NICKEL(II) COMPLEXES CONTAINING NON-CYCLIC AND MACROCYCLIC LIGANDS DERIVED FROM 2,3-BUTANEDIONE MONOHYDRAZONE AND 3,3-DIMETHYL-1,2-BUTANEDIONE MONOHYDRAZONE

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ABSTRACT

NICKEL(II) COMPLEXES CONTAINING NON-CYCLIC AND MACROCYCLIC LIGANDS DERIVED FROM 2,3-BUTANEDIONE MONOHYDRAZONE AND 3,3-DIMETHYL-1,2-BUTANEDIONE MONOHYDRAZONE

By

Douglas Brian Bonfoey

Two new NiN_2O_2 complexes have been prepared and characterized. Reaction of 2,3-butanedione monohydrazone or 3,3-dimethyl-1,2-butanedione monohydrazone with acetone in the presence of nickel(II) ions results in a NiN_2O_2 complex. The complex contains a dinegatively charged tetradentate ligand in a square planar environment about the nickel(II) ion. ^1H nmr studies of these complexes have established that the nickel(II) ion coordinates in an unsymmetrical mode resulting in coordination to one five-membered aza ring, one six-membered diaza ring, and one five-membered triaza ring.

Reaction of the complex based on 2,3-butanedione monohydrazone with 1,2-diaminoethane at 117°C resulted in a macrocyclic NiN_4 complex, but no reaction was observed between this complex and 1,3-diaminopropane. No reaction was observed between the NiN_2O_2 complex based on 3,3-dimethyl-1,2-butanedione monohydrazone and 1,2-diaminoethane at 117°C.

The order of reactivity of the coordinated carbonyl

groups of the NiN_2O_2 complexes is consistent with a mechanism involving nucleophilic attack at the carbon atom of the coordinated carbonyl group.

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D. B. B.

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I. INTRODUCTION

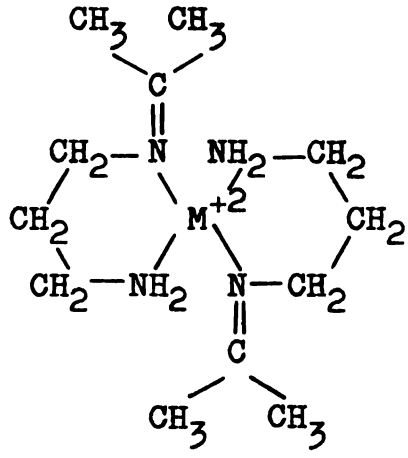
In recent years inorganic chemists have been investigating the effects of the metal ion on a ligand in coordination compounds. Metal ions have been found to catalyze certain reactions and to stabilize ligands that are unstable in the absence of a metal ion.

Coordinated ligands have been found to undergo two types of reactions that provide useful routes for organic synthesis. A "reaction of a coordinated ligand" denotes a chemical reaction in which the ligand undergoes a chemical reaction while it is coordinated to a metal ion. The "template effect"[1] has been proposed to explain how a metal ion controls the steric course of a reaction. Acting as a template, the metal ion holds the ligands in a position that is favorable for a chemical reaction. The reactants then combine to form a product that would not be formed in the absence of the metal ion.

These reactions have been useful for the preparation of both cyclic and non-cyclic compounds. The cyclic compounds, called macrocycles, have 13-16 membered ring systems surrounding the metal ion. Macrocycles, particularly those containing four nitrogen donors coordinated in a plane about a metal ion, are significant in their relation to coordination

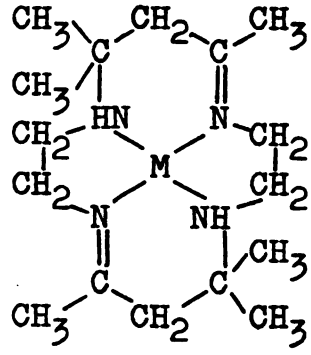
compounds found in biological systems.

The condensation of metal amine complexes with carbonyl compounds has been an area of interest in the reactions of coordinated ligands. These reactions fall into two general classes. The first results in the formation of coordinated Schiff bases:[2]



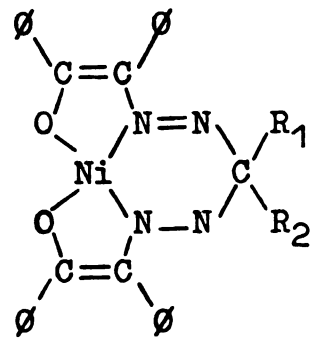
Structure I

The second is characterized by the linking of two coordinated amine groups by a three carbon bridge. Curtis[3] prepared a macrocycle from the condensation of monocarbonyl compounds with coordinated diamines:



Structure II

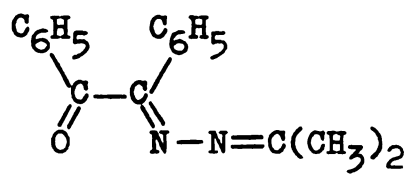
Kerwin and Melson[4,5] have synthesized and characterized the Nickel(II) complexes shown in Structure III:



NiMMK

Structure III

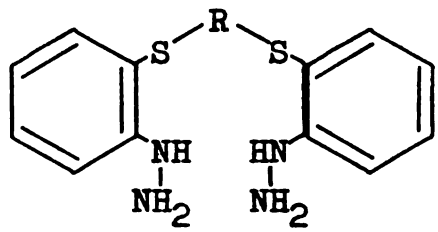
These complexes were prepared by refluxing benzilmonohydrazone, nickel acetate, and a ketone (R_1R_2CO) in ethanol. Each complex contains two benzilmonohydrazone residues linked by a single carbon atom from the ketone. In the absence of the metal ion benzilmonohydrazone condenses with acetone to give benzilacetone azine,



thus demonstrating the ability of the "template effect" to influence the course of a reaction.

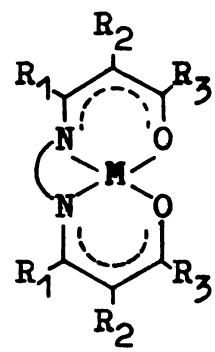
Other authors have recently reported similar results. Goedken and Peng[6] have reported the synthesis of a macrocycle by the reaction of butane-2,3-dione dihydrazone with formaldehyde in the presence of a metal ion. Alcock and

Tosker[7] have reported ring closure of Structure IV by a reaction of the coordinated hydrazine with formaldehyde.



Structure IV

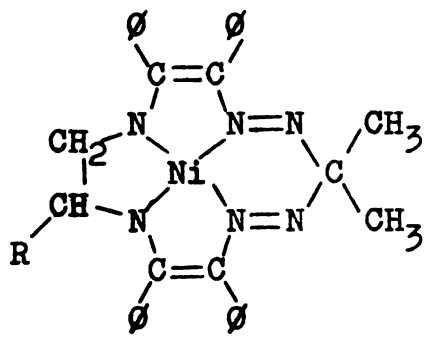
Condensation reactions of coordinated carbonyl groups have been reported but the ability of the coordinated carbonyl group to react is dependent on both the type of amine and the nature of the ligand backbone. Referring to Structure V, it has been reported[8-10] that aliphatic diamines will react with the coordinated carbonyl only if R_2 is -COOR or -COR.



Structure V

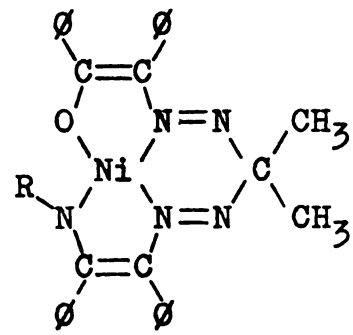
Kerwin[4] also investigated the reactivity of the coordinated carbonyl with aliphatic amines. NiMMK reacted with 1,2-diaminoethane and 1,2-diaminopropane to produce a macrocycle (Structure VI), whereas ethylamine and

1,3-diaminopropane reacted at only one of the coordinated carbonyl sites (Structure VII). These reactions are of interest because the ligand containing the coordinated carbonyl is different from those previously studied.



