THE PREPARATION AND STRUCTURAL CHARACTERIZATION OF NIOBIUM AND TANTALUM COMPLEXES WITH DIPIVALOYLMETHANE

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presented by

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#### ABSTRACT

# THE PREPARATION AND STRUCTURAL CHARACTERIZATION OF NIOBIUM AND TANTALUM COMPLEXES WITH DIPIVALOYLMETHANE

## By

#### George Podolsky

A new series of Nb(V) and Ta(V) dipivaloylmethanate (DPM) complexes have been prepared and characterized. Complexes of the type M(DPM)Cl<sub>4</sub> and M(DPM)<sub>2</sub>Cl<sub>3</sub> were obtained by allowing the metal pentahalide to react with neat H(DPM) (M = Ta) and with H(DPM) in the presence of dichloromethane as a solvent (M = Nb). The complexes of the  $M(DPM)Cl_4$  series exhibit similar infrared and nmr spectra, but the Nb derivative appears to be much less stable in solution in the absence of free ligand. The spectral similarities and differences in stability for the Nb and Ta derivatives also hold true for the M(DPM)<sub>2</sub>Cl<sub>3</sub> complexes. Conductivity data indicate that Ta(DPM)<sub>2</sub>Cl<sub>3</sub> is highly dissociated in nitrobenzene and in nitromethane solution; a dissociation equilibrium involving  $Ta(DPM)_{\lambda}^{+}$  and TaCl<sub>6</sub> is suggested. The constitution of the M(DPM)<sub>2</sub>Cl<sub>3</sub> complexes in the solid state may correspond to an eight-coordinate cationic salt,  $[M(DPM)_{4}][MC1_{6}]$ . Evidence to support this formulation is based primarily on the presence of a band in the ir spectrum near that expected for  $TaCl_{6}$ . The inability to obtain a higher substitution product in the presence of a large excess of ligand or in the presence of a base also suggests the ionic constitution of the complex. An attempt to prepare the Nb(DPM) $_{4}^{+}$  cation by reaction of Nb(DPM) $_{4}$  and anhydrous, oxygen-free Cl<sub>2</sub> in CCl<sub>4</sub> led to abstraction of ligand

oxygen by the metal and the formation of a polymeric oxo-complex, [NbOC1<sub>2</sub>(DPM)].

A new, stable Nb(IV) complex Nb(DPM)<sub>4</sub> was also discovered. This unusual eight-coordinate  $d^1$  metal ion complex was amenable to characterization by various forms of spectroscopy, both in the solid state and in solution. An X-ray structure determination of the complex showed that the coordination polyhedron of the molecule is best described by the D<sub>4</sub> square antiprism, a previously unreported stereoisomer for eightcoordination chemistry. Further studies including electronic absorption and esr spectroscopy indicate that the Nb(DPM)<sub>4</sub> molecule retains its square antiprismatic stereochemistry in solution.

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By

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To Rita

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## TABLE OF CONTENTS

I.	Statement of Purpose
11.	Survey of Niobium and Tantalum Beta-Diketonate Chemistry
111.	Experimental Section
	A. Reagents
	Metal Halides.12C. Purification of Niobium Pentachloride.16D. Syntheses.16E. Physical Methods of Characterization24
IV.	Results and Discussion
	A. Tantalum(V) and Niobium(V) Derivatives of Dipivaloylmethane
	<ul> <li>Tetrakis(dipivaloylmethanato)niobium(IV)</li></ul>
v.	<b>Bibliography</b>
VI.	Appendices
	A. Diketonate Ligand Abbreviations
	of 0.9453)
	Square Antiprismatic Polyhedron of $Nb(DPM)_4$

# LIST OF TABLES

Table		P	age
I.	Chemical Analyses for Products Obtained From the Reactions of TaCl <sub>5</sub> and NbCl <sub>5</sub> With Dipivaloylmethane	•	34
IIA.	Final Atomic Coordinates and Thermal Parameters for Nb(DPM) <sub>4</sub>	•	74
IIB.	Electron Densities (ρ) for Atoms Comprising the Chelate Rings in Nb(DPM) <sub>4</sub>	•	79
III.	Nb-0 and 0-0 Distances (Å) in Nb(DPM) <sub>4</sub>	•	80
IV.	DPM Ligand Bond Distances (Å) in Nb(DPM) <sub>4</sub>	•	82
v.	0-Nb-0 Angles in Nb(DPM) <sub>4</sub>	•	83
VI.	Chelate Ring Interior Angles in Nb(DPM) <sub>4</sub>	•	84
VII.	Average Bond Distances and Angles in the Nb-DPM Chelate Ring	•	85
VIII.	Polyhedral Edge Lengths (Å) When Nb(DPM)4 is Viewed as a D2(aabb) Dodecahedron	•	103
IX.	Polyhedral Edge Lengths (Å) When Nb(DPM)4 is Viewed as a D <sub>2</sub> (gggg) Dodecahedron	•	104
x.	Polyhedral Edge Lengths (Å) When Nb(DPM)4 is Viewed as a D4(llll) Square Antiprism	•	105
XI.	Deviations (Å) of Oxygen Atoms from Best Trapezoidal Planes and Angles of Intersection $(\alpha_T)$ of the Planes When Nb(DPM)4 is Viewed as a D <sub>2</sub> (aabb) Dodecahedron	•	106
XII.	Deviations (Å) of Oxygen Atoms from Best Trapezoidal Planes and Angles of Intersection $(\alpha_T)$ of the Planes When Nb(DPM) <sub>4</sub> is Viewed as a D <sub>2</sub> (gggg) Dodecahedron	•	107
XIII.	Deviations (Å) of Oxygen Atoms from Best Square Planes, Angles of Intersection $(\alpha_s)$ of the Planes, and the Shape Parameter Angles ( $\theta$ ) When Nb(DPM) <sub>4</sub> is Viewed as a D <sub>4</sub> (llll) Square Antiprism	•	108
XIV.	Experimental and Most Favorable Polyhedron Shape Parameters When Nb(DPM)4 is Viewed as a D2(aabb) and D2(gggg) Dodecahedron and a D4(1111) Square Antiprism .	•	109

# LIST OF TABLES (cont'd)

Table		Page
XV.	Experimental and Idealized Plane Deviations (Å) and Angles of Intersection for Nb(DPM) <sub>4</sub> Viewed as a D <sub>4</sub> Square Antiprism and a D <sub>2</sub> (aabb) and D <sub>2</sub> (gggg) Dodecahedron	• <b>1</b> 10
XVI.	UV-Visible Bands of Nb(DPM) <sub>4</sub> In Dichloromethane (2.83 x $10^{-4}$ <u>M</u> )	• 122
XVII.	Second Order Correction Equations for Calculation of g Values	• 135
XVIII.	ESR Parameters for Nb(DPM) <sub>4</sub>	• 136
XIX.	X-Ray Powder Patterns for Nb(DPM) <sub>4</sub> and $Zr(DPM)_4$	• 144

# LIST OF FIGURES

•

Figu	re				P	age
1.	The 9 possible stereoisomers for an eight-coordinate tetrakis chelate	•	•	•	•	3
2.	Apparatus assembly for handling anhydrous solutions during syntheses	•	•	•	•	14
3.	NMR tube assembly for Evans magnetic susceptibility measurement	•	•	•	•	27
4.	Infrared spectrum of Ta(DPM)C14 in a Nujol mull	•	•	•	•	36
5.	Room temperature nmr spectra of Ta(DPM)C1 <sub>4</sub> in dichloromethane	•	•	•	•	39
6.	Room temperature nmr spectra of a dichloromethane solution of the product isolated from the mother liquor of the Ta(DPM)Cl <sub>4</sub> synthesis	•	•	•	•	41
7.	Infrared spectrum of Ta(DPM) $_2$ Cl $_3$ in a Nujol mull	•	•	•	•	46
8.	Room temperature nmr spectra of Ta(DPM) <sub>2</sub> Cl <sub>3</sub> in dichloromethane	•	•	•	•	48
9.	Infrared spectrum of Nb(DPM)Cl <sub>4</sub> in a Nujol mull	•	•	•	•	52
10.	Room temperature nmr spectra of Nb(DPM)Cl <sub>4</sub> in dichloromethane	•	•	•	•	54
11.	Room temperature nmr spectra of Nb(DPM)Cl <sub>4</sub> in dichloromethane after the compound has been allowed to hydrolyze in the solid state	•	•	•	•	57
12.	Infrared spectrum of Nb(DPM) $_2$ Cl $_3$ in a Nujol mull	•	•	•	•	60
13.	Room temperature nmr spectra of Nb(DPM) <sub>2</sub> Cl <sub>3</sub> in dichloromethane	•	•	•	•	62
14.	Infrared spectrum of $[NbOC1_2(DPM)]_x$ in a Nujol mull.	•	•	•	•	66
15.	Infrared spectrum of Nb(DPM) <sub>4</sub> in a Nujol mull	•	•	•	•	71
16a.	The composite electron density along the b axis for Nb(DPM) <sub>4</sub> , Molecule A, showing the half of the molecule containing ligands Ll and L2	•	•	•	•	87
16b.	The composite electron density along the b axis showing the half of Molecule A containing ligands L3 and L4	•	•	•	•	89

# LIST OF FIGURES (cont'd)

Figur	e		Page
17a.	The composite electron density along the b axis for Nb(DPM)4, Molecule B, showing the half of the molecule containing ligands Ll and L2	•	91
17b.	The composite electron density along the b axis showing the half of Molecule B containing ligands L3 and L4	•	93
18.	The motions associated with the transformation of a cube to a $D_{\rm 2d}$ dodecahedron and $D_{\rm 4d}$ square antiprism	•	95
19.	A view of the "idealized" $D_4$ square antiprismatic coordination polyhedron down the "pseudo" $C_4$ axis including the numbering scheme for the ligands, oxygen atoms and carbon atoms for Nb(DPM) <sub>4</sub>	•	97
20.	The Hoard and Silverton polyhedral shape parameter notation for the D <sub>2d</sub> dodecahedron and D <sub>4d</sub> square antiprism	•	100
21.	The average (over Molecules A and B) chelate ring bond distances (A) and their standard deviation of the mean in Nb(DPM) <sub>4</sub>	•	114
22.	The average (over Molecules A and B) interior angles of the chelate ring in Nb(DPM) <sub>4</sub>	•	116
23.	The visible region of the electronic absorption spectrum of Nb(DPM) <sub>4</sub> in dichloromethane (2.83 x $10^{-4}$ M).	•	121
24.	The crystal field splitting diagram for the d orbital energy levels for a D <sub>2d</sub> dodecahedron and a D <sub>4d</sub> squ <b>a</b> re antiprism	•	125
25.	The magnetic circular dichroism spectrum of Nb(DPM)4	•	129
26.	The room temperature esr spectrum of Nb(DPM) <sub>4</sub> in hexane	•	131
27.	The esr spectrum (77°K) of Nb(DPM) <sub>4</sub> in a hexane glass	•	133
28a.	The room temperature esr spectrum of Nb(DPM) <sub>4</sub> powder	•	139
28Ъ.	The esr spectrum of Nb(DPM) <sub>4</sub> powder at 77°K	•	141
29.	The powder esr spectrum at 77°K of Nb(DPM) <sub>4</sub> doped in Zr(DPM) <sub>4</sub>	•	143

#### I. Statement of Purpose

Although the number of species exhibiting discrete eight-coordination<sup>1</sup> has grown rapidly, the observed stereochemistry is still dominated by two coordination polyhedra: the square antiprism and dodecahedron.<sup>1-4</sup> In the case of tetrakis chelate complexes,  $M(chel)_4$ , these two polyhedra can give rise to nine stereoisomers (Figure 1). Among the various  $M(chel)_4$ complexes investigated, only the D<sub>2</sub> antiprism and the D<sub>2d</sub>, D<sub>2</sub>(gggg), and S<sub>4</sub> dodecahedron have yet been observed in the solid state. Very little stereochemical information is available for such complexes in solution. Previous attempts to deduce their stereochemistry by nmr spectroscopy have been thwarted by their rather remarkable stereochemical lability.<sup>5</sup>

The initial object of the research was to investigate the reactions of Nb(V) and Ta(V) pentachlorides and beta-diketones<sup>‡</sup> in solution, with the hope of preparing eight-coordinate  $M(dik)_4^+$  cations suitable for stereochemical studies by nmr spectroscopy. Diketonate ligands were selected for two important reasons: (1) they are known to form higher coordination number complexes with transition metal elements to the left of the periodic table,<sup>6</sup> and (2) the terminal R groups on the ligand provide a convenient means of deducing stereochemistry and possible isomer distributions by conventional  $F^{19}$  and  $H^1$  nmr spectroscopy.

These synthetic studies led to the discovery of several new Ta(V) and Nb(V) complexes, including one possibly containing the  $M(dik)_4^+$  ion. Despite the positive charge on the ion, which was expected to provide a

<sup>\*</sup> A beta-diketonate anion may be represented as (R'COCHCOR) where R may be identical to R'. See Appendix A for a list of ligand abbreviations.

Figure 1. The 9 possible stereoisomers for an eight-coordinate tetrakis chelate.



Figure 1

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substantial barrier of activation for stereochemical rearrangement <u>via</u> intramolecular bond-rupture pathways, the lifetime of the complex in its stereochemical ground state was much too short on the nmr time scale to obtain the desired information.

A new, stable Nb(IV) complex of the type, Nb(dik)<sub>4</sub> was also discovered. This unusual eight-coordinate d<sup>1</sup> metal ion complex was amenable to characterization by various forms of spectroscopy, both in the solid state and in solution. Therefore, an X-ray structure determination of the complex was undertaken, and its spectroscopic properties in the solid state and in solution were correlated with its stereochemistry in the two phases.

## II. Survey of Niobium and Tantalum Beta-Diketonate Chemistry

A review of the chemistry of niobium and tantalum beta-diketonates reveals that a variety of species have been reported. There are two general classes of complexes for the elements in the +5 oxidation state:

(1) Oxo complexes of the type,  $[MOX_2(dik)]_x$ ,  $[MOX(dik)_2]_x$ , and  $[MX_3(dik)]_20$ , where X = halogen and dik = beta-diketonate ligand.

(2) Mixed alkoxo and/or halo complexes of the type,  $MX_2(OR)_2(dik)$ , M(OR)<sub>5-x</sub>(dik)<sub>x</sub> (x = 1,2, or 3) and  $MX_4(dik)$ .

The +4 oxidation state also exhibits two classes of complexes:

(1) Mixed complexes containing halides of the type,  $MX_{4-x}(dik)_x$  where x = 2 or 3.

(2) Tetrakis diketonates, M(dik)<sub>4</sub>.

The first class of the M(V) group includes  $[NbOC1_2(acac)]_x$ ,<sup>7-9</sup>  $[NbOBr(ACAC)_2]_x$ ,<sup>10</sup> and  $[TaC1_3DBM]_20$ .<sup>11b</sup> Rosenheim and Roehrich reported still another oxo complex of the type,  $NbO(C_5H_6O_2)_3^{3-.12}$  This complex was the first example of a Nb beta-diketonate. Hydrated Nb(V) oxide (niobic acid<sup>13</sup>) was allowed to react with a basic solution of acetylacetone to obtain the salt,  $K_2H[NbO(C_5H_6O_2)_3] \cdot 1.5(C_5H_8O_2)$ . The guanidinium salt,  $(CN_3H_6)H_2[NbO(C_5H_6O_2)_3]$ , was also prepared. In these compounds the acetylacetonate anion was formulated as a dinegative species based on elemental analyses, but the formulation has yet to be verified.

The compound,  $[(NbOCl_2(ACAC))]_x$ , was prepared by the reaction of NbOCl\_3 with acetylacetone. The analogous reaction with NbOBr\_3 yielded the disubstituted derivative,  $[NbOBr(ACAC)_2]_x$ , which also retained the Nb-O-Nb linkage. The only Ta example in this class is a dibenzoylmethanate derivative,  $[TaCl_3DBM]_2^0$ , which was prepared by heating a mixture of TaCl\_4 and HDBM in refluxing acetonitrile for five minutes. It was suggested that the diketone acts as the oxidizing agent in the reaction. No MO(dik)\_3 complexes are known with beta-diketonates but the related ligand, tropolone does form NbO(Tp)\_3.

The  $MX_2(OR)_2(dik)$  complexes where M = Nb(V) and Ta(V), X = Cl and Br,  $R = CH_3$  and  $C_2H_5$ , and dik = ACAC or BZAC, were first prepared by allowing the metal pentachloride and diketone to react in the appropriate alcohol.<sup>15</sup> This synthetic method has been used more recently to prepare related derivatives with salicylaldehyde, acetoacetanilide, benzoylacetanilide, 2-hydroxyacetophenone, and o-hydroxybenzophenone in place of the diketones.<sup>16</sup> NbX<sub>2</sub>(OR)<sub>2</sub>ACAC can also be prepared from the oxychloride<sup>8</sup> and oxybromide<sup>10</sup> of Nb(V) by solvolysis of the Nb-O-Nb bond with the appropriate alcohol. The mixed alkoxide-diketonates,  $M(OR)_{5-x}(dik)_x$  where x = 1,2, and 3, M = Nb(V) and Ta(V), R = CH<sub>3</sub>,  $\underline{t}$ -C<sub>4</sub>H<sub>9</sub> and C<sub>2</sub>H<sub>5</sub>, and dik = ACAC, BZAC, and DBM, represent the most extensive series of complexes yet prepared.<sup>17-19</sup> Beta-ketoester derivatives have also been prepared.<sup>20-22</sup> The ethoxide and methoxide complexes were isolated from the reaction of the metal pentalkoxide and corresponding beta-diketone in benzene solution. The  $\underline{t}$ -C<sub>4</sub>H<sub>9</sub> derivatives were prepared by metathesis reaction of the ethoxide complex and  $\underline{t}$ -butanol in benzene. The methoxy-acetylacetonate derivatives, MC1(OMe)<sub>3</sub>ACAC, were prepared from the reaction of M(OMe)<sub>4</sub>ACAC with MC1<sub>2</sub>(OMe)<sub>2</sub>ACAC.<sup>19</sup> The only example of a MX<sub>4</sub>(dik) complex is TaCl<sub>4</sub>(DBM).<sup>11b</sup> It was isolated from a mixture of TaCl<sub>4</sub> and dibenzoylmethane in acetonitrile.

No complexes of the type, MCl(dik)<sub>4</sub> are known with beta-diketonates, but again, tropolone forms both the Nb and Ta derivatives.<sup>14a,14b</sup> The Nb complex was obtained by adding a dichloromethane solution of the ligand to NbCl<sub>5</sub> in dichloromethane and ether. The Ta species was isolated after heating a mixture of TaCl<sub>5</sub> and tropolone in refluxing acidic methanol for fifteen minutes.

Examples of Nb(IV) chelates of the type,  $MX_{4-x}(dik)_x$  are NbCl<sub>2</sub>(DBM)<sub>2</sub> and NbCl(Tp)<sub>3</sub>.<sup>11b</sup> NbCl<sub>2</sub>(DBM)<sub>2</sub> was prepared by heating a mixture of the free ligand and NbCl<sub>4</sub> in refluxing acetonitrile. As noted above, the analogous reaction with TaCl<sub>4</sub> led to oxidation of the metal to give TaCl<sub>4</sub>(DBM) or [TaCl<sub>3</sub>(DBM)]<sub>2</sub>O depending on the reaction time. NbCl(Tp)<sub>3</sub> was prepared by heating NbCl<sub>4</sub> and tropolone in refluxing acetonitrile.

Five tetrakis (beta-diketonato)niobium(IV) complexes are known with ACAC, TTFA, BTFA, BZAC, and DBM.<sup>11a,11b</sup> The tropolone derivative also exists.<sup>11a,11b</sup> The only Ta(IV) species is Ta(DBM)<sub>4</sub>.<sup>11b</sup> With the

exception of Nb(ACAC)<sub>4</sub>, the complexes were prepared from NbCl<sub>4</sub> and the diketone by using triethylamine to help drive the reaction to completion. Nb(ACAC)<sub>4</sub> was prepared by heating a mixture of NbCl<sub>4</sub> and Tl(ACAC) in acetonitrile at reflux temperatures for five minutes. When dioxane was used as the solvent, Nb(ACAC)<sub>4</sub>.Dioxane was obtained. Two methods were successful in preparing the TTFA derivative. In the first case, acetonitrile was the solvent and the reflux time was five minutes. In the second method, the reflux time was reduced to one minute and the reaction was conducted in dioxane. The BTFA, BZAC, and DBM chelates were all similarly prepared with toluene, dioxane, and acetonitrile used, respectively, as solvents. The reflux times varied from one to five minutes. The complexes are readily hydrolyzed in solution. Nb(TTFA)<sub>4</sub> and Nb(BTFA)<sub>4</sub> in the crystalline state are stable toward atmospheric oxygen and water. The remaining derivatives, however, are decomposed by atmospheric oxygen and water at room temperature.

In general, the constitution and structure of the complexes described above in both the solid and solution state are poorly defined. The presence of Nb-O-Nb bridging in the polymeric  $[NbOCl_2(ACAC)]_x$  and  $[NbOBr(ACAC)_2]_x$  species has been indicated by strong, broad infrared bands near 820 cm<sup>-1</sup> and 825 cm<sup>-1</sup>, respectively.<sup>10</sup> These frequencies lie closer to the corresponding Nb-O-Nb vibrational mode observed at 770 cm<sup>-1</sup> for NbOCl<sub>3</sub> than to the Nb = 0 stretching modes at 945, 935 cm<sup>-1</sup> and 910, 890 cm<sup>-1</sup> in NbOBr<sub>3</sub> and NbOCl<sub>2</sub>(OC<sub>2</sub>H<sub>5</sub>)Bipy, respectively.<sup>10</sup> A crystal structure of the latter compound has shown it to be six-coordinate, thus verifying the Nb = 0 formulation.<sup>23</sup> [TaCl<sub>3</sub>(DBM)]<sub>2</sub>0 is apparently a discrete oxo-bridged dimer as supported by the presence of a fairly strong Ta-O-Ta band at 809 cm<sup>-1</sup>.<sup>11b</sup> As in the case of the

Nb = 0 stretching frequency, the Ta = 0 stretch exhibits strong doublets at 935 and 919 cm<sup>-1</sup> in TaOCl<sub>3</sub>(Dioxane)<sub>2</sub>.<sup>11b</sup> Metal-oxygen (ligand) and metal-halogen frequencies have also been assigned, but they have not contributed to additional structural insight.<sup>8,9</sup> Powder diffraction data have been obtained for [NbOCl<sub>2</sub>ACAC]<sub>x</sub> but no new information beyond the conclusion that the complex is not isomorphous with NbOCl<sub>3</sub> was gained.<sup>10</sup>

Monomeric formulations have been suggested for the members of the  $MX_2(OR)_2(dik)$ ,  $M(OR)_{5-x}(dik)_x$ , and  $MX_4(dik)$  families. However, possible solvolysis and/or dissociation in solution leave the question of solution state stereochemistry unanswered. Ebulloscopic molecular weight studies of the  $MX_2(OR)_2ACAC$  series in the parent alcohols led Djordjevic, <u>et al.</u>, to suggest that solvolysis may occur to form neutral and ionic species:<sup>8</sup>

(1) 
$$Nbx_2(OR)_2ACAC \xrightarrow{ROH} Nbx_2(OR)_3 + H^+ + ACAC^-$$
  
 $1/2 Nb_2x_4(OR)_6$ 

(2) 
$$Nbx_2(OR)_2ACAC \xrightarrow{ROH} Nbx(OR)_3ACAC + H^+ + x^-$$
  
1)  
Nb(OR)\_4ACAC + H^+ + x^-

Thus, the low molecular weight values observed could represent an average of the above dissociation products. Acidity of the alcoholic solutions has been cited as further supporting evidence for the dissociations. However, conductivity measurements by Syamal, <u>et al.</u>,<sup>16</sup> are consistent with a 2:1 electrolyte and suggest the existence of  $M(OR)_2(HOR)_2(dik)^{2+}$  ions in solution. Quantitative precipitation of silver chloride further substantiates halogen dissociation in methanol. In acetonitrile, the molar conductance values are between those expected

for a 1:1 and a non-electrolyte, implying that the weaker donor solvent replaces fewer halogen atoms. Vapor pressure osmometric data measured in both chloroform and benzene solutions<sup>16</sup> gave high molecular weight values which increased as a function of time. This time dependence is believed to be due to polymerization of the molecule in the less polar solvents.

Evidence that the MX<sub>2</sub>(OR)<sub>2</sub>(dik) complexes undergo diketonate ligand dissociation and decomposition in solution also exists.<sup>16</sup> Optical spectra in methanol and aged benzene and acetonitrile resemble free ligand spectra. The presence of acetone in carbon tetrachloride and methanol solutions of the complexes has been detected by gas chromatography. Ligand decomposition is further indicated by nmr spectra of the aged solutions which resemble neither fresh solution nor free ligand spectra. Other nmr studies indicate diketone and alkoxide exchange is slow on the nmr time scale since the spectra of the complex and free ligand are identical to the sum of the component spectra. Attempts were made to deduce the stereochemistry of the neutral monomeric molecule in solution by studying a derivative with an asymmetric diketonate ligand.<sup>16</sup> Although a definitive assignment was not possible, a <u>trans</u>-dichloro arrangement was favored.

Further investigations of solution state equilibria have been conducted by titration of Nb(V) and Ta(V) alkoxides in methanol solution.<sup>19</sup>  $M(OR)_{2}ACAC^{2+}$ ,  $M(OR)_{3}ACAC^{+}$ , and  $M(OR)_{4}ACAC$  were found to exist, with the Nb species being more stable than the Ta analogs. Infrared assignments have been made for many of the complexes but no structural information was deduced.<sup>8,9</sup> Powder diffraction data on the  $MX_{2}(OR)_{2}ACAC$  system indicate that the methoxy-chloro and -bromo derivatives are isomorphous,

whereas the ethoxy complexes form a separate isomorphous group.<sup>8</sup>

Aside from ebulloscopic molecular weight measurements and elemental analyses, no other meaningful data are available on the  $M(OR)_{5-x}(dik)_x$ series. Molecular weights of these oils in benzene indicate monomeric species. They may be six, seven, and eight-coordinate, respectively, when x = 1,2, and 3.<sup>17,18</sup> The Nb derivatives are more volatile than the Ta analogs. Also, alkoxide ligand exchange is faster in the niobium complexes than in the tantalum derivatives.<sup>17</sup>

Very little structural information is available for the two known Nb(IV) complexes in the NbX<sub>4-x</sub>(dik)<sub>x</sub> class. A low effective magnetic moment (0.40 B.M.) at room temperature for NbCl(Tp)<sub>3</sub> has been interpreted in terms of a polymeric structure.<sup>11b</sup> The value of 1.58 B.M. for NbCl<sub>2</sub>(DBM)<sub>2</sub>, however, is typical for six-coordinate monomeric Nb(IV) complexes.<sup>11b</sup>

The tetrakis chelates,  $M(dik)_4$ , are eight-coordinate monomers, with the possible exception of the tropolone derivatives being polymeric.<sup>11b</sup> In the dioxane adduct,  $Nb(ACAC)_4$  (Dioxane), the coordination number of Nb may be nine. This complex exhibits an infrared spectrum similar to oxygen-coordinated dioxane complexes, and the visible spectrum is significantly different from  $Nb(ACAC)_4$ .<sup>11b</sup> Ultraviolet and visible spectral data are also reported for the other tetrakis species and are interpreted in terms of possible metal d-d transitions, intraligand singlet to triplet transitions, and charge transfer transitions.<sup>11b</sup>

Attempts at making a specific stereochemical assignment in this class of compounds are based on non-documented X-ray powder diffraction data and sketchy esr data. Deutscher and Kepert<sup>11b</sup> report that Nb(TTFA)<sub>4</sub> is not isomorphous with M(TTFA)<sub>4</sub> where M = Zr, Hf, Th, Ce, U, and Pu, but the structure of this latter isomorphous series of compounds has not yet been reported. Nb(DBM)<sub>4</sub> is not isomorphous with Th(DBM)<sub>4</sub> (a  $D_{2d}$  dodecahedron<sup>24</sup>), and Nb(ACAC)<sub>4</sub> is not isomorphous with Zr(ACAC)<sub>4</sub> (a  $D_2$  square antiprism<sup>3b</sup>). The authors also describe the esr spectra at room temperature of Nb(ACAC)<sub>4</sub> and Nb(DBM)<sub>4</sub> as consisting of a broad asymmetric signal showing the shape predicted for a signal with  $g_{\perp}$  greater than  $g_{\parallel}$ . The values for  $g_{\perp}$  are 1.95 and 1.98, respectively, but  $g_{\parallel}$  values were not reported. Thus, on the basis of these data, they conclude that a dodecahedral, rather than square antiprismatic stereochemistry, is indicated.

III. Experimental Section

A. Reagents

The following commercially available reagents were used without further purification unless otherwise indicated.

- (1) Aquasorb, P<sub>2</sub>O<sub>5</sub> Mallinkrodt Analytical Reagent
- (2) Chlorine gas, Cl<sub>2</sub> Matheson Co.
- (3) Cupric Acetate,  $CuC_{2}H_{3}O_{2}$  Fischer Scientific Reagent
- (4) Methyl pivalate,  $C_6^{H}_{12}^{O}_2$  Aldrich Chemical Company
- (5) Niobium pentachloride, NbCl<sub>5</sub> Research Organic/Inorganic Chemicals, 99.5%
- (6) Niobium shot, Nb Alfa Organics, m2n8-t2n7
- (7) Pinacolone,  $C_6H_{12}O$  Aldrich Chemical Company
- (8) Sodium amide, NaNH, K and K Laboratories
- (9) 2,2,6,6-tetramethy1-3,5-heptanedione,  $C_{11}H_{20}O_2$ -Eastman Chemicals
- (10) Triethylamine, (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N Eastman Chemicals
- (11) Tetramethylsilane, (CH<sub>3</sub>)<sub>4</sub>Si Aldrich Chemical Company

B. General Techniques Used in the Reactions of Metal Halides

In view of the air sensitivity of the Nb and Ta halides and of most of the products they form upon reaction with beta-diketones, special procedures were necessary to maintain anhydrous conditions in the preparative reactions. All glassware contained sidearm stopcocks to allow entry of dry nitrogen or argon gas. This included erlenmeyer and round bottom flasks, filter frits, and dropping funnels. Prior to use, the apparatus was cleaned in a KOH - EtOH bath (except for fritted glassware) followed by a soaking in a  $K_2Cr_2O_7 - H_2SO_4$  bath and rinsing with distilled water. After drying for at least 24 hrs. at <u>ca</u>. 180°C, the glassware was cooled in a CaCl<sub>2</sub> desiccator and flushed with dry nitrogen. It was then transferred to a nitrogen-filled glove bag (obtained from Instruments for Research and Industry, Model X-17-17) which contained a beaker of Aquasorb to help maintain a dry atmosphere. All transfers of hygroscopic reagents were performed in the glove bag, although in a few cases, a dry box was used.

