NICKEL (II) COMPLEXES CONTAINING NON-CYCLIC AND MACROCYCLIC LIGANDS DERIVED FROM BENZIL MONOHYDRAZONE

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This is to certify that the

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Nickel (II) Complexes Containing Non-Cyclic and Macrocyclic Ligands Derived from Benzil Monohydrazone

presented by

Courtney Michael Kerwin

has been accepted towards fulfillment of the requirements for

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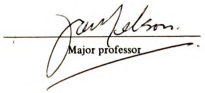

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ABSTRACT

NICKEL (II) COMPLEXES CONTAINING NON-CYCLIC AND MACROCYCLIC LIGANDS DERIVED FROM BENZIL MONOHYDRAZONE

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As a result of this project, a new type of non-cyclic Ni cis N_2O_2 complex, a new 13-membered macrocyclic system, and an unusual non-cyclic Ni N_3O type system have been characterized. The non-cyclic Ni cis N_2O_2 complexes, nickel ketazines, result from the reaction of some ketones, R^1R^2CO, and benzil monohydrazone in the presence of nickel (II) ions. The resulting dinegatively charged tetradentate ligands are coordinated in a square planar arrangement about the nickel (II) ion. A characteristic of this type of condensation reaction is that the carbon atom from the carbonyl group of the ketone forms the sole bridge between terminal nitrogen atoms of two coordinated benzil monohydrazone residues.

The Ni N_4 macrocycles and the Ni N_3O type compounds result from the direct reaction of the coordinated oxygen atoms of the nickel ketazines with di- or mono-amine

compounds. The reactivity of coordinated carbonyl groups has been demonstrated previously, but an apparent need has been noted for β (meso) carbonyl substituents in coordinated Ni cis N_2O_2 type compounds in order for cyclization reactions involving aliphatic diamines to occur. In the nickel ketazine system, the coordinated -CO group reacts with aliphatic amines at room temperature or higher to yield cyclic or noncyclic products depending on the reacting amine. For 1,2 diaminoethane and 1,2 diaminopropane, both coordinated oxygens are replaced and Ni N_4 tetradentate macrocyclic compounds are obtained. For ethylamine, at 100° in a pressure tube, and for 1,3 diaminopropane, at from room temperature to 100°, only one coordinated oxygen is replaced, resulting in the formation of unusual Ni N_3O type compounds; in the case of 1,3 diaminopropane the ligand is potentially pentadentate.

A mechanism is proposed for the reactivity of these coordinated -CO groups. The initial step in this mechanism is suggested to be the coordination of the incoming amine to the central metal ion.

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The author also wishes to thank the Dow Chemical Company for a Summer Fellowship and for their generous assistance in obtaining high resolution mass spectra.

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I. INTRODUCTION

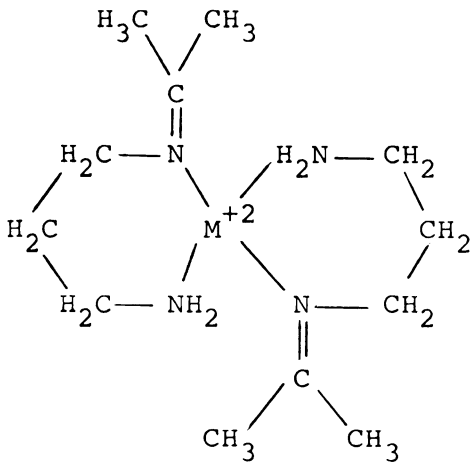
Chemists as early as Werner have recognized the altered properties of ligands coordinated to metal ions, however until just recently the inorganic chemists who have been studying coordination compounds were mainly interested in the effect of the ligands on the metal atoms. Recent advances in the field of biochemistry though have shown the importance of coordinated metal ions in reactions of biological significance. Also the discovery of metal ion catalyzed syntheses of polymers has emphasized the roles of coordination compounds as reaction intermediates. The recent literature dealing with reactions of coordinated ligands is quite vast.[1]

The effects of the metal ion are readily studied in systems where the ligand remains coordinated to the metal ion during and after a chemical reaction. The metal ion may serve to catalyze unusual reactions, impart special steric effects, stabilize otherwise unstable molecules, or have several other effects on the reactivity of the coordinated ligand. One of the most interesting aspects of this area is the ability of the metal ion to function

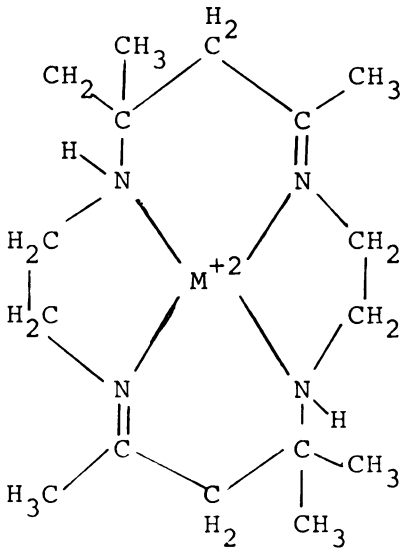
as a template in holding reactive groups in proper positions for sterically selective, multistep reactions. Many researchers have made use of this "template effect" to synthesize compounds which are difficult or impossible to make using other techniques.

One area in the field of reactions of coordinated ligands, which has received a great deal of attention, is the condensation of metal amine complexes with carbonyl compounds. Reference here will be made to two of the numerous review articles[2, 3] whose contents describe this area of chemistry. This type of reaction has proved useful in the synthesis of both cyclic and non-cyclic compounds. These condensation reactions fall into two general classes. The first results in the formation of a Schiff base from the coordinated amine, Structure I, whereas the second type is characterized by the linking of two coordinated amine groups by a three carbon bridge, Structure II. Depending on the metal amine complex employed, macrocyclic compounds with 13-16 member ring systems can be synthesized. The 13 member ring systems, Structure III, have previously been obtained only from condensation reactions of metal triethylenetetramine complexes.

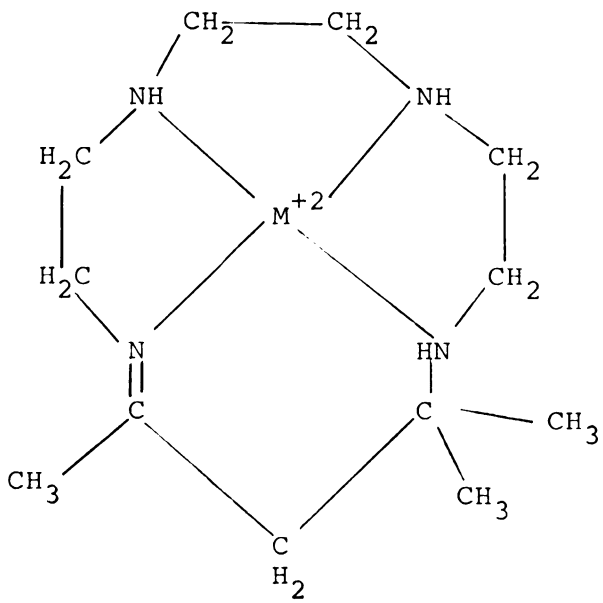
Condensation reactions have resulted from reactions of coordinated aldehydes or ketones with amines.[4] Schiff first used a reaction of this type to prepare bis (salicylaldimino) copper complexes in 1869 and many such



Structure I



Structure II

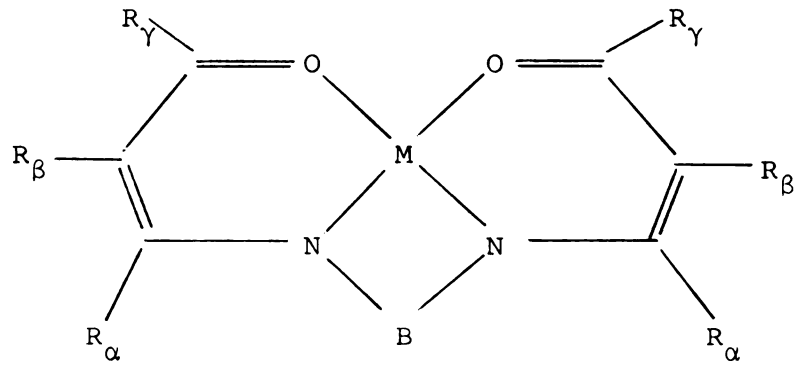


Structure III

reactions involving coordinated salicyclaldehyde have been performed since then.[5] This Schiff base condensation is facilitated by the presence of a second donor atom which assists in the formation of a strong chelate ring. Then, polarization of the carbonyl caused by coordination makes it more susceptible to nucleophilic attack by the lone pair of the amine. For a diamine there is a further "chelate effect" which facilitates the reaction of the other amine group in a similar manner.

Condensation reactions of coordinated carbonyl groups do not usually lead to the formation of macrocyclic compounds. However, Jager[6] has synthesized some macrocyclic complexes by reactions between tetradentate β-ketoamine complexes and primary diamines. Other authors[7, 8, 9] have also investigated the reactions of coordinated carbonyl compounds with amine compounds. These cyclization reactions using aliphatic diamines have failed in the absence of a substituent β or meso to the coordinated carbonyl group, see Structure IV. This requirement does not hold for aromatic diamines,[6, 7] but other factors, such as the steric rigidity of aromatic diamines, the differences in basicity between aromatic and aliphatic amines, or the higher temperatures used, may be involved.

This dissertation is a report on some nickel (II) complexes derived from benzil monohydrazone and the products of the reactions of one of these compounds with



Structure IV

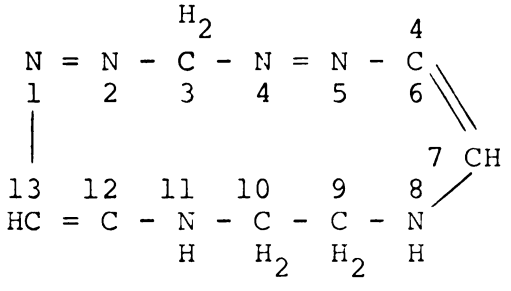
some amine compounds. This study has resulted in the characterization of a new type of condensation reaction of a metal amine type complex with a carbonyl compound, in which the carbon atom from the carbonyl group of a ketone forms the sole bridge between terminal nitrogen atoms of two coordinated benzil monohydrazone residues. The dinegatively charged tetradentate ligands resulting from these condensation reactions are shown in Structure V (p. 9). A compound of this type was first proposed by Taylor, Callow, and Francis[10] in 1939 when they isolated a small quantity of red needles from a synthesis of the nickel complex of benzil monohydrazone in boiling acetone. These authors suggested that a condensation reaction had occurred, but they were unable to ascertain the structure of the new complex. This earlier study was the starting point for this project which has now resulted in the characterization of a series of these nickel ketazine compounds.[11]

The second part of this project was undertaken to investigate the reactivity of the coordinated carbonyl

groups of one of these nickel ketazines, NiMM′K, towards mono- and di-amine compounds. In view of other workers' investigations of the reactivity of coordinated carbonyl groups (vide supra), it seemed appropriate to investigate the reactivity of the nickel ketazines. It was hoped that if these coordinated carbonyl groups were to react with amine compounds, that data might be obtained which would contribute to a better understanding of the conditions necessary for these reactions to occur and of the mechanism involved in this type of reaction. This has resulted in the characterization of two macrocyclic Ni N_4 type complexes, a noncyclic Ni N_3O type complex, and a potentially pentadentate, non-cyclic NiN_4O type complex. These compounds are shown in Structures VI and VII (pp. 9-10).