Ni-Hcyclo 13 (R=H)
Ni-Mcyclo 13 ($R=CH_3$)

Structure VI



Ni-Ap So ($R=(CH_2)_3NH_2$)
Ni-E So ($R=C_2H_5$)

Structure VII

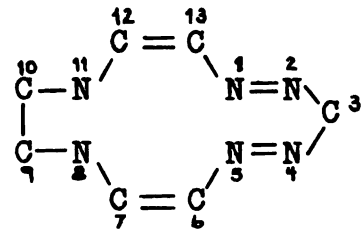
The proposed mechanism for the condensation reaction involves nucleophilic attack by the amine at the carbon atom of the coordinated carbonyl. The carbon atom is believed to be electropositive due to the electron-withdrawing nature of the phenyl group and the positively charged metal ion. Since alkyl groups have less electron-withdrawing power than phenyl groups, or are electron-releasing, it was proposed to synthesize nickel ketazines with alkyl groups in place of the phenyl groups and to investigate the reactivity of these nickel ketazines towards amines.

This thesis describes the preparation of two new nickel ketazines and the reactivity of these nickel ketazines towards amines. Nickel ketazines with methyl and t-butyl groups bonded to the coordinated carbonyl have been prepared and characterized.

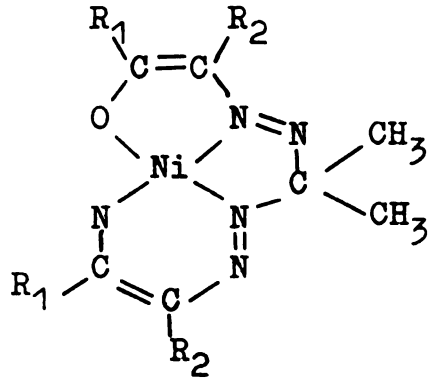
II. NOMENCLATURE

The IUPAC nomenclature and structures of the compounds synthesized in the course of this project are shown in Structures VIII and IX. Compounds of the type shown in Structure III were previously named nickel ketazines, and this general structure will be referred to as a nickel ketazine. NiDMK will refer to the nickel ketazine derived from 2,3-butanedione monohydrazone. The "DM" indicates dimethyl substitution on the hydrazone. NiTBK will refer to the nickel ketazine derived from t-butylglyoxal monohydrazone, where "TB" indicates t-butyl.

The macrocycle, illustrated in Structure IX, derived from NiDMK will be abbreviated NiDMcyclo 13. The IUPAC name is derived from the fundamental ring system shown below:



1,2,4,5,8,11-Hexazacyclotrideca-1,4,6,12-tetraene



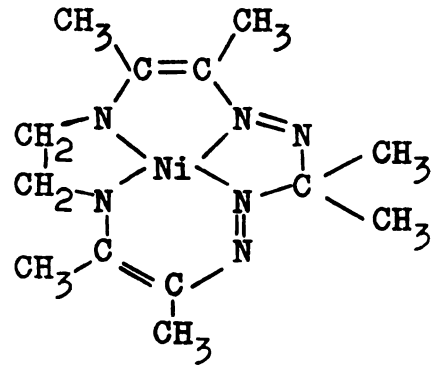
Structure VIII

NiDMK (R_1=R_2=CH_3)

[3,3'-isopropylidenebis(azo)di-2-buten-2-olato] nickel(II).

NiTBK (R_1=$C(CH_3)_3$, R_2=H)

[[1,1'-isopropylidenebis(azo)]bis(3,3'dimethyl-1-buten-2-olato)] nickel(II).



Structure IX

NiDMcyclo 13

(3,3,6,7,12,13-hexamethyl-1,2,4,5,8,11-hexazacyclotrideca-1,4,6,12-tetraenato-N¹,N⁴,N⁸,N¹¹)nickel(II).

III. EXPERIMENTAL

Materials

The following chemicals were used as supplied:

2,3-Butanedione (Aldrich)

3,3-Dimethyl-2-butanone (Aldrich)

Glyoxal - 40% aqueous solution (Aldrich)

Hydrazine hydrate - 85% solution (Fisher Scientific Company)

1,2-Diaminoethane and 1,3-diaminopropane were distilled from sodium hydroxide under nitrogen and stored in a dry box under nitrogen. All other chemicals were of reagent grade or the equivalent.

Preparation of 2,3-Butanedione Monohydrazone

A single neck 250 ml round bottom flask was assembled with a reflux condenser, heating mantle, and magnetic stirring bar. 2,3-Butanedione (7.0 ml, 0.08 moles) was added to 100 ml absolute ethanol in the round bottom flask, and the solution was stirred vigorously while hydrazine monohydrate (4.8 ml, 0.08 moles) was injected rapidly from a syringe. The solution was refluxed for one hour and then immediately reduced to approximately 15 ml by rotary evaporation. The product crystallized as transparent needles at room temperature. The product was isolated by vacuum filtration, and

the crystals were washed three times with one-half milliliter of ethanol.

yield 2.4 g, 30%

Comments on Synthesis

2,3-Butanedione monohydrazone was found to be unstable, forming a yellow powder upon standing at room temperature or in a warm concentrated ethanol solution. The yellow powder was believed to be cyclic or polymerized 2,3-butanedione monohydrazone. The polymer has no melting point but slowly decomposes up to a temperature of 250°C. 2,3-Butanedione monohydrazone is very soluble in ethanol. The polymer is insoluble in ethanol and appears as a precipitate from ethanol. Isolation of 2,3-butanedione monohydrazone depends on rapid low temperature crystallization.

Preparation of [3,3'-Isopropylidenebis(azo)di-2-buten-2-olato]nickel(II), NiDMK

A 500 ml round bottom flask was assembled with a reflux condenser, heating mantle, and magnetic stirring bar. 2,3-Butanedione (1.75 ml, 0.02 moles) was added to 100 ml absolute ethanol in the round bottom flask, and the solution was heated to reflux. The solution was stirred vigorously while hydrazine monohydrate (1.2 ml, 0.02 moles) was injected rapidly from a syringe. The solution was refluxed for one hour, and then a hot solution of nickel acetate tetrahydrate (2.5 g, 0.01 mole) in 100 ml of 95% ethanol and 7.4 ml of acetone (0.1 mole) were added. An intense red color

appeared upon addition of the first few drops of the nickel acetate solution. After addition of all the nickel acetate, the solution was brown and appeared to be a suspension of very small particles.

After six days the flask was removed, and the hot solution was filtered through a medium porosity fritted funnel leaving a grey residue. The filtrate was allowed to evaporate from a beaker at room temperature until approximately 50 ml remained. Small golden crystals and an amorphous black solid were noted. Recrystallization of the golden crystals from ethanol and n-butanol at room temperature produced larger red-brown crystals. Anal. Calculated for $C_{11}H_{18}N_4O_2Ni$: C, 44.44; H, 6.06; N, 18.85. Found: C, 44.64; H, 5.85; N, 19.03.

yield 0.3 g, 18% (based on nickel)

Comments on Synthesis

2,3-Butanedione has an intense yellow color, and it was noted that the drops from the condenser in the alcohol reflux were also yellow. Two minutes after the addition of the hydrazine to the solution the drops were clear, suggesting that the 2,3-butanedione reacts rapidly with the hydrazine. The one hour reflux at this point was arbitrary.

The nickel acetate solution was prepared by slowly heating on a steam bath. Rapid heating produced insoluble nickel hydroxide.

Purification

Recrystallization from ethanol and n-butanol must be done slowly or the crystals produced are extremely small making filtration difficult. The black material obtained in the first crystallization formed a sludge in the solution making filtration difficult and repeated recrystallization necessary to obtain a pure product. Experience indicates that the amount of black material increases with longer reaction times. A shorter reaction time may, therefore, give higher yields of product.

It was found that the product could be sublimed at 110°-120°C under reduced pressure. The sublimed product was recovered as a yellow-brown powder that gave a cherry-red color in ethanol.