Most reactions were conducted in a small erlenmeyer flask (50-250 ml) equipped with a gas inlet tube to admit dry nitrogen. A gentle flow of dry nitrogen or argon served to both insure anhydrous reaction conditions and to help remove product gases (e.g. HCl) that formed during the reaction.

To filter the reaction mixture, a medium porosity  $(10-20 \mu)$  sidearm filter frit, attached to a sidearm erlenmeyer receiving flask, was attached to the reaction flask. The sidearm stopcock on the filter frit enabled a flow of nitrogen to be passed through the frit as well as the reaction flask while the apparatus was being assembled (see Figure 2). Figure 2. Apparatus assembly for handling anhydrous solutions during syntheses: (1) A-original reaction flask, B-S 24/40 medium porosity filter frit, C-receiving flask; (2) A-dropping funnel with wash solvent, B-S 24/40 female-female joint, C-S 24/40 medium porosity filter frit with magnetic stirring bar inside, D-receiving flask.





Development of excessive pressure was avoided by use of a mineral oil-filled nitrogen bubbling tower included in the nitrogen line. Once the filtration apparatus was inverted, rapid filtration could be assured by either passing nitrogen into the reaction flask through the sidearm and/or attaching a periodic vacuum to the sidearm of the receiving flask.

Washing of the solid residue was accomplished by replacing the reaction flask with a dropping funnel containing the appropriate amount of nitrogen-flushed wash solvent. The solvent was flushed at least fifteen minutes before use. The wash solvent was flushed through the frit in a manner analogous to the filtration procedure by using the three-way stopcock on the dropping funnel to attach the nitrogen line. After the washing was complete, the dropping funnel and receiving flask were replaced by adapters (see Figure 2) and the product was dried in vacuo.

Recrystallization of the product was conducted in a similar manner. The recrystallizing solvent or solvent mixture was added by means of the dropping funnel to the solid residue contained in the filter frit. Heat was applied, as necessary, with the aid of a heat gun while the desired product solution was being flushed into the receiving flask with nitrogen. An alternative method of recrystallization involved transferring a pre-weighed portion of the crude product to a sidearm erlenmeyer and adding the appropriate solvent(s) in the glove bag. The mixture was heated and stirred magnetically while passing nitrogen over the solution surface. Filtration was achieved as in the original filtration process, and the flask was set aside in the refrigerator or at room temperature, as desired.

All solvents were dried at least several days and usually, several weeks, over drying agents prior to use. Calcium hydride was used to dry dichloromethane, chloroform, acetonitrile and carbon tetrachloride. Molecular sieves were used to dry nitrobenzene, which was pre-purified according to the procedure outlined by Taylor and Kraus.<sup>25</sup> Triethylamine was freshly-distilled over barium sulfate at 84°C. All other solvents were refluxed over lithium aluminum hydride.

## C. Purification of Niobium Pentachloride

Niobium pentachloride was purified by sublimation <u>in vacuo</u>. A pre-dried pyrex glass tube, equipped with a ground glass joint and vacuum stopcock, was loaded with 6-8 grams of yellow NbCl<sub>5</sub> powder in a dry box. It was slowly evacuated and placed into a tube furnace so that the end containing the NbCl<sub>5</sub> was near the middle of the heating coils. A small piece of aluminum foil wrapped around the end of the tube kept an iron-constantan thermocouple in place. The furnace was placed on an incline (<u>ca</u>. 30°) with the loaded end of the tube slanting downward. The temperature was slowly increased over a three day period to 125°C. The first trace of sublimate was visible after approximately 24 hours and a temperature of 64°C. A very crystalline (plate-like prisms and feathery, needle-like networks) yellow product had sublimed into the cold end of the tube after three days. The reaction tube was dismantled in a dry box, and the product was scraped out with the aid of a bent spatula. Tantalum pentachloride was sublimed in an analogous manner.

D. Syntheses

#### 1. Preparation of niobium tetrachloride.

NbCl<sub>4</sub> was prepared by reaction of Nb and NbCl<sub>5</sub> at elevated temperatures:<sup>26</sup>

 $Nb + 4NbC1_5 = 5NbC1_4$ 

Freshly-sublimed NbCl<sub>5</sub> (27.6 g, 0.102 moles) and niobium shot (2.37 g, 0.0256 moles) were loaded into a dry 45 cm (30 mm o.d.) pyrex tube in a dry box. The tube was evacuated to a pressure of  $10^{-5}$  torr and carefully sealed with a flame. The tube was placed into a two-zone tube furnace with the temperature of each 30 cm zone individually controlled by Variacs. The entire tube was wrapped in aluminum foil to help secure the two iron constantan thermocouples and help improve the uniformity of the temperature gradient along the reaction tube. The zone containing the loaded end of the tube was warmed to 70° before activating the second zone. The temperature of the loaded end was then increased to 400-410° while increasing the temperature of the second zone to 250-260°. After a reaction time of five days, a special shutdown procedure was followed. During the cooling period, the temperature of the "hot" zone was kept approximately 50°C above the "cool" zone to prevent disproportionation of the product. Approximately 23 grams of a dark purple, finely-crystalline product was obtained in the "cool" zone. The NbCl, was purified by sublimation in vacuo at 150°. Approximately 2 days were required to complete the sublimation. The product was placed in a Schlenk tube and stored in a dry box.

## 2. Preparation of 2,2,6,6-tetramethy1-3,5-heptanedione.

The synthesis was patterned after the method reported by Adams and Hauser.<sup>27</sup> The following reactions are used in the synthesis:

$$CH_3COC(CH_3)_3 + NaNH_2 \neq Na^+[CH_2COC(CH_3)_3]^- + NH_3$$
  
pinacolone I

$$H_{2}O$$
II  $\neq$  (CH<sub>3</sub>)<sub>3</sub>CCOCH<sub>2</sub>COC(CH<sub>3</sub>)<sub>3</sub>  
H<sup>+</sup>  
dipivaloylmethane  
(HDPM)

A solution of pinacolone (225 ml, 1.8 moles) in 270 ml of diethyl ether was added dropwise, with stirring, to a grey suspension of sodium amide (70.2 g, 1.8 moles) in 1500 ml of diethyl ether. The addition was completed in about 1 1/2 hours. Methyl pivalate (235 ml, 1.8 moles) in ca. 20 ml of ether was then added to the greyish-green suspension over a 30 minute period. The mixture was heated at reflux temperature overnight. The reaction mixture then was cooled to room temperature and carefully poured into a 4 liter beaker containing ca. 1500 ml of water. Approximately 600 ml of 6<u>N</u> HCl was added to adjust the pH to 7.0 (as indicated with Hydrion paper). The aqueous and ethereal layers were separated, and the water layer was extracted eleven times with 200 ml portions of ether. The following color changes were observed in the ether and water layers before and after neutralization:

 ETHER LAYER
 orange
 HCl
 orange-yellow

 H20
 LAYER
 greenish-brown
 HCl
 orange-yellow

 pH7
 bright yellow
 during extraction
 orange

 greyish-green
 pale yellow

 final extraction
 colorless

 light yellow
 light yellow

The ether solutions were combined (<u>ca</u>. 3700 ml) and evaporated on a steam bath until boiling ceased. Approximately 350 ml of orange liquid product remained. To this product was added a solution of cupric acetate (120 g, 0.600 mole) in 350 ml of methanol and 1050 ml of water. The conversion of the ligand to the copper salt was necessary to isolate a product of higher purity i.e., without accompanying side products of the initial acylation reaction. After heating the copper salt solution to near boiling, it was quickly filtered through a hot Büchner funnel to remove any undissolved cupric acetate. During the heating process the color of the solution changed from orange to dark green. Cooling the solution to room temperature afforded dark purple crystals of copper(II) dipivaloylmethanate, which were collected by filtration. The compound was recrystallized from 1700 ml of hexane which resulted in a yield of 110 g (28.4Z).

The copper salt was divided into three equal portions, and each portion was treated in the following manner. The crystals were dissolved in 500 ml of ether, and the solution was shaken in a separatory funnel with one liter of 10% sulfuric acid. The layers were separated, and the blue aqueous layer was washed twice with 100 ml of ether. The yellow ethereal solutions obtained by treating the three portions of  $Cu(DPM)_2$ were combined and evaporated on a steam bath until boiling ceased. The remaining dipivaloylmethanate was dried over 20 g of anhydrous sodium sulfate for 3 hours and then was transferred to a distilling flask. The product was fractionally-distilled through an insulated vigreaux column under dry nitrogen at a pressure of 20 torr. Three fractions boiling in the following ranges were collected:  $80-93.5^\circ$ ;  $93.5-96^\circ$ ;  $96-97^\circ$ . The first two fractions exhibited the expected tertiary butyl proton

resonance at  $\tau 8.85$  and methylene proton resonance at  $\tau 4.23$  in the nmr spectrum. However, impurities were also present as indicated by a weak set of multiplets between  $\tau 7.66$  and  $\tau 8.16$ , and a strong, sharp resonance at  $\tau 8.80$ . Thus the first two fractions were discarded. The third fraction showed no impurities in the nmr spectrum. The yield was 90 ml (27%, 11t.<sup>27</sup> 28%).

## 3. Preparation of Dipivaloylmethanato Tantalum(V) Tetrachloride.

Dipivaloylmethane (22.2 ml, 120 mmoles) was added at room temperature to  $TaCl_5$  (8.63 g, 24.1 mmoles) to form immediately a yellow suspension. The yellow suspension was stirred for 30 minutes, and a vacuum was applied to remove the by-product HCl. After filtration of the mixture, the yellow solid (3.40 g) was washed with hexane and dried <u>in vacuo</u> for 6 hours. To facilitate the removal of any insoluble impurities and occluded free ligand, the compound was dissolved in dichloromethane, and the solution was filtered and pumped to dryness. The bright yellow solid was dried <u>in vacuo</u> at room temperature for 15 hours and then at 80° for 3 hours; m.p. 123-128°. The yield was 3.40 g (28%).

<u>Anal</u>. Calc'd. for Ta(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)Cl<sub>4</sub>: C, 26.10; H, 3.78; Cl, 28.05; Ta, 35.74. Found: C, 25.87; H, 3.86; Cl, 25.22; Ta, 36.07.

The filtrate of the above compound which had become cloudy after aging for <u>ca</u>. 1 hour was filtered, and a bright yellow solid was obtained. It was dried <u>in vacuo</u> at room temperature for 4 hours. M.P. 190-215° (with decomposition).

4. Preparation of Bis(dipivaloylmethanato)tantalum(V) Trichloride.

Dipivaloylmethane (10 ml, 54 mmoles) was added to  $TaCl_5$  (3.90 g, 10.9 mmoles) as in the preparation of TaDPMCl<sub>4</sub>. The reaction mixture

was stirred for 30 minutes and then heated on a steam bath for 1 1/2 hours. After additional stirring at room temperature for 12 hours, hexane was added to the solution. A pale yellow precipitate formed which was filtered and dried <u>in vacuo</u> for 1 hour. The crude product was washed with hot hexane, recrystallized from dichloromethane-benzene, and dried <u>in vacuo</u> for 12 hours at 80°; m.p. 268-271°, (with decomposition). The yield was 1.76 g (25%).

<u>Anal</u>. Calc'd. for  $Ta(C_{11}H_{19}O_2)_2Cl_3$ : C, 40.41; H, 5.86; Ta, 27.67; mol. wt., 659. Found: C, 40.22; H, 5.88; Ta, 27.22; mol. wt.  $(C_6H_5NO_2)$ , 644;  $\Lambda$  (1.08 x  $10^{-3}$  <u>M</u> in  $C_6H_5NO_2$  at 25°), 12.4 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>;  $\Lambda$  (0.33 x  $10^{-3}$  <u>M</u> in  $CH_3NO_2$  at 25°), 54 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>.

After aging for <u>ca</u> 24 hours, the filtrate of the above compound produced a crop of yellow crystals which were filtered. They were recrystallized in dichloromethane-diethylether and analyzed. The mother liquor of the above filtration also continued to produce more crystals upon aging.

Anal. (first crop): C, 37.05; H, 5.22; Cl, 15.81.

#### 5. Preparation of Dipivaloylmethanatoniobium(V) Tetrachloride.

A solution of dipivaloylmethane (0.91 ml, 4.95 mmoles) in 20 ml dichloromethane was added dropwise, with stirring, to NbCl<sub>5</sub> (1.21 g, 4.50 mmoles). An immediate reaction was indicated by vigorous frothing and the formation of an orange solution. A vacuum was applied during a 30 minute stirring period, after which, 30 ml of hexane was added. After further stirring for 20 minutes the orange reaction mixture was filtered. The orange solid residue (0.27 g) was washed with hexane and dried in vacuo for 1 1/2 hours; m.p. 167°, (with decomposition). The red-orange filtrate became cloudy after addition of 60 ml of hexane, and a precipitate began to form after removal of 30 ml of solvent by evaporation under a stream of dry nitrogen. The finelydivided red-orange precipitate was filtered and dried <u>in vacuo</u> for 2 hours; m.p. 139-142°. The yield was 1.09 g (59%).

<u>Anal</u>. Calc'd. for Nb(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)Cl<sub>4</sub>: C, 31.61; H, 4.58; Cl, 33.93; Nb, 22.23. Found: C, 31.76; H, 4.98; Cl, 29.48; Nb, 22.68.

#### 6. Preparation of Bis(dipivaloylmethanato)niobium(V) Trichloride.

A solution of dipivaloylmethane (8.7 ml, 47.4 mmoles) in 35 ml of dichloromethane was added to NbCl<sub>5</sub> (2.56 g, 9.49 mmoles), and the orange reaction mixture was stirred for 3 hours. During this time a vacuum was applied to remove the HCl. After an initial reaction time of 40 minutes the color of the solution changed from clear orange to opaque red-orange. An orange precipitate began to form after 50 ml of hexane was added to the mixture. The mixture was allowed to age for one hour while the volume was reduced by a gentle stream of dry nitrogen. The orange precipitate was filtered and dried in vacuo for 3 hours.

The filtrate was allowed to age for 24 hours and was filtered again to remove some crystals that had formed. The new filtrate was allowed to age for one week. During this time a mixture of orange needle-like and prismatic crystals had formed. The mother liquor was decanted and the crystals were dried with a stream of dry nitrogen for 3 hours; m.p. 139-144°. The yield was 0.85 g (15%).

<u>Anal</u>. Calc'd. for Nb(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>3</sub>: C, 46.70; H, 6.77; Cl, 18.80; Nb, 16.42. Found: C, 46.96; H, 6.94; Cl, 14.26; Nb, 17.86.

# 7. <u>Preparation of tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)-</u> <u>niobium(IV).</u>

An acetonitrile solution of dipivaloylmethane (39.5 ml, 214 mmoles) containing triethylamine (11.2 ml, 80.3 mmoles) was added dropwise, with stirring to an acetonitrile suspension of NbCl<sub>4</sub> (4.51 g, 192 mmoles). After 2 days the blue-black suspension was filtered and a similarly-colored solid was obtained. The product was washed through a filter frit with hexane, leaving behind a greyish-white solid (triethylaminehydrochloride) and resulting in an opaque purple filtrate. The filtrate was evaporated under vacuum at room temperature, and the finelycrystalline dark purple residue was dried <u>in vacuo</u> at room temperature for 5 hours; m.p. 219-233°. The yield was 7.13 g (53%).

Anal. Calc'd. for Nb( $C_{11}H_{19}O_{2}$ )<sub>4</sub>: C, 63.98; H, 9.27; Nb, 11.25; mol. wt. 826. Found: C, 63.86; H, 9.23; Nb, 11.46; mol. wt. ( $C_{6}H_{5}NO_{2}$ ), 777;  $\Lambda$  (2.93 x 10<sup>-3</sup> <u>M</u> in CH<sub>2</sub>Cl<sub>2</sub> at 26°), 0.0901 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>;  $\Lambda$  (1.11 x 10<sup>-4</sup> <u>M</u> in C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> at 26°), 6.88 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>;  $\mu_{eff}$ (Evans), 2.1 B.M.;  $\mu_{eff}$ (Faraday), 1.9 B.M.

### 8. Preparation of oxodichlorodipivaloylmethanatoniobium(V).

Anhydrous oxygen-free chlorine (8.94 mmoles) dissolved in 200 ml carbon tetrachloride was added in four-50 ml portions to a carbon tetrachloride solution of Nb(DPM)<sub>4</sub> (2.51 g, 3.04 mmoles). After each successive addition, the solution changed color from the initial deep purple to blue-green and finally to yellow when the fourth portion of chlorine was added. The diamagnetic yellow solution was evaporated <u>in</u> <u>vacuo</u> to yield a brown oil. Addition of hexane resulted in the formation of a golden yellow precipitate which was filtered and dried <u>in vacuo</u> at room temperature for 3 hours. The compound decomposes to a black solid at  $280^{\circ}$ . The yield was 0.35 g (32%).

<u>Anal</u>. Calc'd. for NbC<sub>11</sub>H<sub>19</sub>O<sub>3</sub>Cl<sub>2</sub>: C, 36.39; H, 5.28; Cl, 19.53; Nb, 25.59. Found: C, 36.61; H, 5.32; Cl, 19.41; Nb, 25.36.

E. Physical Methods of Characterization

#### 1. Elemental Analysis

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Niobium was determined by atomic absorption.

2. Melting Point

Melting points were determined with a Thomas-Hoover 6406-H capillary melting point apparatus. Capillaries were sealed with a plug of plasticene to avoid hydrolysis or oxidation of compounds during the determination of melting points.

3. Molecular Weight

Molecular weights were determined cryoscopically in nitrobenzene or benzene. The apparatus was equipped with a S 19/38 Beckman thermometer graduated at 0.01°C intervals. An attached magnifying reader made possible readings estimated to  $\pm$  0.001°C.

The molal freezing point depression constants  $(K_f)$  were determined with recrystallized benzil as the reference solute. The freezing depressions were measured in the concentration range of <u>ca</u>. 0.005 <u>m</u> to 0.01 <u>m</u>.

## 4. Molar Conductance

Conductance measurements on the Ta(V) complexes were made with a Beckman Model -RC-16B2 bridge, whereas the Nb(IV) complexes were measured with a Wayne Kerr Model B221 Universal Bridge. Two Freas type conductivity cells with bright platinum electrodes were used. The cell
constants, determined with a standard KCl solution, were 0.2139 cm<sup>-1</sup> and 0.1941 cm<sup>-1</sup>. Solution concentrations in nitrobenzene, dichloromethane and nitromethane ranged from <u>ca</u>. 0.0003 <u>M</u> to 0.07 <u>M</u>.

5. <u>Magnetic Susceptibility</u>

(a) Evans Method<sup>28</sup> - Dichloromethane solutions were measured into an nmr tube assembly as shown in Figure 3. The nmr spectra were obtained with a Varian 56/60-D high resolution spectrometer operated at 60 MHz. Both  $CH_2Cl_2$  and TMS resonances were measured to obtain the paramagnetic shift. The following equation was used to calculate  $x_M$ , the molar magnetic susceptibility:

$$\chi_{\rm M} = \frac{3\Delta v (\rm MW)}{2\pi v \rm C}$$

- where  $\Delta v =$  paramagnetic shift or frequency separation, in Hz, of either TMS or dichloromethane,
  - MW = molecular weight of solute,
    - v = frequency of nmr spectrometer (60 x 10<sup>6</sup>Hz),
  - and C = concentration of solute in g/ml.

(b) Faraday Method - Measurements were made with an Alpha Magnetic Susceptibility System equipped with a Model 3002-1 current regulated power supply, a Model 3022 vacuum controller, and a Model 4600 4 inch adjustable electromagnet. The field strength of the magnet at 30 amps and a one inch gap was 11,300 Gauss. A quartz bucket, which was used as the sample holder, was calibrated with  $Hg[Co(CNS)_4]$ . Readings were taken at 500.0 and 800.0 amps to an accuracy of  $\pm$  0.00003 g. Sample Figure 3. NMR tube assembly for Evans magnetic susceptibility measurement.



weights were approximately 20 mg. Diamagnetic corrections for the ligand<sup>29</sup> and niobium atom<sup>30</sup> were applied. In a typical Faraday experiment, the observed  $\chi_M$ , was 690 x 10<sup>-6</sup> cgs units, and the diamagnetic correction term was 720 x 10<sup>-6</sup> cgs units. The following formula was used to calculate  $\chi_M$ , the molar magnetic susceptibility:

$$x_{\rm M} = (\frac{\alpha + \beta F'}{W \times 106}) \ \rm MW$$

- where  $\alpha$  = correction for displaced air (assumed negligible),
  - β = calibration constant which corrects for susceptibility of sample holder,

$$\mathbf{F'} = \mathbf{F} - \mathbf{\delta}$$

where F = change in weight of the sample holder plus the sample when the field is applied,

- $\delta$  = change in weight of the empty sample holder when the field is applied,
- W = weight of sample in grams,

and MW = molecular weight of the sample.

## 6. Infrared Spectra

Infrared spectra were obtained with a Perkin-Elmer 237B grating infrared spectrophotometer (4000-600 cm<sup>-1</sup>) and a Perkin-Elmer 457 grating infrared spectrophotometer (4000-250 cm<sup>-1</sup>). The samples were prepared in a glove bag as Nujol mulls on CsI plates or as dichloromethane solutions in CsI cells of 0.1 mm pathlength.

29

#### 7. Ultraviolet and Visible Spectra

UV-Vis spectra were obtained with a Unicam SP. 800B ultraviolet spectrophotometer and a Cary 14 recording spectrophotometer. Dichloromethane solutions prepared in a glove bag were measured in the concentration range of <u>ca</u>. 0.0003 <u>M</u> to 0.001 <u>M</u>. In addition, electronic absorption spectra in the solid state were obtained from nujol mulls dispersed on filter paper.

#### 8. Nuclear Magnetic Resonance Spectra

Proton nmr spectra were obtained with a Varian 56/60-D high resolution spectrometer operated at 60 MHz. Chemical shifts were measured by using tetramethylsilane as an internal standard. All samples were prepared in a glove bag. Temperatures were determined from the chemical shift differences between the proton resonances of methanol.

### 9. Electron Spin Resonance Spectra

ESR spectra were obtained with a Varian E-4 spectrometer operated between 9.2 and 9.5 GHz.<sup>‡</sup> Spectra were recorded at room temperature and at 77°K, the latter temperature made possible by insertion of a liquid nitrogen dewar into the probe. Samples were prepared in a glove bag by using pre-dried 3 mm quartz tubes which had been alternately evacuated and flushed with purified nitrogen. After a preliminary seal with stopcock grease, the sample tube was removed from the glove bag and carefully sealed in a flame.

ESR spectra of Nb(DPM)<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature and 77°K were duplicated by Dr. R. D. Bereman, State University of Buffalo. An X-band Varian 4502-19 linear field spectrometer was used.

#### 10. X-Ray Powder Diffraction

X-ray powder patterns were obtained with a Debye-Scherrer and Guinier camera using  $Cu-K_{\alpha}$  radiation. Finely-powdered samples were loaded into 0.3 mm capillaries for the Debye-Scherrer experiments. In the Guinier experiments, crushed samples containing a trace of powdered Platinum as a reference were placed on sample discs containing a strip of transparent cellophane tape on the back side. X-ray d-spacings were determined from the exposed films with the aid of a Picker x-ray film viewer.

### 11. Single Crystal X-Ray Structure Determination

Many of the details of the theory and techniques used in the single crystal structure determination of Nb(DPM)<sub>4</sub> have been presented in several texts.<sup>31-33</sup> Only the general procedures used in the study are described here.

Air-stable, dark purple needles of Nb(DPM)<sub>4</sub> were recrystallized from a benzene-acetonitrile mixture. Two crystals were necessary to collect a complete set of intensity data due to decay of the initial crystal.

The compound was found to possess Laue symmetry m, from oscillation, equi-inclination Weissenberg, and precession photographic techniques. Systematic absences of the type, h0l, l = (2n+1), were found and the space group was identified as Pc with 4 molecules in the unit cell and 2 molecules per asymmetric unit. The density, as determined by the floatation technique in ethylene bromide-acetonitrile, is  $1.12 \text{ g-cm}^{-3}$ . The calculated density is  $1.12 \text{ g-cm}^{-3}$  based on the cell dimensions of:  $a = 22.30 \pm 0.05$ ,  $b = 11.86 \pm 0.02$ ,  $c = 19.58 \pm 0.05$  Å, and

30

 $\beta = 107.46 + 0.05^{\circ}$ . A complete set of intensity data was collected to a d-spacing of 1.0 Å (20 = 100°) using Cu K<sub> $\alpha$ </sub> radiation on a Picker Four Circle Automatic X-Ray Diffractometer controlled by a DEC 4K PDP-8 computer. The "wandering"  $\omega$  step scan procedure.<sup>34</sup> with balanced Ni-Co filters, was used to obtain 3667 independent, observable reflections (total data merged from 2 sets corresponding to the 2 crystals measured). Absorption, decay, and Lorentz-polarization corrections were applied to the intensities to convert them to  $F^2$  values on a relative scale. The Nb positions were derived from a sharpened three dimensional Patterson synthesis, and the remaining atoms were located subsequently by using Fourier methods. The Patterson and Fourier syntheses were performed with the "Two-and Three-Dimensional Crystallographic Fourier Summation Program" written by J. Gyildys at the Argonne National Laboratory and least squares refinement was accomplished with the "ANLFLS, a FORTRAN Crystallographic Least-Square Program" also written by J. Gvildys. Both programs were versions modified by R. L. Vandlen of MSU. Best least squares plane calculations were performed with a "Program B-125 (3600F) Least Squares Plane and Line Fitter" written at the Argonne National Laboratory. Bond distances and angles were calculated with the DISTAN program written by Dr. R. L. Bodner at Michigan State University. All computer computations were performed on the CDC 6500 at Michigan State University. The R factor,  $R = \frac{\Sigma | Fo - Fo |}{\Sigma Fo}$ , was reduced to 0.086 by the full matrix least squares refinement with unit weights for all atoms and anisotropic thermal parameters for the Nb and oxygen atoms.

#### IV. Results and Discussion

- A. Tantalum(V) and Niobium(V) Derivatives of Dipivaloylmethane
  - 1. Products Obtained From the Reaction of TaCl, and H(DPM).

In an effort to prepare an eight-coordinate Ta(V) complex with H(DPM), reactions of the metal pentachloride with the ligand were investigated. The choice of H(DPM) as the ligand was dictated by the greater degree of solubility imparted to chelates of this ligand than to chelates of other beta-diketones. Reaction products were typically yellow powders that were qualitatively characterized by their melting points, infrared spectra and nmr spectra. The compounds were readily hydrolyzable in both the solid state and in solution. In many cases, even under anhydrous conditions, decomposition to free ligand and other by-products occurred as solutions were aged. Because of these factors, reproducibility of results was a major challenge in this area of investigation.

A product with a chemical composition approximately corresponding to the empirical formula Ta(DPM)Cl<sub>4</sub> was obtained as a <u>precipitate</u> from the reaction of the anhydrous chloride and neat H(DPM) at a 1 to 5 molar ratio after a reaction time of 30 minutes at room temperature. The product is a bright yellow powder which is readily soluble in dichloromethane. Upon exposure to air for several hours, the compound hydrolyzes, as indicated by the evolution of HCl gas, to a white insoluble powder. The white solid shows no DPM ligand absorptions in the infrared spectrum. A white insoluble precipitate also forms when a dichloromethane solution of the compound is exposed to air for several hours. Although no elemental analysis was obtained for the hydrolysis product, it is postulated to be a tantalum oxychloride.

32

The elemental analysis of  $Ta(DPM)Cl_4$ , which is presented in Table I shows an appreciable negative deviation for chlorine. The possibility of contamination by oxo-complexes with a Ta-O-Ta or Ta=O formulation as described in Section II above (p.7) is unlikely because presence of an oxo-complex should cause a concomitant increase in the carbon content. Negative deviations of greater than 9% for chlorine analyses have also been reported by Syamal, et al.,<sup>16</sup> for the series of mixed chloroalkoxy-diketonates of Ta(V) and Nb(V) described in Section II above (p.8). The authors note that the negative deviations increased as the period of time that the complexes were subjected to a vacuum increased. No attempt was made to correlate drying time in vacuo to chlorine content in the case of the DPM derivatives discussed here. However, it should be noted that the mixed alkoxy complexes were isolated by rotary evaporation whereas the DPM complexes were filtered and dried as solids in vacuo. A possible cause for the low chlorine analyses may be due to erroneous chlorine analyses. The same sample of Ta(DPM)Cl, that analyzed for 25.22% chlorine (Galbraith) was also analyzed for 12.85% chlorine by the Spang Microanalytical Laboratory (Ann Arbor, Michigan). In addition, the same sample of Nb(DPM)Cl<sub>4</sub> that was analyzed for 29.48% chlorine by Crobaugh Laboratories (Cleveland, Ohio) was analyzed for 12.9 and 13.0% chlorine by Coors Laboratories (Golden, Colorado).

The solid state infrared spectrum of  $Ta(DPM)Cl_4$  is shown in Figure 4. The bands at 1576 and 1562 cm<sup>-1</sup> are assigned to the carbonyl stretching mode. This is well below the free ligand carbonyl bands which are observed above 1600 cm<sup>-1</sup> and shows that the DPM molecule is

33

# Table I

# Chemical Analyses for Products Obtained from the Reactions of TaCl<sub>5</sub> and NbCl<sub>5</sub> with Dipivaloylmethane

Compound	%C	<b>%</b> H	%C1	%M
Ta (DPM) C1 <sub>4</sub>	25.87	3.86	25.22	36.07
	(20.10)-	(3./8)	(28.05)	(35.74)
Ta (DPM) 2 <sup>C1</sup> 3	40.22	5.88		27.22
	(40.41)	(5.86)	(16.27)	(27.67)
N <b>d (dpm)</b> C1 <sub>4</sub>	31.76	4.98	29.48	22.68
	(31.61)	(4.58)	(33.93)	(22.23)
ND (DPM) 2 <sup>C1</sup> 3	46,96	6.94	14.26	17.86
	(46.70)	(6.77)	(18.80)	(16.42)

 $\frac{a}{2}$  Values in parentheses are calculated values.

Figure 4. Infrared spectrum of Ta(DPM)Cl<sub>4</sub> in **a** Nujol mull.



acting as a bidentate ligand. No evidence is present in the spectrum at 900 and 800 cm<sup>-1</sup> for a Ta = 0 or Ta-O-Ta formulation, respectively (see Section II), and a strong broad band at 350 cm<sup>-1</sup> is assigned to overlapping Ta-Cl and Ta-O modes.<sup>9,35,36</sup>

The behavior of Ta(DPM)Cl<sub>4</sub> in solution under anhydrous conditions was investigated by means of nmr spectroscopy. The nmr spectrum of the compound in dichloromethane is shown in Figure 5. The resonances at  $\tau$  8.72 and  $\tau$  3.43 are due to the <u>t</u>-butyl and gamma protons of the ligand, respectively. No decomposition products were observed after the solution was allowed to age 4 days.