II. NOMENCLATURE

The first non-cyclic nickel complex synthesized in the course of this project is shown in Structure V, along with its IUPAC name. The second name listed under the structure is the name under which this compound was previously published. To remain consistent with previous publications these complexes will be referred to as nickel ketazines in the abbreviations used here and are further related to the ketone used in the condensation reactions by which these compounds are synthesized. For example, Ni MMK corresponds to the nickel ketazine formed by use of methyl methyl ketone (acetone). The macrocyclic compounds derived from Ni MMK are illustrated in Structure VI. The fundamental ring system involved in these compounds is named, numbered, and oriented as shown below:



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

In abbreviating these names the key words "cyclo 13" will refer to the generalized compound in Structure VI and an abbreviation for the substituent on carbon #9 will serve as a prefix, i.e., Ni M cyclo 13 will indicate the presence of a methyl substituent at position #9 in the macrocycle. Structure VII shows another type of compound which has been synthesized whose IUPAC names are related to that of the parent compound, Ni MMK, by the "stilbenolato (abbreviated So)" stem. These compounds differ only in the amino group bonded to the #2 carbon, so an abbreviation for these substituents, plus "So," for the stilbenolato stem, can represent these compounds; i.e., Ni-Ap So corresponds to Structure VII with R = 3-aminopropyl. The compound shown in Structure VIII is a complex of benzil monohydrazone with nickel (II) and will be referred to as the nickel hydrazone complex.

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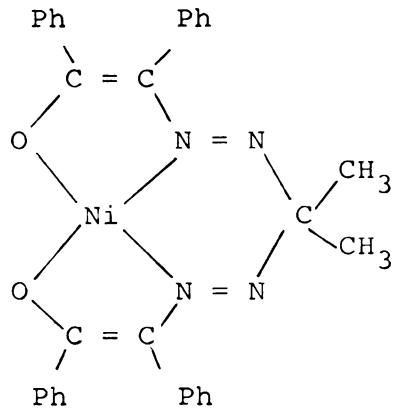
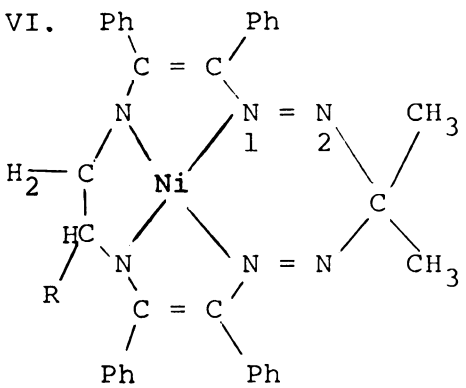
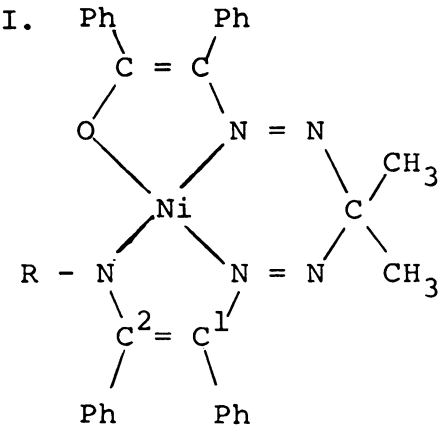
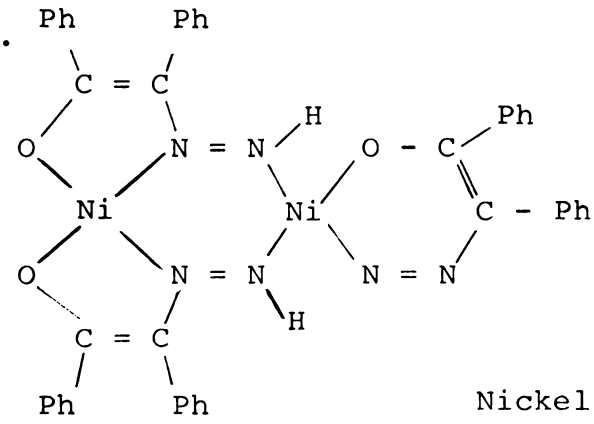
*The names for these compounds were supplied by Kurt L. Loening, Director of Nomenclature for the Chemical Abstract Service.

Structures	IUPAC Names--Abbreviation
V. 	[[α',α'''-[Isopropylidenebis (azo)]-di-α-stilbenolato] (2-)] nickel (Previously published as: 1,2,8,9 tetraphenyl - 3,4,6,7-tetraza-5,5-dimethyl- nona-1,3,6,8-tetraen-1,9- dioxynickel (II)) Ni MMK
VI. 	a. (R=H):[3,3-Dimethyl- 6,7,12,13-tetraphenyl-1,2,4, 5,8,11-hexazacyclotrideca- 1,4,6,12-tetraenato(2-)- $\underline{N}^1,\underline{N}^5,\underline{N}^8,\underline{N}^{11}$] nickel Ni-H cyclo 13
	b. ($R=CH_3$):[3,3,9-trimethyl- 6,7,12,13-tetraphenyl-1,2,4, 5,8,11-hexazacyclotrideca- 1,4,6,12-tetraenato(2-)- $\underline{N}^1,\underline{N}^5,\underline{N}^8,\underline{N}^{11}$] nickel Ni-Mcyclo 13

Structures	IUPAC Names--Abbreviation
VII. 	a. (R=$(CH_2)_3NH_2$):[α'[[1-[[2-[(3Aminopropyl)amino]-1,2-diphenylvinyl] azo]-1-methylethyl]azo]-α-stilbenolato (2-)] nickel Ni-Ap So b. (R=C_2H_5):[α'-[[1-[[2-(Ethylamino)-1,2-diphenylvinyl] azo]-1- methylethyl]azo]-α-stilbenolato(2-)] nickel Ni-E So
VIII. 	Nickel hydrazone complex

III. EXPERIMENTAL SECTION

Materials.--Benzil monohydrazone (Aldrich) was used as supplied. The diamines were distilled over sodium hydroxide under nitrogen and stored in a dry box. All other chemicals employed were of reagent grade or equivalent.

Preparation of Complexes: 1,2,8,9-Tetraphenyl-3,4,6,7-tetraza-5,5-dimethylnona-1,3,6,8-tetraen-1,9 dioxynickel (II) (Ni MMK)

Procedure I.--To a hot solution of 4.5g (0.02 moles) of benzil monohydrazone [$O=C(C_6H_5)-C(C_6H_5)=N-NH_2$] in 125 ml of 95% ethanol was added 7.4 ml (0.10 moles) of acetone and a solution of 2.5g (0.01 moles) of nickel acetate tetrahydrate in 80 ml of hot 95% ethanol. The resulting mixture immediately turned dark red and became difficult to stir. Upon refluxing and stirring for a period of seven days the mixture gradually turned to a light orange red color and an orange red precipitate formed. At this point the mixture was filtered by suction and the filtrate cooled to allow precipitation of the product. Several batches of product were obtained by the

successive filtration and concentration of this solution. The residue from the initial filtration also contained the product, which could be extracted from the nickel hydroxide byproduct with benzene. The various batches of product were combined and recrystallized from n-butanol. The product was obtained as red and red-orange needles and was dried under vacuum at room temperature. For analytical data and yields, see Table 1.

Comments on Synthesis.--(1) The solution of nickel acetate tetrahydrate in 95% ethanol was prepared using a steam bath as heating on a hot plate led to the formation of nickel hydroxide by decomposition of the nickel acetate; (2) various molar ratios of ketone to nickel were tried, with ratios of 10 or 25-1 resulting in optimum yields of product; (3) the reaction mixture, in the initial mixing steps, should be stirred rapidly to prevent the mixture from bumping; (4) various reaction times were tried to optimize conditions for this reaction, seven days were essential for the ketones giving lower yields and resulted in purer products in all cases (apparently the initially formed complex decomposed over this period, leaving behind almost entirely the ketazine and nickel hydroxide); (5) in the extraction of the product from the nickel hydroxide containing residue, the benzene solution should be filtered through a medium or fine fritted funnel to remove the nickel hydroxide and then the benzene should be removed

quickly to prevent photodecomposition of the nickel ketazine; (6) other solvents used to recrystallize the product were 95% ethanol, a solution of 3 parts 95% ethanol and 1 part benzene, or acetone, but these did not lead to the separation of ferromagnetic impurities.

Chromatographic purifications.--In order to obtain high-purity samples of some of these compounds, column chromatography was employed. This method was necessary to obtain magnetically pure samples of Ni MMK, as determined by a Gouy method magnetic susceptibility investigation, and to obtain pure samples of Ni MPhK, as determined by ^{1}H nmr studies.

The technique employed is described in Fieser's Organic Experiments, and briefly summarized here. The end of the tube was plugged with glass wool, covered with sand, and the tube filled about one-half full with the initial solvent, usually benzene. Next, the adsorption alumina was added slowly while tapping the side of the tube. Usually a column length of eight to ten inches was used. An initial amount of solvent approximately the volume of the column was allowed to run through to flush the column. The sample was then loaded onto the column dissolved in a minimum of warm benzene or other solvent. Additional solvent was added slowly at first, to complete the loading process, and then in larger amounts for the

extraction process. Fortunately the desired compounds had absorptions in the visible range and thus could be followed through the column visually. If the compound moved too slowly, or if bands did not separate well, then solvent mixtures were employed in the following order: benzene, diethylether, and methanol. The solvents were changed gradually by mixtures with ratios 3/4A, 1/4B; 1/2A, 1/2B; 1/4A, 3/4B; B; etc. Generally, these three solvents were sufficient. Note! One attempted chromatographic separation involving xylene as the solvent was ruined when something reacted on the column, generating enough heat to crack the alumina column. Xylene is suspected as the culprit.

Other Ketazine Complexes

Using the above described procedure complexes were also prepared using the following ketones: methyl ethyl ketone, ethyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, and methyl phenyl ketone. All products were obtained as orange red crystals. Analytical data are presented in Table 1, along with percentage yields.

Nickel Hydrazone Complex

When benzophenone, in large excess, was used, a dark red-brown crystalline product was produced by the initial mixing of the reactants and did not change during prolonged refluxing and stirring. This product was

removed by suction filtration, triturated with ethanol, and dried under vacuum at room temperature. Analysis of this compound showed that it apparently consisted of three benzil monohydrazone residues and two nickel atoms.* Anal Calcd for $C_{42}H_{32}N_6O_3Ni_2$; C,64.16; H,4.11; N,10.69; Ni,14.93. Found: C,63.98; H,4.05; N,10.60; Ni,14.67.

The infrared spectrum of this compound showed N-H bands at 3228 and 3158 cm^{-1}, and though it lacked the C-O band at 1420 cm^{-1}, it contained all of the other common bands of the nickel ketazines (see Table 2). Some bands in this spectrum were similar to bands observed for the parent compound, benzil monohydrazone. The following is a list of some of the infrared bands in this spectrum: 3228w, 3158m, 3053m, 1597m, 1576m, 1497m, 1449s, 1340s, 1313m, 1275vs, 1181s, 1155m, 1074m, 1031m, 1022m, 1000m, 971s, 790m, 784s, 773s, 766vs, 746m, 725m, 715m, 709vs, 701vs, 685s, 570s, 549s, 508s, 500vs, 452s, 443s, and 291s cm^{-1}. In the mass spectrum, no molecular ion was observed, probably due to decomposition of the compound under the conditions present in the instrument. Attempts to dissolve this compound in benzene resulted in its rapid decomposition. A portion of its UV-vis spectrum was observed in a carbon disulfide solution. This solvent is opaque below 380nm, but absorptions were observed at

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*The proposed structure for this nickel hydrazone is shown in Structure VIII.

540nm (ε 18,400) and 480nm (ε 13,300). Magnetic susceptibility measurements on this compound, by the Gouy method, yielded a magnetic moment of ~ 1.7 B.M. which is between the value of >0.5 B.M. for a diamagnetic nickel(II) ion and ~ 3 B.M. for a paramagnetic nickel (II) ion.

Reaction of Benzil Monohydrazone with Acetone in the Absence of Nickel (II) Ions

Procedure II.--To a hot solution of 2.25g (0.01 moles) of benzil monohydrazone in 100 ml of hot 95% ethanol was added 3.7 ml (0.05 moles) of acetone. The solution was refluxed and stirred for 7 days; on cooling and reducing the volume, yellow crystals were obtained. After recrystallization from methanol, thick yellow, hexagonal crystals were obtained, removed by suction filtration, and dried under vacuum at room temperature; mp 76-77°C. This compound was characterized as benzilacetone azine, $O=C(C_6H_5) - C(C_6H_5) = N-N = C(CH_3)_2$. Anal. Calcd for $C_{17}H_{16}N_2O$: C,77.23; H,6.11; N,10.60. Found: C,77.05; H,6.06; N,10.50. A molecular ion, at a m/e of 264, was observed in the mass spectrum.