Preparation of (3,3,6,7,12,13-hexamethyl-1,2,4,5,8,11-hexazacyclotrideca-1,4,6,12-tetraenato-$\underline{N}^1$,$\underline{N}^4$,$\underline{N}^8$,$\underline{N}^{11}$) nickel(II), NiDMcyclo 13

NiDMK (0.103 g, 0.45 mmoles) was weighed into a 25 ml flask. The flask was placed in a dry box under a nitrogen atmosphere. Approximately 5 ml of 1,2-diaminoethane was added, and the flask was heated and stirred. The NiDMK did not completely dissolve but after ten minutes red-orange crystals appeared. After thirty minutes the flask was allowed to cool, and the crystals were vacuum filtered using a medium porosity glass fritted funnel. The product was recrystallized twice from acetone. Small red-orange needles were obtained. Anal. Calculated for $C_{13}H_{22}N_6Ni$: C, 48.59;

H, 6.85; N, 26.17. Found: C, 48.34; H, 6.82; N, 26.54.

yield 0.060 g, 35%

Reaction of NiDMK with 1,3-Diaminopropane

1. Three days at room temperature. NiDMK (0.1 g, 0.45 mmoles) was stirred in 5 ml of 1,3-diaminopropane for three days at room temperature under a nitrogen atmosphere. The ketazine did not completely dissolve, and there was no color change during the reaction period. After three days the mixture was filtered through a medium porosity glass fritted funnel. Small orange-red crystals were recovered on the funnel and were recrystallized from acetone. The mass spectrum obtained on the crystals was identical to the mass spectrum of NiDMK.

2. Thirty minutes in warm 1,3-diaminopropane. NiDMK (0.1 g) was weighed into a 25 ml flask. The flask was placed in a dry box under a nitrogen atmosphere, and 5 ml of 1,3-diaminopropane were added. The flask was heated on a hot plate with constant stirring. The temperature was controlled so that the solvent vapors slowly condensed on the sides of the flask. The NiDMK dissolved, giving a dark red solution. The color did not change during the reaction period. After thirty minutes the solution was allowed to cool, and crystals appeared. The crystals were removed by vacuum filtration through a medium porosity glass fritted funnel and recrystallized from acetone. The recrystallization produced orange-red crystals with a mass spectrum

identical to NiDMK.

3. One hour at the boiling point of 1,3-diaminopropane (135°C). NiDMK (0.1 g) was weighed into a 25 ml flask. The flask was placed in a dry box under a nitrogen atmosphere, and 5 ml of 1,3-diaminopropane were added. The mixture was heated with constant stirring on a hot plate for one hour. The temperature was maintained at just below the boiling point of 1,3-diaminopropane. The NiDMK dissolved at this temperature and did not recrystallize upon standing overnight at room temperature. The solution was transferred to a round bottom flask, and the 1,3-diaminopropane was removed by rotary evaporation. An attempt to recrystallize the product from acetone produced a dark red oil.

4. Six days at 50°C. A Schlenk tube containing 0.1 g NiDMK and 5 ml of 1,3-diaminopropane (handled under a nitrogen atmosphere) was connected to a nitrogen source and partially immersed in an oil bath maintained at 50°C. The NiDMK did not completely dissolve but the solution turned to a very dark red color. After six days the NiDMK appeared to be completely dissolved and did not recrystallize on cooling. The solution was transferred to a round bottom flask, and the liquid was removed by rotary evaporation. A dark red oil remained in the flask. The oil was insoluble in acetone but was soluble in ethanol. Attempts to recrystallize from ethanol and t-amylalcohol produced only the red oil.

Preparation of 3,3-Dimethyl-1,2-butanedione

Following the method of Taylor[11] 3,3-dimethyl-2-butanone (65 g, 0.65 moles) was refluxed with selenium dioxide (47 g, 0.42 moles) at 110°-120°C for 20 hours. The apparatus consisted of a 250 ml single neck round bottom flask assembled with a reflux condenser, oil bath, and magnetic stirring bar. After 20 hours the reflux column was replaced with a condenser, and a distillation was carried out at the reaction temperature. Below 80°C a yellow liquid and an immiscible clear liquid were distilled. At 85°C a homogeneous yellow oil was distilled. This liquid was allowed to stand in a stoppered flask, and after two days it solidified to a waxy white solid which had a melting range of 84.5°-85.5°C. Taylor[11] identified the white solid as 3,3-dimethyl-1,2-butanedione hemihydrate with a melting point of 85°C.

yield 15 g, 31% (based on selenium dioxide)

Preparation of [1,1'-Isopropylidenebis(azo)]bis(3,3-dimethyl-1-buten-2-olato)]nickel(II), NiTBK

A 500 ml round bottom flask was assembled with a reflux condenser, heating mantle, and magnetic stirring bar. 3,3-Dimethyl-1,2-butanedione (2.5 g, 0.02 moles) was added to 100 ml absolute ethanol, and the solution was heated. Hydrazine monohydrate (1.2 ml, 0.02 moles) was added, and the warm solution was stirred for thirty minutes. During the stirring period the solution slowly turned yellow. After thirty minutes a hot solution of nickel acetate tetrahydrate (2.5 g, 0.01 moles) in 100 ml of 95% ethanol and 7.4 ml (0.1 moles)

of acetone were added. The initial drops of nickel acetate produced a red precipitate and a cherry-red solution. After addition of the nickel acetate solution, the mixture was a very intense dark red. The solution was then heated to reflux.

During six days of refluxing the solution became red-brown, and a precipitate was noted on the sides of the flask. After six days the flask was removed, and the hot solution was vacuum filtered through a medium porosity glass fritted funnel. A light green solid was removed. The filtrate was allowed to stand in a beaker at room temperature. Brown crystals formed and were removed by vacuum filtration. Recrystallization from ethanol gave dark red crystals. Anal. Calculated for $C_{15}H_{26}N_4O_2Ni$: C, 50.99; H, 7.36; N, 15.86. Found: C, 51.23; H, 7.40; N, 16.02.

yield 0.4 g, 11.4% (based on nickel)

Comments on Synthesis

The nickel acetate solution was prepared by slowly heating on a steam bath. Rapid heating produces insoluble nickel hydroxide.

Reaction of NiTBK with 1,2-Diaminoethane

1. Thirty minutes near the boiling point. NiTBK (0.1 g) was weighed into a 25 ml flask. The flask was placed in a dry box under a nitrogen atmosphere. 1,2-Diaminoethane (5 ml) was added, and the mixture was heated, with

stirring, to just below the boiling point on a hot plate. After thirty minutes the solution was allowed to cool, and the solids were removed by filtration through a medium porosity glass fritted funnel. Recrystallization from acetone produced orange crystals which were identified by their mass spectrum as NiTBK.

2. One hour at the boiling point (117°C). The procedure described above was followed except that the solution was allowed to boil gently for one hour. The NiTBK dissolved under these conditions, and upon cooling only a small amount crystallized out of solution.

The mixture was transferred to a round bottom flask, and the 1,2-diaminoethane was removed by rotary evaporation. The acetone-soluble residue was removed and recrystallized from acetone. Orange crystals, identical to those recovered in procedure 1, were recovered.

3. Five hours at the boiling point. The procedure described above was followed except that the solution was boiled gently for five hours. The NiTBK dissolved and did not recrystallize upon cooling. The 1,2-diaminoethane was removed by rotary evaporation. The acetone soluble material was removed leaving a dark red residue which was found to be soluble in ethanol. Attempts to recrystallize this material from ethanol and n-butanol failed, leaving a dark red oil.