A second product was isolated from the 1:5 TaCl<sub>5</sub> to H(DPM) reaction mixture by allowing the mother liquor to age at room temperature for one hour. This product was not analyzed, but its proton nmr spectrum (Figure 6) contained several interesting features. In addition to resonance lines at  $\tau$  8.72 and 3.43 which are characteristic of Ta(DPM)Cl<sub>2</sub>, a much more intense set of lines is observed at  $\tau$  8.84 and 3.80. Closer examination of the t-butyl region at a 50 cycle sweepwidth reveals the presence of a shoulder at  $\tau$  8.85 which is probably due to the presence of free ligand. The gamma proton resonance of the free ligand which should appear at  $\tau$  4.23 is too weak to be observed. After the solution ages two days, the free ligand resonances have grown and the gamma proton resonance at  $\tau$  4.23 is clearly visible. The presence of the new peaks at  $\tau$  8.84 and 3.80 in the initial nmr spectrum is apparently due to a product consistent with a higher degree of ligand substitution, since the position of the peaks coincides with the resonances of the Ta(DPM)<sub>2</sub>Cl<sub>3</sub> complex to be discussed below. This result is not surprising

Figure 5. Room temperature nmr spectra of Ta(DPM)Cl<sub>4</sub> in dichloromethane: (1) <u>t</u>-butyl resonance at 50 cycle sweepwidth; (2) -CH= ( $\pi$  3.43) and <u>t</u>-butyl ( $\pi$  8.72) resonances at 500 cycle sweepwidth.

2 0 (2) Ξ

Figure 5

Ta (DPM)Cl<sub>4</sub> synthesis: (1) <u>t</u>-butyl resonances at 50 cycle sweepwidth; (2) -CH= ( $\tau$  3.80) and <u>t</u>-butyl ( $\tau$  8.72, 8.84) resonances at 500 cycle sweepwidth; (3) <u>t</u>-butyl resonance at 50 cycle sweepwidth after the solution has aged for 3 days. Room temperature nmr spectra of a dichloromethane solution of the product isolated from the mother liquor of the Figure 6.



Figure 6

since the mother liquor contains mainly free ligand. Furthermore, a correlation exists between the reaction time and the intensity of the  $\tau$  8.84 line in the crystallized product. For a reaction time of 24 hours, the mmr spectrum of the product shows only a trace of the low field <u>t</u>-butyl resonance at  $\tau$  8.72. The product crystallized from the mother liquor after it had aged <u>ca</u>. 1 day reveals only a high field resonance at  $\tau$  8.84.

In view of the probable existence of a higher substitution product in the 1:5  $TaCl_5$  to H(DPM) reaction mixture, the reaction was repeated at 100° in order to obtain higher yields of the compound. The carbon, hydrogen, and tantalum analyses (see Table I) are in agreement with the formulation  $Ta(DPM)_2Cl_3$ . The product is a pale yellow powder and exhibits a greater degree of solubility in dichloromethane than  $Ta(DPM)Cl_4$ . This is consistent with a higher degree of substitution on the metal atom. As in the case of  $Ta(DPM)Cl_4$ , the compound forms a white powder upon its exposure in the solid state or in solution to atmospheric moisture.

The molar conductivity at 26° of  $Ta(DPM)_2Cl_3$  is 54 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup> in nitromethane at a concentration of 3.30 x 10<sup>-4</sup> <u>M</u> and 12.4 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup> in nitrobenzene at a concentration of 1.08 x 10<sup>-3</sup> <u>M</u>. The 1:1 electrolyte tetraethylammonium iodide exhibits a molar conductivity of 97 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup> at 20° in nitromethane at a concentration of 5 x 10<sup>-4</sup> <u>M</u>.<sup>37</sup> The electrolyte [Ti(acac)<sub>3</sub>)][SbCl<sub>6</sub>] in nitrobenzene is reported to have a molar conductance of 26.2 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup> at infinite dilution.<sup>5</sup> Thus Ta(DPM)<sub>2</sub>Cl<sub>3</sub> appears to be <u>ca</u>. 50% dissociated in nitrobenzene and nitromethane. This should be regarded as a minimum

42

value, since independent evidence suggests that the compound undergoes decomposition upon aging in solution at room temperature (see below). As the decomposition proceeds, the conductivity decreases. For example, after the solution of  $Ta(DPM)_2Cl_3$  in nitromethane had aged for 5 days, the molar conductance decreased from 54 to 16 ohm<sup>-1</sup> cm<sup>2</sup>mole<sup>-1</sup>.

In nitrobenzene solution, the molecular weight of  $Ta(DPM)_2Cl_3$ corresponds to that expected for a monomer. However, the freezing point depression of the nitrobenzene solution decreased as a function of time. This is consistent with a decrease in the number of dissociated species in solution as decomposition proceeds.

The following equilibrium is suggested to account for the conductivity and molecular weight data:

2 Ta(DPM)<sub>2</sub>Cl<sub>3</sub> 
$$\neq$$
 Ta(DPM)<sub>4</sub><sup>+</sup> + TaCl<sub>6</sub><sup>-</sup>

Heckley and Holah<sup>38</sup> have reported complexes of the type,  $M(dtc)_2 X_3$ , where M is Ta(V) and Nb(V), X is Cl and Br and dtc is the N,N-diethyldithiocarbamate anion. The authors state that on the basis of preliminary conductivity, infrared, and nmr data, the compounds are probably ionic and could possibly be formulated as  $[M(dtc)_4][MX_6]$ . No conductivity or nmr data were reported but a strong band at 320 cm<sup>-1</sup> was assigned to the Ta-Cl stretching mode. Other examples of previously reported eightcoordinate cations of the type  $M(chel)_4^+$  are reported by Muetterties and Wright.<sup>39</sup> The ligand, tropolone, was found to form this cation with both Nb(V) and Ta(V). Although another equilibrium involving the dissociation of a chloride ion to form a six-coordinate cation, Ta(DPM)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, may also be present, there is no evidence in the literature for the existence of such a cation for beta-diketonate ligands.

The solid state infrared spectrum of Ta(DPM)<sub>2</sub>Cl<sub>3</sub> is shown in Figure 7. Complete chelation is again indicated by carbonyl stretching bands at 1578 and 1568 cm<sup>-1</sup>. A strong broad absorption, at 338 cm<sup>-1</sup>, similar to the band in the Ta(DPM)Cl<sub>4</sub> spectrum (see Figure 4), is again assigned to Ta-O and Ta-Cl stretching modes. Earlier infrared studies of a series of hexachlorotantalate salts have led to the assignment of a strong, broad absorption with maxima ranging from 307 to 333  $\rm cm^{-1}$  to the  $v_3$  Ta-Cl stretching mode.<sup>40,41</sup> The shift of the Ta-Cl band from  $350 \text{ cm}^{-1}$  for Ta(DPM)Cl<sub>4</sub> to 338 cm<sup>-1</sup> for Ta(DPM)<sub>2</sub>Cl<sub>3</sub> brings the absorption in the vicinity of the above  $v_3$  range and may suggest the existence of [Ta(DPM)<sub>4</sub>][TaCl<sub>6</sub>] in the solid state. However, the low energy shift of 12  $\rm cm^{-1}$  is also consistent with an increase in coordination number of Ta from six to seven. Figure 8 shows the nmr spectrum of Ta(DPM)<sub>2</sub>Cl<sub>3</sub> at room temperature. One <u>t</u>-butyl resonance at  $\tau$  8.84 and one gamma proton resonance at  $\tau$  3.80 are present. The <u>t</u>-butyl resonance occurs <u>ca</u>. 0.1 ppm upfield of the <u>t</u>-butyl resonance for  $Ta(DPM)Cl_4$  (see Figure 5). If equal amounts of neutral seven-coordinate species and the eightcoordinate cation were present, as described in the equilibrium on p. 43, at least two t-butyl and gamma proton resonances would be predicted to occur. Furthermore, the positive charge on the cation would effect a downfield shift relative to the neutral Ta(DPM)C14 species. The observed upfield shift suggests that the equilibrium favors the sevencoordinate species in dichloromethane. In view of the lower polarity of dichloromethane compared to nitrobenzene, the solvent in which both conductivity and molecular weight data were obtained, this result would

Figure 7. Infrared spectrum of Ta(DPM)<sub>2</sub>Cl<sub>3</sub> in a Nujol mull.

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Room temperature mmr spectra of Ta(DPM)  $_{2}$ Cl<sub>3</sub> in dichloromethane: (1) <u>t</u>-butyl resonance at 50 cycle sweepwidth; (2) -CH= ( $\tau$  3.80) and <u>t</u>-butyl ( $\tau$  8.84) resonances at 500 cycle sweepwidth. Figure 8.



Figure 8

be expected. Based on all possible seven-coordinate stereoisomers arising from a pentagonal bipyramid, capped octahedron, capped trigonal prism, and tetragonal base-trigonal base, only the C<sub>2v</sub> trigonal prism, with a chlorine capping, a rectangular face and the three ligands spanning equivalent rectangular edges, would account for the observation of one t-butyl line, in the absence of ligand exchange. The dichloromethane solution was cooled to  $-60^{\circ}$ C, but no new resonance or line-broadening was observed. Consequently, there are two possible explanations for the nmr spectrum of the complex in dichloromethane, if one assumes that the fortuitous existence of only the  $C_{2v}$  isomer is unlikely. First, an intramolecular ligand exchange process may be invoked which would average the t-butyl environments of the seven-coordinate isomer. This explanation would apply if an appreciable amount of eight-coordinate cation was not present in solution. However, if one does assume the presence of an appreciable amount of the cation, then an intermolecular exchange process must be invoked to explain the presence of only one t-butyl line. In this case, the line would represent an average of the t-butyl environments of both seven- and eight-coordinate species. In either case, the spectrum at -60°C indicates a rapid exchange process.

Appreciable decomposition of  $Ta(DPM)_2Cl_3$  complex in dichloromethane was observed in the course of the nmr studies. After 40 minutes of aging, free ligand peaks at  $\tau$  8.85 and 4.23 begin to appear, and after 4 months, they grow to an intensity equivalent to that of the original <u>t</u>-butyl and gamma proton resonances. An identification of the Ta decomposition product was not attempted. 2. The Reactions of NbCl, and H(DPM).

NbCl<sub>5</sub> and neat H(DPM) react very vigorously with evolution of HCl at room temperature. In order to control the reaction at a convenient rate, the reagents were mixed in the presence of a solvent, dichloromethane. At a molar ratio of NbCl<sub>5</sub> to H(DPM) of 1:1.1, an orange solution was obtained after a 30 minute reaction period. Addition of hexane to the solution afforded a red-orange powder. The C, H, and Nb analyses for the product were in acceptable agreement with Nb(DPM)Cl<sub>4</sub> (see Table I), but as in the case of the analogous Ta derivative, the chlorine analysis was anomalously low.

The infrared spectrum of Nb(DPM)Cl<sub>4</sub> in solid state is shown in Figure 9. The features of the spectrum are qualitatively similar to the spectrum of the Ta derivative (see Figure 5). The diketonate ligand is chelated, as evidenced by the positions of the C=O stretching modes. The band due to overlapping frequencies for Nb-Cl and Nb-O vibrations is positioned <u>ca</u>. 10 cm<sup>-1</sup> higher in energy than the analogous band for the Ta derivative.

 $Nb(DPM)Cl_4$  in the solid state rapidly hydrolyzes, upon exposure to atmospheric moisture, to form HCl and a pale yellow residue. The residue, however, contains coordinated DPM as indicated by infrared spectroscopy. The intensity of the 360 cm<sup>-1</sup> band is markedly decreased on hydrolysis, as expected for the loss of chlorine.

The nmr spectrum of Nb(DPM)Cl<sub>4</sub> in dichloromethane is shown in Figure 10. Two <u>t</u>-butyl resonances are clearly resolved at  $\tau$  8.72 and 8.69, and the presence of a third line is suggested by a shoulder on the low-field side of the  $\tau$  8.72 line. Two -CH= lines are present at  $\tau$  3.38

50

Figure 9. Infrared spectrum of Nb(DPM) $CI_4$  in a Nujol mull.





Room temperature nmr spectra of Nb(DPM)Cl<sub>4</sub> in dichloromethane: (1) -CH= (spectrum amplitude = 12.5) and <u>t</u>-butyl (spectrum amplitude = 2.5) resonances at 50 cycle sweepwidth; (2) -CH= ( $\tau$  3.38, 3.47) and <u>t</u>-butyl ( $\tau$  8.69, 8.72) resonances at 500 cycle sweepwidth; (3) -CH= and <u>t</u>-butyl resonances at 50 cycle sweepwidth after the solution has aged for 24 hrs. Figure 10.



Figure 10

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and 3.47. The lines at  $\tau$  8.72 and 3.47 are assigned to the complex; the remaining lines are probably due to decomposition products. For example, allowing the solution to age at room temperature for 24 hours causes the line at  $\tau$  8.69 to increase in intensity. The decomposition observed by nmr spectroscopy is consistent with the fact that Nb(DPM)Cl<sub>4</sub> cannot be recrystallized from dichloromethane.

Shown in Figure 11 is the nmr spectrum of Nb(DPM)Cl<sub>4</sub> after it had been allowed to hydrolyze in the solid state by exposure at room temperature to atmospheric moisture. The lines at  $\tau$  8.84 and 3.80 are identical in position to those observed for Ta(DPM)<sub>2</sub>Cl<sub>3</sub>, and the lines at  $\tau$  8.85 and 4.23 are those expected for free ligand. Thus it appears that the hydrolysis of Nb(DPM)Cl<sub>4</sub> leads in part to formation of H(DPM) and the higher substitution product Nb(DPM)<sub>2</sub>Cl<sub>3</sub>, whereas the hydrolysis of Ta(DPM)Cl<sub>4</sub> forms an oxide or oxychloride not containing DPM.

The existence of a higher substitution complex of the type, Nb(DPM)<sub>2</sub>Cl<sub>3</sub>, was also suggested by the appearance of lines at  $\tau$  8.84 and 3.80 in the nmr spectrum of a solution of Nb(DPM)Cl<sub>4</sub> and free H(DPM) in dichloromethane after it had been allowed to age 13 days at room temperature. As noted above, these chemical shifts are identical to those observed for Ta(DPM)<sub>2</sub>Cl<sub>3</sub>.

The reaction of NbCl<sub>5</sub> and H(DPM) at a molar ratio of 1 to 5 in dichloromethane at room temperature afforded an orangered crystalline product with a carbon and hydrogen content near that expected for Nb(DPM)<sub>2</sub>Cl<sub>3</sub> (see Table I). The chlorine analysis is characteristically low, and the Nb content is somewhat high. The presence of an oxo impurity is indicated by a band at 807 cm<sup>-1</sup> in the infrared

state: (1) <u>t</u>-butyl resonances at 50 cycle sweepwidth; (2)  $-CH=(\tau 3.80)$  and <u>t</u>-butyl ( $\tau 8.72$ , 8.84, 8.85) resonances at 500 cycle sweepwidth; the -CH= line at  $\tau 3.80$  was observed at a 50 cycle sweepwidth. Room temperature nmr spectra of Nb(DPM)Cl\_4 in dichloromethane after the compound has been allowed to hydrolyze in the solid Figure 11.

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Figure 11

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spectrum of the product shown in Figure 12. A band in this region  $(825 \text{ cm}^{-1})$  for NbO(ACAC)<sub>2</sub>Br has been assigned by Djordjevic<sup>10</sup> to a Nb-O-Nb stretching mode. The oxo impurity probably is a decomposition product of Nb(DPM)<sub>2</sub>Cl<sub>3</sub>, perhaps formed by abstraction of oxygen from the diketonate ligand. Oxygen abstraction by Nb and Ta has been observed previously with various solvents and donor ligands such as phosphine oxides, <sup>42,43</sup> sulphoxides, <sup>44</sup> and beta-diketonates.<sup>11b</sup> The infrared spectrum also contains a strong, broad band at 339 cm<sup>-1</sup> which is assignable to overlapping Nb-Cl and Nb-O stretching frequencies. As in the case of Ta(DPM)<sub>2</sub>Cl<sub>3</sub>, the possibility of the ionic formulation,  $[Nb(DPM)_4][NbCl_6]$ , is suggested as the Nb-Cl stretch lies just outside the range of 331-335 cm<sup>-1</sup> for the v<sub>3</sub> vibration of the NbCl<sub>6</sub><sup>-</sup> ion.<sup>40,41</sup>

The reaction of NbCl<sub>5</sub> and H(DPM) in dichloromethane at room temperature was also investigated at molar ratios of 1:3 and 1:10. The 1:3 reaction mixture, after a reaction time of 4 hours, afforded a mixture of Nb(DPM)Cl<sub>4</sub> and Nb(DPM)<sub>2</sub>Cl<sub>3</sub> as indicated by elemental analyses and nmr spectroscopy. After a reaction of 26 hours, the 1:3 mixture afforded primarily Nb(DPM)<sub>2</sub>Cl<sub>3</sub>: Found; 46.60% C, 7.06% H; Calc'd, 46.70% C, 6.77% H; nmr in CH<sub>2</sub>Cl<sub>2</sub>,  $\tau$  8.84 and 3.80 with relative intensities of 18:1. The nmr spectrum of the 1:10 reaction mixture indicated the presence of only Nb(DPM)Cl<sub>4</sub> after a 20 minute reaction time, approximately equal amounts of Nb(DPM)Cl<sub>4</sub> and Nb(DPM)<sub>2</sub>Cl<sub>3</sub> after 3 hours, and only Nb(DPM)<sub>2</sub>Cl<sub>3</sub> after 21 hours. The presence of excess free ligand in the reaction mixture apparently retards the decomposition of Nb(DPM)<sub>2</sub>Cl<sub>3</sub>, as well as Nb(DPM)Cl<sub>4</sub>. Figure 13 illustrates the rapid decomposition of Nb(DPM)<sub>2</sub>Cl<sub>3</sub> in dichloromethane in the absence of free ligand. After
Figure 12. Infrared spectrum of Nb(DPM) $_2$ Cl<sub>3</sub> in a Nujol mull.



Figure 12

Room temperature nmr spectra of Nb(DPM)  $_{2}$ Cl<sub>3</sub> in dichloromethane: (1) <u>t</u>-butyl resonances at 50 cycle sweepwidth; (2) -CH= ( $\pi$  3.80) and <u>t</u>-butyl ( $\pi$  8.71, 8.84) resonances at 500 cycle sweepwidth; (3) <u>t</u>-butyl ( $\pi$  8.71, 8.84 with low field shoulder indicated by arrow, 8.85) at 50 cycle sweepwidth and -CH= ( $\pi$  3.67, 3.80, 4.23 as indicated by arrows) resonances at 500 cycle sweepwidth after the solution has aged for 3 days. Figure 13.

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the solution has aged only 10 minutes an impurity line appears at  $\tau$  8.71 and another appears as a low field shoulder on the  $\tau$  8.84 line. After three days both lines increase significantly in intensity and 3 -CH= lines can be observed at  $\tau$  4.23 and  $\tau$  3.67 and  $\tau$  3.80. The  $\tau$  8.85 and 4.23 lines are characteristic of free H(DPM) and the  $\tau$  8.84 and 3.80 lines may be due to Nb(DPM)<sub>2</sub>Cl<sub>3</sub>.

The reaction of NbCl<sub>5</sub> with H(DPM) was also conducted in the presence of triethylamine at room temperature at a metal to ligand molar ratio of 1:4.1 for 20 hours. In addition to the by-product triethylamine-hydrochloride, a product, whose infrared and nmr spectrum was identical to the Nb(DPM)<sub>2</sub>Cl<sub>3</sub> complex above, was isolated. Thus, in spite of the presence of base and a long reaction time, further substitution of ligand for chlorine was not achieved.

### 3. The Reaction of Nb(DPM), and Cl<sub>2</sub>.

In an effort to prepare the chloride salt of the eightcoordinate cation, Nb(DPM)<sub>4</sub><sup>+</sup>, and verify the possible existence of the cation in the above syntheses, Nb(DPM)<sub>4</sub> was oxidized by means of anhydrous, oxygen-free chlorine. However, instead of the desired salt, a compound with the stoichiometry,  $[NbOCl_2(DPM)]_x$ , was prepared. The progress of the preparation of this oxo-complex was monitored by esr spectroscopy. Immediately upon addition of the first aliquot of chlorine solution, the deep purple (almost black) solution became bluegreen and remained this color when a sample was removed 40 minutes later. The presence of Nb(IV) was still indicated by a 10 line esr spectrum, and only after the solution became orange in color (3 hours later), was the complete absence of the signal observed. The golden yellow solid that was isolated from the reaction mixture was sparingly soluble in benzene (ca. 0.001 g/ml) and dichloromethane, and insoluble in either, acetone, and carbon tetrachloride. The poor solubility properties of the compound are, of course, consistent with a polymeric formulation. The elemental analysis was also in agreement with the suggested formula-The infrared spectrum of the solid is shown in Figure 14. The tion. striking feature of the spectrum is the presence of a very strong, broad band at 802 cm<sup>-1</sup>. This is assigned to a Nb-O-Nb stretching mode. The two strong, broad bands at 350  $\text{cm}^{-1}$  and 380  $\text{cm}^{-1}$  are assigned to the Nb-Cl stretching mode (the former band likely overlaps a Nb-O (ligand) stretching mode). Both assignments are consistent with those made by Djordjevic for NbOCl<sub>2</sub>ACAC which was prepared from NbOCl<sub>2</sub>.<sup>10</sup> In the ACAC complex, a strong, broad band at 820 cm<sup>-1</sup>, and a strong broad doublet at 355 cm<sup>-1</sup> and 379 cm<sup>-1</sup> were assigned to the Nb-O-Nb and Nb-C1 modes, respectively. It is interesting to note that even the lower energy band at 350  $\rm cm^{-1}$  for the DPM complex is still at a higher energy than the band at 338 cm<sup>-1</sup> assigned to the Nb-Cl stretching mode for Nb(DPM)<sub>2</sub>Cl<sub>3</sub>.

A weak nmr spectrum (due to low solubility) was obtained in dichloromethane. A multiplet of broad resonances was observed in the <u>t</u>-butyl region with at least 5 peaks resolvable at  $\tau$  8.82, 8.77, 8.73, 8.72 and 8.70. This result is not unexpected since numerous isomers are possible even when x is only 2. The nmr solution was too dilute to observe -CH= resonances.

The preparation of this compound appears to be yet another example of the tendency of niobium to abstract oxygen from a ligand (see p. 58).

64

Figure 14. Infrared spectrum of  $[NbOC1_2(DPM)]_x$  in a Nujol mull.



Figure 14

66

#### 4. Summary.

The preparation and characterization of a series of new Nb(V) and Ta(V) complexes containing the beta-diketonate ligand, H(DPM), have been described. Complexes of the type, M(DPM)C14 and M(DPM)2C13, were obtained by allowing the metal pentahalide to react with neat H(DPM) (for M = Ta) and with H(DPM) in presence of dichloromethane as a solvent (for M = Nb). The complexes of the  $M(DPM)Cl_{1}$  series exhibit similar infrared and nmr spectra, but the Nb derivative appears to be much less stable in solution in the absence of free ligand. The above spectral similarities and solution behavior also hold true for the M(DPM)<sub>2</sub>Cl<sub>2</sub> series. Conductivity data indicate that Ta(DPM),Cl, is highly dissociated in nitrobenzene and nitromethane solution: a dissociation equilibrium involving Ta(DPM)<sup>+</sup><sub>4</sub> and TaCl<sub>6</sub> is suggested. The constitution of the M(DPM)<sub>2</sub>Cl<sub>3</sub> complexes in the solid state may correspond to an eightcoordinate cationic salt, [M(DPM),][MC1,]. Evidence to support this formulation is based primarily on the presence of a band in the ir spectrum near that expected for  $TaCl_6$ . The inability to obtain a higher substitution product in the presence of a large excess of ligand (ligand to metal ratio of 10 to 1) or in the presence of base also suggests the ionic constitution of the complex. An attempt to prepare the Nb(DPM) $_{4}^{+}$  cation by reaction of Nb(DPM) $_{4}$  and anhydrous, oxygen-free Cl<sub>2</sub> in CCl<sub>4</sub>, led to abstraction of ligand oxygen by the metal and the formulation of a polymeric oxo complex, [NbOC1, (DPM)].

67

B. Preparation and Characterization of Tetrakis(dipivaloylmethanato)niobium(IV)

The reaction of NbCl<sub>4</sub> and H(DPM) was conducted in acetonitrile in the presence of triethylamine. The procedure is analogous to that used by Deutcher and Kepert<sup>11a</sup> in their preparation of other niobium(IV) diketonates. Based on melting point, infrared, and esr data, the same product was obtained upon varying the ligand to metal ratio from 10:1 (reaction time = 46 hours) to 4:1 (reaction time = 3 hours). In both cases, the yield was between 50 and 60%.

An nmr spectrum of a dichloromethane solution of the dark purple (almost black) solid showed no free ligand resonances and elemental analyses were obtained without prior recrystallization. The compound, however, does form opaque, dark purple needles when recrystallized in benzene-acetonitrile. In the solid state, Nb(DPM)<sub>4</sub> apparently does not undergo any decomposition when stored under anhydrous, oxygen-free conditions, as judged by comparison of the ir spectrum of a fresh sample and one which had aged over 1 year. However, after several months of exposure to air, the solid becomes coated with a white film, suggesting that oxidation and/or hydrolysis occurs.

The compound is extemely soluble in most nonpolar organic solvents. Deep purple solutions are formed which become yellow upon exposure to air for several days. The infrared spectrum of a yellow dichloromethane solution shows a strong broad band at 800 cm<sup>-1</sup> as well as bands at 1700 and 1730 cm<sup>-1</sup>. The same spectrum is obtained when oxygen is bubbled into a dichloromethane solution of Nb(DPM)<sub>4</sub>. The band at 800 cm<sup>-1</sup> suggests an oxidation to some type of bridging oxoniobium(V) species (see

Section II). The bands at 1700 and 1730 cm<sup>-1</sup> suggest a Nb by-product that has a free carbonyl function or, perhaps, the by-product is free HDPM.

Deutscher and Kepert<sup>11b</sup> report that Nb(ACAC)<sub>4</sub> also decomposes in wet solvents. No mention is made of the behavior in anhydrous solvents, but one must infer that the complex is stable, since solution spectral data in toluene are reported. It is interesting to note that the authors report that Nb(ACAC)<sub>4</sub> in the solid state decomposes rapidly in air, in contrast to Nb(DPM)<sub>4</sub>. Thus with the successful synthesis of such an unusually stable Nb(IV) beta-diketonate, a stereochemical investigation was eagerly undertaken.

The infrared spectrum of Nb(DPM)<sub>4</sub> is shown in Figure 15. Since no absorptions are observed in the carbonyl region  $(1600-1720 \text{ cm}^{-1})$  of the free ligand, chelation by the beta-diketonate ligand is indicated. The carbonyl stretching modes are assigned at 1585 cm<sup>-1</sup>, 1562 cm<sup>-1</sup>, and 1410 cm<sup>-1</sup> which is consistent with previously reported assignments for transition metal beta-diketonates.<sup>35,36</sup> The low energy portion of the spectrum shows two absorptions at 352 cm<sup>-1</sup>, and 285 cm<sup>-1</sup> which are assigned to Nb-0 (ligand) stretching modes. These assignments are consistent with the analysis of the low energy portion of the infrared spectra for the niobium(V) complexes described in section IV-A.2.

The molecular weight was determined in benzene because the hydrolysis of Nb(DPM)<sub>4</sub> appeared to occur less rapidly in this solvent than in other solvents. The observed value of 777 g/mole is in agreement with the value expected for a monomer (826). The molar conductance  $(0.0901 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ , 2.93 x  $10^{-3}$  M) is consistent with a non-electrolyte in dichloromethane. Fay and Lowry<sup>45</sup> report  $\Lambda$  to be 0.092 Figure 15. Infrared spectrum of  $Nb(DPM)_4$  in a Nujol mull.





 $(5 \times 10^{-3} \text{ M})$  for the non-electrolyte, Ti(ACAC)Cl<sub>2</sub>, and 40 (5 x  $10^{-3} \text{ M})$ for the 1:1 electrolyte,  $[Si(ACAC)_3]$ Br, in the same solvent. A time dependence is observed for the conductivity of Nb(DPM)<sub>4</sub> in dichloromethane. The initial value of  $\Lambda$  reported above was observed 7 minutes after the preparation of the solution. After aging for 15 minutes,  $\Lambda$ increased to 0.169 ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>, after 50 minutes to 0.326, and after 9 days the deep purple solution had changed to a yellow-brown color, and  $\Lambda$  had increased to 13.3. After 10 days of aging, the color became yellow, and  $\Lambda$  had leveled off, as indicated by a value of 13.2. Thus, the time dependence was due to oxidation, and possibly hydrolysis, upon aging in the conductivity cell (see ir data above). The value of 6.88  $(1.11 \times 10^{-4} \text{ M})$  reported for Nb(DPM)<sub>4</sub> in nitrobenzene was observed after the solution had aged for 60 minutes and hydrolysis had likely already occurred to a significant extent.

The room temperature effective magnetic moment of Nb(DPM)<sub>4</sub> was determined by both the Evans and Faraday technique. In view of the comparable magnitudes of the paramagnetic and diamagnetic molar susceptibilities (see Section III), the observed values of 2.1 B.M. (Evans) and 1.9 B.M. (Faraday) are consistent with one unpaired electron.

Consequently, all of the above preliminary experiments (infrared, molecular weight, conductance, and magnetic susceptibility) are consistent with a discrete molecular eight-coordinate formulation for Nb(DPM)<sub>4</sub> and a +4 oxidation state for the Nb atom.

C. The X-Ray Structure Determination of Nb(DPM)

Nb(DPM)<sub>4</sub> crystallizes in the space group, Pc, with four molecules in the unit cell and two molecules in the asymmetric unit.

The experimental density is  $1.12g \text{ cm}^{-3}$  ( $\rho_{\text{calc.}} = 1.12g \text{ cm}^{-3}$ ) and the unit cell dimensions are as follows:

a = 22.30 
$$\pm$$
 0.05 Å  
b = 11.86  $\pm$  0.02 Å  
c = 19.58  $\pm$  0.05 Å  
 $\beta$  = 107.46  $\pm$  0.05°

Table IIA and B lists the final atomic coordinates, thermal parameters, and electron density of the 106 atoms comprising the two molecules in the asymmetric unit. The observed and calculated structure factors are listed in Appendix B. Tables III-VII list the bond distances and angles of both molecules. The interior angles of planes of the Nb(DPM)<sub>4</sub> polyhedron are listed in Appendix C. Figures 16a and b and 17a and b illustrate the electron density contour maps of the two molecules obtained from the observed Fourier map with an R factor of 0.086.