Other Variations Investigated

Other Bridging Species

a.2,4 Pentanedione.--In the above described Procedure I, 10g (10.3 ml; 0.10 mole) of 2,4 pentanedione was substituted for the acetone. Upon mixing the reagents the

solution turned a dark yellow-green color. After 20 hours the reaction mixture was filtered by suction and the filtrate allowed to cool. On cooling some pale green crystals precipitated out and were removed by suction filtration. When dry the precipitate appeared to be a mixture of green and yellow crystals. These were separated by dissolving the green substance in water in which the yellow was insoluble. Both compounds were then recrystallized from methanol. The green substance was identified as hydrated nickel acetylacetonate on the basis of its infrared spectrum. The yellow compound was obtained as thick yellow hexagonal crystals. Analysis of this compound showed it to be benzilacetylacetone azine $O = C(C_6H_5) - C(C_6H_5) = N - N = C(CH_3) - CH_2 - C = O(CH_3)$. Anal. Calcd for $C_{19}H_{18}N_2O_2$; C,74.48; H,5.93; N,9.15. Found: C,74.32; H,5.85; N,9.19.

In a second attempt to form a ketazine complex with 2,4 pentanedione a molar ratio of 0.013 : 0.01, moles of 2,4 pentanedione to moles of nickel (II) was used. Upon initial mixing of the reactants the usual dark red color resulted After five days of refluxing and stirring, the solution was filtered by suction and the filtrate allowed to cool. A small amount of irridescent-red residue remained in the fritted funnel. The infrared spectrum of this material was similar to that

of the ketazines. No further batches of this material could be isolated and the small amount obtained was insufficient for characterization. This was probably the desired product and probably could be synthesized in larger quantities by carefully controlling the molar ratios of the reactants. The other products of this reaction were a red oil, a tan powder, and some yellow crystals. The yellow compound was probably benzilacetylacetone azine, based on the earlier experiment, and the tan powder probably contained $Ni(OH)_2 \cdot xH_2O$, based on its infrared spectrum.

Aldehydes.--Attempts were made to substitute an aldehyde for the acetone in Procedure I. A molar ratio of 0.20 : 0.01 moles of butyraldehyde to nickel(II) ions was used. Immediately after mixing the reactants the resulting mixture turned dark red and, after stirring at reflux temperature for seven days the solution turned violet. No residue remained after filtering this hot solution, but the filtrate turned red when stored overnight in a refrigerator and a small amount of green material (probably nickel hydroxide) precipitated out of the solution and was removed by filtration. Step-wise reduction of the volume of this filtrate resulted only in a viscous red oil after the removal of all solvent. This oil was very soluble in 95% ethanol, but insoluble in petroleum ether, so a mixture of these solvents was tried

to induce crystallization. The result was a two-layer system, the lower being a purple alcohol solution which was removed with a separatory funnel. These solvents are normally miscible, which suggests that the separation may have been induced by saturating the alcohol with the purple material. A purple solid was obtained from the alcohol by solvent evaporation. Attempts to recrystallize this material from acetone, or a solution of three parts ethanol and one part benzene, resulted in purple tars.

No meaningful mass spectra could be obtained as the compound decomposed too rapidly in the mass spectrometer. The infrared spectrum of this compound is listed below:

3100 - 3600 cm^{-1} (very broad), 1580 cm^{-1} vs (broad), 1055m, 1030m, 725m, 683s, 622m, 395m, and 310m.

Both butyraldehyde and acetaldehyde showed promise of yielding pure new compounds if sufficient work were invested in the project, but they were not pursued beyond the preliminary stage described above. Acetaldehyde performed similarly to butyraldehyde, so only the work with the latter is described here, as a guide to future workers.

Di-chlorides.--Methylene chloride and 1,1-dichloroethane were substituted for acetone in Procedure I. The principle product obtained from these reactions was a brown-reddish brown solid with characteristics similar to the nickel hydrazone complex (see page 14). These reactions were investigated to determine whether 1,1-dichloro compounds

could serve as bridging agents in the reaction in which the nickel ketazines were formed. A possible "driving force" for these reactions might have been the formation, and subsequent removal from the reaction mixture, of hydrogen chloride, similar to the formation of water when a ketone was used.

1,1,1 trifluoroacetone.--1,1,1 trifluoroacetone was substituted for acetone in Procedure I. The uniform result of several such experiments was a brown solid with characteristics similar to the nickel hydrazone complex (see page 14).

Other Metal Ions

Copper (II), mercury (II), zinc (II), and manganese (II) acetates were substituted for nickel acetate in Procedure I, but no products similar to the nickel ketazines were obtained. The reaction mixture before the addition of the metal had considerable reducing ability as evidenced by the formation of elemental copper and mercury after their acetate compounds were added. In the zinc case, zinc hydroxide was produced. The manganese acetate solution in ethanol was unstable, and once carefully placed in solution in ethanol and added to the reaction mixture appeared again to undergo decomposition to the hydroxide. The products of these

reactions were not completely characterized, but they did not resemble those found in reactions using nickel acetate.

Reactions of Ni MMK With Amines

[3,3-Dimethyl-6,7,12,13-tetraphenyl-1,2,4,5,8,11-hexazacyclotrideca-1,4,6,12-tetraenato(2-)-N^{1},N^{5},N^{8},N^{11}] nickel

Procedure IIIa.--To 10ml of ethylenediamine was added 0.54g (0.001 moles) Ni MMK under a dry nitrogen atmosphere. The reaction mixture was stirred and heated to a temperature just below the boiling point for 30 minutes. After cooling the solution to ambient temperature a bright red powder was removed by filtration. A second batch of product was obtained by the complete rotary evaporation of the ethylenediamine from the filtrate. The two fractions of product were combined for recrystallization from acetone. The product was obtained as a bright red powder, or as dark red crystals. For analytical data see Table 1.

Procedure IIIb.--To 10 ml of ethylenediamine was added 0.54g (0.001 moles) Ni MMK under a dry nitrogen atmosphere. The reaction mixture was stirred at ambient temperature for 48 hours, during which time the solid component changes color to a brighter shade of red. At the end of this time a bright red powder was removed by

Table 1.--Analytical Data for the Complexes.

Compound	% Yield[a]	% Calculated			% Found		
		C	H	N	C	H	N
Ni MMK	78.5	68.27	4.82	10.28	68.16	4.89	10.30
Ni MEK	60.9	68.71	5.06	10.02	68.91	5.25	10.22
Ni EEK	39.4	69.12	5.28	9.77	69.19	5.33	9.87
Ni MPrK	58.2	69.12	5.28	9.77	68.76	5.35	9.70
Ni MBuK	60.3	69.52	5.50	9.54	69.32	5.32	9.44
Ni MPhK	14.5	71.18	4.66	9.23	71.05	4.76	9.14
Ni Hcyclo 13	[b]	69.60	5.32	14.76	69.22	5.28	14.71
Ni Mcyclo 13	[b]	69.99	5.54	14.41	69.28	5.54	14.36
Ni ApSo	[b]	67.89	5.71	13.98	67.54	5.93	14.75

[a]Based on nickel (II).

[b]Due to difficulty in recrystallization accurate yields could not be attained.

filtration. A second batch of the product was obtained by the complete rotary evaporation of the ethylenediamine. The two fractions of product were combined for recrystallization from acetone. The product was obtained as a bright red powder or as a bright red crystals. This material was shown to be identical to the product of Procedure IIIa.

Racemic 1,2 diaminopropane, when substituted for ethylene diamine in Procedures IIIa and b yielded similar products. A reaction involving ℓ-1,2 diaminopropane was carried out using Procedure IIIa and resulted in the formation of an optically active product. This product was obtained as a waxy red material.

Comments.--The products described in this section could not be crystallized well from a wide range of available solvents. The products generally dissolved with difficulty and then precipitated only after the loss of most of the solvent. The reaction times indicated in Procedures IIIa and b have been shown to yield the desired products, but shorter reaction times may also have been effective if they had been investigated.

[α'-[[1-[[2-[(3 Aminopropyl)amino]-1,2-diphenyvinyl]azo]-1-methylethyl]azo]-α-stilbenolato(2-)] nickel

When 1,3 diaminopropane was substituted for ethylenediamine in Procedure IIIb a red powder was obtained.

This material could be recrystallized from methanol or ethanol, yielding a bright red crystalline material. For analytical data see Table 1. When 1,3 diaminopropane was substituted for ethylenediamine in Procedure IIIa, some of the starting material, Ni MMK, was isolated, as well as a red oil which could not be induced to crystallize, even by a chromatographic purification procedure.

Reaction of Ni MMK with Ethylamine

Procedure IV*.--Use of Pressure Tubes. To 0.54g (0.001 moles) Ni MMK, which had been placed inside of a pressure tube, was added 15 ml of ethylamine. A stopcock was attached to the end of the tube by means of a short section of vacuum tubing. The reaction mixture in the tube was gradually cooled to -196° by immersing the tube in a liquid nitrogen bath. After being frozen, the tube was evacuated by pumping for 15 minutes. The stopcock was then closed and the tube was allowed to warm to near room temperature, at which point the tube was shaken and then reimmersed in the liquid nitrogen bath. The cycle of gradually freezing, pumping, warming, and shaking was repeated three times before the contents of the tube were finally frozen and sealed with a torch. The tube was slowly warmed to room temperature and then clamped in an

*This procedure was used to control the atmosphere over a reaction and also the temperature at which the reaction was allowed to occur.

oil bath behind a shield. The oil bath was heated to about 100°, but not over 115°, and held there for three hours, then it was allowed to cool to room temperature. At room temperature, the tube was removed from the oil bath, wiped clean, and gradually cooled to -196°. While the tube was still cold, the glass was broken to open it. The tube was warmed slowly in an upside down position, while wrapped to catch condensed water. The solution dripped into a receiving vessel when it reached its melting point, and on further warming the amine evaporated, leaving the red product behind. A pure sample of this product could not be isolated, in part this seemed to be caused by decomposition during purification steps. Caution! During the heating cycle of one of these reactions the end of the pressure tube shattered and the reaction mixture shot out. Comments.--Both the time and temperature indicated in this procedure appeared to be necessary for the reaction to occur.

1,3 Diaminopropane was allowed to react with NiMMK in a manner similar to Procedure IV. The changes reflected the higher boiling point of the diamine (160° vs 14°). The product was initially obtained as a red oil, from which a white substance could be removed by dissolving the red material in methylene chloride. A thick red oil was obtained by rotary evaporation of the filtrate.

An attempt to purify this material by chromatographic means yielded Ni Ap So.

p-Toluenesulfonyl derivative of Ni Ap So.--To a solution of sodium hydroxide in 10 ml of water was added 0.1 g (excess)p-toluenesulfonyl chloride. A second solution, composed of 0.10 g of Ni Ap So dissolved in 5 ml of benzene, was shaken together periodically with the first solution over a period of several hours, after which the benzene layer was removed and the solvent was removed by rotary evaporation. This residue contained unreacted p-toluenesulfonyl chloride which was removed by sublimation, leaving behind an orange-red material. This product was identified as a mono-p-toluenesulfonyl derivative of Ni Ap So by its parent ion at m/e 784 in its mass spectrum.

Dehydrogenated Compound

A solution of 0.24g Ni Ap So in 350 ml of n-butanol was refluxed for six hours. After reducing the volume of the solvent and cooling, a red solid was obtained. The mass spectrum had a parent ion (m/e 596) which was four mass units lower than Ni Ap So. A summary of the infrared spectrum of this product is presented in Table 6.