4. Twenty hours at 80°C. NiTBK (0.1 g) and 1,2-diaminoethane (5 ml) were placed in a Schlenk tube. The 1,2-diaminoethane was handled in a dry box under a nitrogen atmosphere. The Schlenk tube was connected to a drying tube packed with Aquasorb and placed in an oil bath maintained at 80°C. After twenty hours the NiTBK had dissolved, and the solution was a very dark red color. Recrystallization did not occur upon cooling. The 1,2-diaminoethane was removed by rotary evaporation, leaving a dark red material. This material was insoluble in acetone but soluble in alcohol. Attempts to recrystallize this material from ethanol, n-butanol, isopropyl alcohol and t-amyl alcohol produced only a red oil or an amorphous solid.

IV. PHYSICAL MEASUREMENTS

Infrared spectra were obtained using Nujol and Fluorolube mull techniques with a Perkin-Elmer Model 457 spectrometer. The ^1H nmr spectra were obtained with a Varian HA-100 in $CDCl_3$ using TMS as an internal reference. Mass spectra were determined with a Hitachi-Perkin-Elmer RMU-60. Elemental analyses were performed by Chemalytics, Tempe, Arizona. Molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

V. RESULTS AND DISCUSSION

The starting point of this project was the preparation of 2,3-butanedione monohydrazone and 3,3-dimethyl-1,2-butanedione monohydrazone from α-diketones. It was soon discovered that the monohydrazones were unstable, tending to polymerize, and that handling would be difficult. It was also found that the reactivity of the carbonyl group of the α-diketone or monohydrazone was dependent upon the nature of the alkyl substituent. Glyoxal reacted with hydrazine so rapidly that isolation of a monohydrazone was not possible. 2,3-Butanedione reacts rapidly with hydrazine to form the monohydrazone and polymerizes in the solid state at room temperature. Newman and Kahle[12] reported that preparation of dipivaloyl monohydrazone from dipivaloyl took two days with an acid catalyst. The reactivity of the carbonyl therefore depends upon the alkyl substituent and decreases in the order $H > CH_3 > C(CH_3)_3$. This series proved useful in the preparation of monohydrazones from unsymmetrical diketones. 3,3-Dimethyl-1,2-butanedione monohydrazone with hydrazine condensation at the carbonyl group with the hydrogen substituent was prepared using mild reaction conditions.

In order to avoid the handling difficulties associated with the monohydrazones these compounds were prepared "in

situ" by reaction of equimolar amounts of α-diketone and hydrazine monohydrate in alcohol. A short reaction period was observed, and then nickel acetate and acetone were added to the solution. The color of the solution changed from yellow to red upon addition of the nickel acetate, indicating that the nickel ions had been complexed in a square planar environment. The solution was filtered. The nickel ketazines were recrystallized from the filtrate at room temperature. This procedure is very similar to the procedure described by Kerwin and Melson[4,5] for the preparation of nickel ketazines based on benzilmonohydrazone.

NiDMK and NiTBK were prepared in this manner, and yields in the neighborhood of 10-20 percent were obtained. It was believed that the yields could be improved by optimizing the reaction conditions for the preparation of the monohydrazones and the reaction period of the nickel ketazines.

Characterization of NiDMK and NiTBK

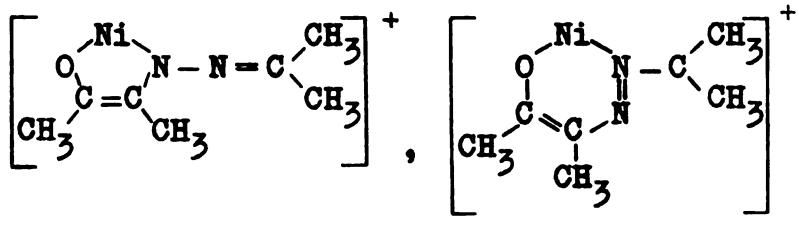
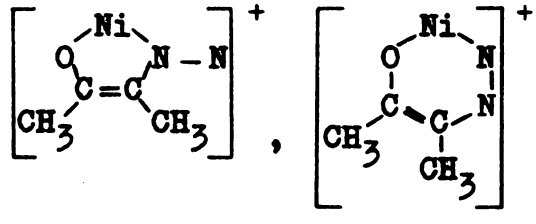
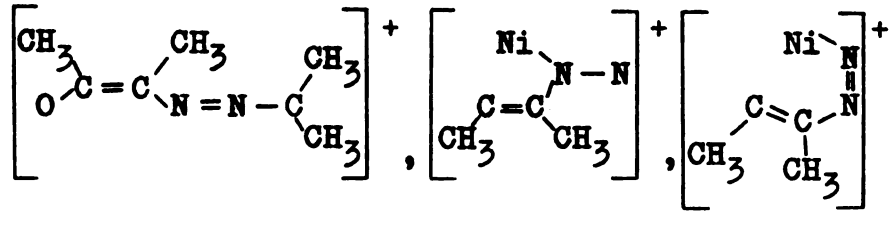
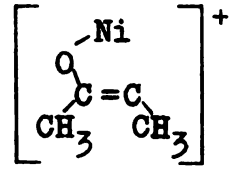
The elemental analyses for NiDMK and NiTBK, given in Section III, are in close agreement with the theoretical values calculated from the proposed structures. NiDMK was found to be monomeric in carbon tetrachloride by vapor phase osmometry.

In the infrared spectra of NiDMK and NiTBK (Appendix, Table V, p. 43), the absence of NH_2 stretching vibrations indicates that a chemical reaction has taken place with

elimination of the hydrogens from the primary amine groups of the monohydrazone. The absence of a carbonyl absorption is consistent with the formation of a C-O-Ni bond. The strongest absorptions in the spectrum of NiDMK were at 1322 and 1150 cm^{-1}. The spectrum of NiTBK contained three strong absorptions at 1450, 1340, and 1180 cm^{-1}. Two of these absorptions were common to the spectra of NiDMK and NiTBK. The common bands at 1322,1340, 1150, and 1180 cm^{-1} are in the C-O and C-N stretching region of the infrared.

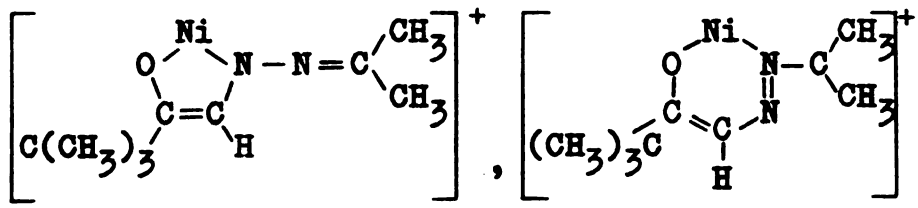
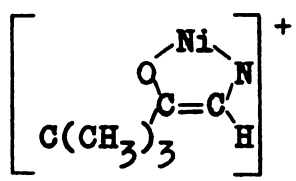
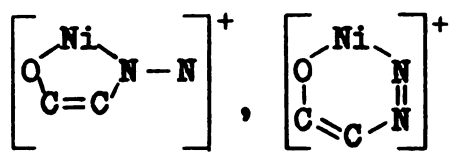
A study of the fragmentation patterns of their mass spectra provided evidence of the structures of the nickel ketazines. The mass spectra of NiDMK and NiTBK are listed in Tables 1 and 2. In each case the highest mass observed corresponded to the parent ion for the proposed structure of the nickel ketazines. Nickel containing fragments were identified by the relative abundance of the nickel isotopes. The tentative assignment of the fragments supported the proposed structure, however, the fragmentation pattern did not provide evidence that would establish which mode of coordination is preferred by the nickel ion. In the symmetrical mode (Structure X) the nickel ion coordinates to two five-membered aza rings and a six-membered tetraaza ring. In the unsymmetrical mode (Structure XI) the nickel ion coordinates to a five-membered aza ring, a six-membered diaza ring, and a five-membered triaza ring. The nickel ion is associated with chelate rings in several of the fragments. These fragments could be attributed to either a five-membered aza ring

Table I. Mass Spectrum of NiDMK

M/e*	Assignment
296	$[\text{parent}]^+$
P-15	$[p - CH_3]^+$
P-28	$[p - CO]^+$, $[p - N_2]^+$
198	
156	
140	
128	
99	?