The motions associated with the transformation of a cube into a  $D_{4d}$  square antiprism or a  $D_{2d}$  dodecahedron are shown in Figure 18. The structure of Nb(DPM)<sub>4</sub> appears to approximate the square antiprismatic geometry. A convenient perspective for viewing the square antiprism is along the fourfold rotation axis ( $C_4$ ). This view of the two molecules comprising the asymmetric unit of the unit cell (molecules A and B) is shown in Figure 19. It is clear from this representation that the structure may be visualized as a "propeller" or "pinwheel" with idealized  $D_4$  symmetry. However, because the dodecahedron is so closely related to a square antiprism<sup>1-3a,4</sup> (a square antiprism with puckered square planes may be viewed as a dodecahedron), it is necessary to consider the Nb(DPM)<sub>4</sub> structure in terms of the most closely related dodecahedral isomer(s) to unambiguously establish it as an idealized  $D_4$  square

								7		
					Molecule A	-1				
Atom Number	×	y	N	β <sub>11</sub>	<sup>8</sup> 22	β <sub>33</sub>	β <sub>12</sub>	<sup>8</sup> 13	<sup>8</sup> 23	Ŕ
Nb	000145	.369707	.007956	.002352	.009130	.004063	.00009	.000191	000034	
01	.086488	.429671	.085016	.002680	.009607	.004176	.000803	.000798	.000414	
02	018083	.506851	.069271	.002275	.005160	.005185	.000353	.001045	.00009	
03	057937	.310187	.066783	.003514	.009119	.003660	.000006	000426	001926	
04	.039997	.237014	.072055	.003788	.006694	.005968	.000743	.000771	.000758	
05	.018640	.509284	048755	.003299	.011008	.002739	.001267	000253	.001273	
90	091724	.419880	056328	.002086	.009838	.002515	000142	.000150	000267	
07	041662	.225093	059366	.002181	.008895	.003894	.000437	.000523	000401	
08 1	.069381	.315905	039601	.001173	.010891	.003509	.000553	.000274	001863	
c1-1 <sup>-</sup>	.125561	.503056	.080539							4.822
C2-1	.119699	.580091	.016312							6.199
C3-1	.063369	.589112	043977							5.047
C4-1	.059724	.657070	108098							7.771
C5-1	015126	.723384	110474							7.896
C6-1	.050482	.599501	174147							9.729
C7-1	.101950	.755630	089779							10.042
C8-1	.182021	.520854	.151464							6.707
C9-1	.222583	.408502	.143728							7.849
C10-1	.165982	.511915	.209260							8.107
C11-1	.224357	.611962	.138769							11.642
c1-2	061874	.575493	.054207							5.791
C2-2	109169	.591724	007045							4.668
C3-2	123931	.513005	056728							5.984
C4-2	186336	.507757	121013							6.340

Table II(A)

Final Atomic Coordinates<sup>a</sup> and Thermal Parameters for Nb(DPM)<sub>1</sub>

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	£	•	8.419	9.616	922.6	4°0/0	7.0/2 11 252	7.728	7.003	7.317	5.190	6.880	12.377	8.884	9.258	5.823	10.047	9.623	760.0	/21.0		4-814	7.286	7.860	10.459	9.321	6.336
	8	^23																									
		713																									
	8.0	712																									
nt'd)	8000	733																									
II (A) (co	<u>Baa</u>	~22																									
Table	8.	111,																									
	N	1	101268	140869	19432/	100011.	110600.	.156720	.048868	008937	054820	119993	103991	190583	114615	.107331	.106407	.116/28	.102234	9645/0°	045/10.	U38140	095112	080142	164043	068692	.137618
	^		.436270	.641925	101604°	770/00.	.104009	.690823	.225610	.155759	.162764	.071425	041273	.146559	.010418	.215479	.337367	.10199/	2/2602.	.LJ4435	6T/0CT.	101652.	.240236	.132620	.214332	.322130	.077543
	×		233902	206187	C/700T	020200 -	00/039 081457	.012609	103553	112953	078607	108871	123704	109639	038812	136108	177644	10440UZ	007060	.091435	C6C0TT.	• T04984	.143385	.185848	.092899	.192180	.092566
	Atom	Number	C5-2	C6-2	7-70		2-67 C10-2	C11-2	c1-3	C2-3	C3-3	C4-3	C5-3	C6-3	c7-3	C8-3	C9-3			C1-4	C2-4	5.0-4 0.0	C4-4	C5-4	C6-4	C7-4	C8-4

	ß	2.884 1.974 1.707										5.192	6.851	6.014	.1.968	.3.776	.2.759	2.788	6.215	6.646	7.620	9.358
	<sup>8</sup> 23			.000472 - 000013	001275	000387	000850	000744	000125	002181	.001212				-	Г	Г	1				
	<sup>8</sup> 13			.000338	.000808	.000944	.001727	.000134	000437	000177	.000618											
	<sup>8</sup> 12			000038	000960	.001396	.000584	.000095	.000704	000437	.002024											
	<sup>6</sup> 33			.003389 003437	.002791	.003799	.004074	.003483	.004938	.003081	.004130											
Molecule A	<sup>8</sup> 22		Molecule B	.008386	.009813	.004800	.010140	.009240	.008745	.007308	.013058											
	β11			.002309	.002509	.003619	.002280	.002228	.000395	.002710	.001821											
	N	.167398 .142274 .198023		.507808 569674	.573851	.572999	.572413	.448201	.447325	.447592	.445255	.559422	.504504	.445400	.402897	.396502	.333066	.372626	.627268	.695850	.615197	.623727
	Y	.058221 .006668 .131771		.082921 140603	.221782	.024266	056938	.220988	.135197	053794	.032972	.226096	.300952	.295177	.448380	.443372	.340914	.422470	.215842	.239621	.114085	.337012
	×	.046257 .160705 .146753		.499654 590133	.487515	.444487	.548716	.509828	.407690	.456082	.560234	.629198	.613908	.552436	.563661	.498027	.509113	.596626	.692686	.675492	.728060	.724390
	Atom Number	C10-4 C10-4 C11-4		<del>ୟ</del>	02	03	04	05	90	07	08	C1-1	C2-1	C3-1	C4-1	C5-1	C6-1	C7-1	C8-1	C9-1	C10-1	c11-1

Table II(A) (cont'd)

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				Table	II(A) (co	nt'd)				
					Molecule B					
Atom Number	×	Ŷ	N	β <sub>11</sub>	<sup>8</sup> 22	β <b>3</b> 3	β <sub>12</sub>	β <sub>13</sub>	<sup>β</sup> 23	B
c1-2	.443307	.292043	.564321							4.587
C2-2	.391091	.299325	.508613							5.496
C3-2	.376738	.216216	.452011							4.585
C4-2	.312454	.235828	.396284							4.413
C5-2	.282103	.350853	.390716							8.998
C6-2	.265047	.149696	.417499							7.241
C7-2	.319463	.180154	.322557							7.478
C8-2	.458322	.375146	.627468							2.572
C9-2	.422119	.335149	.676126							12.164
C10-2	.483424	.309420	.705685							14.018
C11-2	.533961	.409927	.657192							12.067
C1-3	.405218	049269	.566627							5.698
C2-3	.392560	138302	.509677							5.789
C3-3	.417117	121723	.453727							3.524
C4-3	.383481	212581	.387225							6.141
C5-3	.377946	330044	.419419							7.884
C6-3	.358473	154660	.323753							10.812
C7-3	.462052	270167	.385630							8.218
C8-3	.370361	044862	.625629							4.937
C9-3	.331472	.061888	.622320							8.105
C10-3	.350842	180647	.635156							8.339
C11-3	.429804	065118	.702430							7.793
C1-4	.591728	135023	.562424							7.138
C2-4	.618712	123288	.507052							4.776
C3-4	.597233	056069	.447563							4.596
C4-4	.621830	072481	.386103							4.932

(cont'd)
<b>II(A)</b>
Table

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B	8.371 6.559 8.747 4.648 7.175 8.190 7.881
<sup>β</sup> 23	
β <sub>13</sub>	
β <sub>12</sub>	
β <sub>33</sub>	
β22	
<sup>β</sup> 11	
N	.394083 .318577 .403956 .621433 .663496 .681043 .611943
у	154076 029337 .018536 216404 231480 161254 313739
x	.674040 .576832 .675818 .600115 .559238 .669649 .645247
Atom Number	C5-4 C6-4 C7-4 C3-4 C3-4 C3-4 C10-4 C11-4

<sup>a</sup> Fractional decimal coordinates.

 $rac{\mathrm{b}}{\mathrm{D}}$  The last number to the right of the dash corresponds to the ligand number.

### Table II(B)

### Electron Densities ( $\rho$ ) for Atoms Comprising

## the Chelate Rings in Nb(DPM)4

Atom	Molecule A	Molecule B
Number		
	a	
Nb	44.5-	41.9
01	6.1	5.5
02	7.0	6.5
03	5.7	6.2
04	5.3	6.1
05	6.4	6.3
06	6.2	6.4
07	5.9	6.4
08	6.1	6.4
C1-1	4.1	4.1
C2-1	3.9	3.8
C3-1	3.5	4.0
C1-2	4.5	4.3
C2-2	4.1	4.0
C3-2	3.6	3.9
C1-3	3.6	3.6
C2-3	3.5	3.9
C3-3	4.0	4.8
C1-4	3.1	3.7
C2-4	4.0	4.6
C3-4	4.2	4.5

 $\frac{a}{2}$  Corrected for F<sub>000</sub> term.

### Table III

Nb-O and O-O Distances Å in Nb(DPM)<sub>4</sub>

Molecule A	Molecu	ule B
Atom Distance	Atom	Distance
Number (A)	Number	c (Å)
Nb-O Distances		
Nb-01 2.184 $\frac{a}{2}$	ND-01	2,132
Nb-05 2.104	Nb-05	2.062
Nb-02 2.129	Nb-02	2.160
Nb-06 2.138	Nb-06	2.131
Nb-03 2.091	Nb-03	2.136
Nb-07 2.192	Nb-07	2.068
Nb-04 2.044	Nb-04	2.172
Nb-08 2.131	Nb-08	2.160
Mean Distance: 2.128 $\pm$ 0.048 $\frac{b}{}$		$2.128 \pm 0.042^{\underline{b}}$
0-0 Distances Along Diagonals of	of Squar	re Face
01-03 3.438 <sup>C</sup>	01-03	3.547
02-04 3.447	02-04	3,580
05-07 3.612	05-07	3.471
06-08 3.719	06-08	3.623
Mean Distance: 3.554 <u>+</u> 0.136 <sup>b</sup>		$3.555 \pm 0.064^{b}$
0-0 Distances Defining Che	late Bin	tes
01 05 2 760C	01 05	 2 607
01-03 2.709-	02-06	2.00/
02-00 2.710	02-00	2.770
0/-08 2 63/	0/-08	2.707
04-00 2:004 h	04-00	2.709 h
Mean Distance: 2.728 <u>+</u> 0.069 <sup>5</sup>		$2.740 \pm 0.051^{-1}$
0-0 Distance Defining Lateral Edges Not	Involvi	ng Chelate Bites
01-08 2.712	01-08	2.652
02-05 2.672	02-05	2.651
03-06 2.642	03-06	2.692
04-07 2.674	04-07	2.687
Mean Distance: 2.675 + $0.029^{b}$		$2.670 \pm 0.0223^{b}$

Table III (cont'd)

Molecule A	Molecule B			
Atom Distance	Atom Distance			
Number (Å)	Number (Å)			

0-0 Distances	Defining	Edges of	Square	e Faces
01-02 2.437			01-02	2.506
02-03 2.491			02-03	2.530
03-04 2.324			03-04	2.519
04-01 2.491			04-01	2.525
05-06 2.643			05-06	2.490
06-07 2.574			06-07	2.487
07-08 2.621			07-08	2.553
08-05 2.540			08-05	2.506
Mean Distance	: 2.515 <u>+</u>	0.104 <u>b</u>		$2.514 \pm 0.022^{b}$

- $\frac{a}{a}$  The average standard deviation for a single Nb-0 distance as calculated from the uncertainties in atomic coordinates (equations on p. 417 of ref. 33), is  $\pm$  0.020 Å.
- $\frac{b}{c}$  Standard deviation ( $\sigma$ ) of the mean ( $\sigma = [\Sigma \sigma_1^2/n-1]^{1/2}$ ).
- $\frac{c}{b}$  Based on uncertainties in atomic coordinates, the average standard deviation of a single 0-0 distance is  $\pm$  0.030 Å.

### Table IV

# DPM Ligand Bond Distances (Å) in Nb(DPM)4

	Mole	ecule A				Mo	lecule 🛛	В	
Atom	Ligano	1	Numbe	r <sup>a</sup>	Atom	Ligar	nd	Numb	ber
Numbers	<b>1</b> ·	2	3	4	Numbers	1	2	3	4
C-O Dista	nces								
C1-0	$1.253^{b}$	1.237	1.397	1.494	C1-0	1.261	1.390	1.388	1.216
C3-0	1.358	1.316	1.130	1.202	C3-0	1.202	1.308	1.333	1.217
Mean Dist	ance:	1.298 <u>+</u>	0.117 <u>으</u>				1.290	<u>+</u> 0.077	<u>,c</u>
C-C Dista	nces in	Chelate	Ring						
C1-C2	1.528d	1.353	1.367	1,408	C1-C2	1.357	1.339	1.500	1.395
C2-C3	1.447	1.317	1.346	1.411	C2-C3	1.508	1.445	1.377	1.374
Mean Dist	ance:	1.397 <u>+</u>	0.067 <u>c</u>				1.412	<u>+</u> 0.065	<u>jC</u>
<u>C-C Dista</u>	nces in	Termina	1 t-But	yl Grou	1ps				
C1-C8	1.585 <u>e</u>	1.558	1.532	1.514	C1-C8	1.630	1.537	1.574	1.473
C8-C9	1.643	1.604	1.714	1.348	C8-C9	1.528	1.498	1.525	1.410
C8-C10	1.289	1.651	1.522	1.715	C <b>8-</b> C10	1.499	1.659	1.693	1.764
<b>C8-</b> C11	1.504	1.441	1.559	1.555	C8-C11	1.612	1.663	1.698	1.578
C3–C4	1.473	1.574	1.656	1.595	C3–C4	2.045	1.537	1.683	1.476
C4–C5	1.833	1.496	1.434	1.564	C4-C5	1.432	1.512	1.549	1.486
C4–C6	1.421	1.666	1.640	1.507	C4-C6	1.994	1.611	1.383	1.491
C4–C7	1.476	1.689	1.696	1.435	C4-C7	1.116	1.636	1.889	1.576
Mean Dist	ance:	1.559 <u>+</u>	0.094 <sup>C</sup>				1.586	<u>+</u> 0.180	عر
<u>a</u> Ligands	are de	fined in	Figure	19.					
<u>b</u> Based o standar	n uncer d devia	tainties ation <sup>33</sup>	in ato of a si	mic coo ngle C-	ordinates -0 distan	, the avce is +	verage 0.040	Å.	
<u>c</u> Standar	d devia	tion of	the m <b>ea</b>	n, σ =	$\Sigma(\sigma_1^2/n_{-})$	$1)^{1/2}$ .			
$\frac{d}{d}$ Average standard deviation of a single C-C distance in a chelate ring is + 0.060 Å.									
<u>e</u> Average standard deviation of a single C-C distance for the terminal <u>t</u> -butyl groups is <u>+</u> 0.150 Å.									

### Table V

## 0-Nb-0 Angles in Nb(DPM)<sub>4</sub>

Atom Numbers	Angle, degrees <u>Molecule A</u>	Atom Numbers	Angle, degrees Molecule B
	<b>0-Nb-0 Angles o</b> :	f Chelate Rings	
01-Nb-05	80.4	01-Nb-05	79.7
02-Nb-06	79.1	02-Nb-06	80.7
03-Nb-07	81.2	03-Nb-07	80.1
04-Nb-08	78.2	04-Nb-08	80.1
Mean Angle:	79.7 <u>+</u> 1.3 <u>a</u>	Mean Angle:	80.2 <u>+</u> 0.4
	0-Nb-0 Angles bet	ween Chelate Ring	38
02-Nb-05	78.3	02-Nb-05	77.7
03-Nb-06	77.3	03-Nb-06	78.2
04-Nb-07	78.2	04-мъ-07	78.6
01-Nb-08	77.9	01-Nb-08	76.3
Mean Angle:	77.9 <u>+</u> 0.4	Mean Angle:	77.7 <u>+</u> 1.0
Mean of all Angles	<b>:</b> 78.8 <u>+</u> 1.3	Mean of all	Angles: 78.9 <u>+</u> 1.5

 $\frac{a}{2}$  Standard deviation of mean

.

### Table VI

## Chelate Ring Interior Angles in Nb(DPM)4

Atom <u>Numbers</u>	-	Angle, <u>Mole</u>	degree cule A		Atom Numbers		Angle, Molec	degrees ule B	
Nb-O-C Angles									
	L1	L2	L3	L4		L1	L2	L3	L4
Nb-0-C1 Nb-0-C3	131.9 140.4	129.5 131.3	128.8 130.6	136.2 141.1	Nb-0-C1 Nb-0-C3	132.8 139.6	130.3 132.0	134.3 133.7	132.5 133.2
Mean Nb-O-C Angle: 133.7 ± 4.9 Mean Nb-O-C Angle: 133.6 ± 2.6				6					
			(	0-C-C <sub>r</sub>	Angles				
	L1	L2	L3	L4		L1	L2	L3	L4
0-C1-C2 0-C3-C2	125.6 118.1	130.9 125.1	124.3 131.8	115.0 119.7	0-C1-C2 0-C3-C2	124.9 120.2	127.9 127.1	123.4 129.7	121.3 123.0
Mean O-C-	C <sub>r</sub> Ang	gle: 1	123.8 -	<u>+</u> 5.9	Mean O-C-	C <sub>r</sub> Ang	;le: 12	4.7 <u>+</u> 3	.3
C-C <sub>2</sub> -C Angles									
	L <b>1</b>	L2	L3	L4		L1	L2	L3	L4
C1-C2-C3	123.7	120.7	122.5	128.5	C1-C2-C3	122.2	121.3	117.3	126.5
Mean C-C <sub>r</sub>	-C An	gle:	123.8 -	<u>+</u> 3.3	Mean C-C <sub>r</sub>	-C Angl	.e: 121	.8 <u>+</u> 3.	8

### Table VII

Average Bond Distances	and	Angles	in	the	Nb-DPM	Chelate	Ring
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Distance, A	Molecule A	Molecule B	Average over both Molecules
ND-0	2.128 <u>+</u> 0.048	2.128 <u>+</u> 0.042	2.128 <u>+</u> 0.045
0-0 (ligand bite)	2.728 <u>+</u> 0.069	2.740 <u>+</u> 0.051	2.734 <u>+</u> 0.060
C-0	1.298 <u>+</u> 0.117	1.290 <u>+</u> 0.077	1.294 <u>+</u> 0.096
C-C <sub>r</sub> <sup>a</sup>	1.397 <u>+</u> 0.067	1.412 <u>+</u> 0.065	1.404 <u>+</u> 0.064
C-C <sub>t</sub>	1.553 <u>+</u> 0.056	1.619 <u>+</u> 0.186	1.586 <u>+</u> 0.136
<sup>C</sup> t <sup>-C</sup> m	1.558 <u>+</u> 0.131	1.575 <u>+</u> 0.173	1.566 <u>+</u> 0.151
Angle, deg.	Molecule A	Molecule B	Average over both molecules
0 <b>MO</b>	78.8 <u>+</u> 1.3	78.9 <u>+</u> 1.5	78.8 <u>+</u> 1.4
	$(79.7 \pm 1.3)^{b}$	(80.2 <u>+</u> 0.4)	(80.0 <u>+</u> 0.9)
MOC	133.7 <u>+</u> 4.9	133.6 <u>+</u> 2.7	133.6 <u>+</u> 3.8
occ <sub>r</sub>	123.8 <u>+</u> 5.9	124.7 <u>+</u> 3.3	124.2 <u>+</u> 4.7
cc <sub>r</sub> c	123.8 <u>+</u> 3.3	121.8 <u>+</u> 3.8	122.8 <u>+</u> 3.5

 $\stackrel{a}{=}$  C, C<sub>r</sub>, C<sub>t</sub>, and C<sub>m</sub> denote carbonyl carbon, ring carbon, tertiarybutyl carbon, and methyl carbon atoms, respectively.

 $\frac{b}{c}$  ( ) denotes the chelate ring angles only.

Figure 16a. The composite electron density along the b axis for Nb(DPM)<sub>4</sub>, Molecule A, showing the half of the molecule containing ligands L1 and L2. With the exception of Nb, contours are at 1 electron/(Å)<sup>3</sup> beginning with 1 electron. For Nb, contours are at 4 electrons/(Å)<sup>3</sup> beginning with 1 electron. The ligand number corresponds to the last number of each carbon atom.



Figure 16b. The composite electron density along the b axis showing the half of Molecule A containing ligands L3 and L4; contours as in Figure 16a.



Figure 17a. The composite electron density along the b axis for Nb(DPM)4, Molecule B, showing the half of the molecule containing ligands L1 and L2; contours as in 16a.

Figure 17b. The composite electron density along the b axis showing the half of Molecule B containing ligands L3 and L4; contours as in Figure 16a. The motions associated with the transformation of a cube to a D2d dodecahedron and D4d square antiprism.  $\mathbf{l}$ Figure 18.





Figure 19. A view of the "idealized"  $D_4$  square antiprismatic coordination polyhedron down the "pseudo"  $C_4$  axis including the numbering scheme for the ligands, oxygen atoms and carbon atoms for Nb(DPM)4. The b axis is indicated.


Figure 19

antiprism. To do this, we must consider the merit of the two most closely related dodecahedral stereoisomers:<sup>2,3a</sup> the  $D_2(gggg)$ , and the  $D_2$  (aabb) dodecahedron. These isomers, along with the remaining stereoisomers possible for a tetrakis chelate, are illustrated in Figure 1. The polyhedral shape parameters that must be calculated to distinguish between the three possibilities are the angles defined by the metal ligand bond axis and the principal rotation axis of the idealized polyhedron, the degree of planarity in the trapezoidal planes of the dodecahedra and the square planes of the antiprism, and the angles of intersection of these planes.

Hoard and Silverton<sup>3a</sup> have defined the dodecahedron in terms of two angles,  $\theta_A$  and  $\theta_B$ , formed by the two unique types of metal-ligand atom bonds, M-A and M-B, with the fourfold inversion axis ( $\overline{4}$ ) and the ratio of the M-A and M-B bond lengths (see Figure 20).

In addition, the four unequal edge lengths of the dodecahedron, a, b, m, and g are useful in discussing the polyhedron despite being redundant in terms of defining it. The definitive shape parameters for the square antiprism are the angle,  $\theta$ , made by a metal-ligand atom bond, M-A, with the  $\overline{8}$  axis (for a D<sub>4d</sub> square antiprism) and the ratio of the lateral edges, 1, to the square edges, s (see Figure 20). Once the above parameters have been determined, a choice of the proper polyhedron may be made on the basis of a comparison to those calculated for models based on a closed-shell, non-bonded ligand repulsion analysis that minimizes ligand repulsions. These parameters are referred to as the "most favorable" polyhedron parameters by Hoard and Silverton.<sup>3a</sup> Recently, Lippard and Russ<sup>46</sup> have suggested a third criterion for The Hoard and Silverton  $^{3a}$  polyhedral shape parameter notation for the D2d dodecahedron and  $D_{4d}$  square antiprism. Figure 20.



distinguishing dodecahedral and square antiprismatic stereochemistry in cases where the criteria of Hoard and Silverton may not provide an unambiguous choice. Lippard and Russ point out that one of the drawbacks of the Hoard and Silverton criteria is that the  $\overline{8}$  axis of the  $D_4 d$  square antiprism and the  $\overline{4}$  axis of the  $D_2 d$  dodecahedron are mutually orthogonal and thus, direct comparisons of the  $\theta$  angles are not meaningful. Furthermore, although calculations of edge lengths are normalized by the metal-ligand atom bond distance, ambiguities arise since the dodecahedron does not possess a single value for this distance as does the antiprism. Further problems arise due to the presence of four non-equivalent edges (a, b, m, g) in the dodecahedron and only two (1, s) in the antiprism. Consequently, to complement the polyhedral selection, the authors suggest trapezoidal planes, whose line of intersection contains the central metal atom (as described by Hoard and Silverton<sup>3a</sup>) and coincides with the  $\overline{4}$  axis. Once the best planes corresponding to the two trapezoids have been calculated, the angle of intersection of these planes may also be calculated and compared to the theoretical values of 90° and 77.4° for the perfect dodecahedron and square antiprism, respectively. This procedure, however, also has its disadvantages since the angle of intersection of the trapezoidal planes is only theoretical, i.e., it is a result of two nonexistant planes when the polyhedron is actually a square antiprism. It would seem that the most definitive test would be to calculate both the trapezoidal planes of the polyhedron viewed as a dodecahedron and the square planes of the polyhedron viewed as a square antiprism, and then to compare the deviations from these best planes. In addition, the deviation of the angle of intersection of the square planes from 0° would provide a good

criterion for the proper choice.

Tables VIII-X list the edge lengths used to calculate shape parameters for the three polyhedra being considered. It is obvious that for each polydron, both molecules (A and B) must be considered, and in the case of the dodecahedral stereoisomers, there are two sets of trapezoidal planes (Sets I and II) which can be defined. Tables XI and XII list the deviations of the oxygen atoms comprising the possible dodecahedral planes from the best plane and also the angles of intersection of these planes. Table XIII lists the deviations of the oxygen atoms comprising the two square planes of the square antiprism, the angles of intersection of these planes, and the shape parameter, 0, as defined above. Tables XIV and XV summarize the results of these data and compare them to the idealized polyhedron shape parameters.<sup>3a,46</sup> The average Nb-0 bond lengths which were identical (2.128 Å) in molecules A and B were used to normalize the shape parameters.

An analysis of the results of the above calculations clearly establishes the structure of Nb(DPM)<sub>4</sub> to be most closely approximated by the D<sub>4</sub> square antiprism. The overall agreement between the experimental and "MFP" shape parameters for a square antiprism is good. However, the most striking evidence to support the choice of the square antiprism lies in the plane calculations. The <u>maximum</u> average deviation from planarity for four oxygen atoms comprising a square plane is 0.058 Å, whereas the <u>minimum</u> average deviation from planarity for four oxygen defining a trapezoidal plane is 0.26 Å. Furthermore, the square planes are parallel in molecule  $A(\alpha_g = 0^\circ)$  and very nearly parallel in molecule B ( $\alpha_g = 0.7^\circ$ ). Among the various dodecahedral views of the molecule, the best trapezoidal planes, which should be orthogonal, intersect at a

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Polyhedral Edge Lengths (Å) when Nb(DPM)  $_4$  is Viewed as a D $_2$ (aabb) Dodecahedron

Edge-	Oxygen Atom Numbers <u>b</u>	Trapezoidal Molecule A	<mark>Set I</mark> Molecule B	Oxygen Atom Numbers	<u>Trapezoida</u> Molecule A	l Set II Molecule B
a 1	2-6 2 -6	2.718	2.778	1-5 1-5	2.769	2.687
82	4-0	2.034 (2.676 <u>+</u> .059) <sup>C</sup>	2.784 ± .020)	<b>1</b> -1	2.779 ± .014)	2./0/ (2.697 + .014)
	1-5	2.769	2.687	2-6	2.718	2.778
р <del>,</del>	3-7	2.789	2.707	4-8	2.634	2.789
م م	5-7	3.612	3.471	2-4	3.447	3.580
ף ק	1-3	3.438	3.547	4-5	3.719	3.623
t		$(3.152 \pm .437)$	$(3.103 \pm .598)$		$(3.130 \pm .536)$	$(3.192 \pm .473)$
Ē	5-8	2.540	2.506	5-6	2.643	2.490
∃ E	4-3	2.324	2.519	1-4	2.491	2.525
۲ ۲	1-2	2.437	2.506	2-3	2.491	2.530
о ~	6-7	2.574	2.487	7–8	2.621	2.553
t		(2.469 + .112)	(2.504 + .023)		(2.562 + .082)	(2.524 + .046)
81	2-5	$2.672^{-}$	$2.651^{-}$	2-5	2.672	$2.651^{-}$
8, L	3-6	2.642	2.692	3-6	2.642	2.692
8 7 8	4-7	2.674	2.687	4-7	2.674	2.687
00°,	1-8	2.712	2.652	1-8	2.712	2.652
τ 1 υ	5-6	2.643	2.490	1-2	2.437	2.506
00 00	7-8	2.621	2.553	6-7	2.324	2.519
0 K 80 L	2-3	2.491	2.530	5-8	2.540	2.506
80	1-4	2.491	2.525	4-8	2.574	2.487
0		(2.618 ± .083)	(2.598 <u>+</u> .081)		(2.572 ± .134)	(2.588 <u>+</u> .090)

 $\frac{a}{b}$  Notation according to reference 3a.  $\frac{b}{b}$  Notation according to Figure 19.  $\frac{c}{c}$  ( ) denotes average value and standard deviation of the mean.

	Pol	Lyhedral Edge Leng	ths (Å) when Nb(I	)PM) <sub>4</sub> is Viewed	as a D <sub>2</sub> (gggg) Do	decahedron
Edge <sup>a</sup>	Oxygen Atom Numbers <mark>b</mark>	<u>Trapezoidal</u> Molecule A	Set I Molecule B	Oxygen Atom Numbers	Trapezoidal Molecule A	Set II Molecule B
a_	2-5	2.672	2.651	1-8	2.652	2.712
а Г	4-7	2.674	2.687	3-6	2.692	2.642
7		(2.673 + .001) <sup>C</sup>	(2.669 + .025)		(2.672 + .028)	(5.677 + .049)
þ,	1-8	2.712	2.652	2-5	2.651	2.674
ч с Д	3-6	2.642	2.692	4-7	2.687	3.471
ہ ر م	1-3	3.438	3.547	5-7	3.612	3.580
ۍ ر	6-8	3.719	3.623	2-4	3.447	2.437
4		(3.128 + .534)	(3.128 + .528)		(3.099 + .502)	(3.099 + .574)
Ē	5-8	2.540	2.506	1-2	2.506	2.437
⊐ c ≣	2-3	2.491	2.530	7-8	2.553	2.621
о и В	1-4	2.491	2.525	5-6	2.490	2.643
л,	6-7	2.574	2.487	3-4	2.519	2.324
4		(2.524 + .041)	(2.512 + .019)		(2.517 + .026)	(2.506 + .153)
6	1-5	2.769 -	2.687	1-5	2.687	2.769
ц В Г	2-6	2.718	2.778	2-6	2.778	2.718
2 60	3-7	2.789	2.707	3-7	2.707	2.789
0 2 2	4–8	2.634	2.789	4-8	2.789	2.634
1 00 1 1	5-6	2.643	2.490	5-8	2.506	2.540
00 00	7–8	2.621	2.553	6-7	2.487	2.574
0 60 7	1-2	2.437	2.506	1-4	2.525	2.491
80,	3-4	2.324	2.519	2-3	2.530	2.491
0		(2.617 ± .161)	(2.629 ± .126)		(2.626 ± .127)	(2.626 ± .121)

104

Table IX

Polyhedral Edge Lengths (Å) when Nb(DPM) is

<sup>&</sup>lt;u>a, b, c</u> See Table VIII.