Reactions of Ni MMK With Other Amines

To 50 ml of liquid ammonia was added 0.5 g Ni MMK. The reaction mixture was stirred under a dry nitrogen atmosphere for 1 hour while refluxing with a dry ice condenser. The ammonia was then allowed to evaporate and be carried off by the nitrogen flow. The red product which remained in the reaction vessel, was recrystallized from n-butanol to give red needles. The mass spectrum of this product identified it as Ni MMK.

In separate reactions, aniline and 3,3'iminobispropylamine [$H_2N(CH_2)_3NH(CH_2)_3NH_2$] were substituted for ethylenediamine in Procedure IIIb. In both cases, the red product obtained was recrystallized from n-butanol and identified as Ni MMK by its mass spectrum. 3,3' Iminobispropylamine was also substituted for the ethylamine in a procedure very similar to Procedure IV. A red solution was removed from the pressure tube and subjected to rotary evaporation to remove the amine. The product obtained was a red oil which could not be induced to crystallize. The mass spectrum of this oil did not indicate the presence of Ni MMK nor any of the products which were expected to be formed in this reaction.

When o-phenylenediamine was substituted for either the ethylenediamine in Procedure IIIa, or the ethylamine in Procedure IV, the red products obtained from both of these reactions were identical. These

products were both identified as Ni MMK by their mass spectra. Ni MMK was allowed to react with o-phenylenediamine by the method of Jager[6] (similar to Procedure IIIa). The products of this reaction appeared to be decomposition products of the starting materials, o-phenylenediamine and Ni MMK. When 1.1 g o-phenylenediamine was added to a hot solution of 0.54 g Ni MMK in n-butanol and stirred at reflux temperature for three hours, a red product was obtained in the form of red needles. The mass spectrum of these needles identified them as NiMMK.

Other Reactions Investigated

About 30 ml of ethyl iodide was distilled (66-68°) into a round bottom flask containing 0.27 g of Ni MMK. The reaction mixture was stirred at reflux temperature for 6 hours, after which the ethyl iodide was removed by rotary evaporation, leaving behind a red residue. The red material was recrystallized from acetone and identified as Ni MMK on the basis of its infrared and mass spectra.

To 0.27 g Ni MMK was added 50 ml of pyridine. The Ni MMK dissolved completely and the solution was stirred for 3 hours. The pyridine was then removed by rotary evaporation and the red residue was recrystallized from n-butanol. The product was obtained as red needles and

was identified as Ni MMK on the basis of its mass spectrum. Also a 4.97×10^{-5} M solution of Ni MMK in pyridine was prepared. The UV-visible spectrum was taken both immediately after the solution was prepared, and several days later. In both cases the spectrum observed was identical to that of Ni MMK in benzene.

Two 3.68×10^{-3} M solutions of Ni MMK in chloroform were prepared under a dry nitrogen atmosphere and amounts of 1,2 diaminopropane were added to give respective molar ratios of amine to Ni MMK of 25-1 and 120-1. The volumetric flasks were sealed with electrical tape and stored in the dark for 7 days. Aliquots were then taken and diluted to give a theoretical concentration of Ni MMK of 7.4×10^{-5} M. At this point purple crystals were observed in the original flasks. The UV-visible spectrum of the diluted solution was taken and compared to the spectrum of a known solution of 7.4×10^{-5} M Ni MMK in chloroform. The solution with the amine indicated the presence of Ni MMK, but in a lower concentration than the known solution, indicating that decomposition had taken place.

When 1,3 diaminopropane was substituted for 1,2 diaminopropane in the above procedure, similar results were obtained.

Reactions of Benzil Monohydrazone With Amines

To a hot solution of 2.25 g (0.01 moles) benzil monohydrazone in absolute ethanol was added 0.34 ml (0.005 moles) ethylenediamine. The clear yellow solution was refluxed for 24 hours and then cooled overnight in a refrigerator. The next day a white crystalline precipitate was removed by filtration. This material was identified as benzil monohydrazone on the basis of its infrared and mass spectra. This was the only product of this reaction. This reaction was repeated but with the addition of 1 drop of concentrated sulfuric acid to serve as a catalyst. The white crystalline product of this reaction was identified as benzil monohydrazone on the basis of its infrared and mass spectra.

0.34 ml (0.005 moles) ethylenediamine was added to 175 ml absolute ethanol in a round bottom flask. 0.25 g (0.01 moles) benzil monohydrazone was placed in an asbestos thimble of a soxhlet extraction apparatus. The ethanol solution was refluxed and the condensate was used to leach the benzil monohydrazone from the thimble into the round bottom flask containing the diamine. The white product isolated after the reaction was identified as benzil monohydrazone by its infrared and mass spectra.

To a 95% ethanol solution containing 0.01 moles of benzil monohydrazone and 0.012 moles of ethylenediamine

was added 0.005 moles of hydrated nickel chloride. The reaction mixture was stirred at reflux temperature for 6 hours. The white product obtained from this reaction was identified as benzil monohydrazone on the basis of its infrared and mass spectra.

To 50 ml of fresh 91-93% ethylenediamine was added 2.25 g benzil monohydrazone. The solution was stirred at reflux temperature for two hours. The excess amine was then removed by rotary evaporation and the yellow residue was recrystallized from 95% ethanol. The product was obtained as yellow crystals and was identified as 2,3 diphenyl-1,4 diazine* on the basis of its mass spectrum.

To a hot ethanolic solution of 0.01 moles of benzil monohydrazone were added 1 drop of concentrated sulfuric acid and 0.005 moles of o-phenylenediamine. The solution was stirred at reflux temperature for 3 hours. After reduction of the solvent volume, a small amount of white needles were obtained. This product was identified

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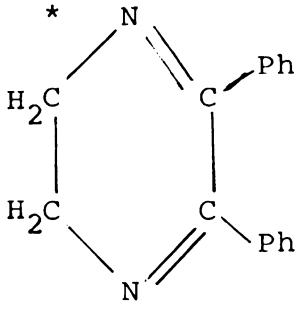

as 2,3 diphenyl quinoxaline* on the basis of its infrared and mass spectra.

To a hot ethanolic solution of 0.01 moles benzil monohydrazone were added .005 moles of hydrated nickel chloride and 0.005 moles of o-phenylendiamine. The reaction mixture was stirred at reflux temperature for 2 hours. A pale green precipitate was removed by filtration. After cooling overnight in a refrigerator, a lavender crystalline material precipitated from the filtrate and was removed by filtration. The green product was identical to a green material produced in 87% yield when the reaction was repeated in the absence of benzil monohydrazone. This substance was Ni (o-phenylenediamine) Cl_2. The lavender crystals could not be characterized. No mass peaks higher than m/e of 160 were seen in the mass spectrum. The infrared spectrum gave strong broad absorptions between 3100 and 3500 cm^{-1}, probably due to N-H absorptions also several unusual bands of medium intensity were observed between 2100 and 2300 cm^{-1}. The following is a list of the major infrared absorptions of the material in cm^{-1}: 3100-3500 s(br), 2260m, 2180m, 2120m, 1655s, 1608vs, 1590vs, 1328vs, 1273vs, 1155vs, 1096s, 1075s, 1010vs (br), 981vs, 720s, 660vs(br), 525vs, 501vs, 325m.

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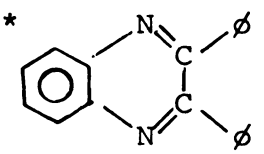
* 

IV. PHYSICAL MEASUREMENTS

Infrared spectra were obtained using Nujol or Fluorolube mulls on a Perkin-Elmer Model 457 spectrometer. Visible and ultraviolet spectra were obtained by use of a Unicam SP 800 B spectrophotometer. The reported proton magnetic resonance spectra were determined using a Varian HA-100 nmr spectrometer by a repetitive scanning technique. H_2SO_4 was used as an external reference for the instrument to "lock on" during the scanning. Chemical shifts were determined by the subsequent introduction of TMS as an internal reference. This procedure was necessitated by the high molecular weights and low solubility of the compounds in suitable solvents. Mass spectra were determined with an Hitachi-Perkin-Elmer RMU-6 O, and CEC 21-110 B double-focusing mass spectrometer. Accurate masses were measured with a Nier type peak matching unit attached to the latter instrument (accuracy ~ 4ppm). Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan, by Galbraith Laboratory, Inc., Knoxville, Tennessee, by Chemaltyics, Tempe, Arizona, and by the Water Resources Department of Michigan State University.

V. RESULTS AND DISCUSSION

Reaction between benzil monohydrazone and a series of ketones R^1R^2CO in the presence of nickel (II) ions has been found to yield a series of neutral Ni cis N_2O_2 tetradentate complexes containing a ligand formed by condensation between the ketone and two benzil monohydrazone residues. The reactivity of one of these coordinated ligands toward amine compounds has resulted in the formation of two types of complexes, the macrocyclic Ni N_4 and the non-cyclic Ni N_3O complexes. These new compounds are formed by the condensation of the nickel ketazine with one or two amine groups and the elimination of one or two molecules of water. The analytical data which were obtained for these complexes are presented in Table 1. The nickel ketazines and the compounds formed from them will be discussed in separate sections below.

Nickel Ketazines

The structures of the ketazine ligands were deduced by their infrared, ^1H nmr and mass spectra. The infrared spectra of the nickel ketazines exhibited numerous

absorptions but many similarities existed in the series. Table 2 contains a list of the common features of the infrared spectra of these complexes. These spectra differed significantly from the spectrum observed for benzil monohydrazone, which exhibited strong absorption bands at 3390, 3275, and 3180 cm^{-1} assigned to $\nu(NH_2)$ and a strong broad band at 1620 cm^{-1} assigned to $\delta(NH_2)$ and $\nu(C=O)$. The absence of these absorptions in the nickel ketazines was accompanied by a new strong band centered near 1280 cm^{-1} attributed to $\nu(C-N)$ and $\nu(C-O)$. Also the strong complex band at 1530 cm^{-1} in benzil monohydrazone, assigned to $\nu(C=C)$ from the phenyl rings and $\nu(C=N)$, is generally absent in the nickel ketazine spectra. These changes are consistent with the NH_2 groups of benzil monohydrazone having undergone condensation with the reacting ketone.

A summary of the ^1H nmr spectra obtained from the nickel ketazines is presented in Table 3. The solubility of the nickel ketazines was very low in solvents suitable for nmr studies, including CCl_4 in which the spectra were obtained. As a result of this problem, repetitive scan, time averaging techniques were employed to obtain reasonable resolution of the spectra. However, even using these techniques, some of the more complicated resonances could not be resolved. The spectra consist of two regions, an alkyl region, δ 0.9-2.2 and a phenyl region about

TABLE 2.--Common Absorption Bands in the Infrared Spectra of Nickel Ketazines.

Band Center	Band Range	Intensity \ Ketazine						I.R. Assignments for Ketazines
		NiNMK	NiMEK	NiEEK	NiMPrK	NiMBuK	NiMPhK	
1596	1592-1601	s	m	m	m	w	m	conjugated C=C; -N=N-
1577	1573-1580	m	w	w	m	w	w	aromatic absorptions; -N=N-; C-N
1494	1491-1496	m	m	m	s	w	s	mono substituted ø;
1420	1415-1428	s	s	s	vs	s	vs	C-O
1313	1311-1316	s	m	s	vs	m	m	C-O; ν(C-N)[12]
1174	1164-1177	s	s	m	vs	m	s	$C(CH_3)_2$; C-O
1155	1152-1160	vs	s	s	vs	m	s	$C(CH_3)_2$; C-O; mono substituted ø
1073	1071-1076	s	m	s	s	m	vs	mono substituted ø; C-O
1025	1023-1028	s	m	m	vs	m	vs	
1000	998-1003	m	m	m	s	m	s	Benzene ring breathing vibrations[12]
791	788- 794	vs	s	s	vs	m	vs	$C(CH_3)_2$; γ CH phenyl
522	519- 525	s	m	m	s	w	s	

TABLE 3.--Proton Magnetic Resonance Spectra of Nickel Ketazines.