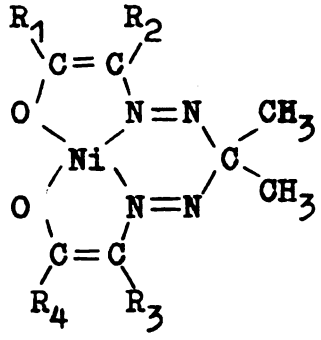
*For nickel-containing species the value for ^{58}Ni is given.

Table 2. Mass Spectrum of NiTBK

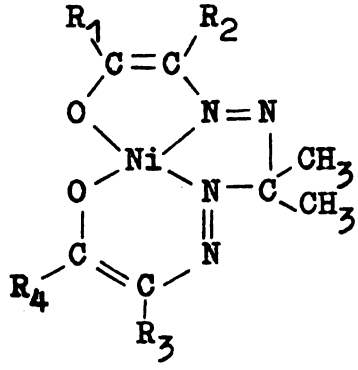
M/e*	Assignment
352	$[\text{parent}]^+$
P-15	$[\text{p} - CH_3]^+$
P-28	$[\text{p} - N_2]^+$, $[\text{p} - CO]^+$
P-85	$[\text{p} - OCC(CH_3)_3]^+$
P-113	$[\text{p} - OCC(CH_3)_3CHCH_3]^+$, $[\text{p} - NNC(CH_3)_2NNCH_3]^+$
226	
170	
126	
115	$[NiC(CH_3)_3]^+$

*For nickel-containing species the value for ^{58}Ni is given.

with a pendant nitrogen atom or a six-membered diaza ring.



Structure X



Structure XI

The fragmentation patterns of the nickel ketazines were consistent with either the symmetrical or the unsymmetrical mode of coordination.

The ^1H nmr spectra of the nickel ketazines provided evidence that the nickel ion coordinates in an unsymmetrical mode. In the symmetrical mode of coordination the methyl groups on the five-membered ring are related by a mirror plane perpendicular to the plane of the molecule so that R_1 is identical to R_4, and R_2 is identical to R_3. The geminal methyl groups are related by a mirror plane in the plane of the tetradentate ligand and are therefore equivalent. The ^1H nmr spectrum of NiDMK coordinated in a symmetrical mode would consist of three singlets of equal intensity. The observed spectrum (Figure 1) consists of five singlets with area ratios of 2:1:1:1:1 and is not consistent with a symmetrical structure. The spectrum is consistent with a structure in which the nickel ion coordinates in an unsymmetrical mode (Structure XI), and the geminal methyl groups are in equivalent chemical environments above and below the plane

Figure 1. ^{1}H nmr Spectrum of NiDMK

of the tetradentate ligand. In the unsymmetrical structure, R_1 is not equivalent to R_4, and R_2 is not equivalent to R_3. A singlet was observed for each methyl group bonded to the monohydrazone residues.

The ^1H nmr spectrum of NiTBK (Figure 2) is also consistent with the unsymmetrical structure. Five singlets with area ratios of 9:9:6:1:1 were observed. Absorption assignments are based on area ratios. The geminal methyl groups absorb as a singlet at δ 1.52 ppm. Two singlets at δ 1.21 and 1.23 ppm are observed for the t-butyl groups. Since the hydrogen atoms on the t-butyl groups are separated from the chemical environment of the chelate rings by two carbon bonds a very small difference in chemical shift is observed. The hydrogens bonded directly to the chelate rings exhibit a large difference in chemical shifts with absorptions at δ 6.56 and 7.26 ppm.

The effect of the solvent on the structure was investigated by obtaining ^1H nmr spectra of NiDMK in solvents with different dielectric constants. Table 3 lists the chemical shifts observed in pyridine, bromoform, carbon disulfide, and carbon tetrachloride. Small shifts were noted but the unsymmetrical structure was the only structure observed in each solvent.

Molecular framework models indicated that unfavorable strain was not produced in either the symmetrical or unsymmetrical structure. Why was the unsymmetrical structure preferred? A possible explanation was found by considering

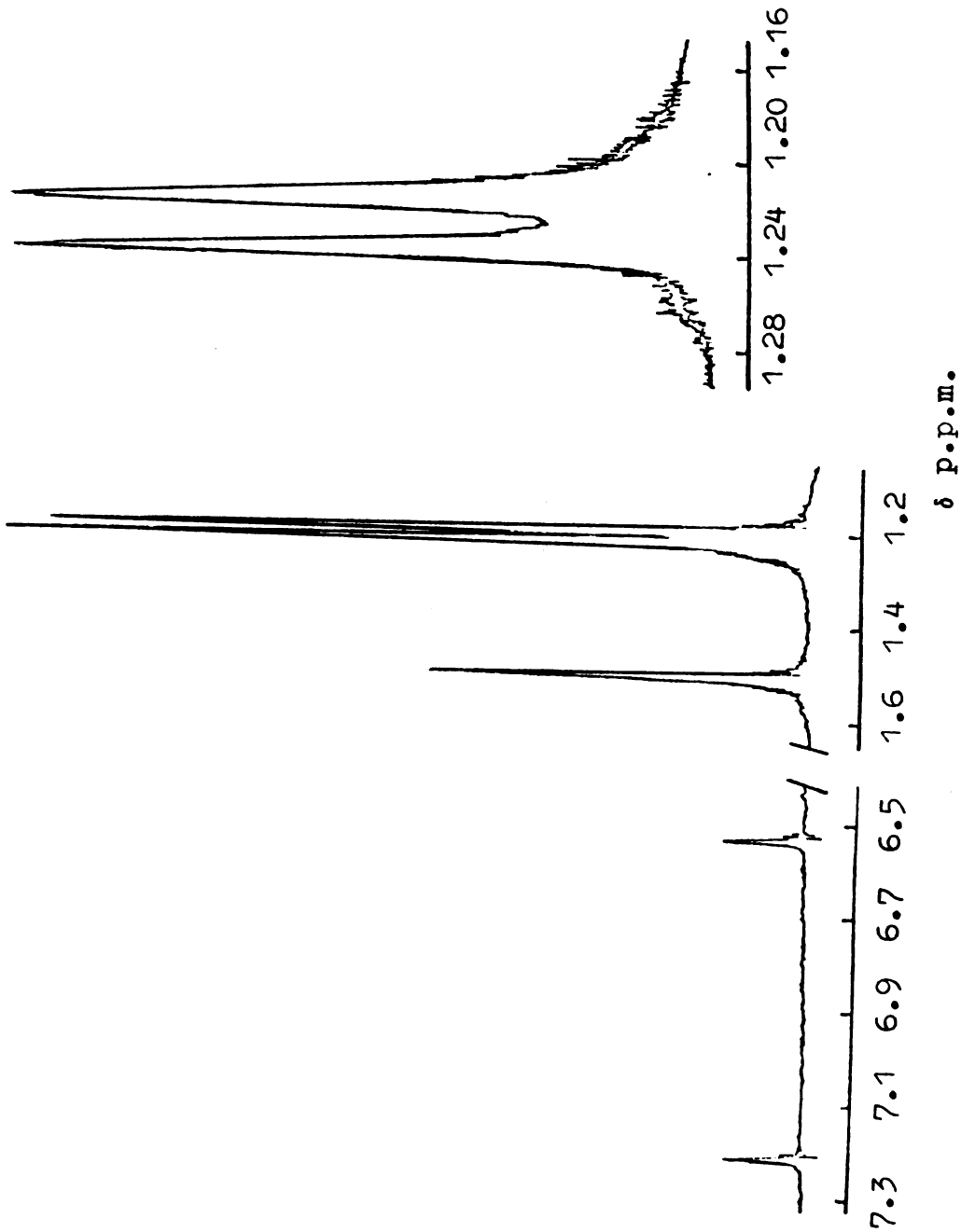
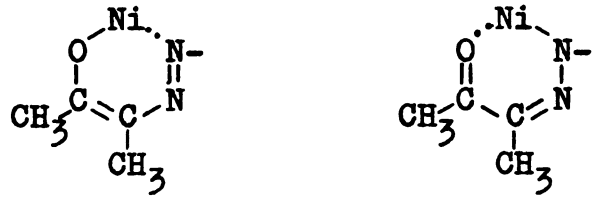