## Table X

Polyhedral Edge Lengths (Å) when  $Nb(DPM)_4$  is Viewed as a  $D_4(1111)$  Square Antiprism

Edge <sup>a</sup>	Oxygen Atom Numbers <mark>b</mark>	Molecule A	Molecule B
1 <sub>1</sub>	1-5	2.769	2.687
<sup>1</sup> 2	2-6	2.718	2.778
<sup>1</sup> 3	4-8	2.634	2.789
<sup>1</sup> 4	3–7	2.789	2.707
<sup>1</sup> 5	1-8	2.712	2.652
1 <sub>6</sub>	2–5	2.672	2.651
1 <sub>7</sub>	3–6	2.642	2.692
1 <sub>8</sub>	4-7	2.674	2.687
		(2.728 <u>+</u> .069) <sup>C</sup>	(2.740 <u>+</u> .051)
<sup>s</sup> 1	1-2	2.437	2.506
<sup>s</sup> 2	2-3	2.491	2.530
<sup>s</sup> 3	3-4	2.324	2.519
s <sub>4</sub>	1-4	2.490	2.525
<sup>s</sup> 5	5-6	2.643	2.490
<sup>s</sup> 6	6-7	2.574	2.487
<sup>s</sup> 7	7–8	2.621	2.553
s <sub>8</sub>	5-8	2.540	2.506
		(2.514 + .104)	(2.514 <u>+</u> .021)

<u>a</u>, <u>b</u>, <u>c</u> See Table VIII

Devi	ations (Å) of Oxygen	Atoms From Best T	rapezoidal Planes	and Angles of Inter	section
	$(\alpha_{\mathrm{T}})$ of the Plan	es When Nb(DPM) <sub>4</sub> 1	s Viewed as a D <sub>2</sub> (	aabb) Dodecahedron	
Oxygen Atom Number <u>a</u>	<u>Trapezoidal</u> Molecule A	<u>Set I</u> Molecule B	Oxygen Atom Number	<u>Trapezoidal S</u> Molecule A	<u>et II</u> Molecule B
1	0.2097	0.2552	ω	0.2775	-0.2483
2	-0.3228	-0.3752	7	-0.4230	0.3847
6	0.3064	0.3770	e	0.4547	-0.3847
7	-0.1933	-0.2570	2	-0.3092	0.2483
(1) <sup>C</sup>	(0.2580 <u>+</u> .0660) <sup>b</sup>	· (0.3161 <u>+</u> .0693)	(1)	(0.3661 ± .0860)	(0.3165 ± .0787)
S	0.1914	0.2481	4	-0.3043	-0.2318
80	-0.3066	-0.3619	1	0.4410	0.3632
4	0.3376	0.3629	S	-0.4220	-0.3696
£	-0.2225	-0.2491	ę	0.2852	0.2382
(2)	(0.2645 <u>+</u> .0665)	(0.3055 <u>+</u> .0657)	(2)	(0.3631 ± .0797)	(0.3007 ± .0760)
cos م <sub>ا</sub>	0.08663	0.07150		0.07323	0.08385
$\alpha_{T}$ , degrees	85.03	85.90		85.80	85.19

Table XI

 $\frac{a}{2}$ ,  $\frac{b}{2}$  See Table VIII, Footnotes  $\underline{b}$  and  $\underline{c}$ .

<u>c</u> Trapezoidal plane no. l.

Devia	tions (Å) of Oxyger	n Atoms From Best Tı	capezoidal Planes	and Angles of Inter	section.
	$(lpha_T)$ of the Pla	nes When Nb(DPM) <sub>4</sub> 1:	s Viewed as a D <sub>2</sub>	(gggg) Dodecahedron	
Oxygen Atom Numberª	<u>Trapezoida</u> Molecule A	<u>l Set I</u> Molecule B	Oxygen Atom Number	<u>Trapezoidal</u> Molecule A	Set II Molecule B
1	-0.2857	-0.2614	2	0.2653	0.2652
4	0.4524	0.4164	1	-0.4118	-0.4165
7	-0.4195	-0.4296	ω	0.3902	0.4027
6	0.2582	0.2746	7	-0.2437	-0.2514
(1) <sup>C</sup>	$(0.3562 \pm .0981)^{1}$	<u>b</u> (0.3455 <u>+</u> .0898)	(1)	(0.3278 ± .0855)	$(0.3340 \pm .0877)$
8	0.2618	0.2734	Ŋ	0.2327	0.2658
Ŋ	-0.4099	-0.4402	9	-0.3746	-0.4153
2	0.4181	0.4290	ო	0.4236	0.4162
£	-0.2699	-0.2622	4	-0.2818	-0.2667
(2)	(0.3399 ± .0856)	(0.3512 <u>+</u> .0965)	(2)	(0.3282 <u>+</u> .0867)	(0.3410 ± .0863)
$\mathbf{L}_{\mathbf{v}}$ soc	0.08411	0.08718		-0.7817	-0.7160
$^{\alpha}\mathrm{_{T}}$ , degrees	85.18	85.00		85.52	85.89

 $\frac{a}{2}$ ,  $\frac{b}{2}$  See Table VIII, Footnotes  $\underline{b}$  and  $\underline{c}$ .

<u>c</u> See Table XI.

Table XII

#### Table XIII

Deviations (Å) of Oxygen Atoms From Best Square Planes,

Angles of Intersection ( $\alpha_{g}$ ) of the Planes,

and the Shape Parameter Angles ( $\theta$ ) when Nb(DPM)<sub>4</sub> is Viewed as

## a D<sub>4</sub>(1111) Square Antiprism

Oxygen Atom Number <sup>a</sup>	Molecule A	Molecule B
1	0.04566	-0.01690
2	-0.04565	0.01686
3	0.04789	-0.01678
4	-0.04790	0.01681
(1) <u>c</u>	$(0.04678 \pm .00130)^{-1}$	(0.01684 + .00005)
5	-0.05807	0.01501
6	0.05730	-0.01511
7	-0.05777	0.01474
8	0.05854	-0.01464
(2)	(0.05792 <u>+</u> .00052)	(0.01488 <u>+</u> .00068)
cos α <sub>s</sub>	1.0000	0.9999
$\alpha_s$ , degrees	0	0.6836
Oxygen	$\theta, \frac{d}{d}$ Molecule A	$\theta$ , Molecule B
1	52.73	56.66
2	54.63	55.83
3	54.33	55.76
4	56.70	55.60
5	58.80	57.18
6	60.69	57.16
7	55.62	57.18
8	60.50	58.07
	(56.75 <u>+</u> 2.97)	(56.68 <u>+</u> 0.77)

- $\frac{a}{b}$ ,  $\frac{b}{b}$  See Table VIII, Footnotes  $\underline{b}$  and  $\underline{c}$ .
  - $\frac{c}{c}$  Square plane (1).
  - $\frac{d}{d}$  Defined according to reference 3a; the C<sub>4</sub> axis was the best least squares line passing through the centroids of the two square planes and the Nb atom.

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Experimental and Most Favorable Polyhedron Shape Parameters<sup>3a</sup> when

Nb (DPM) $_4$  is Viewed as a D $_2$ (aabb) and D $_2$ (gggg) Dodecahedron and

a  $D_{\Delta}(llll)$  Square Antiprism

	D <sub>4</sub> Squ	lare Antiprism		А	2 (aabb) Dod	ecahedron	D <sub>2</sub> (gggg)	Dodecahedron	
Mole	cule A	Molecule B	MFP	X	olecule A	Molecule B	Molecule A	Molecule B	MFP
1	. 28	1.29	1.26	đ	1.26 <sup>a</sup> 1.31	1.31 1.27	1.26 1.26	1.25 1.26	1.17
				م	1.48 1.47	1.46 1.50	1.47 1.46	1.47 1.46	1.47
S L	.18	1.18	1.19	E	1.16 1.20	1.18 1.19	1.19 1.18	1.18 1.18	1.17
				00	1.23 1.21	1.22 1.22	1.23 1.23	1.24 1.23	1.24
1/s 1	60•	1.09	1.06	ባ ዋ	39.5 40.5	40.2 40.0	41.3 38.3	41.0 38.7	35.2
				θ	71.8 69.4	70.5 70.2	72.2 72.3	62.8 72.4	73.5
θ <b>, 5</b> 6 deg.	8.	56.7	57.3	M-A/M-B	0.985 1.01	1.03 0.974	1.01 0.991	1.01 0.989	1.03
AFP & Antir Antir axis axis the 1 the t the t the t the t	hape par rrismatic was appr igands s row) and est leas est leas ints of	ameter calcula configuration oximated by th panning oxygen oxygen atoms, t squares line and 03-06, fo	ted for The The Le best Latoms, 01-05, C1-05, t the f	one of second s least sq 04-08, and 03- g throug irst pos	two possibl et's param uares line and 02-06, 07, for the the Nb at sible D2(88	e dodecahedral eter is listed passing throug for the first second possib om and the mid gg) dodecahedr	sets which can directly below h the central r possible D2(aab le D2(aabb) dod points of the 1 on (top row) an	be derived fr <b>b</b> The pseud ing carbon atc b) dodecahedrc ecahedron (sec ines defined b d the Nb atom	om a D <sub>4</sub> lo- 4/2 of m (C2) of n cond row); y oxygen and the

dodecahedron (second row), approximated the pseudo- 4 axis.

#### Table XV

Experimental and Idealized Plane Deviations (Å) and Angles of Intersection for Nb(DPM)<sub>4</sub> Viewed as a D<sub>4</sub> Square Antiprism and a D<sub>2</sub>(aabb) and D<sub>2</sub>(gggg) Dodecahedron

	1977,	Molecule A	Molecule B	Idealized Polyhedron
D <sub>4</sub> (1111)	$d_{s}(1) =$	0.058	0.015	0
	d <sub>s</sub> (2)	0.047	0.017	0
	α s	0.00°	0.68°	0
D <sub>2</sub> (aabb)	d <sub>T</sub> (1) <u>b</u>	0.26 0.37	0.32 0.32	0(0.4) <sup>c</sup>
	d <sub>T</sub> (2)	0.26 0.36	0.31 0.30	0(0.4)
	α <sub>T</sub>	85.0° 85.8°	86.0° 85.2°	90.0(77.4) <sup>d</sup>
D <sub>2</sub> (gggg)	d <sub>T</sub> (1)	0.35 0.33	0.34 0.33	0(0.4) <sup>c</sup>
	d <sub>T</sub> (2)	0.34 0.33	0.35 0.34	0(0.4)
	α <sub>T</sub>	85.2° 85.5°	85.0° 85.9°	90.0(77.4) <sup>d</sup>

 $\frac{a}{a}$  Average deviation of the 4 oxygen atoms (Å) comprising the square plane as defined in Table XIII.

 $\frac{b}{b}$  Average deviation of the oxygen atoms comprising the trapezoidal plane defined in Tables XI and XII: the two rows per plane correspond to the two possible dodecahedral sets which can be derived from a D<sub>4</sub> antiprismatic configuration.

 $\frac{c}{d}$  () represents deviation from planarity of the theoretical trapezoidal plane derived from a perfect antiprism.

 $\frac{d}{d}$  () represents the angle of intersection of the two theoretical trapezoidal planes derived from a perfect square antiprism. maximum angle of 86.0°. The deviation of this angle from the perfect antiprism value of 77.4° exemplifies the caution which should be exercised when one chooses to use  $\alpha_{_{\mathrm{T}}}$  as a criterion to aid a polyhedral selection. As discussed above,  $\alpha_{T}$  is an angle based on <u>theoretical</u> planes when the isomer is a square antiprism and consequently, would be expected to deviate significantly from ideality as minor distortions are introduced into the square antiprismatic polyhedron. The structure of the bis (4-picoline) adduct of tris (2,2,6,6-tetramethy1-3,5-heptanedionato)holmium(III)<sup>47</sup> is another example where the utility of this angle is found to be secondary to the planarity criteria in aiding a stereochemical assignment. The structure was determined to be a square antiprism with the theoretical trapezoidal planes intersecting at an angle of 85.8°. The average deviation from planarity for the square planes was only 0.06 Å, however, whereas the deviations of the best trapezoidal planes ranged from 0.29 to 0.47 Å.

It is strikingly obvious from the electron density contour maps (see Figures 16 and 17 and Table IIb, that as one leaves the inner coordination sphere of the Nb(DPM)<sub>4</sub> molecule, the electron density falls off significantly for the carbon atoms. For example, Figure 17a shows a density for a <u>t</u>-butyl carbon, C3-1, of three electrons per cubic Angstrom. However, the density of one of the methyl carbon atoms, C6-1, belonging to the same ligand has fallen to one electron. With the exception of the Nb atoms, in fact, the electron densities of all the atoms are lower than expected. This phenomenon may be attributed to a significant degree of disorder introduced into the molecule by the abundance of <u>t</u>-butyl groups. No previous structure with four DPM ligands per molecule has been reported, but seven-coordinate monomeric and dimeric lanthanide metal-DPM structures have been reported with unusually high thermal parameters for the <u>t</u>-butyl carbon atoms. 48-50Erasmus and Boyens 48 suggest that for the Dy(DPM)<sub>3</sub>H<sub>2</sub>O structure, the high thermal parameters may be symptomatic of static disorder rather than thermal vibrations. To support this hypothesis, the authors cite the noticeably lower thermal parameters for several methyl carbon atoms of the t-butyl groups. Bennet, et al., also report a similar effect for the CF<sub>3</sub> groups in Cs[Y(HFA)<sub>4</sub>]. Although the thermal parameters of the methyl carbon atoms of the <u>t</u>-butyl groups in the Nb(DPM), structure were also high, no unusually low values were observed. Thus, it is not clear whether the disorder is static or due to thermal vibrations. The effect of the disorder is evidenced by the large standard deviation for the carbon-carbon single bond distance which is shown, along with the other average bond distances and angles, in Table III-VII and Figures 21 and 22. Despite the large standard deviation of the mean  $(\pm 0.15 \text{ Å})$  for the methyl carbon single bond distance, the average bond distances and angles are in satisfactory agreement with previously reported DPM-chelate structures. 47-50,52,53 Furthermore, since the question of which polyhedron best describes the structure is dependent primarily on the accuracy with which the inner coordination sphere has been determined (i.e., the oxygen positions), the inability to precisely determine the carbon atom positions was only a minor disappointment.

As Tables III and IV indicate, the Nb-O bond length has been determined to a much greater degree of precision than the C-C single bond length. Since this is the first crystal structure of a Nb betadiketonate, a direct comparison of Nb-O bond lengths is not possible. The average (over molecules A and B) chelate ring bond distances (Å) and their standard deviation of the mean in Nb(DPM) $_4$ . Figure 21.



The average (over Molecules A and B) interior angles of the chelate ring in  $Nb(DPM)_4$ . Figure 22.



116

However, the structures of several niobates containing the oxalate ligand show Nb-0 bond distances ranging from 2.07 to 2.16 Å.<sup>55,56</sup> The structure of  $[NbOCl_2(OC_2H_5)(bipyridy1)]$  reveals a suprisingly short Nb-0 (ethoxy) bond length of 1.87 Å.<sup>54</sup> To account for this, the authors suggest the presence of considerable double bond character for this bond. The nioby1, Nb=0 distance is 1.71 Å in the molecule and varies from 1.66 to 1.71 Å in other Nb=0 containing structures.<sup>55,56</sup> The average Nb-0 distance of 2.13 Å for Nb(DPM)<sub>4</sub> compares favorably with the above Nb-0 single bond distances.

It is of interest to consider the possible reasons why Nb(DPM), adopts a  $D_{\underline{A}}$  square antiprismatic configuration rather than one of the two D<sub>2</sub> dodecahedral molecular arrangements. Qualitatively, one might predict that the D<sub>2</sub>(aabb) stereoisomer would be least likely to be the coordination polyhedron for Nb(DPM)<sub>4</sub>. Such a configuration would require the four identical bidentate DPM ligands to span polyhedral edges differing by 25% (see Table XIV). Hoard and Silverton, <sup>3a</sup> in fact, rule out the D<sub>2</sub>(aabb), C<sub>1</sub>(abmg), C<sub>2</sub>(mmgg) dodecahedra and the C2(11ss) square antiprism from consideration as possible stereoisomers for neutral tetrakis bidentate chelates on the basis that the related isomers with equivalent edges can better simultaneously minimize the effects of both closed-shell repulsions and ring constraints. However, as mentioned above, the polyhedron which best describes the structure of Ho(DPM)<sub>3</sub>(4-Pic) $_{2}^{47}$  is based on a C<sub>2</sub>(11ss) square antiprism in which a diketonate ligand spanning an 1 edge is substituted by four picoline ligands. Although this is not a tetrakis chelate, two of the DPM ligands span s edges and one spans an 1 edge. To add further insight into the prediction of eight-coordinate stereochemistries, Kepert<sup>57</sup>

extended Hoard and Silverton's <sup>3a</sup> ligand-ligand repulsion energy calculations for eight monodentate ligands and showed that the potential energy minima corresponding to the square antiprism and the dodecahedron are very similar and that these stereochemistries are easy to distort. Further calculations by Blight and Kepert<sup>58</sup> showed that a potential energy barrier between these stereochemistries does not exist, as earlier assumed, 2,4,59 and therefore, in the absence of other stereochemically-directing forces, there may be a continuous ligand movement, creating a fluxional structure. More recently, Blight and Kepert have extended their ligand-ligand repulsion energy calculations to eightcoordinate complexes with four bidentate ligands. 60 The relative stabilities of the various stereoisomers were calculated as a function of the "normalized" ligand bite i.e., the distance between the two oxygens of the ligand divided by the metal-oxygen bond length. For bites of 1.20 and 1.25, separate minima on the calculated potential energy surfaces occur for the  $D_2$  and  $D_4$  square antiprisms. The  $D_2$ dodecahedron appears as a saddle between these two stereoisomers with a slightly higher energy. Consequently, the authors note that the similar energies of these three stereochemistries make a prediction of a given isomer impossible. Additional energy terms such as crystal field stabilization, covalent  $\sigma$  bonding,  $\pi$  bonding, and crystal packing or solvation forces become important in determining the stereochemistry. It is relevant to note that the ACAC bite in the Zr(ACAC)4 structure  $^{3b}$  is 1.22 and the observed D<sub>2</sub>(ssss) stereochemistry is consistent with the above predictions. As the bite of the ligand is increased to 1.30, a single minimum corresponding to a  $D_4$  antiprism appears on the potential energy surface. The authors state that ligands

with such a large bite would not be expected to form discrete eightcoordinate chelates since the ligand-ligand repulsion would be lowered if the ligands bridged different metal atoms to form a polymeric structure. This is the reason, the authors summarize, that molecules with this stereochemistry have not been observed. The bite of both molecules in the asymmetric unit of the Nb(DPM)<sub>4</sub> structure is 1.28. Consequently, the observed D<sub>4</sub> stereochemistry is again consistent with Blight and Kepert's theoretical prediction. However, the ligand-ligand repulsion does not appear sufficiently important to cause the compound to adopt a polymeric structure.

D. The Stereochemistry of Nb(DPM)4 in Solution

The stereochemistry of Nb(DPM)<sub>4</sub> in solution was investigated by means of electronic absorption spectrophotometry and esr spectroscopy. In both cases the same stereochemical assignment was implied.

The electronic absorption spectrum of Nb(DPM) $_4$  in dichloromethane solution is shown in Figure 23. Table XVI lists the absorption maxima and the corresponding molar absorptivities. The qualitative features of the spectrum include a broad absorption at 17.8 kK with a broad shoulder at 15.4 kK and a sharper asymmetric band at 24.0 kK. The band which appears off scale in Figure 23 is one of two bands in the ultraviolet region at 32.0 (shoulder) and 35.0 kK. Deconvolution of the spectrum results in two sets of bands containing either 4 or 5 bands between 33.3 and 12.5 kK. Upon aging, the solution becomes pale yellow (almost colorless due to dilution), and a concomitant decay of the spectrum in the 33.3 to 12.5 kK region occurs until only the two bands at 32.0 and 35.0 kK remain. This time dependence parallels the The visible region of the electronic absorption spectrum of Nb(DPM)<sub>4</sub> in dichloromethane (2.83 x  $10^{-4}$  M). The dashed and dotted lines represent 2 deconvolutions of the spectrum. Figure 23.



### Table XVI

UV VISIDIE Dana	<i>a or no (bring</i> 4		<u>(100 x 10</u> )
	$\lambda$ , nm	<u>E,kK</u>	$\varepsilon, cm^{-1}-M^{-1} \times 10^{-2}$
Experimental:	650	15.4	
-	561	17.8	
	416	24.0	
Resolved:	680	14.7	6.89
(dashed lines)ª	550	18.2	21.4
	415	24.1	18.9
	387	25.8	16.2
Resolved:	705	14.2	2.80
(dotted lines) <u>a</u>	655	15.3	6.36
(dotted imes)=	545	18.4	20.0
	415	24.1	18.9
	387	25.8	16.2
Charge transfer:	312	32.0	28.8
-	286	35.0	57.6

<sup>a</sup> Dotted and dashed lines of resolved spectrum shown in Figure 23.

# UV-Visible Bands of Nb(DPM), in Dichloromethane $(2.83 \times 10^{-4} \text{M})$

conductivity observations discussed above (see p. 69) and again is believed to be due to oxidation, possibly accompanied by hydrolysis. Thus, the bands in the visible region may be due to transitions involving the single d electron of the Nb in the +4 oxidation state, but the two bands in the ultraviolet region are due to ligand charge transfer. The validity of the latter assignment was confirmed by observing the identical bands at 32.0 and 35.0 kK for a dichloromethane solution of  $Zr(DPM)_{4}$ .

There are three possibilities for assigning the bands in the visible region: the bands may be due to (1) d-d transitions, (2) metal to ligand charge transfer, and, (3) ligand to metal charge transfer. In view of the large difference in intensities between the two bands at 14.2 and 15.3 kK ( $\varepsilon$  = 280 and 636 cm<sup>-1</sup>M<sup>-1</sup>, respectively) as estimated from the "dashed lines" in Figure 23 and the three bands at 18.4, 24.1, and 25.8 kK ( $\epsilon$  = 2000, 1890, and 1620, respectively) as judged from the deconvoluted spectrum in Figure 23, it is tempting to assign the two low energy bands to d-d transitions. Figure 24 shows the crystal field splitting diagram for a  $D_{4d}$  square antiprism.<sup>61,62</sup> As the eight monodentate ligands of D<sub>4d</sub> square antiprism are replaced by four bidentate ligands, the symmetry is lowered to D, and the degeneracy of the E<sub>2</sub> level is removed. Consequently, three d-d transitions would be predicted. The observation of only two bands may be due to spectral deconvolution inaccuracies or to a non-detectable energy difference between the  $B_2$  and  $B_1$  energy levels. Deutscher and Kepert<sup>11b</sup> were unable to assign any of the observed bands in the uv-visible spectra of several tetrakis diketonates to d-d transitions. However, the above authors do make d-d assignments for three weak bands at 9.8, 12.8 The crystal field splitting diagram for the d orbital energy levels for a  $D_{2d}$  dodecahedron and a  $D_{4d}$  square antiprism. $^{61},^{62}$ Figure 24.



Figure 24

(shoulder at 14.7), and 17.5 kK for the dodecahedral NbCl<sub>4</sub>( $C_2H_5$  diars)<sub>2</sub> in toluene. Agreement with the theoretically predicted number of transitions for a dodecahedron (see Figure 24) is cited but the appearance of shoulders at 14.7 and 23 kK is not explained. The bands of lowest intensity in Nb(DPM)<sub>4</sub> at 14.2 kK and 15.3 appear to be the most reasonable candidates for assignment as d-d transitions, even though the molar absorptivities are unusually high. However, bands of unusually high intensity for d-d transitions have been assigned previously for several tetrakis(8-quinolinolato)tungsten(IV) chelates in benzene solution.<sup>63,64</sup> Bands at 9.9 ( $\epsilon$  = 500) and 11.2 kK ( $\epsilon$  = 450), for example, have been assigned for both W(QCl<sub>2</sub>)<sub>4</sub> and W(QBr<sub>2</sub>)<sub>4</sub> (halogen substitution at the 5,7 positions of the 8-quinolinol).

The remaining bands in Nb(DPM)<sub>4</sub> at 18.4, 24.1, and 25.8 kK are presumed to be charge transfer bands on the basis of intensity. An attempt to make a specific assignment in terms of direction of the transfer was hampered by the absence of consistent data on analogous Nb(IV) chelates. It is probable that the transitions are due to ligand to metal charge transfer in view of the electron-rich ligand  $\pi$  orbitals and the high positive charge on the metal atom. An experiment that may confirm this assignment would be to prepare, if possible, the trifluoroand hexafluoro acelylacetonate analogs of the DPM complex and look for the expected high energy shift in the transitions as a function of increasing fluorination. Deutscher and Kepert<sup>11b</sup> assign a band at 24.0 kK ( $\varepsilon = 1200$ ) to a d to  $\pi_4^*$  transition and a band at 19.4 kK ( $\varepsilon = 890$ ) to a  $\pi_3$  to d transition for Nb(ACAC)<sub>4</sub> in toluene. However, the band at 24 kK is assigned to a  $\pi_3$  to d transition in a subsequent discussion in the publication. In spite of this confusion, the assignment of the three bands between 18.4 and 25.8 kK in Nb(DPM) $_4$  to charge transfer transitions involving the Nb atom and the DPM ligands is reasonable.

The magnetic circular dichroism spectrum shown in Figure 25 was recorded in an effort to confirm the deconvolution of the electronic absorption spectrum.<sup>‡</sup> With the exception of a shoulder at 23.6 kK, no new additional bands were observed. Thus it appears that the deconvoluted spectrum represented by the dashed lines is the appropriate choice, as was assumed in the above discussion (see Figure 23).

In an attempt to correlate the solid state stereochemistry with the stereochemistry in solution, an electronic absorption spectrum of a mull of Nb(DPM)<sub>4</sub> was recorded. The spectrum is identical to the solution spectrum both in terms of relative band intensities and band energies. Thus, this evidence suggests that the complex retains a square antiprismatic stereochemistry in solution.

To test this hypothesis, an esr study of Nb(DPM)<sub>4</sub> was undertaken. The room temperature esr spectrum of the complex in hexane is shown in Figure 26. Ten well-resolved nuclear hyperfine components are observed, as expected (I = 9/2, 100% <sup>93</sup>Nb). The anisotropic components are observed in the hexane glass spectrum shown in Figure 27. The isotropic and anisotropic g values (<g>, g<sub>||</sub>, g<sub>⊥</sub>) and the coupling constants (<g>, A<sub>||</sub>, and A<sub>⊥</sub>) were calculated with the aid of second order corrections, since the high field approximation for determination

<sup>&</sup>lt;sup>+</sup> The author wishes to acknowledge Professor C. Djerassi, Stanford University, for recording the spectrum.

The magnetic circular dichroism spectrum of Nb(DPM) $_4$ ; the visible region of the electronic absorption spectrum is shown below the MCD spectrum. Figure 25.



Figure 26. The room temperature esr spectrum of Nb(DPM)\_4 in hexane.

The esr spectrum (77°K) of Nb(DPM) $_4$  in hexane glass. Figure 27.


of g values was precluded by the rather large magnitude of the hyperfine splittings<sup>65</sup> (see Table XVII and XVIII). The room temperature spectrum yielded  $\langle g \rangle$  and  $\langle a \rangle$ , and  $g_{\perp}$ ,  $g_{\parallel}$ ,  $A_{\perp}$ , and  $A_{\parallel}$  were obtained from the hexane glass spectrum. Only five of the ten possible parallel components were resolved. Consequently, the positions of the third and eighth, and fifth and sixth lines were used to determine  $A_{\parallel}$  and  $g_{\parallel}$ . The experimentally-observed parameters are tabulated and compared to "calculated" parallel g and A values which were obtained by substituting the experimental perpendicular and isotropic values into the following equations:

 $g_{||} = 3 \langle g \rangle - 2 g_{\perp}$  $A_{||} = 3 \langle a \rangle - 2 A_{|}$ 

The experimental anisotropic values were substituted into the above equations to obtain the "calculated" <g> and <a> parameters.

Theoretical calculations of esr parameters for a  $D_{2d}$  dodecahedron and  $D_{4d}$  square antiprism have shown that  $g_{||} < g_{\perp}$  and  $A_{||} > A_{\perp}$  for a dodecahedron and  $g_{\perp} < g_{||} = 2.0023$  and  $A_{||} < A_{\perp}$  for a square antiprism.<sup>61,67</sup> The anisotropic parameters for Nb(DPM)<sub>4</sub> show that  $g_{\perp} = 1.928 < g_{||} = 1.997$  and  $A_{||} = 52.7G < A_{\perp} = 141.1G$ . It is evident, therefore, that a square antiprismatic configuration is the correct choice for the stereochemistry in hexane solution. The identical spectrum was obtained in dichloromethane at room temperature but the parallel components were not resolvable from the glass spectrum due to a solvent line-broadening effect which apparently has decreased the spin-lattice relaxation time.<sup>66</sup>

#### Table XVII

# Second Order Correction Equations For Calculation of g Values<sup>65</sup>

For resonance, 
$$hv = g\beta H_{0}$$

For 
$$\langle g \rangle$$
,  $H_0 = H_m + \langle a \rangle m_I + \frac{\langle a \rangle^2}{2H_0} [I(I+1) - m_I^2]$ 

~

For 
$$g_{\|}$$
,  $H_{o} = H_{m} + A_{\|} M_{I} + \frac{A_{\|}^{2}}{2H_{o}} [I(I+1) - m_{I}^{2}]$ 

For 
$$g_{\perp}$$
,  $H_{o} = H_{m} + A_{\perp}m_{I} + \frac{A_{\perp}^{2} + A_{\parallel}^{2}}{4H_{o}^{2}} [I(I+1) - m_{I}^{2}]$ 

Where  $H_m =$  the magnetic field position of the ESR Jine due to the nuclear spin quantum number,  $m_I$ , v is the klystron frequency and <a>,  $A_{||}$ , and  $A_{\perp}$  are the hyperfine coupling constants.

#### Table XVIII

- $\langle g \rangle = 1.9507^{\underline{a}}$   $\langle g \rangle_{(calc.)} = 1.9508$  $\langle a \rangle = 109.9 \ G^{\underline{a}}$   $\langle a \rangle_{(calc.)} = 111.6 \ G$
- $g_{||} = 1.9967 \frac{b}{c}$   $g_{||} = 1.9278 \frac{b}{c}$  $g_{||(calc.)} = 1.9965$
- $A_{\perp} = 141.1^{\underline{b}}$   $A_{\parallel} = 52.7 \text{ G}^{\underline{b}}$  $A_{\parallel}(\text{calc.}) = 47.4 \text{ G}$
- <sup>a</sup> Measured in hexane at room temperature.
  <sup>b</sup> Measured in hexane at 77°K

The esr spectra of the Nb(DPM)<sub>4</sub> powder at room temperature and 77°K are shown in Figures 28a and 28b. At least 14 lines are visible which may be a result of two sets of 10 lines, some of which are overlapping. This would imply the presence of two magnetically-nonequivalent Nb sites as is expected from the observation of two Nb(DPM)<sub>4</sub> molecules in the asymmetric unit of the unit cell.