Compound	Chemical Shift[a]	Type	Assignment
NiMNK	1.68	singlet	$-CH_3$
	7.06-7.47	multiplet	$-C_6H_5$
NiMEK	0.96[b]	triplet	$-CH_2.\underline{CH_3}$
	1.65	singlet	$-CH_3$
	2.17[c]	quartet	$-\underline{CH_2}.CH_3$
	7.06-7.44	multiplet	$-C_6H_5$
NiEEK	0.92[b]	triplet	$-CH_2.\underline{CH_3}$
	2.20[c]	quartet	$-\underline{CH_2}.CH_3$
	7.05-7.40	multiplet	$-C_6H_5$
NiMPrK	0.91[b]	triplet	$-CH_2.CH_2.\underline{CH_3}$
	~1.40	multiplet	$-CH_2.\underline{CH_2}.CH_3$
	1.65	singlet	$-CH_3$
	2.12[b]	triplet	$-\underline{CH_2}.CH_2.CH_3$
	7.06-7.39	multiplet	$-C_6H_5$
NiMBuK	0.92[b]	triplet	$-CH_2.CH_2.CH_2.\underline{CH_3}$
	1.22-1.43	multiplet	$-CH_2.\underline{CH_2}.\underline{CH_2}.CH_3$
	1.64	singlet	$-CH_3$
	2.15[b]	triplet	$-\underline{CH_2}.CH_2.CH_2.CH_3$
	6.94-7.49	multiplet	$-C_6H_5$
NiMPhK	2.06	singlet	$-CH_3$
	7.11-7.30	multiplet	$-C_6H_5$

[a] p.p.m. downfield from tetramethylsilane.

[b] Center of triplet.

[c] Center of quartet.

δ 7-7.5, both downfield from TMS. As an example of the spectra obtained, the spectrum of NiMEK is presented in Figure 1.

No resonances which might be attributable to N-H groups, were observed. The relative areas under the peaks appeared to be in ratios consistent with the assignments made (coupling constants, J_{H-H}, were calculated to be 7.0-7.7 cps from spectra exhibiting triplets and quartets). For all of the ketazine complexes containing R^1 = Me, except the case where R^2 = Ph, a sharp singlet, attributable to this methyl resonance, was observed close to δ 1.65 However, when R^2 = Ph, this methyl singlet was shifted downfield to δ 2.06, indicating that the methyl group had been deshielded by the phenyl group. A molecular framework model of NiMPhK based on the proposed structure showed the methyl group to be positioned, relative to the phenyl group, in such a way as to make possible the observed deshielding.

The observed ^1H nmr spectra are consistent with the formulation of the tetradentate ligands of the nickel ketazines as proposed in Structure V.

Further confirmation of the structure of the ketazines was provided by a study of their fragmention patterns in their mass spectra. For each pure compound in the series, the set of highest mass peaks corresponded to the singly charged molecular ion for the compound. The

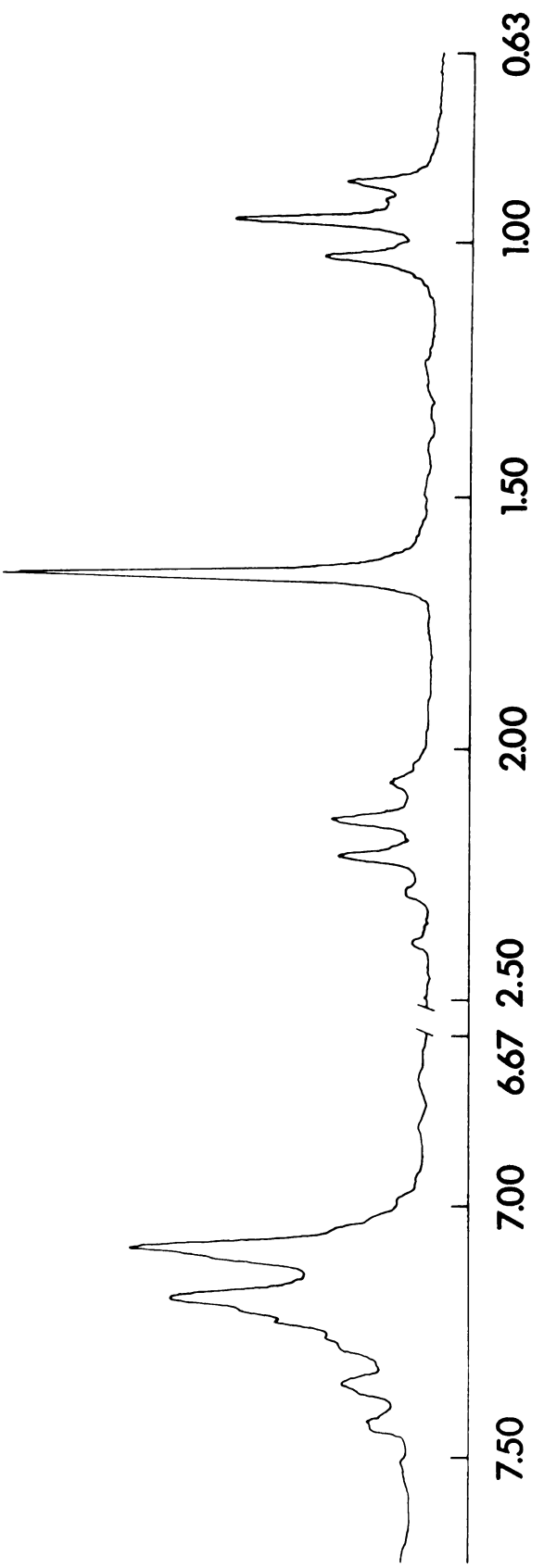
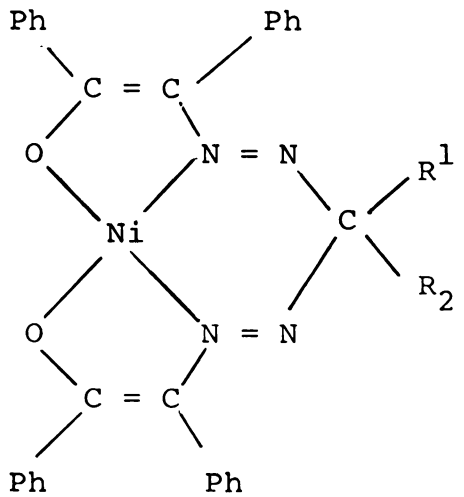


Fig. 1. 100 MHz ^{1}H nmr spectrum of nickel methyl ethyl ketazine, (NiMEK).



Structure V

peak of highest intensity in this set corresponded to an ion containing ^{58}Ni followed by peaks at higher masses with lower intensities representing the presence of other isotopes of nickel, carbon, and nitrogen. The fragmentation pattern for this series of compounds was quite uniform and is summarized in Table 4. The tentative assignments made in this table can easily be accounted for on the basis of the proposed structure. A notable feature of these residues is the stability of the five-membered chelate ring, possibly stabilized by electron delocalization. A similar stability of a six-membered chelate ring has been observed by Cummings and Sievers in the mass spectra of two nickel (II) macrocylic complexes.[13]

One of the most notable characteristics in these mass spectra was the feature of the three highest mass peaks. The highest peak corresponded to the molecular ion

TABLE 4.--Mass Spectra of Nickel Ketazines.

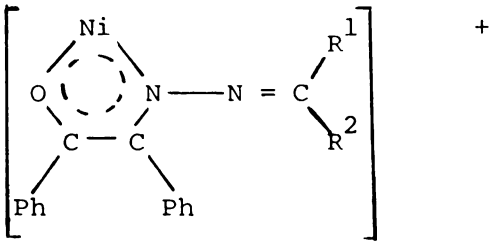
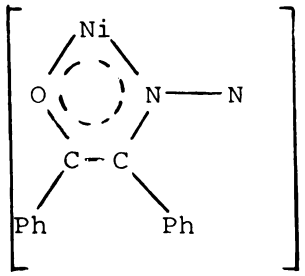
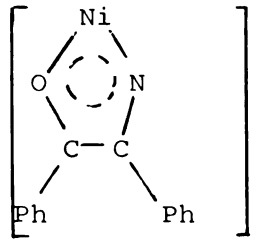
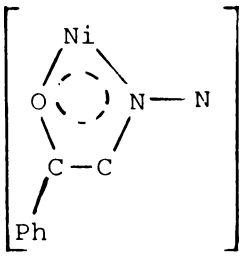
M/e[a]	Assignment
P	[Parent Ion]+
P-28	$[P - N_2]+$
P-56	$[(P - N_2) - CO]+$
P-222	
280	
266	
240	$[Ni.O.C.(Ph)_2]+$
238	$[Ni.N.C.(Ph)_2]+$
224	$[Ni.C.(Ph)_2]+$
203	
192	[Ph.C.C.(N).Ph]+
178	[Ph.C.C.Ph]+

TABLE 4.--(Con't.).

M/e[a]	Assignment
166	$[C.(Ph)_2]+$
135	?
117	[Ph.C.CO]+ or $[Ph.C.N_2]+$
105	[Ph.CO]+
99	?
91	[Ph.N.]+
77	[Ph]+

[a]For nickel containing species, the value for ^{58}Ni is given.

and the next two peaks occurred at P-28 amu and at P-56 amu (again a separation of 28 amu from the next higher peak). These losses could correspond to the loss of CO or N_2, or some combination of the two, since they both have the same nominal mass of 28 amu. High resolution mass spectrometry was used to resolve the uncertainty. Table 5 presents the theoretical possibilities and the results of an exact mass measurement for NiMMK. Thus it can be seen that the [P-28 amu]+ peak for NiMMK represents the loss of an N_2 fragment and that the [P-56 amu]+ peak represents the loss of a CO fragment from the [P-28 amu]+ residue. It was further shown that these losses were consecutive rather than concurrent by a measurement of metastable ions by the defocusing technique. A similar consecutive fragmentation pattern has been observed in the mass spectra of some triazinones* (compounds which contain both > C=O and -N=N- groups).[14] This similarity strongly suggests the presence of an -N=N- linkage in the nickel ketazines and is consistent with the proposed structure (see Structure V). On the basis of these measurements and the similarity of the mass spectra of the other nickel ketazines, it was concluded that their fragmentation also proceeds by an

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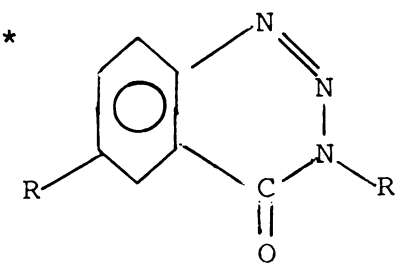
* 

TABLE 5.--Results of High Resolution Mass Spectroscopy Investigation for NiMMK, (R^1 = R^2 = Me).

m/e	Possible Assignment	Exact Mass. Theoret.	Exact Mass. Measured
544	$M^{+\cdot}$	544.1409	544.1387
516	$M^{+\cdot}-N_2$	516.1348	516.1343
	$M^{+\cdot}-CO$	516.1460	
488	$M^{+\cdot}-N_2-CO$	488.1399	488.1375
	$M^{+\cdot}-2N_2$	488.1286	
	$M^{+\cdot}-2CO$	488.1511	

initial loss of N_2, followed by a loss of CO from the initial residue. However, for benzilacetone azine, the initial loss of 28 amu probably represents the elimination of a CO fragment because the two nitrogen atoms are linked by only a single bond and their loss would break the molecule into several fragments.

The ultraviolet-visible spectra of the nickel ketazines, from 300-850 nm, were obtained in approximately $5x10^{-5}$M benzene solutions (in which they were quite soluble). Care was taken to run the spectra soon after preparation of the solutions because benzene appeared to accelerate photodecomposition. All of the nickel ketazines gave very similar spectra, which suggests that the nickel (II) ion is in a similar environment in all of the complexes. These spectra are presented in Table 6. The absorption band near 495 nm has been assigned to the $^1A_1 \rightarrow {}^1B_1$ transition for nickel (II) in a Ni cis N_2O_2 planar environment,[15, 16] which satisfies the requirements imposed by the nature of the tetradentate ligand. If this assignment is made, then the other bands may be assigned as charge-transfer and ligand bands. The position and molar extinction coefficients of the lower lying bands are probably influenced by the strong ligand bands at 390 and ~ 340 nm.