Figure 2. ^1H nmr Spectrum of NiTBK

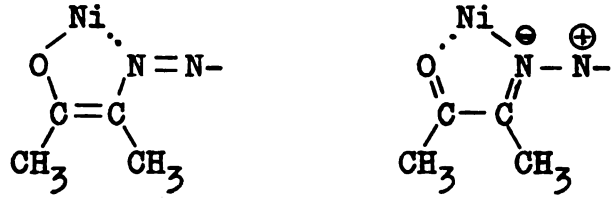
Table 3. Chemical Shifts in ^1H nmr Spectrum of NiDMK

Solvent	Dielectric Constant	Geminal Methyl Groups (δ ppm)	Methyl Groups from the Monohydrazone Residue (δ ppm)			
Pyridine	12.30	1.62	1.86	1.95	2.00	2.18
Bromoform	4.39	1.56	1.91	2.11	2.14	2.29
Carbon Disulfide	2.6	1.49	1.83	1.94	2.02	2.25
Carbon Tetrachloride	2.22	1.50	1.85	1.99	2.07	2.26

resonance structures of the five- and six-membered rings. The six-membered diaza ring contains a pair of conjugated double bonds. A resonance structure involving the double bonds can be written:



The resonance structure results in a delocalization of charge within the chelate ring and would be expected to increase the stability of the six-membered chelate ring. The five-membered aza ring does not contain a pair of conjugated double bonds. The resonance structure involves a separation of charge between two adjacent nitrogen atoms and involves atoms located outside of the chelate ring:



Further work is necessary to establish the electron distribution within the chelate rings; however, if the six-membered ring is favored by resonance stabilization over the five-membered ring, then the unsymmetrical structure would be preferred.

To summarize, NiDMK and NiTBK have been characterized by their infrared, ^1H nmr, and mass spectra as complexes

containing dinegatively charged ligands in which two monohydrazone residues are linked by a single carbon atom from the acetone. The tetradentate ligand is coordinated about the nickel(II) ion in a square planar environment. In addition, the ^1H nmr spectra of the nickel ketazines are consistent with a structure in which the nickel(II) ion is coordinated in an unsymmetrical mode. The unsymmetrical structure was not detected in the nickel ketazines prepared by Kerwin and Melson[4,5] because of the complexity of the ^1H nmr absorptions of the phenyl groups.

Reaction of Nickel Ketazines with Amines

The reactivity of the coordinated carbonyl groups of NiDMK and NiTBK toward amines was investigated using reaction conditions similar to those described by Kerwin[4] for the preparation of NiN_4 and NiN_3O complexes from NiMMK. The reactions of the nickel ketazines with neat amines were found to be temperature dependent. Many of the reactions failed at high temperatures producing a red oil. The structures of the oily products could not be deduced from their mass spectra, and attempts to recrystallize the oil from various solvents were unsuccessful. Low temperatures resulted in recovery of the nickel ketazine from the reaction mixture. Failure to obtain a product from the reaction conditions investigated was not taken as evidence that the product could not be prepared but only that the reaction did not take place under the specified conditions.

Reaction of NiDMK with 1,2-Diaminoethane

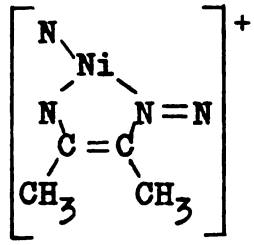
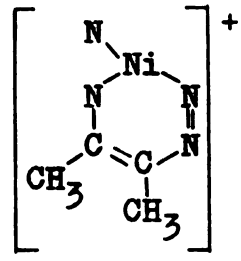
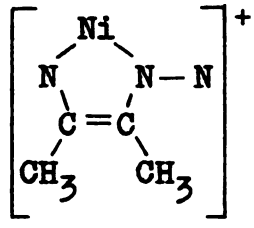
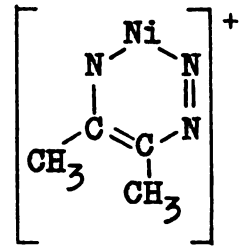
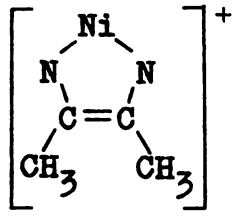
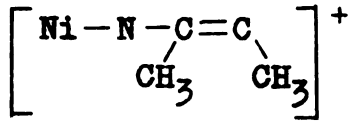
A boiling mixture of NiDMK and 1,2-diaminoethane produced orange-red crystals. The crystals were isolated and characterized as a macrocyclic NiN_4 complex formed by condensation of both coordinated carbonyl groups of the nickel ketazine with the amine groups of 1,2-diaminoethane.

The elemental analysis of NiDMcyclo 13, given in Section III, is in close agreement with the theoretical values calculated from the proposed structure.

The infrared spectrum of NiDMcyclo 13 (Appendix, Table 5, p. 43) differs significantly from the spectrum of NiDMK. The spectrum of NiDMK contained absorptions in the C-O and C-N stretching region at 1322 and 1150 cm^{-1}. The absorption at 1322 cm^{-1} in the spectrum of NiDMK is absent from the spectrum of NiDMcyclo 13. However, the absorption at 1150 cm^{-1} is present, and a strong absorption appears at 1170 cm^{-1}. A reasonable explanation of this data would be to assign the absorption at 1322 cm^{-1} to a C-O stretching vibration, which is lost upon reaction of NiDMK with 1,2-diaminoethane; the band at 1150 cm^{-1} to the C-N stretching vibration of the nickel ketazine; and the band at 1170 cm^{-1} to the C-N stretching vibration of the ethylenediamine bridge. Numerous absorptions in the spectrum of NiDMcyclo 13 could not be assigned to specific functional group vibrations and were believed to be group vibrations of the chelate rings.

The mass spectrum of NiDMcyclo 13 (Table 4) provided evidence to support the proposed reaction. The highest

Table 4. Mass Spectrum of NiDMcyclo 13

M/e*	Assignment
320	$[\text{parent}]^+$
P-15	$[\text{p} - CH_3]^+$
P-28	$[\text{p} - N_2]^+$,
P-56	$[\text{p} - NCH_2CH_2N]^+$, $[\text{p} - NC(CH_3)_2]^+$
P-69	$[\text{p} - CH_3CNCH_2CH_2]^+$
P-84	$\left[\text{p} - NNC(CH_3)_2\right]^+$ (N)
P-97	$[\text{p} - CH_3CNNC(CH_3)_2]^+$
P-111	$[\text{p} - CH_3CNNC(CH_3)_2N]^+$
P-125	$[\text{p} - CH_3CNNC(CH_3)_2NN]^+$
168	 , 
154	 , 
140	
126	

*For nickel-containing species the value for ^{58}Ni is given.

observed mass corresponded to the singly charged parent ion. The fragmentation pattern contained residues that could be assigned to either a five-membered aza ring with a pendant nitrogen atom or a six-membered diaza ring. Thus, the fragmentation pattern was consistent with either a symmetrical or an unsymmetrical structure.