To further confirm the postulation of a square antiprismatic stereochemistry in solution, a Zr(DPM), host was doped with Nb(DPM), by dissolving both complexes in hexane and evaporating the solution to dryness. Zr(DPM), is expected to adopt an antiprismatic configuration based on the prediction of Blight and Kepert<sup>60</sup> and the fact that  $Zr(ACAC)_{A}$  is known to be antiprismatic.<sup>3b</sup> The esr spectrum of the doped powder at 77°K is shown in Figure 29; the spectrum is identical to the hexane glass spectrum of Nb(DPM), (see Figure 27). To be meaningful, an experiment of the above type is usually contingent upon the host being isomorphous with the paramagnetic solute; otherwise a distortion may occur in the structure of the solute when it occupies lattice points of the host. However, in the above case, the question of isomorphism is less critical since positive evidence was obtained in that  $g_{||} > g_{|}$  is consistent with a square antiprismatic geometry and not a dodecahedral structure. Powder diffraction data were compared for Zr(DPM), and Nb(DPM), as shown in Table XIX. The two patterns look very similar, but small differences in the powder patterns make an unequivocal statement regarding isomorphism impossible. The important point, however, is that the doped powder and solution esr spectra were identical and, therefore, consistent with the theoretical predictions for a square antiprism, even though the symmetry in

The room temperature esr spectrum of Nb(DPM) $_4$  powder. Figure 28a.

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ì.



Figure 28b. The esr spectrum of Nb(DPM) $_4$  powder at 77°K.



Figure 29. The powder esr spectrum at 77°K of Nb(DPM) $_4$  doped in Zr(DPM) $_4$ .



#### Table XIX

# X-Ray Powder Patterns for

Nb(DPM)<sub>4</sub> and  $Zr(DPM)_4$ 

Zr (DPM) 4	<u>Nb(DPM)</u> 
10.97 <sup>a</sup> - v.s. <sup>b</sup>	10.43 - v.s., br
10.14 - v.s.	
9.57 - v.s.	9.43 - v.s., br
8.56 - s.	8.44 - s., br
7.53 - m.	7.53 - s.
6.59 - w.	6.51 - m.
0.40	6.17 - w.
5.81 - v.w.	5.72 - w.
5.51 - v.w.	5.38 - v.w.
5.12 - v.w.	5.05 - m.
4.95 - w.m.	
4.81 - v.w.	4.87 – w.
4.67 – m.	4.71 - m.
4.52 - m.	4.58 - v.w.
	4.44 - m.
4.27 - s.	4.29 - m.
4.01 - w.	4.06 - w.
3.76 - w.	3.86 - w.
	3.72 - w.
3.41 - v.w.	3.51 - v.w.
3.29 - v.w.	3.30 - v.w.
3.18 - w.	
3.15 - w.	3.16 - v.w.
	3.05 - v.w.
	2.95 - v.w.
	2.86 - v.w.
2.32 - w.	

- $\stackrel{\circ}{-}$  d-spacing in  $\stackrel{\circ}{A}$  units.
- <sup>b</sup> Visual estimates of intensity with the following abbreviations used: v.s. = very strong, s. = strong, m. = medium, w. = weak, v.w. = very weak, br. = broad.

solution may be  $D_2$  or  $C_2$  rather than  $D_4$ .

The question of retention of the solid state stereochemistry in solution has been a widely-studied aspect of the chemistry of many complexes and in particular, the Mo(V) and W(V) octacyano system.<sup>2,58,61,67-69</sup> Emission spectral data from frozen powders and solutions of lanthanide metal beta-diketonates has been presented as evidence for the presence of the D<sub>4</sub> antiprism.<sup>70</sup> However, in both of the above systems, the nature of the influence of cations and solvents on the stereochemistry in solution is unclear and consequently, the interpretation of the experimental observations is surrounded by controversy.<sup>68,69,71</sup> On the other hand, as described above, the square antiprismatic polyhedral framework of Nb(DPM)<sub>4</sub> <u>is</u> retained in solution.

BIBLIOGRAPHY

- 1. S. J. Lippard, Prog. Inorg. Chem., 8, 109(1967).
- 2. E. L. Muetterties and C. M. Wright, <u>Quart. Rev. Chem. Soc.</u>, <u>21</u>, 109(1967).
- 3. (a) J. L. Hoard and J. V. Silverton, <u>Inorg. Chem.</u>, <u>2</u>, 235(1963);
  (b) J. V. Silverton and J. L. Hoard, <u>Inorg. Chem.</u>, <u>2</u>, 243(1963).
- 4. R. V. Parish, Coord. Chem. Rev., 1, 439(1966).
- 5. R. C. Fay and T. J. Pinnavaia, Inorg. Chem., 7, 502(1968).
- 6. J. P. Fackler, Jr., Prog. Inorg. Chem., 7, 361(1966).
- 7. C. Djordjevic and V. Katovic, Chem. and Ind., 411(1963).
- 8. Ibid., J. Inorg. Nucl. Chem., 25, 1099(1963).
- 9. C. Djordjevic, Spect. Acta., 21, 301(1965).
- 10. N. Brnicevic and C. Djordjevic, J. Less Com. Met., 13, 470(1967).
- 11. (a) R. L. Deutscher and D. L. Kepert, <u>J. Chem. Soc. D.</u>, 121(1969);
  (b) <u>Ibid.</u>, <u>Inorg. Chim. Acta.</u>, <u>4</u>, 645(1970).
- 12. A. Rosenheim and E. Roehrich, Z. Anorg. Chem., 204, 342(1932).
- 13. F. Fairbrother, "The Chemistry of Niobium and Tantalum", Elsevier Publishing Co., New York, N. Y., 1967, p. 33.
- 14. (a) E. L. Muetterties and C. M. Wright, <u>J. Am. Chem. Soc.</u>, <u>87</u>, 21(1965); (b) <u>Ibid.</u>, 4706(1965).
- 15. H. Funk, Chem. Ber., <u>67</u>, 1801(1934).
- A. Syamal, D. H. Fricks, D. C. Pantaleo, P. G. King, and R. C. Johnson, J. Less Com. Met., 19, 141(1969).
- 17. P. N. Kapoor and R. C. Mehrotra, J. Less Com. Met., 8, 339(1965).
- R. N. Kapoor, S. Prakash, and P. N. Kapoor, <u>Bull. Chem. Soc. Jap.</u>, 40, 1384(1967).
- 19. R. Gut, H. Buser, and E. Schmid, Helv. Chim. Acta., 48, 878(1965).
- 20. R. C. Mehrotra and P. N. Kapoor, J. Less Com. Met., 7, 176(1964).
- 21. Ibid., 453(1964).
- R. C. Mehrotra, P. N. Kapoor, S. Prakash, and P. N. Kapoor, <u>Aust. J. Chem.</u>, <u>19</u>, 2079(1966).

- 23. B. Kamenar and C. K. Prout, <u>J. Chem. Soc.</u>, <u>(A)</u>, 2379(1970).
- Von Leopold Wolf and Hartmut Barnighausen, <u>Acta Cryst.</u>, <u>13</u>, 778(1960).
- 25. E. G. Taylor and C. A. Kraus, J. Am. Chem. Soc., 69, 1731(1947).
- 26. R. E. McCarley and B. A. Torp, Inorg. Chem., 2, 540(1963).
- 27. J. T. Adams and C. R. Hauser, J. Am. Chem. Soc., 66, 1220(1944).
- 28. D. F. Evans, J. Chem. Soc., 2003(1959).
- 29. A. Earnshaw, "Introduction to Magnetochemistry", Academic Press London, 1968, p. 6.
- 30. "Handbook of Chemistry and Physics", 47th Edition, The Chemical Rubber Company, Cleveland, 1966.
- N. F. M. Henry, H. Lipson, and W. A. Wooster, "The Interpretation of X-Ray Diffraction Photographs", MacMillan and Company, Ltd., London, 1961.
- 32. H. Lipson and W. Cochran, "The Determination of Crystal Structures", Cornell University Press, New York, 1966.
- 33. G. H. Stout and L. H. Jensen, "X-Ray Structure Determination", The MacMillan Company, New York, 1968.
- 34. R. L. Vandlen and A. Tulinsky, Acta. Cryst., B27, 437(1971).
- 35. T. J. Pinnavaia and R. C. Fay, Inorg. Chem., 7, 508(1968).
- K. Nakamoto, C. Udovich, and J. Takemoto, <u>J. Am. Chem. Soc.</u>, <u>92</u>, 3937(1970).
- 37. N. S. Gill and R. S. Nyholm, J. Chem. Soc., 3997(1959).
- P. R. Heckley and D. G. Holah, <u>Inorg. Nucl. Chem. Letters</u>, <u>6</u>, 865(1970).
- E. L. Muetterties and C. M. Wright, <u>J. Am. Chem. Soc.</u>, <u>87</u>, 21(1965); <u>ibid.</u>, <u>87</u>, 4706(1965).
- 40. S. M. Horner, R. J. H. Clark, B. Crociani, D. B. Copley, W. W. Horner, F. N. Collier, and S. Y. Tyree, Jr., <u>Inorg. Chem</u>., <u>7</u>, 1859(1968).
- 41. D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, <u>J. Chem. Soc</u>., 2189(1963).
- 42. D. Brown, J. F. Easey and J. G. H. Du Preez, <u>J. Chem. Soc. (A)</u>, 258(1966).

- 43. D. B. Copley, F. Fairbrother, and A. Thompson, <u>J. Less. Com. Met.</u>, <u>8</u>, 256(1965).
- 44. D. B. Copley, F. Fairbrother, K. H. Grundy, and A. Thompson, J. Less. Com. Met., <u>6</u>, 407(1964).
- 45. R. C. Fay and R. N. Lowry, Inorg. Chem., 9, 2048(1970).
- 46. S. J. Lippard and B. J. Russ, Inorg. Chem., 7, 1686(1968).
- 47. W. DeW. Horrocks, Jr., J. P. Sipe, III, and J. R. Luber, <u>J. Am. Chem.</u> <u>Soc.</u>, <u>93</u>, 5258(1971).
- 48. C. S. Erasmus and J. C. A. Boeyens, <u>J. Cryst. Mol. Struct.</u>, <u>1</u>, 83(1971).
- 49. C. S. Erasmus and J. C. A. Boeyens, Acta. Cryst., B26, 1843(1970).
- 50. J. P. R. DeVilliers and J. C. A. Boeyens, <u>Acta. Cryst.</u>, <u>B27</u>, 692(1971).
- 51. M. J. Bennet, F. A. Cotton, P. Legzdins, and S. J. Lippard, <u>Inorg</u>. <u>Chem.</u>, <u>7</u>, 1770(1968).
- 52. F. A. Cotton and J. S. Wood, Inorg. Chem., 3, 245(1964).
- 53. F. A. Cotton and J. J. Wise, <u>Inorg. Chem.</u>, <u>5</u>, 1200(1966).
- 54. N. Galesic, B. Matkovic, M. Herceg, and M. Sljukic, <u>J. Less. Com.</u> <u>Met.</u>, <u>25</u>, 234(1971).
- 55. G. Mathern and R. Weiss, Acta. Cryst., <u>B27</u>, 1610(1971).
- 56. G. Mathern and R. Weiss, *ibid.*, Acta. Cryst., B27, 1572(1971).
- 57. D. L. Kepert, J. Chem. Soc., 4736(1965).
- 58. D. G. Blight and D. L. Kepert, Theor. Chim. Acta., 11, 51(1968).
- 59. J. L. Hoard, T. A. Hamor, and M. D. Glick, <u>J. Am. Chem. Soc.</u>, <u>90</u>, 3177(1968).
- 60. D. G. Blight and D. L. Kepert, <u>Inorg. Chem.</u>, <u>11</u>, 1556(1972).
- 61. B. R. McGarvey, Inorg. Chem., 5, 476(1966).
- 62. R. V. Parish and P. G. Perkins, J. Chem. Soc., (A), 345(1967).
- 63. W. D. Bonds, Jr., and R. D. Archer, <u>Inorg. Chem.</u>, <u>10</u>, 2057(1971).
- 64. R. A. Pribush, University of Massachusetts, private communication.

- 65. D. P. Johnson and R. D. Bereman, J. Inorg. Nucl. Chem., 34, 679(1972).
- 66. J. E. Wertz and J. R. Bolton, "Electron Spin Resonance", McGraw-Hill, Inc., New York, 1972, Chapter 9.
- 67. R. G. Hayes, J. Chem. Phys., 44, 2210(1966).
- 68. B. J. Corden, J. A. Cunningham and R. Eisenberg, <u>Inorg. Chem.</u>, <u>9</u>, 536(1970).
- 69. T. V. Long, II, and G. A. Vernon, J. Am. Chem. Soc., <u>93</u>, 1919(1971). See also references therein.
- 70. (a) H. Samelson, V. A. Brophy, C. Breecher, and A. Lempicki, <u>J. Chem. Phys.</u>, <u>41</u>, 3998(1964). (b) Von E. Butter and W. Seifert, <u>Z. Anorg. Allg. Chem.</u>, <u>67</u>, 384(1971).
- 71. M. O. Workman and J. H. Burns, <u>Inorg. Chem.</u>, <u>9</u>, 1542(1969).

APPENDIX A

Diketonate Ligand Abbreviations

### APPENDIX A

# Diketonate Ligand Abbreviations

Abbreviation	Trivial Name	R COCHCC R1	$R_2^{R_2}$
ACAC	acetylacetonate	СН3	CH <sub>3</sub>
BZAC	benzoylacetonate	<sup>С</sup> 6 <sup>Н</sup> 5	<sup>СН</sup> 3
BTFA	b <b>enzoyltrifluoroace</b> tonate	<sup>с</sup> 6 <sup>н</sup> 5	CF3
DBM	dibenzoylmethanate	с <sub>6</sub> н <sub>5</sub>	<sup>С</sup> 6 <sup>Н</sup> 5
DPM	dipivaloylmethanate	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	<u>t</u> -C <sub>4</sub> H <sub>9</sub>
TTFA	the <b>noyltrifluoroacetonate</b>	ſ	CF <sub>3</sub>
Tp	tropolonate		

#### APPENDIX B

Observed and Calculated Structure Factors (multiplied by 10 and using a scale factor of 0.9453)

#### APPENDIX B

Observed and Calculated Structure Factors (multiplied

by 10 and using a scale factor of 0.9453)

н	κ	FOBS	FCAL	н	к	FOBS	FCAL	н	κ	FOBS	FCAL
¥ #	L	= 0	**								
0	S	335	358	4	3	1213	1184	8	4	521	551
0	3	131	62	4	4	556	514	8	5	106	149
0	4	425	395	4	5	159	188	8	6	388	317
0	5	104	49	4	6	270	307	8	7	610	577
0	6	181	253	4	7	717	709	8	8	171	162
0	7	787	706	4	8	200	198	8	9	72	80
0	8	142	128	4	9	103	92	9	0	86	130
0	9	83	68	4	10	81	109	9	1	656	546
0	11	113	168	4	11	320	320	9	2	124	143
1	Ō	49	52	5	0	172	218	9	3	314	303
1	1	2649	2682	5	1	983	769	9	4	53	78
1	2	202	159	5	2	439	385	9	5	685	689
1	3	84	79	5	3	677	647	9	6	293	256
1	4	118	99	5	4	264	348	9	7	58	85
1	5	688	577	5	5	111	115	9	8	331	312
1	6	489	513	5	6	861	775	9	9	334	325
1	7	74	27	5	8	567	492	9	10	134	143
1	8	459	499	5	9	153	137	10	0	1260	1501
1	9	53	117	5	10	95	89	10	1	62	135
1	10	67	31	6	0	206	257	10	3	326	250
2	0	3415	3605	6	1	176	257	10	4	701	694
2	1	113	175	6	2	198	551	10	5	143	142
2	2	193	168	6	3	141	133	10	6	311	285
2	3	930	944	6	4	102	133	10	7	422	389
2	4	72	221	6	5	260	325	10	8	186	157
S	5	123	131	6	6	150	49	11	0	_61	75
2	6	519	522	6	1	890	863	11	1	741	742
2	7	683	617	0	8	244	248	11	3	488	468
2	8	74	75	6	19	101	106	11	4	188	154
2	. 9	135	141	0	10	120	118	11	5	306	274
2	11	96	40	7	11	318	287	11	6	328	320
3	0	263	214		1	220	151	11	н 0	186	184
3	1	332	411	7	1	237 E1E	221	11	. 9	168	186
3	2	1237	1060	7	2	212	400	11	10	91	97
3	3	380	421	7	3	220	213	12	0	709	123
3	4	287	285	7	4	150	100	12	1	115	108
3	5	124	630	7	2	190	185	12	2	2.51	274
3	6	667	617	7	0	601	60.3 E()	12	5	100	110
5	/	73	55	י ד	0	210	204 211	12	4 5	170	121
<b>ر</b>	8	340	342	י 7	7	219	211	12	, 6	142	144
ر د	7	55	70	י 2	10	670	141	12	7	202	179
<b>5</b>	10	138	124	с) Ц	1	1/1	001	12	, 8	2.V2 Q5	90
4	0	040		n a	1	141		13	้า	583	607
4	เ ว	1145	1001	сі А	2	200	77	13	2	173	198
	r	471	→ / )	• • •	.)	200	6.07		•.		• *

н	κ	FORS	FCAL	н	κ	FOBS	FCAL	н	к	FOBS	FCAL
13	3	440	402	0	2	548	507	-3	7	343	304
13	4	172	140	0	3	89	104	3	7	241	284
13	5	435	389	Ō	4	212	155	-3	8	265	230
13	6	137	163	Ô	5	663	630	3	8	351	361
13	- 8	148	133	Ó	6	325	377	-3	10	335	310
13	9	81	108	Ō	8	167	192	3	10	228	243
14	0	336	332	0	9	331	356	3	11	85	104
14	2	133	146	-1	1	2083	2101	-4	1	192	164
14	3	371	383	ī	ī	1626	1787	4	1	2007	1942
14	4	453	442	-1	2	382	309	-4	2	2131	1903
14	5	64	90	ī	S	444	406	4	2	1343	1342
14	6	67	109	-1	3	630	487	-4	3	357	319
14	7	278	251	1	3	88	70	4	3	342	385
15	1	457	454	ī	4	574	571	-4	4	508	469
15	2	177	165	-1	5	114	76	4	4	136	175
15	3	226	220	ī	5	173	141	-4	5	389	352
15	4	319	334	-1	6	402	412	4	5	398	426
15	5	166	163	ī	6	364	328	-4	6	532	499
15	6	360	335	-1	7	420	416	4	6	142	183
15	7	93	81	ī	7	345	319	-4	7	122	123
15	8	167	181	-1	8	293	278	-4	8	164	141
16	0	570	572	ī	8	320	372	4	8	.334	338
16	2	87	79	-1	10	197	160	-4	9	444	382
16	3	265	290	ī	10	210	180	4	9	332	280
16	4	111	143	-2	1	291	312	-4	11	151	150
16	5	95	76	2	ī	103	77	4	11	130	138
16	7	283	290	-2	2	839	647	-5	1	1130	903
17	0	66	111	2	2	266	262	5	1	861	781
17	ĭ	482	447	-2	3	142	166	-5	2	97	100
17	3	115	125	2	2	625	661	5	2	136	126
17	4	225	246	-2	4	299	334	-5	3	1672	1379
17	5	151	145	2	4	48	91	5	จ้	718	676
17	6	215	237	-2	5	716	661	-5	4	440	427
18	0	538	543	2	Ś	447	444	Ś	4	718	673
18	3	277	275	-2	6	529	468	5	5	103	133
18	4	234	229	2	6	548	580	-5	6	707	724
18	6	119	109	-2	Å	171	188	5	6	816	699
19	1	214	241	2	8	82	85	-5	7	461	462
19	2	191	184	-2	9	422	377	5	7	438	420
19	3	124	123	2	á	470	457	-5	8	517	483
19	4	109	175	-3	í	251	311	5	8	399	388
19	5	218	232	3	i	925	886	-5	10	170	156
20	Ó	291	340	้า	2	477	505	5	10	224	225
20	ĭ	99	104	-7	۲. ۲	1568	1577	-6	Ĩ	153	140
20	3	175	168	ر ۲	7	271	308	6	i	136	255
21	õ	84	99	-7	4	252	347	-6	2	1234	1246
21	ĩ	199	214	ר ר	4	444	438	6	2	1170	1161
	•			-7	ς	169	157	-6	3	1.38	144
# #	1	= 1	44	3	Ś	140	155	6	ŕ	ЪЧ	117
	-	•		-7	6	569	524	-6	4	93	142
0	1	478	461	- 7	6	483	419	6	4	272	285
-	-		-		• •		• • •		-		

н	K	FODS	FCAL	н	κ	FOBS	FCAL	н	κ	FOBS	FCAL
-6	5	567	586	c,	8	228	217	13	2	97	106
6	5	1297	1273	9	9	95	85	-13	3	847	823
-6	6	482	400	-9	10	280	247	13	3	734	684
-6	8	343	297	9	10	273	254	-13	4	333	283
6	8	242	239	-10	2	768	703	13	Å	300	301
-6	9	447	433	10	2	878	866	13	5	211	79
6	9	331	350	-10	3	103	104	_13	5	150	154
-6	11	170	152	10	3	382	331	-13	6	175	105
6	11	132	126	-10	4	288	292	13	7	1/5	100
-7	1	182	258	10	4	209	238		6	105	100
7	1	456	492	-10	5	613	502	-13	e B	220	105
7	2	308	354	10	5	566	493	13	ר ר	700	177
-7	3	321	189	-10	6	236	218	-14	2	122	134
7	3	930	951	10	6	285	270	14	2		
-7	4	148	132	-10	8	197	194	-14	່ງ າ	105	154
7	4	554	561	10	Ŕ	284	257	14	5	133	124
-7	5	120	110	-10	à	221	231	-14	4	283	260
-7	6	739	730	10	ó	300	201	14	4	93	220
7	6	538	525	-11	í	539	577	-14	2	298	334
-7	7	612	566	11	ī	627	642	14	2	451	421
7	7	453	388	11	ż	113	125	14	0	91	98
-7	8	550	520	-11	3	928	856	14	0	174	10/
7	8	317	307	11	3	799	755	-15	1	284	283
-7	10	251	218	-11	4	426	377	17	2	362	353
7	10	292	304	11	4	230	217	17	5	103	135
8	1	332	243	11	5	136	125	10	4	299	244
-8	2	771	751	-11	6	216	200	12	07	211	241
8	2	896	858	11	6	245	228		0	151	110
8	3	56	65	-11	7	178	175	17	о Э	<pre>&lt;11</pre>	205
8	4	588	580	11	7	203	206	-10	2	409	411
-8	5	558	511	-11	Ŕ	198	192	10	2	481	411
8	5	498	480	11	8	192	184	-10	3	88	99
-8	6	580	460	11	9	67	72	-10	4	117	114
Я	6	346	289	-11	10	222	213	-10	2	489	520
-8	8	232	207	12	ĩ	137	152	10	2	437	407
8	8	213	516	-12	2	908	407	10	0	142	108
-8	9	478	502	12	2	1061	995	-1/	1	251	270
8	9	281	315	-12	3	78	60	1/	1	340	319
-9	1	590	504	12	3	84	65	-1/	3		216
9	1	897	837	-12	4	278	262	17	3	193	175
9	2	128	136	12	4	259	260	-1/	4	304	321
-9	3	647	705	-12	5	472	465	17	4	360	312
9	3	728	699	12	5	429	395	-17	5	102	214
9	4	93	92	-12	6	179	172	-17	6	120	214
-9	5	257	231	12	6	137	125	_10	ט כ	224	245
9	5	164	172	-12	8	135	117	-10	2	20	295
-9	6	211	235	12	8	213	188	-18	<i>נ</i>	234	141
9	6	340	329	-12	9	210	191	18	ר ר	117	141
-9	7	276	288	12	9	248	233	-18	5	141	107
9	7	309	301	-13	1	420	416	19		120	114
-4	8	342	340	13	1	392	411	-18	יד ג	220	265
								± \ /	<u> </u>	L ( 7	という

н	κ	FORS	FCAL	н	κ	FOBS	FCAL	н	κ	FORS	FCAL
18	5	202	191	2	3	854	983	-4	11	296	282
-18	6	99	115	-2	4	503	439	4	11	251	279
-19	1	135	155	2	4	205	335	-5	0	162	112
19	1	202	217	-2	5	125	174	5	0	58	71
-19	3	211	259	2	5	161	190	-5	1	572	354
19	3	235	211	-2	6	270	241	5	ī	550	575
-19	4	211	216	2	6	351	384	-5	2	1194	1155
19	4	226	183	-2	7	555	564	-5	3	655	574
-20	2	170	203	2	7	660	635	5	3	194	271
20	2	302	290	-2	8	176	231	-5	4	155	169
-20	4	116	151	2	8	62	13	5	4	579	547
-51	1	128	159	2	9	152	150	-5	5	578	570
				2	11	156	171	5	5	217	189
44	L	= 2	* *	-3	0	366	338	-5	6	450	409
				3	0	135	131	5	6	812	780
0	0	3515	4147	-3	1	613	599	-5	7	87	100
0	1	315	359	3	1	<u>515</u> 6	1992	-5	8	609	509
0	2	58	179	-3	S	887	723	5	8	425	438
0	3	160	209	3	2	1122	1063	5	9	186	231
0	4	513	587	-3	3	659	662	5	10	152	140
0	5	237	204	3	3	225	154	-6	0	254	282
0	6	318	349	-3	4	110	178	6	0	131	151
0	7	488	471	3	4	282	268	-6	1	333	315
0	8	94	100	-3	5	286	329	6	1	189	277
0	9	73	52	3	5	426	421	6	2	512	468
-1	0	64	74	-3	6	670	623	-6	3	609	466
1	0	116	148	3	6	524	544	6	3	495	540
-1	1	2069	2223	-3	8	422	403	-6	4	86	94
1	1	1709	1921	3	8	511	550	6	4	526	526
-1	2	1669	1508	-3	9	200	164	-6	5	156	161
1	2	2504	2261	3	9	67	40	6	5	241	238
-1	3	401	396	-3	10	128	140	-6	6	794	737
ī	3	86	42	3	10	81	86	-6	7	982	941
-1	4	98	63	-4	0	507	484	6	7	681	667
ī	4	390	339	4	0	1376	1182	-6	8	194	175
-1	5	896	847	-4	1	1594	1254	6	8	173	168
ī	5	810	794	4	1	1010	964	6	9	85	60
-1	6	480	493	-4	S	484	473	6	10	171	174
1	6	463	495	4	2	543	502	-6	11	326	287
-1	8	296	308	4	3	751	773	6	11	245	250
1	8	380	454	-4	4	638	616	7	Ō	67	76
-1	9	260	310	4	4	84	156	-7	ĩ	257	375
1	9	134	133	-4	5	121	180	7	ī	933	810
i	10	106	110	4	5	166	166	-7	2	484	460
-2	0	2957	3103	-4	6	606	513	7	2	633	546
2	Ū	2052	2102	-4	7	586	619	-7	3	250	172
-2-	1	45	43	4	, 7	922	8010	7	3	294	359
2	ī	63	149	4	8	204	170	-7	4	69	141
-2	2	468	409	-4	9	111	117	7	4	479	504
2	5	287	303	4	9	131	122	-7	5	589	579
-2	3	789	879	4	10	137	151	7	5	214	855

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Н		κ	FOBS	FCAL	н	κ	FOBS	FCAL	Н	κ	FORS	FCAL
-	7	6	757	691	10	3	501	525	-13	4	219	502 E
	7	6	353	377	-10	4	869	9 834	13	4	102	2 144
-	7	8	706	681	10	4	559	9 558	-13	5	327	2 337
	7	8	260	239	-10	5	120	) 96	13	5	282	2 237
-	7	9	107	89	10	5	87	9?	-13	6	20)	1 211
	7	9	327	328	-10	6	18(	) 197	13	6	307	2 327
-	7	10	119	120	10	6	281	228	13	8	296	5 275
	7	10	161	166	-10	7	329	286	-14	0	654	4 623
-	8	0	982	815	10	7	380	385	14	0	354	4 354
	8	0	1653	1596	-10	8	95	5 111	-14	2	165	5 196
-	8	1	99	82	10	8	218	8 230	14	2	108	3 84
	8	1	212	204	10	9	102	2 103	-14	3	399	375
	8	2	223	234	-11	1	647	651	14	3	67	7 82
-	8	3	91	104	11	1	599	559	-14	4	67]	655
	8	3	407	398	-11	2	24(	272 (	14	4	79	<b>) 1</b> 06
-	8	4	200	119	11	2	68	3 149	14	6	126	5 139
	8	4	977	898	-11	3	657	615	14	7	528	3 500
-	8	5	73	71	11	3	297	322	14	8	8(	) 96
-	8	6	386	424	-11	4	346	5 350	-15	0	95	5 123
	8	6	192	190	-11	5	442	2 401	15	0	68	3 36
-	8	7	711	666	11	5	574	• <u>5</u> 12	-15	1	40(	) 423
	8	7	578	538	-11	6	249	236	15	1	437	7 383
-	8	8	168	163	11	6	355	5 337	-15	2	263	3 262
	8	8	250	241	-11	8	166	5 163	15	5	107	7 113
	8	9	72	58	11	8	225	5 211	-15	3	288	3 301
	9	0	264	256	-11	9	107	/ 116	15	3	149	5 134
-	9	1	733	706	11	9	94	► 102	-15	4	249	9 251
	9	1	1076	1028	-12	0	750	) 718	15	4	160	6 174
-	9	2	211	244	12	0	328	3 327	-15	5	274	4 299
	9	2	832	735	-12	1	9(	) 112	-15	6	190	6 192
-	9	3	341	329	-15	2	111	136	15	6	37	7 363
	9	3	304	327	12	2	219	217	-16	0	420	6 485
-	9	5	718	602	-15	3	199	553	16	0	694	4 634
	9	5	403	453	12	3	119	) 109	16	2	11	1 88
-	9	6	397	359	-15	4	648	8 624	-16	3	38	0 386
	9	6	424	388	12	4	694	623	16	3	120	0 144
-	9	8	436	430	15	5	80	) 84	-16	4	34	7 383
	9	8	195	215	-12	6	186	<b>b</b> 194	16	4	7	7 96
-	9	9	121	107	15	6	163	183	16	6	144	4 115
	9	9	288	282	-12	7	222	214	-16	7	137	2 131
-	9	10	100	118	15	(	294	304	16	7	34	1 326
	9	10	119	93	12	8	154	133	-17	1	294	4 290
- 1	0	0	1620	1699	-13	0	101	96	17	1	43	2 390
1	0	0	795	749	-13	1	555	592	-17	2	99	9 156
<b>-</b> 1	0	1	94	144	13	1	406	366	17	2	125	5 128
1	0	1	62	37	-13	2	137	256	-17	3	93	3 120
-1	0	2	154	125	13	2	113	135	17	3	13	1 126
1	0	2	165	194	-13	3	554	592	-17	4	150	0 188
-1	0	3	304	338	13	3	296	244	17	4	21	1 182