All of the nickel ketazines were obtained as dark red to orange-red crystalline solids which were found to be diamagnetic ($\mu eff \leq 0.5$ B M) when pure. As initially

TABLE 6.--Ultra-Violet and Visible Spectra of Nickel Ketazines.[a]

Compound	ν_1[b]	$\varepsilon_M \times 10^{-3}$	ν_2[b]	$\varepsilon_M \times 10^{-3}$	ν_3[b]	$\varepsilon_M \times 10^{-3}$	ν_4[b]	$\varepsilon_M \times 10^{-3}$
NiMMK	495	7.67	460 sh	8.80	390	17.9	344	15.7
NiMEK	498	7.85	460 sh	9.06	390	17.3	342	15.3
NiEEK	498	7.84	460 sh	8.88	390	17.3	342	15.2
NiMPrK	498	7.51	460 sh	8.64	390	16.7	342	14.8
NiMBuK	498	7.48	460 sh	8.75	390	16.8	342	14.8
NiMPhK	495	7.78	455 sh	9.14	390	16.7	336	14.8

[a]All spectra obtained in benzene.

[b]In nm.

isolated, the complexes usually contained small amounts of ferromagnetic impurities. These impurities could be removed by repeated recrystallizations (if stored in the dark) or by passing a benzene solution of the complex through an alumina column (see experimental section for details).

All of the data obtained for the nickel ketazines support the structure as shown in Structure V. In the alternate structure the adjacent nitrogen atoms would be linked by a single bond and the coordinated nitrogens would form a four-membered ring with the nickel ion and the bridging carbon atom. However, the presence of a nitrogen-nitrogen double bond has been demonstrated and molecular framework models have indicated that the alternate structure would involve greater strain than Structure V.

This is the first example in which a ketone reacts with coordinated nitrogen atoms to form a single carbon atom bridge. Thus, it represents a new type of condensation reaction, previous types of condensation reactions resulting in the formation of new chelate rings have necessitated the presence of, or the formation of a three carbon atom bridge between coordinated nitrogen atoms. This type of condensation reaction offers a direct route for introducing a large degree of unsaturation into metal chelate ring systems. Unsaturated chelate ring systems have been a goal of previous synthetic investigations,[3]

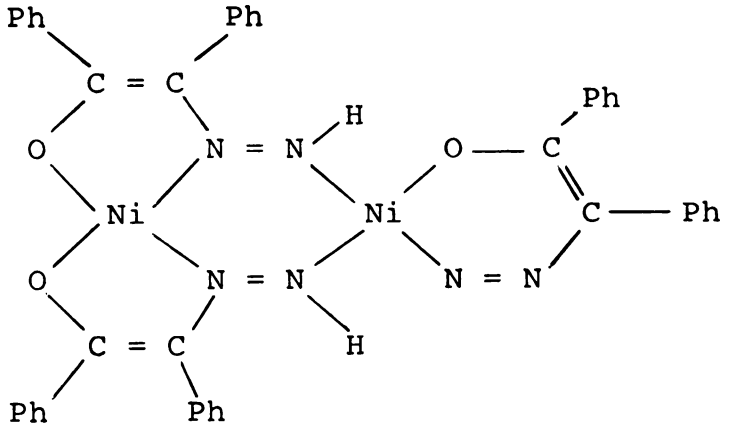
one reason for this being attempts to approximate the conjugated chelate ring systems of naturally occurring compounds. These previous attempts to introduce unsaturation have often required additional dehydrogenation steps after the initial formation of the metal complex. The chelate ring formed by the single bridging carbon atom in this new type of condensation contains six members, this is the same size ring as has been observed in other condensation reactions[2] and the stability of five- and six-membered chelate rings has been observed here and in previous investigations.[13]

The reaction resulting in the formation of these ligands is best described as a template reaction[3] since it is dependent on the presence of the nickel (II) ion. In the absence of nickel (II) ions, benzil monohydrazone and acetone undergo a Schiff's base condensation reaction to give benzilacetone azine. Benzilacetone azine may function as an intermediate in the formation of NiMMK, in that Taylor and associates[10] demonstrated that NiMMK could be formed, in low yield, by refluxing nickel acetate and benzil monohydrazone with this compound. However, excess benzil monohydrazone is necessary for this reaction to take place.

When nickel acetate is added to an ethanolic solution of benzil monohydrazone a dark red-brown product is formed immediately. This same compound appears to form

as an initial precipitate in the condensation reactions of the ketones. Both of these dark reddish-brown substances have infrared spectra similar to the nickel hydrazone complex (vide infra). In the case where the ketone is benzophenone, the only product obtained is a dark reddish-brown crystalline compound which is probably a pure form of this compound. Earlier workers in this area also reported the formation of a similar dark red solid, but they were unable to obtain consistent analyses. The crystalline form of this dark solid (serendepitiously isolated!) has now been characterized as Ni_2 $(L-H)_2$ $(L-2H)$, where (L-H) and (L-2H) are benzil monohydrazone minus one or two amine hydrozen atoms respectively (see Structure VIII). It is likely that the amorphous solids obtained by mixing nickel acetate with alcoholic benzil monohydrazone or as the initial precipitate in the ketazine formation reactions are similar to Ni_2 $(L-H)_2$ $(L-2H)$, but polymeric or more randomly complexed species may also be formulated using the same chemical units. The extremely viscous nature of reaction mixtures containing this substance immediately after its formation may lend credence to these possible species. If this did occur, it might help to explain the inconsistent analyses. Two other possible explanations for these earlier inconsistencies are that the material is insoluble in many organic solvents and does not recrystallize well from those in which it does dissolve and also that it undergoes rapid decomposition in solvents such as benzene which are used

to remove the nickel hydroxide impurities of these reactions.



Structure VIII

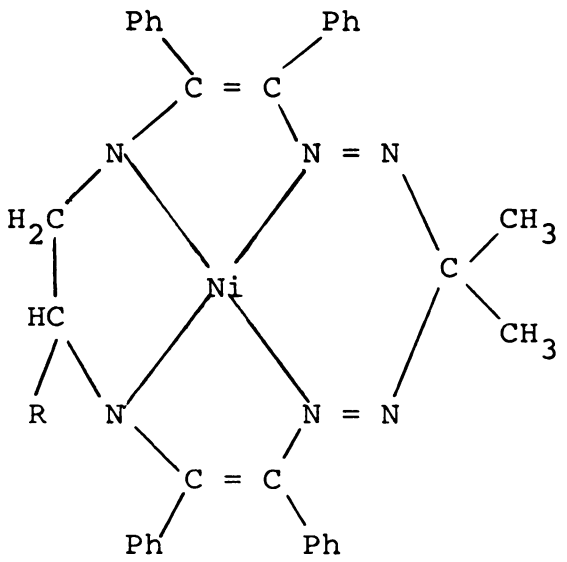
As the ketazine formation reactions progress, this initial complex slowly disappears (probably through a thermodynamic equilibrium favoring other product formation) and the stable orange-red nickel ketazines are formed. The ketazine formation reaction has not been studied in great detail, but it appears to involve an equilibrium concentration of benzil monohydrazone, with the nickel (II) ions coordinating the intermediates or products which are formed.

To summarize briefly, a new series of non-cyclic Ni cis N_2O_2 tetradentate complexes have been synthesized. These complexes have been characterized by infrared, ^1H nmr, ultraviolet-visible, and mass spectroscopy as well as elemental analyses and magnetic susceptibility measurements. In the next section, the reactivity of one of these complexes (NiMMK) toward amines will be examined.

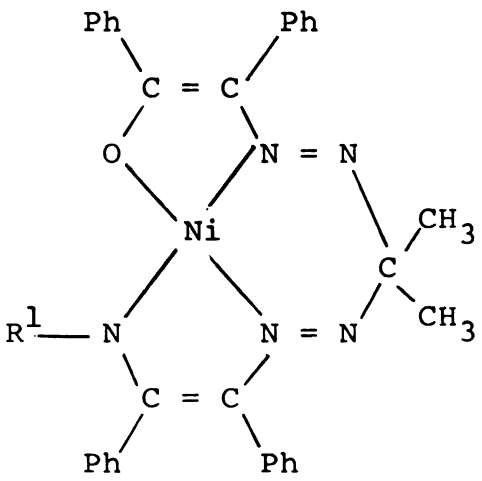
Reaction Products of NiMMK

At about the same time that the nickel ketazine compounds were being characterized, other authors[6, 7, 8] were reporting condensation reactions of coordinated carbonyl groups with amines resulting in the formation of macrocyclic complexes, in compounds similar to the nickel ketazines. Previously, the coordinated carbonyl groups of salicyclaldehydes had been shown to react with amines to form Shiff base type compounds, but the formation of macrocyclic complexes was a new and interesting development. Since the conditions necessary for these cyclization reactions to occur and the mechanisms of these reactions were not entirely understood, an investigation of the reactivity of a nickel ketazine towards amine compounds seemed like a potentially interesting and useful area for research.

Reaction between NiMMK and some neat mono- and diamine compounds yields two types of neutral complexes, a macrocyclic NiN_4 type (Structure VI) and a non-cyclic NiN_3O type (Structure VII). These compounds are condensation products of the ketazine resulting in the replacement of one or both oxygen atoms by nitrogen atoms and the elimination of one or two molecules of water. The analytical data for these compounds have been presented in Table 1. The structures of the ligands have been deduced from the infrared and mass spectra of the complexes.



Structure VI



Structure VII

^{1}H nmr spectra have been unobtainable and purification of some of the compounds has proven to be difficult due to their low solubility in most solvents. The characterization of these two types of compounds will be discussed in separate sections below, beginning with the macrocyclic NiN_4 complexes.

Macrocylic NiN_4 Type Compounds

These macrocyclic complexes are formed by reactions of NiMMK with neat 1,2 diaminoethane or 1,2 diaminopropane at room temperature or higher in a dry nitrogen atmosphere.

Their infrared spectra were complicated in that numberous absorptions were observed, but they bore some resemblance to that of the parent compound. The common features of the infrared spectra of these compounds are reported in Table 7. Also presented in this table are

TABLE 7.--Common Absorption Bands in the Infrared Spectra of NiN_4 and NiN_3O Compounds.[a]

Band Center	Band Range	Intensity \ Compound NiHcydo 13	NiMcyclo 13	NiApSo	NiD-ApSo	NiMMK[b]	I. R. Band Assignments
1598	1597-1602	m	m	s	vs	s	conjugated C=C; -N=N-; C-Ø[12]
1577	1573-1577	m	w	m		m	aromatic absorptions; -N=N-;C-N
1498	1498-1499	s	vs			1493m	mono substituted Ø;
1346	1343-1349	vs	vs	vs	vs	vs	
1313	. .	vs	vs			1315 s	ν(C-N)[12]
1295	1293-1298	vs	vs	vs	vs		ν(C-N)[12]
1272	1270-1275	vs	vs	vs	s	1280vs	
1210	1208-1212	m	m	s	m	m	
1173	1170-1177	vs	vs	1161vs(br)	s	s	$C(CH_3)_2$ aromatic C-H[12]
1070	1066-1072	s	s	vs	s	1075 s	mono substituted Ø; aromatic C-H[12]
1000	997-1002	m	m	s	m	m	benzene ring breathing vibrations[12]
923	921- 925	m	m	s			
844	841- 846	m	w	m	m	m	
785	785- 788	m	m	vs		s	$C(CH_3)_2$
700	699- 701	vs	vs	vs	vs		
590	598- 590	w	w	w	m	592m	
512	509- 512	w	m	w			

[a]NiESO could not be isolated in a sufficiently pure form to give a meaningful infrared spectrum.