The ^1H nmr spectrum of NiDMcyclo 13 (Figure 3) provided evidence that the nickel ion is coordinated in an unsymmetrical mode. The spectrum consisted of five singlets and two sets of triplets with relative areas of 6:3:3:3:3:2:2. Absorption assignments were based on the relative areas. The geminal methyl groups appear as a singlet at δ 1.57 ppm. Four singlets at δ 1.95, 1.99, 2.10, and 2.38 ppm are assigned to the monohydrazone methyl groups. The two methylene groups appear as two sets of "triplets" centered at δ 3.63 and 4.10 ppm. A computer simulation (Figure 4) of this pattern was achieved by assuming an AA'BB' system with J_{AB} = -13 Hz, $J_{AA'}$ = 4.7 Hz, and $J_{AB'}$ = 7.1 Hz. This pattern is consistent with an unsymmetrical structure since the CH_2 groups are bound to nitrogen atoms in chelate rings of different size. Furthermore, the hydrogens of each CH_2 group must be in different chemical environments (axial and equitorial). The axial hydrogens will be deshielded by the electrons in the d_{z^2} orbital of the nickel(II) ion while the equitorial hydrogens almost in the plane of the ligand will not be influenced by these electrons.[13,14] Several conformations of the dimethylene bridge were considered, but based

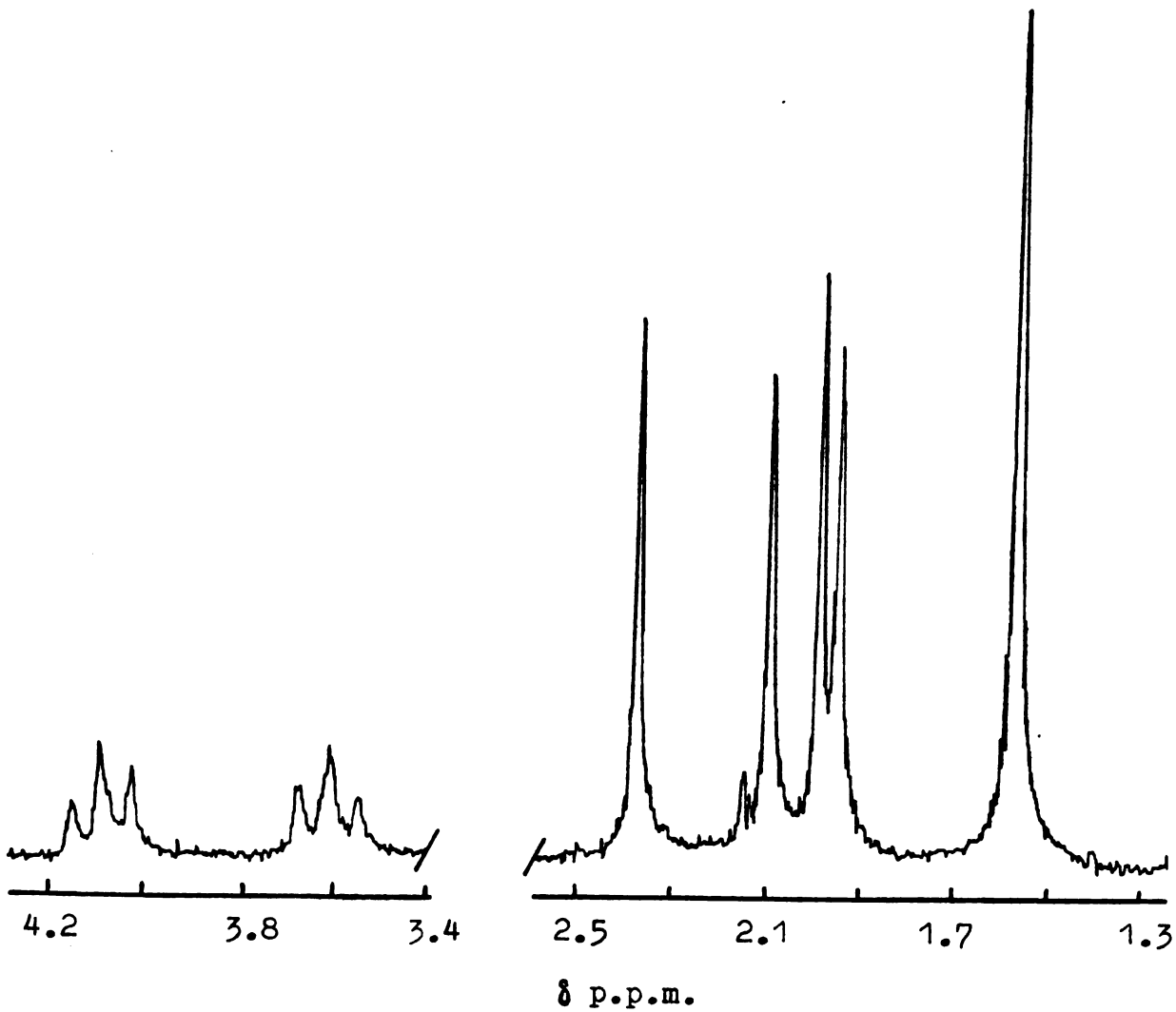


Figure 3. ^{1}H nmr Spectrum of NiDMcyclo 13

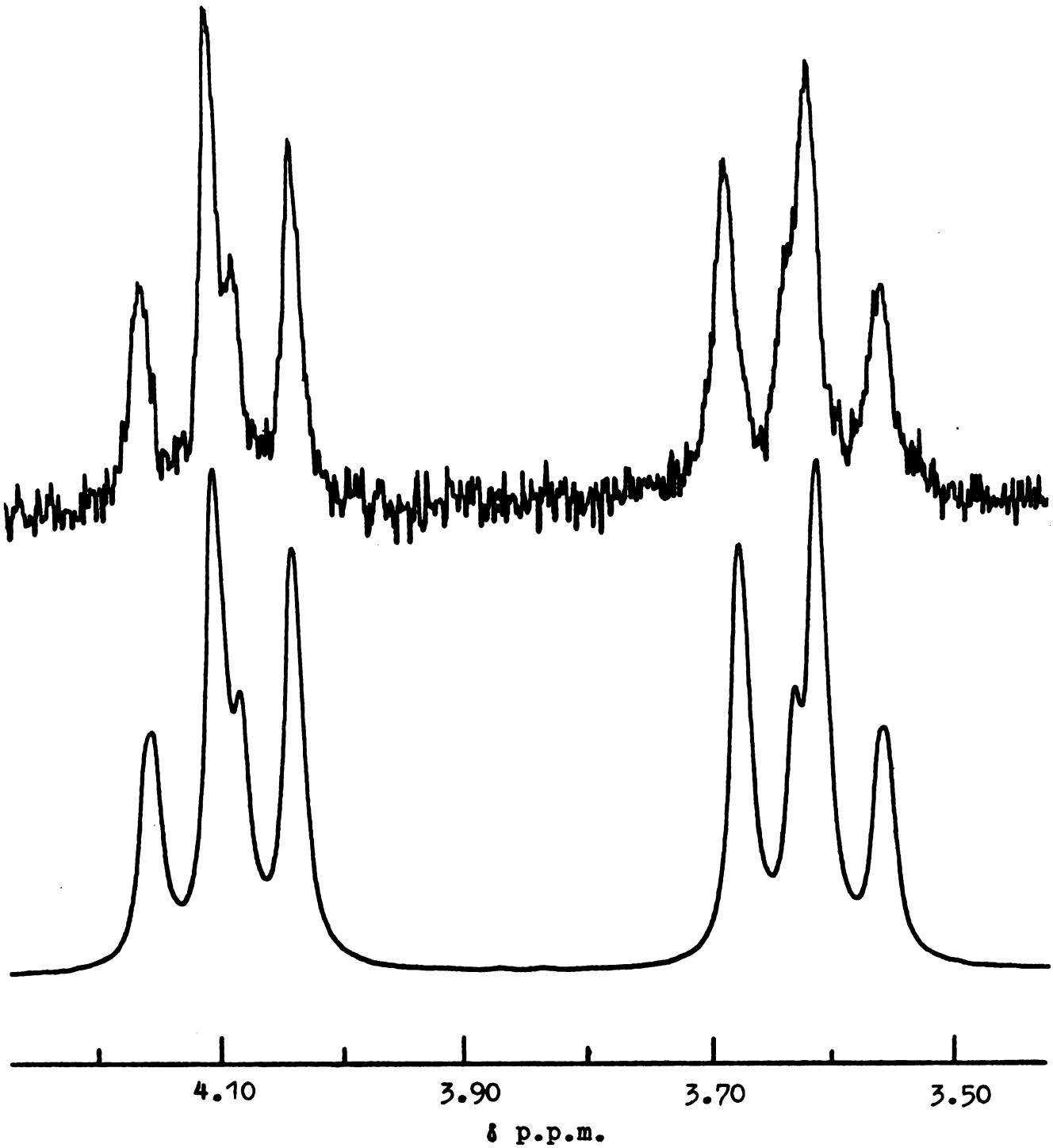


Figure 4. 100 MHz ^1H nmr Spectrum of Dimethylene Bridge of NiDMcyclo 13. (Experimental: above. Computer simulation:

on the computer simulation the proposed conformation was accepted as the best explanation of the ^1H nmr spectrum.