н	κ	FOBS	FCAL	н	κ	FOBS	FCAL	н	κ	FOBS	FCAL
					_				•		1010
-17	5	157	170	1	5	90	116	4	2	1418	1315
17	5	276	240	-1	6	382	417	4	3	445	437
-17	6	188	192	1	6	362	383	-4	4	344	312
17	6	175	166	-1	7	267	308	4	4	40	49
-18	0	388	364	1	7	109	100	-4	5	267	234
18	0	540	554	-1	8	224	555	4	- 5	844	827
18	1	140	143	1	8	299	313	-4	6	659	604
18	2	107	98	-1	10	237	248	4	6	150	204
-18	3	186	223	1	10	248	273	-4	8	141	134
18	3	276	243	1	11	64	92	4	8	182	193
-18	4	163	198	-2	1	279	299	-4	9	374	366
18	4	254	224	5	1	169	213	4	9	211	207
-18	6	95	102	-2	2	2086	1888	4	10	73	93
19	0	76	118	2	2	1080	1055	-4	11	153	130
-19	1	174	185	-2	3	171	560	4	11	123	158
19	1	354	367	2	3	150	242	-5	1	735	611
-19	2	148	186	-2	4	400	392	5	1	202	172
19	2	152	138	2	4	305	321	-5	2	292	282
19	3	123	123	-2	5	574	530	5	2	90	109
19	4	130	125	2	5	985	1080	-5	3	1200	1114
-19	5	209	218	-2	6	340	328	5	3	864	912
-20	0	156	175	2	6	186	293	-5	4	120	64
20	0	507	496	-2	8	290	322	5	4	877	829
-20	1	98	93	2	8	127	106	-5	5	303	316
20	1	81	113	-2	9	287	279	5	6	408	395
-20	3	189	220	2	9	429	401	-5	7	564	550
-20	4	181	208	2	11	95	97	5	7	333	263
-21	0	80	109	-3	1	862	783	-5	8	484	442
-21	1	118	160	3	1	1157	1078	5	8	158	113
-21	2	160	186	-3	2	145	183	5	9	59	55
			-	.3	2	188	249	-5	10	259	251
**	L	= 3	**	-3	3	849	861	5	10	344	347
				3	3	562	543	-6	1	529	534
0	1	296	323	-3	4	66	100	6	1	194	269
0	2	1945	1799	3	4	1123	981	-6	2	704	691
0	3	30	78	3	5	58	113	6	2	1392	1358
Ō	4	178	266	-3	6	302	356	-6	3	287	<b>21</b> 6
Ō	5	1016	1028	3	6	399	361	6	3	361	366
Ő	6	350	328	-3	7	573	588	-6	4	209	204
Ő	8	94	76	3	7	326	354	6	4	251	201
0	9	476	492	-3	8	336	332	-6	5	452	445
ő	11	88	82	3	8	352	331	6	5	752	755
-1	· · ·	1301	1772	-3	9	98	71	-6	6	798	730
1	i	1201	1204	-3	10	229	226	-6	8	228	205
-1	2	252	297	จั	10	185	185	6	8	118	134
-1	ר. כ	2 72	204		11	122	148	-6	9	411	426
ו 1	2	.)2U 193	270	่. ว	11	87	104	6	9	178	206
-1	נ. ר	107	7.	-4	1	2489	2248	-6	11	158	151
1	) //	הת כבחו	14	4	i	454	461	-7	1	177	243
_ 1	-+ C	1035	1077	-4	2	1364	1233	7	ī	1064	994
-1	2	<i>cc</i> 1	C .30		۴.	20.74	A C 3.7		-		· ·

н	κ	FORS	FCAL	н	к	FOBS	FCAL	н	к	FORS	FCAL
-7	2	126	131	10	2	580	594	רו	6	300	212
7	2	354	334	-10	<u>ר</u>	404	384	13	7	299	280
-7	3	194	169	10	3	85	97	13	Ŕ	235	233
7	3	1155	1111	-10	4	349	316	-14	2	688	768
-7	4	162	106	10	4	383	341	14	2	581	567
7	4	671	641	-10	5	551	536	-14	3	193	221
-7	5	137	201	10	5	348	303	-14	4	321	313
-7	6	428	397	-10	6	173	142	14	4	118	116
7	6	343	329	10	6	280	264	-14	5	283	295
-7	7	440	425	10	8	253	242	14	5	444	428
7	7	186	168	-10	9	383	378	-14	6	99	144
-7	8	484	465	10	9	337	305	14	6	92	103
7	8	81	95	-11	1	380	375	14	8	170	175
7	9	82	82	11	1	368	355	-14	9	149	110
-7	10	263	239	11	2	203	185	-15	1	418	470
7	10	306	297	-11	3	792	837	15	1	347	332
-8	1	130	153	11	3	587	590	-15	3	746	745
8	1	388	351	-11	4	568	532	15	3	255	265
-8	2	536	616	11	4	57	32	-15	4	396	444
8	2	/13	/33	11	5	244	231	15	4	291	280
-8	3	161	206	-11	6	183	192	-15	6	177	182
-8	4	188	5 179	11	0	105	192	15	6	253	250
<b>H</b>	4	580	538	-11	'	108	160	15	(	202	190
-8	5	593	521	11	0	211	201	10	1	70	119
8	5	521	500 345	-11		1/5	1/8	-10	2	380	375
-0	0	356	345	11	8	190	172	10	2	422	384
-0	0	243		-11	10	00 222	20	-10	5	118	101
_9	0	507	200 521	-12	10	222	224	-16	3	242	120
-о я	2	257	241	-12	2	771	747	-16	4	242	<i>2</i> 00 4 <b>21</b>
_0	2	406	360	12	2	737	707	-10	5	220	961
9	1	769	690	-12	3	346	351	16	6	170	157
ģ	2	84	86	-12	4	373	340	-17	ĩ	244	242
-9	3	351	429	12	4	132	64	17	1	350	342
9	3	606	541	-12	5	313	301	-17	3	282	295
-9	4	489	458	12	5	198	205	17	ĩ	223	199
9	4	207	210	-12	6	203	189	-17	4	247	267
-9	5	82	? 72	12	6	151	174	17	4	260	245
-9	6	363	3 349	12	8	223	213	17	5	78	78
9	6	456	5 397	-12	9	197	165	-17	6	181	207
-9	7	238	3 225	12	9	223	228	-17	7	98	91
9	7	324	290	-13	1	472	494	18	1	103	98
-9	8	357	7 354	13	1	329	297	-18	2	252	245
9	8	139	9 173	13	2	91	101	18	2	313	315
9	9	71	88	-13	3	825	823	18	3	70	82
-9	10	268	3 254	13	3	455	380	-18	4	121	151
9	10	251	249	-13	4	401	392	-18	5	254	267
-10	1	173	3 217	13	4	148	143	-18	6	125	107
10	1	191	232	13	5	112	113	-19	1	155	152
-10	2	801	l 747	-13	6	195	174	19	1	318	327

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н	κ	FOBS	FCAL	н	κ	FOBS	FCAL	н	Κ	FOBS	FCAL
10	~			-	,				_		
-19	3	180	205	2	6	115	159	5	1	323	408
19	3	143	133	-2	7	371	487	-5	2	857	916
-19	4	135	156	2	7	546	559	-5	3	362	377
-20	2	192	225	-2	8	161	202	5	3	394	388
-20	4	96	115	2	8	53	92	-5	4	197	198
-21	3	235	277	2	9	91	96	5	4	591	586
				2	10	85	70	-5	5	845	812
**	L	= 4	**	-2	11	143	136	5	5	116	126
				· 2	11	201	211	-5	6	173	173
0	0	1748	1523	-3	0	111	175	5	6	510	544
0	1	155	129	3	0	266	253	-5	8	523	500
0	2	190	219	-3	1	1854	1694	5	8	244	272
0	3	97	115	3	1	958	965	5	9	172	193
0	4	902	903	-3	2	203	227	-5	10	125	141
0	5	286	338	3	2	326	313	5	10	158	151
0	6	277	280	-3	3	341	345	-6	Ó	204	152
Û	7	170	188	3	3	349	305	6	0	1218	1205
0	8	72	103	3	4	470	421	-6	ĭ	375	487
0	9	112	161	-3	5	788	821	6	i	704	657
0	11	184	206	3	5	204	161	-6	2	304	256
-1	0	511	496	-3	6	322	258	6	2	410	200
1	0	588	551	3	6	429	456	-6	2	212	356
-1	1	1378	1304	3	7	54	88	6	้า	280	402
1	ī	1418	1274	-3	8	499	486	-6	4	878	885
-1	Š	61	168	3	8	453	452	6	4	622	564
1	2	572	565	-3	9	221	171	-6	5	127	127
-1	3	125	103	3	9	57	47	6	5	165	162
1	3	70	189	3	10	96	96	-6	6	711	725
1	4	528	496	-4	0	1709	1541	6	6	60	12.5
-1	5	1152	1234	4	Ő	218	192	-6	7	740	704
1	5	722	673	-4	ĩ	1159	1055	6	7	535	436
-1	6	347	304	4	ī	172	263	6	Ŕ	74	104
1	6	400	455	-4	2	468	447	6	9	73	64
1	7	86	104	4	2	356	354	-6	10	99	129
-1	8	283	261	-4	3	152	264	6	10	140	140
1	8	397	404	4	3	859	948	-6	11	276	276
-1	9	226	239	-4	4	770	704	-7	Ō	182	212
-1	10	108	148	4	4	145	71	7	Õ	75	67
1	10	131	148	4	5	232	186	-7	ĩ	319	294
-2	0	1369	1439	-4	6	490	463	7	ī	1279	1224
2	0	1714	1572	4	6	215	273	-7	2	1064	947
-2	1	179	123	-4	7	722	793	7	2	795	712
2	1	268	275	4	7	789	769	-7	3	142	155
-2	2	412	398	-4	9	92	114	7	3	445	440
2	2	214	229	4	9	64	65	-7	4	382	322
Ž	3	435	521	4	10	148	147	7	4	377	342
-2	4	1334	1248	-4	11	225	217	-7	5	1004	946
Ž	4	60.3	548	4	11	212	236	7	5	212	220
2	5	308	259	-5	0	118	134	-7	6	374	299
-2	6	289	309	-5	1	639	571	7	6	451	465
			-								

	н	κ	FOBS	FCAL	н	κ	FOBS	FCAL	н	Κ	FOBS F	CAL
	-7	8	459	420	-10	6	115	91	-14	1	161	197
	7	8	78	78	10	6	169	179	-14	2	139	138
	7	9	300	299	-10	6	115	91	14	2	220	204
	-7	10	150	162	10	6	169	179	-14	3	360	365
	7	10	153	126	-10	7	356	341	-14	4	604	590
	-8	0	522	532	10	7	170	221	-14	6	145	142
	8	0	2043	1834	10	8	189	171	14	6	194	184
	-8	1	253	175	10	9	94	102	14	7	572	568
	8	1	171	174	-11	0	126	146	15	0	76	81
	8	2	238	248	11	0	134	116	-15	1	382	<b>3</b> 63
	-8	3	707	757	-11	1	638	615	15	1	356	342
	8	3	205	257	11	1	530	525	-15	2	156	190
	-8	4	419	435	-11	2	268	232	-15	3	289	281
	8	4	799	757	11	2	251	226	15	3	142	144
	8	5	123	122	-11	3	308	292	-15	4	158	147
	-8	6	350	377	11	3	148	185	-15	5	345	381
	-8	7	662	624	-11	4	103	98	15	5	134	127
	8	7	210	169	-11	5	611	567	15	6	252	277
	-8	8	90	86	11	5	559	503	-16	0	481	544
	8	Ř	285	285	-11	6	215	183	16	0	482	459
	8	9	76	54	11	6	291	296	-16	1	76	85
	-9	Ó	75	33	-11	8	222	206	-16	2	117	99
	9	Õ	163	163	11	R	306	284	-16	3	230	269
	-9	ī	632	601	-12	<u> </u>	735	749	16	3	154	136
	9	ī	712	715	-12	0	646	580	-16	4	448	474
	-9	2	448	449	-12	2	74	200	16	4	290	251
	9	2	89	113	-12	2	100	100	-16	6	159	138
	-9	3	232	272	-12	2. 2	660	612	16	6	177	161
	9	3	218	281	-12	2	220	101	17	Õ	86	106
	-9	4	343	337	-12		502	520	-17	ĭ	189	189
	9	4	80	127	-12	4	273	260	17	î	291	315
	-9	5	524	487	12	-	341	70	-17	2	89	97
	ģ	5	507	515	12		14	19	17	2	134	104
	-ý	6	495	484	-12	0	185	195	17	2	165	151
	á	6	797	348	12	0	124	157	-17	5	113	131
	ģ	7	70	10	-12	4	241	234	-17	5	213	120
	_ú	Å	419	415	12	(	5/8	584	-17	ר ג	256	242
	ú	8	128	156	12	8	121	125	-17	6	117	106
	_á	å	105	114	-13	0	13	109	-18	ŏ	258	251
	_ , _	0	103	117	13	0	400	60	18	ň	516	561 .
	_0	10	142	122	-13	1	482	441	-18	้ว	109	148
-		10	142	132	13	1	438	420	-18	5	186	250
•	10	0	1332	1340	-13	2	323	.309	19	4	179	190
	10	1	120	172	-13	3	405	455	-10	~	100	116
	10	1	120	103	13	3	96	118	-10	•	107	164
	10	1	102	240	-13	4	209	210	-19		204	100
	.10	2	472	C14 540	-13	5	338	347	-19	1	374	371
-	10	נ ר	152	עסכ כוכ	-13	0	233	218	-19	6	22(	111
	10	<b>.</b>	123	616	13	6	495	485	-19	5	224	235
•	10	4	502	40.3	13	8	339	349	-19	5	132	101
	10	4 E		סרט	-14	0	728	705	-20	2		143
-	- 1 0	7	148	113	14	0	465	454	-20	3	140	172

н	K	FOSS	FCAL	н	K	FOSS	FCAL	Н	ĸ	FOBS	FCAL
-20	4	209	227	2	11	143	145	5	9	89	81
-21	2	117	131	-3	1	1067	1063	-5	10	335	336
-21	้า	102	118	3	1	381	434	5	10	259	240
<b>L</b> 1				3	2	197	231	-6	1	240	331
* *	1	= 5	**	-3	3	808	767	6	ī	556	503
	-			3	3	989	1024	-6	2	1078	972
0	1	156	168	-3	4	166	171	6	2	1173	1193
Ō	2	292	447	3	4	1333	1332	6	3	74	92
Ō	3	85	131	-3	5	264	270	-6	4	609	604
Ō	4	469	453	3	5	129	158	6	4	350	309
Ō	5	748	740	-3	6	211	267	-6	5	240	238
0	6	255	268	3	6	281	282	6	5	541	598
0	8	138	141	-3	7	501	528	-6	6	564	566
0	9	599	607	3	7	238	199	6	6	140	137
0	11	134	159	-3	8	289	302	-6	8	94	81
- 1	1	884	833	3	8	268	276	6	8	162	183
1	1	832	729	-3	10	205	214	-6	9	295	302
1	2	186	154	3	10	272	273	6	9	201	167
-1	3	131	260	-3	11	110	127	6	10	66	72
1	3	251	332	-4	1	537	497	-6	11	112	139
-1	4	495	486	4	1	283	408	-7	1	566	599
]	4	1310	1194	-4	2	1260	1150	7	1	1031	963
-1	5	271	296	4	2	1541	1442	-7	2	470	422
1	5	168	214	4	.3	344	366	7	2	150	116
-1	6	236	273	-4	4	359	341	-7	3	793	904
1	6	222	280	4	4	79	82	7	3	992	939
-1	7	160	208	4	5	687	670	-7	4	457	467
1	7	98	89	-4	6	473	485	7	4	541	523
-1	8	281	313	4	6	370	374	-7	5	162	143
1	8	310	319	-4	8	244	247	7	5	119	124
1	9	82	98	4	8	84	103	-7	6	110	88
-1	10	295	375	-4	9	214	213	7	6	304	274
1	10	292	349	4	9	243	228	-7	7	337	334
-2	1	120	137	-4	11	111	131	-7	8	296	293
5	1	220	207	-5	1	127	156	7	8	62	22
-2	5	943	979	5	1	217	299	-7	10	329	327
S	S	923	1030	-5	2	228	268	7	10	206	171
-2	3	186	100	5	2	47	92	-8	1	519	426
S	.3	322	363	-5	3	963	1015	8	1	187	154
-2	4	550	561	5	3	1160	1159	-8	2	286	295
2	4	256	261	-5	4	316	350	8	2	683	719
-2	5	436	372	5	4	753	724	-8	3	266	210
2	5	692	667	-5	5	205	185	<u>я</u>	3	119	102
-5	6	252	293	5	5	53	43	-8	4	425	446
2	6	331	296	-5	6	102	165	H A	4	501	494
-2	7	81	105	5	6	180	220	-8	5	399	583
-2	8	249	274	-5	7	545	541	8	5	173	783
-2	9	5/5	376	5	7	103	100	-8	0	191	218
<u>ک</u>	א יו	589 201	313	-5	<u>н</u>	2.35	144	N 0	1	103	103
-6	11	166	140	5	В		12	-8	8	92	124

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н	κ	FOBS	FCAL	н	ĸ	FOBS	FCAL	н	κ	FOBS	FCAL
	•	• • •									
8	8	212	196	12	5	36	6 358	-17	3	345	5 <b>3</b> 58
-8	9	383	398	-12	3	47	4 450	17	3	211	220
8	9	325	304	-15	4	30	9 297	-17	4	159	9 193
-9	1	763	713	12	- 4	6	3 62	17	4	108	3 123
9	1	540	559	-12	5	23	1 187	-17	6	120	) 125
-9	5	71	176	12	5	94	4 105	-18	1	78	3 99
-9	3	98	49	-12	6	17	8 178	-18	2	241	256
9	3	646	680	12	6	304	4 311	18	2	301	318
-9	4	720	709	12	8	15	7 183	-18	4	110	) 130
9	4	340	341	-12	9	239	9 216	-18	5	209	227
9	5	71	92	-13	1	384	4 404	-18	6	101	106
-9	6	372	337	13	1	189	9 174	-19	1	164	153
9	6	318	317	-13	2	12	1 150	-19	3	202	228
-9	7	306	245	13	2	84	4 96	-19	4	120	129
9	7	169	131	-13	3	64:	3 629	-19	6	89	) 104
-9	8	284	299	13	3	551	1 182	-20	S	252	282
9	.8	65	67	-13	4	44]	l 475	-20	4	97	93
-9	10	260	248	13	5	79	5 90	-20	5	165	201
-10	1	210	287	-13	6	127	7 123	-21	3	261	301
10	1	121	97	13	6	277	7 272				
-10	2	554	560	13	7	383	3 398	<b>#</b> #	L	= 6	* *
10	2	450	488	-14	1	182	220				
-10	3	210	494	-14	2	698	691	0	0	93	179
10	3	251	234	14	2	342	2 342	0	1	53	123
-10	4	132	151	-14	3	277	7 286	Ō	2	69	177
10	4	551	507	-14	4	326	5 317	0	3	474	458
-10	5	345	381	-14	5	309	272	0	4	1290	1119
10	5	559	218	14	5	138	3 144	0	5	77	164
-10	6	267	270	-14	6	146	<b>1</b> 46	0	6	271	281
10	6	206	233	14	6	242	219	0	7	273	307
10		109	111	-14	9	154	138	0	8	79	9 117
10	8	130	130	-15	1	336	342	0	9	139	9 181
-10	9	3/5	357	15	1	203	197	0	10	61	86
10	3	310	292	-15	3	123	130	0	11	305	5 333
-11	1	0.32	274	15	3	342	329	-1	0	223	8 281
	2	400	3/0	-15	4	385	422	1	0	213	3 162
-11	2	296	261	10	4	109	108	-1	1	538	3 401
-11	ר ר	300	201	15	5	811		1	1	259	255
_11	4	406	304	15	0	137	162	-1	2	167	352
_11	5	140	140	-10	1	143		1	2	229	9 261
-11	6	223	220	-10	2	417	401	-1	3	483	3 568
-11	6	250	275	10	2	340	334	1	3	48	536
-11	7	192	150	-10	כ ר	75	101	-1	4	231	822
11	7	364	130	10	3	102	8.1	1	4	349	5 329
-11	Å	206	200	-16	4	286	106	-1	5	61:	646
11	Ŕ	225	200	-10	つ 「	156	1/3	1	5	623	3 737
-11	10	206	212	-14	Э 4	125	147	-1	6	337	7 362
-12	ĩ	136	171	-17	o v	207	107	1	6	274	• 266
-12	2	710	724	-17	1	2.31	2.15	-1	8	290	5 326
• •	۰.	.10	1 6 4	17	T	294	249	1	8	30(	) 264

Н	κ	FOBS	FCAL	н	κ	FOBS	FCAL	н	κ	FORS	FCAL
-1	9	96	73	-4	4	1027	1033	7	2	61	106
î	ó	146	179	Å	Å	167	221	-7	2	363	105
_1	ıó	126	166		Ē	107	144	7	ž	352	330
1	10	120	160	4	2	100	274	-7	4	124	176
-2	0	897	790	-4	6	207	210	- 1	~	230	222
2	0	220	200	4	0 7	202 501	200	- 7	5	626	627
-2	3	220	390	-4	7	201	5/1	-7	5	555	550
- 2	1	237	202	4		471	454	-7	6	84	99
-2	2	104	161	-4	0	111	102	7	6	450	395
-2	2	100	120	4	0	99 7)	07 07	7	7	70	58
-2	้า	102	105	4	7	7.	97	-7	8	221	201
	2	1209	1203	4	10	14	204	7	8	82	110
-2	.,	1532	1203	-4	11	171	204	-7	9	217	213
2	4	452	522	-5	0	107	90	7	9	90	134
-2	5	161	222	5	U N	127	104	-7	10	149	158
-2	5	101	232	- 5	1	101	1207	-8	0	1532	1521
-2	5	102	104	-5	2	1330	607	8	ŏ	722	827
-2	6	220	174	-5	2	46	607	-8	ĭ	521	531
-2	7	202	200	-5	2	552	572	8	i	69	95
-2	7	676		- 5	2	207	256	-8	2	93	87
_2	<b>2</b>	435	420	-5	5	277	210	8	2	203	190
-2	å	107	100	-5	4	200	246	-8	3	879	787
-7.	10	102	100	-5	5	750	720	Ř	ă	333	358
-2	11	210	256	-5	с С	120	272	-8	ŭ	793	774
-2	11	140	194	5	2	410	312	Ř	4	671	696
-7	ĩ	737	722	-5	6	202	200	8	5	228	210
- 5	1	202	752	5	0	272	290	-8	6	357	354
-7	2	406	402	-5	0	243	201	Ř	6	78	72
- 7	2	381	773	5	0	232	207	-8	7	467	434
-7	2	312	305	-5	10	151	145	8	7	126	116
2	2	269	202	-6	10	121	171	-8	8	87	106
-7	4	203 80	- JUR 71	-0	0	1044	171	Ř	8	70	83
, 7	4	405	402	- 6	1	1744	1/61	-8	9	93	54
-3	5	796	704	-0	1	134	345	8	9	85	77
- J - R	5	723	1 74	-6	2	300	201	-9	Ó	178	228
-3	6	380	420	-0	2	403	271	9	Ō	108	99
2	6	305	202	-6	2	341	200	-9	ì	798	791
-3	8 8	260	275	-0	2	741	127	9	ĩ	432	478
- J - J	8	304	207	-6	5	122	951	-4	2	1061	1063
-3	ä	130	122	-0	4	636	613	9	2	372	332
- J - J	ó	62	166	6	5	134	122	9	3	263	233
ر د	10	101	44	-6	5	263	271	-9	4	442	504
) 2	10	101	113	-0	6	64	00	ġ	4	206	101
- 4	10	220	161	-6	7	452	77	_9_	5	457	472
-4	0	22U 201	100	<u>ک</u>	7	170	110	9	5	634	506
-4	1	07U 202	1012	4	<u>`</u>	117	103	-9	ĥ	330	266
4	ì	272	268	<b>_7</b>	7 0	227	103	9	6	211	200
-4	2	315	301	7	۰ م	۲ د. ۲۵	176	-9	Ř	231	726
4	2	400	378	7	U N	770	100 764	ģ	8	170	157
-4	3	282	312	- 1	1	022	000	<b>_</b> 9	Q	151	120
4	ร	698	705	י ד_	2	1030	00V 1004	_q	10	134	127
•		070	.05	- 1	C	1024	1004	,	10	1.74	1 2 1

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н	κ	FORS	FCAL	н	κ	FOBSF	CAL	н	κ	FOBS	FCAL
-10	0	913	801	13	1	340	324	-18	4	257	267
10	Õ	846	861	-13	2	374	325	-18	6	121	138
-10	ĩ	221	251	13	2	204	215	-19	1	165	165
-10	2	96	130	-13	3	228	229	-19	4	81	109
10	2	105	99	-13	4	156	164	-19	5	188	205
-10	3	811	746	-13	5	377	373	-19	6	161	190
10	3	309	321	13	5	70	77	-20	0	91	50
-10	4	275	239	-13	6	157	163	-20	2	103	139
10	4	491	437	13	6	344	324	-20	4	191	175
-10	5	132	107	-13	8	215	175	-20	5	82	87
10	5	184	166	-14	0	410	410	-21	3	<u>83</u>	90
-10	6	288	252	14	0	402	4.32			_	
10	6	96	88	-14	1	161	198	**	L	= 7	**
-10	7	423	422	14	1	72	83		_		
10	7	181	230	-14	2	137	150	0	1	92	104
10	8	100	100	14	2	166	157	0	2	66	175
-10	9	108	113	-14	3	240	227	0	3	492	486
-11	0	92	138	14	3	219	218	0	4	555	542
-11	1	612	626	-14	4	459	435	0	5	387	4/1
11	1	463	411	14	. 4	172	172	0	6	305	311
-11	2	593	612	-14	6	152	160	0	8	105	
11	2	138	136	14	6	196	173	U		390	418
11	3	124	143	-14		152	140	-1	L N	212	307
-11	4	86	98	-15	0	10	39	1	1	121	134
11	4	77	71	-13		312 772	274	1	2	100	145
-11	2	533	522	-15	) I ) 7	112	3/0	-1	3	12/0	1275
11	5	187	513	-12	2	123	107	1	5	1147	1110
-11	n K	253	204	-15	2	251	264	-1	4	101	770
11	0 7	214	231	-10	. J	123	403	1	4 E	927	119
11	0	140	120	- 10		402	400	1	~	245	110
-11	0	304	204	-10	) 7 - E	403	463	-1	6	343	205
-12	· · ·	5.50	622	-15	2 2	240	104	-1	7	104	10/
-12	0	500	520	-13		272	204	-1	7	202	194
-12	1	547 79	76	-10			467	_1	Ŕ	202	241
-12	1	90	117	-16	่า	174	165	i	Ř	230	259
-12	2	200	220	16	2	104	103	-1	10	359	436
-12	2	69	60	-16	<u> </u>	382	415	ī	10	358	424
-12	2	652	652	16	4	262	276	2	1	179	176
12	3	144	175	-16	6	216	225	-2	2	492	540
-12	4	478	436	-16	7	107	93	2	2	1054	1025
12	4	67	60	17	0	79	89	2	3	631	561
12	5	105	97	-17	' ĭ	223	213	-2	4	474	435
-12	6	124	122	17	'ī	314	339	2	4	205	276
12	6	146	149	-17	2	77	67	-2	5	516	649
-12	7	210	234	-17	3	126	158	2	5	276	284
12	7	562	591	17	3	102	114	-2	6	180	204
12	8	78	100	-17	5	420	448	2	6	324	377
-13	0	124	110	-18	0	329	310	-2	8	176	167
-13	1	495	529	18	0	437	471	-2	9	407	476
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н	K	FOBS	FCAL	н	κ	FOBS	FCAL	н	κ	FOBS	FCAL
5	9	348	346	-6	2	981	1009	9	4	447	437
-3	1	477	484	6	2	822	853	9	5	66	85
3	1	410	359	-6	3	220	254	-9	6	174	122
-3	2	158	170	6	3	48	54	9	6	93	127
3	2	41	96	-6	4	511	446	-9	7	189	157
-3	3	1446	1526	6	4	238	245	-9	8	275	293
3	3	905	021	-6	5	135	220	9	8	100	73
-3	4	227	15)	6	5	495	460	-9	10	233	278
3	4	564	581	-6	6	366	436	-10	1	108	137
-3	5	226	277	6	6	302	256	-10	2	204	211
3	5	111	129	6	7	97	107	10	2	421	611
-3	6	333	316	6	8	168	159	-10	2	265	409
3	6	212	208	-6	9	237	232	10	2	192	200
-3	7	315	200	6	9	246	223	-10	5	102	201
3	7	181	198	-7	Í	522	577	10	-	202	203
-3	8	176	218	7	i	443	437	-10		340	321
3	8	230	278	-7	2	395	398	-10	5	247	333
3	9	64	85	7	2	68	89	-10	5	212	320
-3	10	308	295	-7	3	836	821	-10	6	201	322
3	10	283	288	7	3	511	478	10	7	141	122
-4	1	256	367	-7	4	445	376	-10	6	2101	137
4	1	490	4.00	7	4	326	345	-11	í	469	471
-4	2	1750	400	-7	5	131	150	ii	i	306	264
4	2	1072	1 301	7	5	301	305	-11	<b>`</b>	168	140
4	2	257	240	7	6	141	115	11	จั	130	307
-4	4	426	241 431	-7	7	319	267	-11	4	447	474
Å	4	255	431	-7	8	113	138	11	4	365	777
-4	5	153	103	7	8	97	102	-11	5	118	108
4	5	405	176	-7	10	289	290	11	5	133	127
-4	6	225	434	-8	1	726	700	-11	ň	255	204
4	6	220	210	8	1	127	109	11	6	255	200
-4	0	202	219	-8	2	213	333	-11	7	105	204
_4	a	230	220	8	2	627	584	11	7	269	121
4	à	222	223	-8	3	236	855	-11	Å	200	272
Ś	í	757	744	8	3	72	52	11	A	172	101
-5	2	100	144	-8	4	500	503	12	1	106	101
-5	ົ້າ	100	100	8	4	235	217	-12	2	690	772
Ś	2	702	400	-8	5	123	119	12	2	369	752
-5	5	266	077	8	5	593	530	-12	2	207	.341
5	4	200	201	-8	6	339	386	12	2	271	310
-5	5	120	300	8	6	215	204	-12	5	124	122
-5	5	120	100	-8	8	86	93	12	4	124	127
-5	4	275	210	-8	9	316	326	-12	5	440	172
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-5	0 7	112	101	-9	1	783	777	-12	6	163	103
5	' <b>7</b>	444	430	9	1	274	292	12	6	202	202
5	é	100	100	-9	5	291	288	12	7	943	673 00
-5	10	204	214	y	2	60	59	-12	9	222	225
 	10	C 74	619	-9	3	104	210	-13	í	318	727
-6	1	561		9	3	541	532	13	ī	208	239
5	T	100	200	-9	4	52 <b>8</b>	516	-13	3	525	494