[b]Absorptions of NiMMK are listed for comparison purposes.

some infrared absorption bands of NiMMK which is presented for comparison purposes. In these spectra the strong band at 1420 cm^{-1} ν(C-O) of the nickel ketazines is absent and a strong new band at 1295 cm^{-1} ν(C-N) appears. Below 1300 cm^{-1} it seems that the bands in common with NiMMK are shifted slightly in the direction of lower wave numbers. Other notable features of these spectra include the consistent intense absorptions at 700 cm^{-1}, in contrast to a frequent, but not characteristic band at 704 cm^{-1} of the ketazines, and the band at 512 cm^{-1} of weak to moderate intensity which is unique to these daughter compounds.

In the mass spectra of these compounds, singly charged molecular ions corresponding to a ^{58}Ni isotope, have been observed for each of the compounds. The envelope of mass peaks surrounding the molecular ion is very similar to that observed for the nickel ketazines. The compounds also exhibit the loss of an N_2 fragment, as shown by high resolution mass spectroscopy (see Table 8). A summary of the fragmentation patterns of these compounds in their mass spectra is presented in Table 9, along with tentative assignments based on the proposed structures for the reported mass peaks. The table is divided into two sections in order to illustrate the similarities observed for these compounds. In the first section, the leaving groups are shown because for each compound the residue

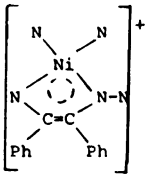
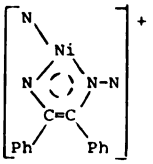
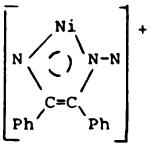
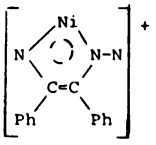
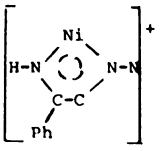
TABLE 8.--Results of High Resolution Mass Spectroscopy Investigation for Ni Mcyclo 13.

m/e	Assignment	Exact Mass	
		Theoret.	Measured
582	$M^{+}\cdot$	582.2042	582.1995
544	$M^{+}\cdot-N_2$	554.1980	554.1930

would be different, while in the second section the remaining molecular fragments have lost the disimilar parts of the parent ions, so the identical residues are shown. The mass spectra of these compounds display a similarity to those of the nickel ketazines in some of the residual fragments and also in the stability of the five-membered chelate ring system. The loss of an N_2 fragment suggests the presence of a nitrogen-nitrogen double band and the resemblance to the nickel ketazine mass spectra suggests structural similarities. The data obtained from the mass spectra of these compounds supports the proposed Structure VI for these compounds.

The ultraviolet and visible spectra over the range of 300-850 nm are reported in Table 10, along with the circular dichroism spectrum of ℓ-NiM cyclo 13. Both the location and the measured absorbances of these bands are probably inaccurate due to the strong charge transfer bands at the high energy end of the spectra. This is shown in Figure 2, where the spectra of the macrocycles

TABLE 9.--Mass Spectra of NiN_4 and NiN_3O Compounds.

m/e[a]	Assignment Leaving Group	Assignment Residue
P	Parent Ion	
P-15[b]	$-CH_3$	
P-28	N_2	
P-56	$NC(CH_3)_2$[c]	
P-84	$N{=}N{-}C(CH_3)_2$ (N) [c]	
P-131[b]	$Ph{-}C{-}N{-}(CH_2)_2$[c]	
P-159	$Ph{-}C{-}N{=}N{-}C(CH_3)_2$[c]	
P-187	$Ph{-}C{-}N{=}N{-}C(CH_3)_2{-}N{=}N$	
P-276	$Ph{-}C{=}C(Ph)N{=}N{-}C(CH_3)_2$[c]	
P-290	$Ph{-}C(N){=}C(Ph)N{=}N{-}C(CH_3)_2$[c]	
P-332	$-(CH_2){-}N{-}(Ph)C{=}C(Ph)N{=}N{-}C(CH_3)_2N$[c]	
306[b]		
292[b]		
278		
265		
250[b]		[Ni-N-C(Ph)-C(Ph)]+
236		[Ni-C(Ph)-C(Ph)]+
202		
193		[PhC(NH)CPh]+
178		[PhCCPh]+
77		[Ph]+

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

[b] For macrocyclic compounds only.

[c] Residue contains a five-membered chelate ring.

TABLE 10.--Ultraviolet and Visible Spectra of NiN_4 and NiN_3O Compounds.

Compound	λ, nm (ε)[a]
Ni H cyclo 13	558(ε3.14), 534(ε4.71), 459(ε12.2), 350(ε17.5)
Ni M cyclo 13 (racemic)	546(ε2.02), 518(ε3.64), 440(ε9.90), 334(ε15.8)
Ni M cyclo 13 (l)	546(ε2.15), 518(ε3.43), 450(ε9.01), 345(ε15.9), 320(ε19.3), 300(ε24.0)
Ni ApSo	558(ε1.20), 532(ε2.79), 440(ε12.2), 420(ε12.2), 340(ε10.8)
NiESo[b]	510(ε7.5), 464(ε8.9), 405(ε17), 348(ε14.5)
CD Spectrum of Ni M cyclo 13 (ℓ)	λ, nm (Δε) 495(+0.11); 426(-0.07); 364 sh (+0.44); 350(+0.63); 307(-0.09)

[a]All ε values are x 10^{-3} and all λ are in nm.

[b]ε are based on an estimated concentration.

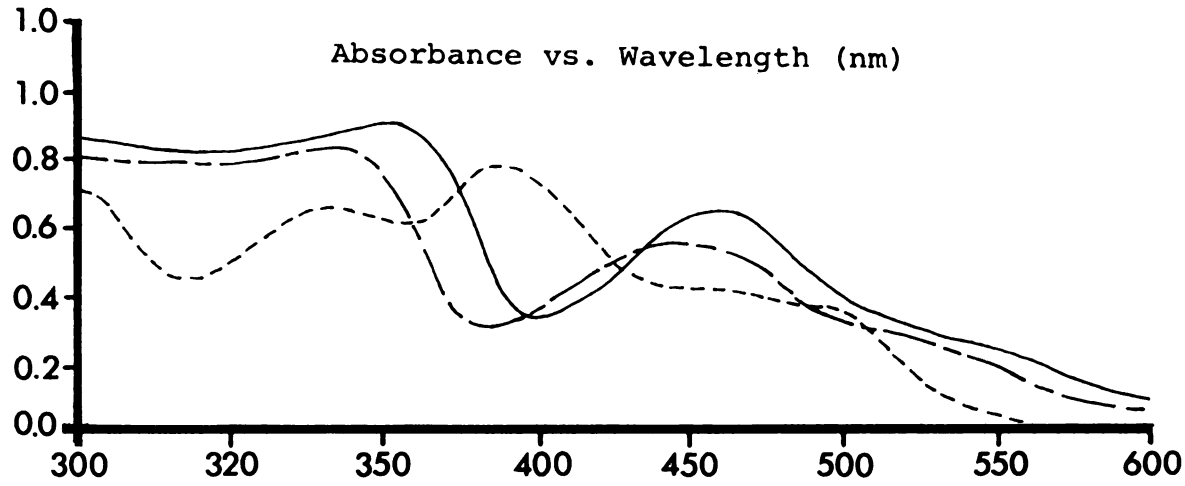


Fig. 2. Electronic absorption spectra, in benzene, of NiMMK (---), Ni H cyclo 13 (———), and Ni M cyclo 13 (— - — -).

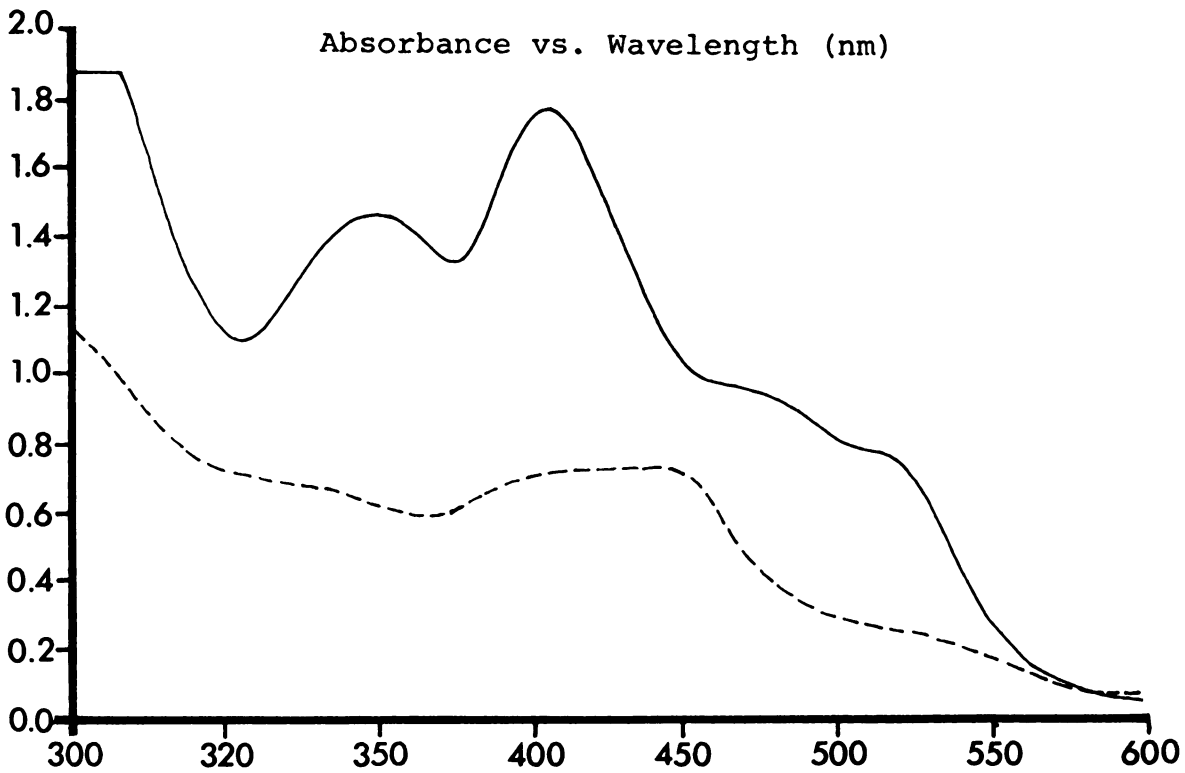
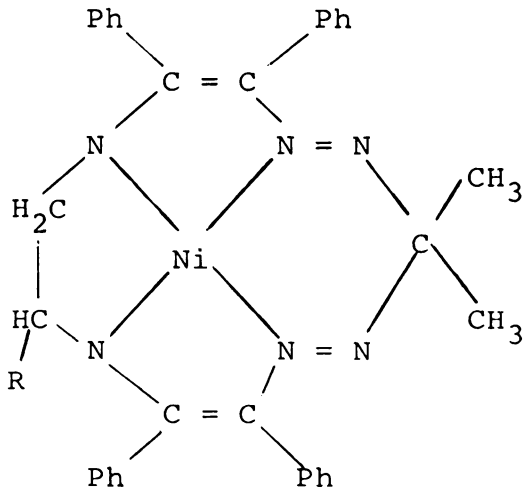


Fig. 3. Electronic absorption spectra, in benzene, of Ni ApSo (----), and Ni ESo (———).



Structure VI

are superimposed on that of NiMMK. Normally the substitution of a methyl group for a hydrogen atom on a chelate ring system produces little change in the electronic spectrum of the compound[12] but some distinct changes are noted in this case. In the electronic spectra of square-planar nickel (II) complexes, theory predicts that three or four transitions, depending on the symmetry of the complex, should occur in the d-orbital manifold of the metal ion. For these compounds, the d-d transitions are probably represented by the low energy shoulders in the spectra; they appear to be partially obscured by the charge-transfer bands which occur at lower energies than in the nickel ketazines. These shoulders may represent the $^1A_1 \rightarrow {}^1B_1$ transition observed in the spectra of the nickel ketazines. Bands near 650 nm would be expected if these complexes were tetrahedral, so their absence suggests a square-planar

environment for the nickel (II) ion. The circular dichroism spectrum of ℓ-Ni M cyclo 13 exhibits a positive cotton effect and is shown in Figure 4. This CD spectrum exhibits better resolved bands than the ultraviolet-visible spectrum, but little interpretation is possible from a single example.