Resonance considerations very similar to those proposed for the nickel ketazines can be proposed for the chelate rings of the macrocycle. The six-membered chelate ring with conjugated double bonds provides a resonance structure resulting in delocalization of charge:

The resonance structure of the five-membered chelate ring results in a charge separation and involves atoms outside the chelate ring:

If resonance stabilization favors the six-membered ring the unsymmetrical structure would be preferred.

Molecular framework models indicate that unfavorable strain is not produced in either the symmetrical or unsymmetrical structures.

To briefly summarize, the infrared, ^1H nmr and mass spectra are consistent with the formation of a dinegatively charged 13-membered macrocyclic ligand coordinated in a square planar environment about the nickel ion. The ^1H nmr

spectrum establishes an unsymmetrical mode of coordination. Molecular framework models indicate that unfavorable strain is not produced in the unsymmetrical structure, however, it is probable that a slight tetrahedral twisting of the ligand system takes place to reduce some apparent strain inherent in the purely planar configuration.[15]

Reaction of NiDMK with 1,3-Diaminopropane

Kerwin[4] obtained an NiN_3O complex from the reaction of NiMMK with neat 1,3-diaminopropane at ambient temperature for three days under a nitrogen atmosphere. These conditions failed to give a reaction between NiDMK and 1,3-diaminopropane. Several attempts, using different reaction conditions, failed to produce a reaction. The conditions and results are summarized below:

1. $\xrightarrow[\text{Ambient temperature}]{\text{3 days}}$ N. R.

2. $\xrightarrow[\text{warm}]{\text{30 minutes}}$ N. R.

3. $\xrightarrow[\text{135°C}]{\text{1 hour}}$ red oil

4. $\xrightarrow[\text{50°C}]{\text{six days}}$ red oil

Reaction of NiTBK with 1,2-Diaminopropane

NiTBK failed to react with 1,2-diaminoethane under conditions which produced macrocyclic products with NiMMK[4] and NiDMK. Several attempts were made to obtain a product from heating NiTBK in neat 1,2-diaminoethane under a nitrogen

atmosphere. The conditions and results are listed below:

1. $\xrightarrow[117°C]{\text{30 minutes}}$ N. R.

2. $\xrightarrow[117°C]{\text{1 hour}}$ N. R.

3. $\xrightarrow[117°C]{\text{5 hours}}$ red oil

4. $\xrightarrow[80°C]{\text{20 hours}}$ red oil

Reactivity of Coordinated Carbonyl Groups

This preliminary investigation of the reactions of the coordinated carbonyl groups with amines suggests that the order of reactivity of the nickel ketazines is consistent with the order expected for a mechanism involving nucleophic attack by the amine group at the carbon atom of the coordinated carbonyl group. The electron density at the carbon atom is influenced by the positively charged nickel ion and the alkyl or aryl group bonded to the carbon atom. Phenyl groups are electron-withdrawing; methyl groups are weakly electron-releasing; and t-butyl groups are electron-releasing. The electropositive nature of the carbon atom depends upon the nature of the substituents and decreases in the order phenyl>methyl>t-butyl. If the mechanism involves nucleophilic attack at the carbon atom, the order of reactivity would be NiMMK>NiDMK>NiTBK. Kerwin[4] found that NiMMK reacted with 1,2-diaminoethane and 1,3-diaminopropane at room temperature to form NiN_4 and NiN_3O

complexes. NiDMK reacted with 1,2-diaminoethane at 117°C to form a NiN_4 macrocycle but did not react with 1,3-diaminopropane at room temperature. NiTBK did not react with 1,2-diaminoethane at 117°C. Various mechanisms involving nucleophilic attack at the carbon atom may be proposed to account for the observed order of reactivity.

The discovery that nickel ketazines are coordinated in an unsymmetrical mode is significant to the study of the mechanism of amine condensation reactions with the coordinated carbonyl. It is now apparent that the coordinated carbonyl groups are not equivalent. If the resonance argument is valid then the carbonyl group in the five-membered ring is essentially a negatively charged oxygen atom bonded to a carbon atom while the carbonyl group in the six-membered ring does not carry a full charge and has more double bond character. The reactivity of these groups towards amines would be expected to be different. Kerwin[4] reported that the reaction of NiMMK with ethylamine or 1,3-diaminopropane at 100°C resulted in amine condensation at only one of the coordinated carbonyl groups. This suggests a large difference in the reactivity of the carbonyl groups. Reaction at both sites is achieved only with 1,2-diamines with the formation of a macrocycle. The second condensation must either take place by a different mechanism or involve a stronger nucleophile, and the chain length of the diamine must be the determining factor in the second condensation reaction.

An interesting similarity is noted between the six-membered ring of the nickel ketazines and the six-membered ring of the bis(acetylacetone)ethylenediamine metal complex. Both ring systems contain conjugated double bonds, and resonance structures resulting in electron delocalization can be written for both ring structures. The failure of the coordinated carbonyl group of the bis(acetylacetone)ethylenediamine metal complex to react with aliphatic amines suggests that the coordinated carbonyl group of the six-membered ring of the nickel ketazines may be less susceptable to nucleophilic attack by primary amines.

Suggestions for Future Work

A crystal structure determination of the complex prepared in the course of this project would confirm the unsymmetrical structure of the complexes providing rearrangement does not occur upon crystallization. The conformation of the dimethylene bridge of NiDMcyclo 13 could also be confirmed by this method. A study of the bond lengths of the five- and six-membered rings would establish the degree of electron delocalization associated with each ring. In addition, a crystal structure study of one of the NiN_3O complexes prepared by Kerwin[4] would establish the site of the first condensation reaction.

VI. CONCLUSIONS

In summary, two new nickel ketazines have been prepared and characterized. The nickel ketazines were found to be coordinated in an unsymmetrical mode. A preliminary investigation of the reactivity of the nickel ketazines towards amines resulted in a macrocyclic NiN_4 complex. The order of the reactivity of the nickel ketazines is consistent with a mechanism involving nucleophilic attack by the amine at the carbon atom of the coordinated carbonyl group.

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APPENDIX

Table 5. Infrared Absorptions of NiDMK, NiTBK, and NiDMcyclo 13

(Technique - Nujol Mulls)

NiDMK
2920(S), 2875(M), 1540(W), 1450(M), 1425(M), 1402(M), 1362(M), 1322(S), 1275(W), 1210(M), 1150(M), 1035(W), 980(M), 795(W), 702(W), 590(W)

NiTBK
2910(S), 2850(S), 1500(Sh,M), 1450(S), 1408(S), 1375(W), 1340(S), 1262(W), 1218(M), 1184(S), 1150-1120(3 bands M), 1045(W), 1120(W), 962(S), 930(W), 895(S), 815(W), 792(W), 748(W), 710(W), 670(W), 625(W), 685(W), 670(W), 650(W)

NiDMcyclo 13
2970(Sh), 2955(Sh), 2910(S), 2860(S), 1520(M), 1460(S), 1430(W), 1397(S), 1370(S), 1345(W), 1328(W), 1315(S), 1268(M), 1218(M), 1170(S), 1150(Sh,M), 1050(W), 1030(W), 990(W), 975(W), 928(W), 880(W), 820(W), 700(M), 625(W)