н	κ	FOBS	FCAL	н	κ	FOBS	FCAL	н	κ	FORS	FCAL
13	3	235	5 246	0	1	119	56	-3	2	494	419
-13	4	419	420	0	2	241	<b>5</b> 50	3	2	271	340
-13	6	130	150	0	3	690	660	-3	3	734	700
13	6	168	165	0	4	891	881	3	3	434	418
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14	2	383	341	-1	0	126	195	-3	8	114	121
-14	3	192	188	1	0	133	222	3	8	252	237
-14	4	224	238	-1	1	326	337	3	9	59	50
14	4	132	132	1	1	291	265	-3	10	118	127
-14	5	274	275	-1	2	352	333	3	10	106	131
-14	6	158	173	1	2	154	90	-4	0	419	500
14	6	248	245	-1	3	837	803	4	0	926	899
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15	5	120	129	-1	6	415	396	4	ž	278	300
-15	7	198	181	1	6	396	306	-4	4	687	714
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17	1	143	186	-2	1	301	324	4	ğ	74	71
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-17	6	83	87	-2	2	157	127	5	ŏ	315	261
-17	7	111	117	2	2	66	89	-5	ĭ	850	828
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-19	1	148	154	2	5	110	191	-5	5	245	276
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-21	3	248	286	-2	8	119	123	с Г	A	203	173
				2	9	79	- 98	-6	ñ	1450	1422
**	L	= 8	# #	-3	0	190	160	6	ñ	1061	1024
	-			3	0	532	486	-6	ĭ	454	476
n	0	240	170	-3	1	168	206	6	i	401	304
~	v	677	1/0	3	1	351	374	-6	ż	384	408
н	κ	FOBS	FCAL	н	κ	FOBS	FCAL	н	κ	FOBS	FCAL
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6	2	228	209	-9	2	545	521	12	3	189	9 199
-6	3	577	605	9	5	287	323	-12	4	27	0 274
6	3	285	300	-9	3	145	5 161	-12	5	204	4 227
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6	4	505	518	-9	4	374	380	12	6	182	2 187
-6	5	115	139	9	4	209	) 187	-12	7	27	7 289
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6	6	243	269	9	5	461	430	-13	1	35	1 337
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7	0	83	58	-9	10	97	95	-13	5	304	4 297
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7	1	722	728	10	0	682	612	-13	6	11	3 123
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-/	3	304	306	10	2	167	170	-14	0	215	5 243
	3	189	228	-10	3	465	5 485 8 8 9 9 9	14	0	34	2 330
-/	4	143	153	10	3	268	292	-14	1	119	9 109
	4	196	189	-10	4	276	266	-14	2	10	1 82
-/	5	566	631	10	4	245	230	14	· 2	74	4 93
4	5	655	635	10	5	238	191	-14	3	19	3 183
- (	6	1/1	192	-10	6	357	304	14	3	10	5 93
	0	1/6	142	10	07	110		-14	. 4	270	252
'	1	02	58	-10	'	310	000 JUD	14	4	200	5 198
- /	8	187	220	-10	0	<i>داع</i>		-14	5		<b>y</b> 84
' '		1/5	159	-10	0 0	104	100	-14	0 7	201	2 173
- /	9	107	1.37	-11	7	152	215	-14	· /	29	7 <u>2</u> 07
-0	0	1073	1/00	-11	ň	92	70	-10	1	20	a 301
- 9	1	620	647 535	-11	ĩ	509	540	-15	່ 1 ວ	2.70	5 306
	1	2020	360	11	i	260	299	-13	່ <u>ເ</u>	15	5 175
_9	2	122	145	-11	2	284	278	-15	<u> </u>	1.5	0 171
-0 8	2	265	224	11	2	207	227	-10		0	R 105
-8	2.	676	664	11	2	82	72	-15		370	3 103 376 C
-0 9	ר. ר	434	453	-11	4	269	318	-15	5	13	<b>7 149</b>
-8		+C+ 606	475	11	4	88	130	-15	ີ <b>ຄ</b>	20	0 217
-n 8	4	530	512	-11	5	298	225	-15	. n	42	Q 427
р В	5	142	130	11	5	137	167	-10		20	7 749
-8	6	332	351	-11	6	277	272	-10 -14	, U	17	L 147
8	ĕ	215	219	11	6	169	213	-10	2	10	7 126
-8	7	159	91	-11	8	296	270	-16	<u> </u>	26	6 262
Ř	7	82	97	-12	0	299	290	-10		17	5 188
-8	8	163	162	12	Õ	169	230	-16	7	20	1 200
Ŕ	R	85	97	12	ĩ	87	77	-17		36	5 366
9	n	68	119	-12	2	260	270	-17	2	16	7 185
-9	ĩ	720	719	12	2	65	5 93	-17	3	11	0 110
9	ì	613	579	-12	3	323	338	-17	5	35	1 349
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н	ĸ	FOBS F	CAL	н	κ	FOBS	FCAL	н	κ	FORS	FCAL
-17	4	120	151	~			•••	-			
-10	0	130	121	-2	8	121	114	- <u>-</u> -	10	146	137
-10	0	300	437	2	8	132	2 1.35	-6	1	409	426
-10	4	309	333	-2	9	31	318	6	1	355	325
-10	, ,	10	93	2	9	296	287	-6	2	145	126
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-19	3	142	1/2	-3	1	106	5 74	-6	3	237	201
-19	د ج	130	149	3	1	363	3 370	6	3	269	247
-70	0	197	210	-3	2	120	) 150	-6	4	291	263
-20	4	159	152	3	2	146	5 168	6	4	144	156
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-71	3	83	103	3	3	818	s 760	6	5	241	226
		-		- 3	4	404	397	-6	6	184	195
ዮጵ	L	= 9	**	3	4	66	n HJ	6	6	225	247
•			• •	-3	5	83	122	6	7	70	78
0	1	39	16	-3	6	242	2 240	-6	9	255	216
0	2	429	483	3	6	189	205	6	9	198	236
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1	3	1054	1021	4	3	251	246	7	7	81	86
-1	4	519	561	-4	4	202	7 240	7	8	196	176
1	4	168	238	4	4	287	7 303	-7	10	153	142
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1	8	195	175	4	9	206	5 209	8	4	160	144
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2	6	186	225	5	8	213	8 211	9	4	515	474

ц	~	FORC	FCAL	н	ĸ	FC	AS	FCAL	н	κ	FOBS	FCAL
п	~	r ()#3										
-9	5	121	158	-14	6		293	3 324	-1	6	261	235
9	5	195	199	-14	8		97	91	ī	6	165	185
-9	6	87	54	-15	1		227	246	-1	8	236	236
-9	8	119	119	15	1		172	2 179	1	8	246	260
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-12	2	513	518	-21	1		142	2 159	3	4	65	5 57
12	2	451	446						-3	5	367	354
-15	3	126	<b>)</b> 114	**	L	z	10	**	3	5	472	2 483
15	3	112	2 120						-3	6	237	241
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-15	5	381	373	0	1		100	) 143	- 3	8	237	234
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13	4	92	95	-1	1			1 38 201	4	3	169	) 154
-13	2	122	145	1	1		271	301	-4	4	400	424
-13	(	251	215	-1	2		184		4	4	625	610
-15	1 1	663	214	1	2		248	5 .506	-4	5	86	5 79
14	1	14	) <u>7</u> 7	-1	5		158	5 135	-4	6	156	184
-14	2	438	) 415 ) 37/	1	5		273	5 307 5 307	4	6	227	240
14 _14	2	100	J J D	-1	4		301	325	-4	7	267	273
-14	ר. ר	00	י א 10 רוו ז	1	4		500	<b>b</b> 70	4	(	298	289
14	<b>ر</b>	10/		-1	) 5		500	1 488 607	4	8	97	98
14	4	129	0 100	1	2		211	. 497	ל-	0	- 581	554

н	κ	FORS	FCAL	н	κ	F08S	FCAL	н	к	FORS	ECAL
5	0	72	89	A	5	69	77	-12	6	210	
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5	1	390	389	8	6	172	190	-12	1	437	400
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5	2	364	363	ğ	'n	137	103	-13	2	244	258
-5	3	334	307	_ <u>_</u>	1	7.08	401	-13	<i>.</i> 2	190	224
5	3	305	350		1	346	250	1)	2	177	1/6
-5	4	196	170	á	2	281	304	-12	- 5 - E		04
-5	5	294	300	- 9	2	220	210	-13	<b>)</b>	1.31	114
5	5	415	399	-9	4	168	150	-13	0	221	281
-5	6	203	178	ģ	4	82	95	-13	0	313	330
5	6	550	203	-9	5	624	630	14	ñ	226	225
-5	8	218	204	9	5	288	308	-14	ì	79	70
5	8	131	96	-9	6	164	149	14	1	70	9 <b>17</b> 9 2
-6	0	1411	1381	9	6	138	158	-14	2	170	225
6	0	671	667	-9	8	125	116	-14	<u>с</u> Э	117	100
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6	1	270	273	-10	0	589	682	-14	5	102	197
-6	2	233	216	10	0	344	391	-14	5	30	1.24
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6	3	248	259	10	1	155	122	-14	7	214 753	600
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-6	5	218	550	10	3	326	328	-15	4	100	321
-6	6	134	112	-10	4	377	406	-15	5	273	262
6	6	294	279	10	4	119	150	-15	6	192	166
-6	7	170	176	10	5	91	107	-16	õ	450	478
6	7	229	234	-10	6	192	207	-16	ĭ	153	157
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-8	0	818	792 .	-11	8	246	<b>515</b>	-20	4	131	167
8	0	813	761 ·	-12	0	591	596	-21	1	177	189
8	1	196	190	12	0	289	252		-	- • •	
-8	2	223	227 ·	-12	1	81	134	# #	L =	: 11	<b>#</b> #
-8	3	246	279 ·	-12	2	118	117		-		
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-8	4	489	505 ·	-12	3	116	78	0	5	52 <b>6</b>	557
8	4	462	429	12	3	215	22A	0	3	84	98
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н	K	FOBS	FCAL	н	κ	FOBS	FCAL	н	κ	FOBS	FCAL
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0	9	266	306	~5	1	598	670	-9	4	362	380
- 1	1	382	390	5	1	44]	392	9	4	339	333
1	1	226	214	-5	3	514	527	-9	5	118	166
1	2	74	48	5	3	401	430	9	5	97	92
- 1	3	496	534	-5	4	590	620	-9	6	103	94
1	3	504	523	5	5	138	144	9	6	119	123
- 1	4	382	378	-5	6	200	279	-10	2	462	446
1	4	125	128	5	6	108	122	10	2	347	321
-1	6	138	127	5	7	226	242	-10	3	91	151
1	6	130	156	-5	8	221	515	10	3	87	89
1		200	225	5	8	193	172	-10	4	335	333
-1	8	186	183	6	1	325	345	10	4	72	87
1	<u>н</u>	161	138	-6	2	920	839	-10	5	408	406
2	I	88	104	6	2	246	251	10	5	209	<b>5</b> 58
-2	2	560	543	D (	3	221	227	-10	6	105	84
2	2	520	516	-0	4	100	126	-10	8	138	153
-2	3	245	223	- 6	4	124	147	-10	9	226	220
-2	4	292	287	-0	2 5	409	480	-11	1	311	319
2	4	359	377	- 6	2	121	125	11	1	247	263
-7	ר ר	446	437	-0	р 4	92	41	11	2	74	122
2	5	133	95	-6	0	100	614	-11	3	390	368
-2	0	93	92	-7	7	622	173	11	.1	2 19	263
- 2	0	209	261	7	, L	215	200	-11	4	254	225
- 2	8	101	89	-7	2	215 4 <b>2</b> 0	272	11	4 E	195	217
-2	0	1/0	205	7	2	322	312	-11	כ ד	94	147
-2	7 0	240	200	-7	4	320	344	-11	<b>0</b>	145	1.50
- 3	7	140	223	7	4	347	321	-12	2	200	202
3	1	107	416	7	5	104	105	-12	2	200	690
-3	2	302	125	-7	6	233	268	12	2	220	401
3	2	123	172	7	6	86	124	12	4	146	157
- 3	2	546	530	7	7	129	139	-12	5	103	116
3	3	496	515	-7	8	135	96	-12	6	173	185
-3	4	672	643	8	1	203	201	-12	8	158	169
3	4	56	107	-8	2	752	735	-13	ī	207	186
-3	6	147	174	8	2	150	167	13	ī	220	239
3	6	155	157	-8	3	126	114	-13	3	190	169
3	7	271	310	8	3	274	271	-13	5	88	97
-3	8	171	147	-8	4	242	244	-13	6	96	125
3	8	176	172	8	4	141	153	-13	7	282	318
-4	2	731	743	-8	5	511	513	-13	8	199	212
4	2	626	586	8	5	168	187	-14	2	220	239
-4	3	<b>?86</b>	305	-8	6	127	115	-14	5	90	129
-4	4	140	150	8	6	185	189	-14	6	268	282
4	4	116	115	-8	9	187	185	-15	1	116	116
-4	5	416	406	-9	1	246	251	-15	3	203	231
-4	6	152	185	9	1	248	254	-15	6	163	182

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н	κ	FOBS F	CAL	н	κ	FOBSF	CAL	н	κ	FORS	FCAL
-15	7	217	260	-2	6	122	146	6	2	74	93
-16	2	238	228	2	6	177	200	-6	3	181	207
-16	5	128	129	-2	7	286	264	6	3	271	283
-16	6	115	117	2	7	330	309	-6	4	281	255
-17	ĩ	212	246	2	<u>.</u>	100	105	ő	4	481	454
-17	3	204	211	2	•	107	105	-6	5	156	168
-17	4	204	611			123	100	-6	6	130	130
-17	6	121	140	-3	Ţ	430	418	-0	4	101	190
_19	2	2/0	260	3	1	521	483	0 4	רי די	171	261
-10	2	103	200	- 3	2	84	74	-0	4	240	201
_18	5	102	120	3	2	160	188			20.3	201
-10	1	100	202	-3	3	87	106	-/	0	120	1/3
-10	2	190	221	3	3	238	242	-/	1	510	519
-10	<b>.</b>	142	144	-3	4	325	343	7	1	261	277
-17	4	90	100	-3	5	194	149	-7	2	124	161
-20	~	195	192	3	5	327	303	7	2	299	307
-21	1	179	207	-3	6	292	266	-7	3	257	263
				3	6	191	183	7	3	158	132
8 <b>8</b>	L	= 12	**	-3	- 8	271	276	7	4	69	70
				3	8	154	168	-7	5	281	251
0	0	368	315	-4	0	304	364	7	5	293	304
0	1	57	42	4	Ň	615	565	-7	6	218	213
0	2	53	53	-4	ĭ	225	250	7	6	171	175
0	3	146	140		i	281	204	-7	8	98	75
0	4	437	434	-4	ו כ	270	200	-7	9	106	146
0	5	93	77	-4	2	210	200	-8	0	635	702
0	6	113	98	-4	5	323	314	8	ő	394	430
0	7	208	158	-4	4	140	124	-8	ň	153	163
-1	0	92	157	- 4	4	300	304		2	140	149
1	0	130	171	-4	, C	141	179	-0	2	170	94
-1	1	322	328	4	7	220	(7)		2	267	364
1	1	450	464	-4	4	363	369		5	(10	614
-1	2	94	96	4	(	332	337	-8	4	410	414
ī	2	267	286	-5	0	127	134	0	4	244	200
- 1	4	123	06	5	0	11	82	-8	5	220	224
i	ŕ	174	159	-5	1	446	457	н –	6	1.31	170
-1	4	215	105	5	1	291	278	-8	8	109	113
_1	5	600	142	-5	2	217	225	-9	1	547	560
-1	5	403	407	5	2	337	327	9	1	282	278
_1	⊃ ∡	421	421	-5	3	261	280	-9	2	88	121
-1	0	120	137	5	3	338	326	9	2	133	174
1	0	87	146	-5	4	178	178	-9	3	155	131
-1	8	191	183	5	4	126	130	9	3	93	130
1	8	193	204	-5	5	121	95	-9	5	399	368
-2	0	393	390	5	5	310	289	9	5	182	225
S	0	619	665	-5	6	288	258	-9	6	195	209
2	1	70	101	5	6	193	190	-9	8	91	82
-2	2	97	100	-5	8	200	180	-10	0	689	676
2	2	190	212	-6	Ő	551	539	10	0	311	335
-2	3	270	275	6	õ	429	382	-10	2	200	210
-2	4	263	255	-6	ĩ	136	98	-10	3	100	129
2	4	350	328	6	ī	183	151	10	3	229	261
				-	-						

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н	κ	FOBS	FCAL	н	κ	FOBS	FCAL	н	κ	FOBS	FCAL
-10	4	497	494	0	3	72	50	-5	4	427	420
10	4	177	208	0	4	249	238	-5	6	191	198
-10	5	97	133	0	5	257	282	5	6	83	78
-10	7	103	55	0	6	126	154	-5	7	144	123
-11	1	359	319	0	8	81	79	5	7	200	217
11	1	247	239	- 1	1	290	300	-5	8	169	154
11	2	114	135	1	1	408	439	-6	1	86	102
-11	3	129	144	1	2	52	43	6	1	207	180
11	3	122	130	-1	3	387	351	-6	2	604	546
-11	4	160	169	1	3	408	407	6	2	204	202
-11	5	273	292	-1	4	278	247	-6	3	178	179
-11	6	228	237	1	4	143	154	6	3	169	148
-11	7	151	187	-1	6	151	98	-6	4	105	117
-11	8	168	154	1	6	169	180	6	4	73	79
-12	0	487	441	-1	7	118	80	-6	5	324	278
15	0	266	283	1	7	110	119	-6	6	104	113
-12	3	98	91	1	8	67	86	6	6	218	200
-12	4	170	127	-2	2	568	525	-7	1	475	438
-12	5	98	137	2	2	529	492	7	1	125	130
-12	6	215	251	-2	3	111	102	-7	3	350	340
-12	7	396	394	-2	4	182	191	7	3	182	156
-13	1	275	299	2	4	556	258	-7	4	363	403
-13	3	92	116	-2	5	355	356	7	4	110	106
-13	4	85	95	5	5	136	147	7	5	98	105
-13	5	90	60	2	6	142	149	-7	6	258	268
-13	6	325	333	2	8	117	143	7	6	103	100
-13	7	109	119	-3	1	336	372	-7	7	97	78
-14	0	316	377	3	1	433	428	-7	8	145	130
-14	Ś	122	150	3	2	98	86	-8	1	243	254
-14	6	157	158	-3	3	299	247	-8	2	448	418
-14	7	421	473	3	3	358	352	8	2	262	238
-15	1	254	243	-3	4	322	330	8	3	101	92
-15	5	79	55	-3	6	165	167	-8	4	170	165
-15	6	241	236	3	6	187	174	-8	5	446	434
-16	0	326	313	-3	7	172	149	- 8	5	155	180
-16	2	99	117	3	7	200	236	-8	8	145	156
-16	3	87	110	-3	8	174	187	-9	1	276	314
-16	4	167	170	-4	1	109	113	9	1	182	186
-16	5	87	103	4	1	193	193	-9	3	375	376
-17	1	202	210	-4	2	533	510	9	3	134	140
-17	3	136	143	4	2	355	366	-9	4	241	220
-17	5	118	140	-4	3	216	210	9	4	103	144
-18	0	344	362	4	4	113	120	-9	6	185	165
-18	4	165	175	-4	5	331	349	-9	7	119	105
-19	1	232	262	4	5	100	55	-10	5	317	337
-20	0	363	384	-4	6	90	151	10	2	246	264
				4	6	187	219	-10	4	168	161
<b>4</b> 4	L	= 13	4 <b>4</b> 44	-5	1	424	438	-10	5	264	266
0	1	66	105	-5	3	350	309	-10	8	151	156
0	5	564	522	5	3	274	252	-11	1	217	208

н	κ	FORS	FCAL	н	κ	FOBS	FCAL	н	κ	FOBS	FCAL
11	1	172	200	2	1	202	230	6	2	150	132
-11	3	328	310	-2	2	160	181	-6	4	150	120
-11	5	127	148	-2	3	293	272	-0	4	142	157
-11	6	83	82	2	3	124	99	-6	5	97	107
-11	7	166	160	-2	4	194	199	-6	7	291	310
-12	2	297	291	Ē	4	187	165	-7	ò	85	78
-12	4	92	102	-2	6	155	152	-7	ň	307	282
-12	6	92	105	Ē	6	150	145	7	i	265	255
-13	1	185	205	-2	7	212	195	-7	2	144	155
-13	3	192	181	Ē	7	219	232	7	2	106	118
-13	6	145	166	-3	Ó	190	204	-7	3	269	277
-13	7	184	221	3	õ	206	212	7	Ř	86	106
-14	2	312	342	-3	ī	506	473	- 7	5	124	81
-14	5	111	108	3	ī	262	251	- 7	6	195	215
-14	6	89	96	-3	Ś	229	234	-8	Ň	678	562
-15	1	138	151	3	5	109	114	A	ň	264	26.9
-15	3	262	272	3	3	269	227	Â	ă	107	122
-15	4	131	144	-3	4	224	239	-8	4	428	306
-15	6	119	147	-3	5	148	155	8	4	177	161
-16	2	250	234	3	5	203	206	-8	5	114	115
-16	3	91	82	-3	6	216	183	-8	7	183	189
-16	5	151	134	3	6	130	127	-9	Ó	91	63
-17	1	142	131	-3	7	111	121	-9	1	385	363
-17	3	170	168	-3	8	183	199	9	1	228	234
-17	4	135	145	-4	0	620	628	-9	2	159	173
-18	2	204	212	4	0	262	246	-9	3	201	228
-19	1	187	211	4	1	257	240	-9	5	213	176
**	L	= 14	**	-4	3	299	295	-9	6	185	195
				4	4	210	179	-10	0	544	534
0	0	587	630	-4	6	174	164	-10	2	138	152
0	2	231	252	4	6	171	173	-10	4	465	433
0	3	68	81	-4	7	336	356	-10	5	150	159
0	4	226	223	-5	0	120	169	-10	7	132	129
0	5	101	113	-5	1	361	352	-11	0	121	152
0	6	107	88	5	1	213	212	-11	1	244	271
0	7	198	157	-5	2	89	80	-11	5	269	268
-1	0	98	104	5	2	254	248	-11	6	191	202
-1	1	514	547	-5	3	138	175	-12	0	142	157
1	1	458	446	5	3	197	139	-12	2	121	134
- 1	2	182	176	-5	4	101	119	-15	4	248	238
1	3	55	56	5	5	239	242	-12	6	122	115
- 1	4	95	90	-5	6	280	274	-15	7	181	208
- 1	5	243	283	5	6	143	149	-13	1	190	193
1	5	193	204	-5	8	165	160	-13	3	119	135
-1	6	202	185	-6	0	438	<b>3</b> 73	-13	5	114	101
1	6	223	214	6	0	182	197	-13	6	198	188
-2	0	624	650	-6	1	97	146	-14	0	203	196
S	0	647	671	6	2	113	105	-14	6	85	98
-2	1	195	148	-6	3	139	140	-15	1	241	250

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н	κ	FOBS	FCAL	н	κ	FOBS	FCAL	н	κ	FOBS	FCAL
-16	0	251	251	-5	3	187	165	-18	2	119	130
-17	1	195	226	5	3	208	194				
-18	0	288	311	-5	4	267	213	<b>#</b> #	L	= 16	<b># #</b>
-18	1	90	124	5	4	96	88				
-18	3	84	102	-5	6	191	204	0	0	904	883
-19	0	103	128	-5	7	124	138	0	1	181	163
-19	1	206	240	-6	1	177	190	0	2	121	124
				-6	2	353	371	0	4	153	143
**	L	<b>=</b> 15	<b># #</b>	6	2	296	277	0	5	60	55
				-6	3	225	238	1	0	391	379
0	2	289	252	6	3	68	63	-1	1	550	529
0	3	87	112	-6	4	158	141	1	1	396	393
0	4	100	82	-6	5	237	231	-1	2	116	87
0	5	178	186	-7	1	156	130	1	3	101	110
0	6	130	120	7	1	175	152	-1	5	162	175
- 1	1	347	340	-7	3	339	351	1	5	130	135
1	1	416	408	7	3	104	111	-1	6	159	160
-1	3	178	170	-7	4	375	344	-2	0	814	789
1	3	553	230	-7	6	166	167	2	0	414	407
-1	4	123	124	-7	7	102	101	2	1	194	187
1	4	100	122	-8	1	163	148	-2	2	170	174
1	6	130	134	-8	2	223	193	-2	3	177	135
-2	2	291	266	-8	4	183	148	2	3	102	90
2	2	371	385	-8	5	285	267	-2	4	154	150
-2	3	103	151	-9	1	200	238	5	4	157	145
2	3	58	77	-9	3	309	277	-2	6	97	104
-2	4	96	84	-9	4	185	149	-3	0	199	248
2	4	117	133	-9	6	129	157	3	0	170	169
-2	5	148	131	-9	7	126	135	-3	1	317	292
2	5	214	201	-10	2	271	246	3	1	193	200
-2	6	172	148	-10	5	186	178	-3	2	238	214
2	6	78	79	-11	1	183	209	3	2	88	98
-3	1	456	436	-11	2	104	115	3	3	84	76
3	1	213	213	-11	3	267	. <u>5</u> 61	-3	5	229	204
-3	3	133	131	-11	6	109	107	-3	6	134	128
3	3	288	276	-12	2	343	305	-4	0	389	363
-3	4	154	139	-12	4	117	146	4	0	118	121
3	4	139	100	-12	5	124	116	-4	1	127	149
-3	6	130	126	-13	1	179	197	4	2	83	92
-3	7	138	144	-13	3	253	254	-4	3	227	225
4	1	70	104	-13	6	107	155	4	3	101	90
-4	2	376	376	-14	2	354	367	-4	4	112	113
4	2	738	353	-14	4	99	101	4	4	72	° 63
-4	3	201	212	-14	5	182	178	-4	6	140	136
4	3	151	109	-15	1	182	175	-5	1	169	162
4	4	152	133	-15	3	162	168	5	1	158	157
-4	5	197	203	-15	4	151	103	-5	3	144	174
4	5	134	146	-16	2	224	237	-5	5	136	96
-5	1	333	301	-17	1	100	69	-5	6	165	166
5	1	101	136	-17	3	97	98	-6	0	235	5 193
							-				

н	κ	FOB	S	FCAL	н	κ	FC	)8S <sup>.</sup>	FCAL	н	κ	F(	OBS	FCAL
6	0	10	54	167	3	1		111	116	5 -7	1		180	166
-6	1	13	34	116	-3	2		120	144	- 7	2		103	92
-6	4	1	13	95	-3	3		200	202	2 -8	0		154	105
-6	6	10	01	84	-3	4		112	2 107	7 -8	1		100	96
- 7	0	1 (	07	118	-4	2		290	288	3 -9	) 1		103	102
-7	1	24	47	246	-4	3		143	139	9 -10	) ()		200	190
-7	2	10	08	100	-4	4		101	. 86	3 -11	1		176	135
-7	3	22	21	198	-4	5		126	128	3 -12	2 0		214	192
-7	6	20	09	226	-5	1		164	164	+ -13	3 1		129	109
-8	0	30	18	315	-5	3		222	2 199	9 -14	+ 0		145	125
-8	4	20	02	170	-5	4		99	108	3				
-8	5	(	94	118	-6	2		303	329		۰ L	=	19	<b>#</b> #
-9	1	27	23	555	-6	5		182	2 174	•				
-9	3	10	64	125	-7	3		209	157	7 -:	3 1		122	117
-9	5	17	27	135	-7	4		105	5 89	) _(	4 2		195	184
-9	6	10	96	179	-8	2		238	8 200	) -(	62	•	204	200
-10	0	30	05	319	-8	5		127	120	) –	71		116	103
-10	4	21	25	216	-9	1		103	102	? -	82		185	181
-10	6	10	03	95	-9	3		173	137	7				
-11	1	50	04	208	-9	4		85	5 96	5				
-11	3	C C	97	87	-10	2		228	189	5				
-11	5	19	58	176	-10	5		107	108	3				
-12	0	19	95	221	-11	1		129	123	3				
-15	2	Ģ	94	107	-11	3		202	5 510	)				
-12	4	17	73	190	-12	2		250	258	3				
-13	1	18	89	161	-12	4		114	122	2				
-13	2		78	92	-13	1		141	156					
-13	5	10	07	114	-13	3		247	260	)				
-14	0	14	87	130	-13	4		119	) 114	•				
-14	4	1	55	119	-14	2		253	254	•				
-15	1	14	46	183	-15	1		142	167	7				
-15	4	-	75	107										
-16	0	10	63	146	**	L	Ξ	18	<b>#</b> #					
-16	3	ł	80	81										
-17	1	19	56	186	0	0		510	540	)				
					0	1		108	89	•				
**	Ł	= 1	7	4 H	1	0		194	222					
_	_				-1	1		298	299					
0	2	1	35	135	1	1		257	282	-				
0	4		58	73	1	5		74	70	)				
- 1	1	3.	30	334	-2	0		492	519					
1	1	19	97	205	-3	0		213	255					
1	2	1	86	97	-3	1		210	225	<b>)</b>				
1	3	Ģ	96	111	-4	0		181	217	1				
1	4	12	28	105	-4	4		145	137	7				
-2	2	16	80	169	-5	1		131	128	3				
2	2	2	13	224	-5	2		93	86	)				
-2	3	12	22	114	-6	0		108	92	2				
-2	5	10		103	-6	4		91	95	5				
-3	1	3:	33	303	-7	0		91	107	7				

#### APPENDIX C

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Interior Angles of the Planes Comprising the  $D_4$ Square Antiprismatic Polyhedron of Nb(DPM)<sub>4</sub>

#### APPENDIX C

# Interior Angles of the Planes Comprising the $D_4$

# Square Antiprismatic Polyhedron of Nb(DPM)4

	Molecule A	Molecule B
Oxygen Atom	Angle,	Angle,
Numbers	deg.	deg.
04 01 02	00 0	00.7
04 - 01 - 02 01 - 02 - 03	00.0 88 5	90.7
02-03-04	01 /	07.0
03-04-01	91.4	89 4
03-04-01	71.1	07.4
08-05-06	91.7	93.0
05-06-07	87.6	88.4
06-07-08	91.4	91.9
07-08-05	88.8	86.6
08-01-05	55.2	56.0
01-05-08	61.3	61.3
05-08-01	63.5	62.7
05 01 02		(1.)
03-01-02	61.4 65.4	61.3
01-02-03	63.4 52.2	02.7
02-03-01	55.2	50.0
05-02-06	58.7	54.5
02-06-05	5 <b>9.</b> 8	60.1
06-05-02	61.5	65.3
03-02-06	60.8	60.7
02-06-03	55.4	55.1
06-03-02	63.9	64.2
07 02 07	5/ 5	5/ 0
07-03-06	56.5	54.9
03-06-07	64.6 50.0	62.9
06-07-03	28.8	02.3
04-03-07	62.3	61.8
03-07-04	50.3	55.7
07-04-03	67.4	62.6
07-04-08	59.2	55.6
04-08-07	61.2	60.2
08-07-04	59.6	64.2
08-04-01	63 0	50 6
04-01-08	03.0 60 6	J7.0 65 1
01-08-04	55 5	0J•T 55 9
01-00-04	JJ.J	۲. در