These compounds were generally obtained as red powders, or rarely, as red crystal platelets; they had a measured magnetic moment of approximately 1 B.M. This relatively high magnetic moment was probably due to the presence of impurities as difficulties were encountered in purifying these compounds, a similar problem was encountered with ferromagnetic impurities in the nickel ketazines which could only be removed by repeated recrystallizations or a chromatographic purification step. However, anomalous magnetic moments[18] have been reported for nickel (II) complexes and this possibility could not be discounted.

The coordination of the ligands to the nickel (II) ion is proposed to be as shown in Structure VI. The macrocyclic ligand contains thirteen members and is coordinated so as to form three five-membered and one six-membered chelate rings with the nickel (II) ion. The ligand donor atoms are situated in an approximately square planar configuration about the nickel (II) ion. Such coordination by 13-membered macrocycles is rare,[2] but a recent X-ray structure determination on a nickel (II)

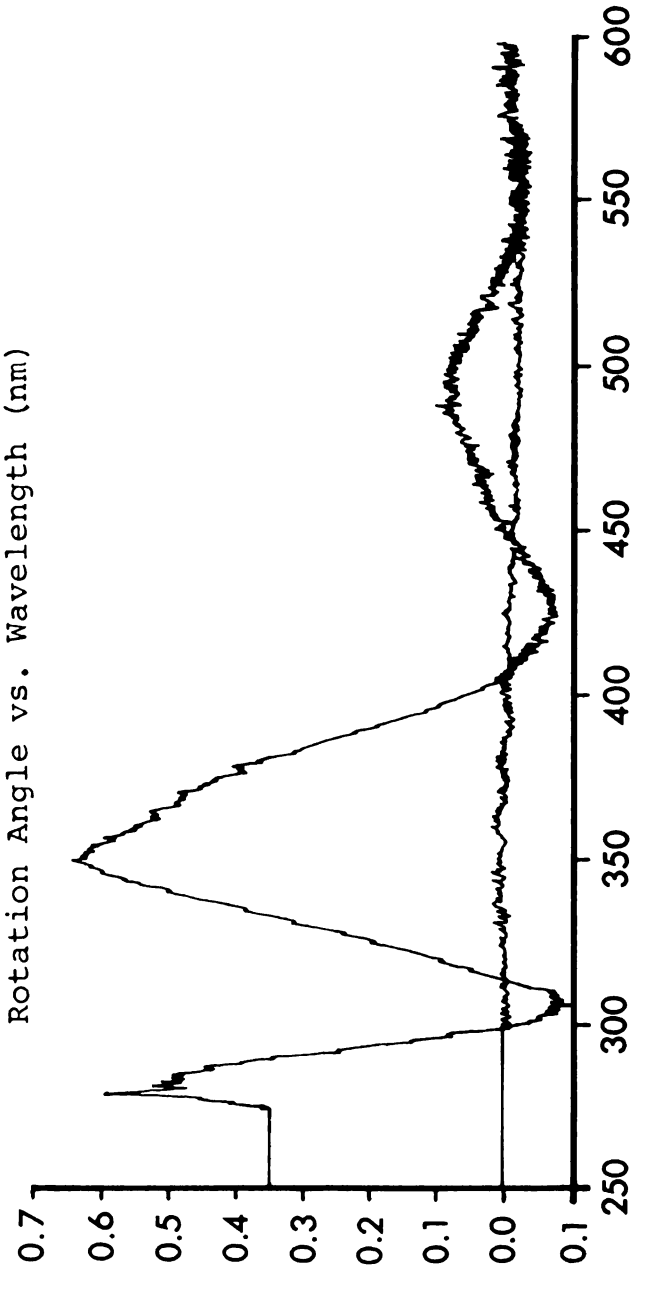


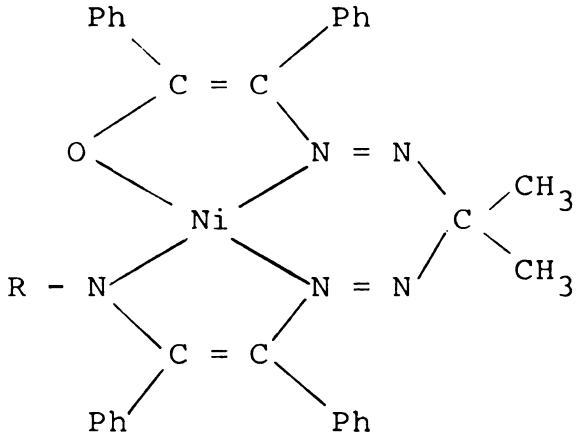
Fig. 4. Circular dichroism spectra, in benzene, of ℓ-Ni M cyclo 13.

complex of a 13-membered macrocycle[19] has shown that such coordination does exist in other compounds. The authors found slight tetrahedral distortions, but noted that similar distortions occur in macrocyclic complexes of larger ring size and in non-cyclic complexes. These authors have further suggested that square-planar coordination may be possible for 12-membered macrocyclic complexes of nickel (II), based on the available data on Ni-N bond distances and N-N "bites." All of the previously reported synthetic 13-membered macrocyclic complexes have been derived from triethylenetetramine, so the synthetic route published in this dissertation represents a new route for the synthesis of these unusually small ring-sized macrocyclic ligands. Electron delocalization throughout the ring system is possible via the central metal ion and may stabilize the compounds. Models based on this structure show very little strain. By reacting NiMMK with optically active diamines it has been shown that optically active macrocycles can be synthesized.

Non-Cyclic Ni-N_3O Type Compounds

A different type of complex is formed when NiMMK reacts with 1,3 diaminopropane at from room temperature to 100° or with ethylamine at 100° for several hours. These reactions result primarily in a Ni N_3O type of

coordination, by displacement of only one of the oxygen atoms of the ketazine, as shown in Structure VII. The



Structure VII

formation of these compounds appears to indicate that the second oxygen atom of NiMMK is more difficult to dislodge than the first. Only a mono-ethylamine product has been detected, although the reaction took place under what would appear to be forcing conditions. This reaction occurred at 100-110°, about 90° above the boiling point of ethylamine, under several atmospheres of pressure in a sealed pressure tube and with precautions taken to exclude water from the reaction mixture.

NiApSo is obtained in near quantitative yields from the reaction of 1,3 diaminopropane with NiMMK and can be recrystallized from common organic solvents. NiESo is obtained in low yield and has not as yet been isolated in a form pure enough for infrared or elemental analysis, but it appears that a purification can be

accomplished in the near future. Some of the infrared absorption bands of NiApSo have been presented in Table 6. This spectrum contains the intense ν(C-N) band at 1295 cm^{-1} and the characteristic band of these condensation products at 700 cm^{-1}; in many aspects this spectrum is similar to those of the nickel macrocyclic complexes. The primary method of characterization for these Ni N_3O type compounds has been mass spectroscopy, and these compounds exhibited fragmentation patterns which were similar to those of the macrocyclic complexes. These compounds also displayed the stability of the five-membered chelate ring which was noted previously. Although NiApSo was the only compound of this group which did not exhibit an initial loss of 28 mass units, the majority of the data obtained from the mass spectra supports the proposed structure for these compounds, as shown in Structure VII.

When 1,3 diaminopropane reacted with NiMMK at 100° in a pressure tube, a peak was seen in the mass spectrum of the product which corresponded to the macrocycle which could be formed in the reaction. However, the major component of the mixture obtained was NiApSo and an attempt to isolate this macrocycle by chromatographic techniques yielded only a fraction containing the non-cyclic NiApSo compound. Apparently the 1,3 diaminopropane macrocycle hydrolyzed on the water containing alumina column. Also a sample of NiESo was apparently hydrolyzed

to NiMMK in a similar way. Chromatographic purifications of NiESo have been accomplished, though, when the alumina and solvents used were treated to remove any moisture; a similar procedure might work for the 1,3 diaminopropane macrocycle.

The reactions of ethylamine and 1,3 diaminopropane were temperature dependent. For 1,3 diaminopropane, a red oil was obtained from its reaction with NiMMK at the boiling point of the amine (~ 150°). Although this red oil was not characterized, it was probably a polymer. Jager[6] has reported polymer formation in similar reactions with diamines, and a molecular framework model showed that the propyl chain was sufficiently long to enable the terminal amine group to react intermolecularly with a second nearby molecule of NiMMK. At 100-110°, about the boiling point of 1,2 diaminoethane and 1,2 diaminopropane, 1,3 diaminopropane reacted to form NiApSo and, what appeared to be, a small amount of a 14-membered macrocyclic complex. At ambient temperature, NiApSo appeared to be the only product of the reaction. For the case of ethylamine, NiESo was only obtained after heating the reactants to 100-110° for several hours. The product isolated when this reaction occurred at the boiling point of the amine, about 14°, or in a pressure tube at 60°, was the NiMMK starting material. In these condensation-reactions the temperature appeared to be a crucial factor in determining the course of these reactions.

The NiApSo compound contained a potentially pentadentate ligand. A five coordinate intermediate similar to this has been proposed by Green et al,[8] but has not been isolated. The presence of the amino group was confirmed by the formation of a mono-p-toluenesulfonyl derivative. A similar reactivity was observed for nickel complexes of ornithine[20] where a terminal amino group, which was coordinated to the nickel ion, formed only a mono benzoyl derivative. A project is now underway to determine the structure of this compound in the solid state by X-ray crystallography. It is hoped that this structural analysis will confirm the five coordinate nature of this compound.

After NiApSo was characterized and the temperature dependent nature of the reactivity of 1,3 diaminopropane with NiMMK was discovered, attempts were made to bring about a ring closure reaction to form a macrocyclic product. Heating NiApSo, at 100° for several hours under vacuum in a drying pistol containing phosphorus pentoxide, produced no reaction. The next idea tried was to dissolve NiApSo in a solvent and then heat the solution to reflux. It was hoped that under conditions of high dilution and elevated temperature the ring closure reaction might be induced to occur. It was thought that the applied heat might supply sufficient energy to overcome the apparent barrier to reaction at the second oxygen site, and under

conditions of high dilution the "template effect" might work to hold the terminal amine group in close enough proximity to allow a reaction to occur. The compound was soluble in alcohols, so it was decided to attempt the reaction in a series of alcohols of increasing boiling point to try to determine the height of the barrier to reaction. The first alcohol used was absolute ethanol (b.p. 78°) selected partially on the basis of its water absorbing abilities, but after refluxing a solution of NiApSo in ethanol for several hours, NiApSo was the only product isolated. The next alcohol tried was n-butanol (b.p. 114°). This appeared a likely candidate since its boiling point was close to that of 1,2 diaminoethane which was known to form macrocycles at reflux temperature. The red product obtained after refluxing NiApSo in n-butanol for several hours had a molecular weight of four less than NiApSo. The mass spectrum of this compound was quite different from that of NiApSo. This compound was apparently formed by a dehydrogenation of NiApSo with the resulting loss of two molecules of hydrogen. The nickel ketazines were routinely recrystallized from boiling n-butanol without undergoing any such change, which rules out dehydrogenation at the bridging carbon atom, so the loss probably occurred on the aminopropyl chain. Elemental analysis would probably not be sensitive enough to detect a loss of four hydrogens from a compound with a molecular

weight of 596 and which still retained 30 hydrogen atoms, so it was not attempted. The infrared spectrum showed changes in the N-H absorptions and showed bands which could be attributed to hydrogens attached to doubly-bonded carbon atoms. The available information, on the small sample obtained, suggested the following change in the amino propyl chain, from $-\underset{\underset{Ni}{|}}{N}-CH_2-CH_2-CH_2-NH_2$ of NiApSo, to $-\underset{\underset{Ni}{|}}{N}-CH=CH-CH=NH$ of a dehydrogenated compound. Possible precedents for this type of a reaction might be found in the work of Bailar and co-workers* on platinum complexes which catalyzed selective partial hydrogenation of unsaturated fatty acids. A complete understanding of this unusual reaction awaits further investigation. As a result of this reaction it appears that NiApSo would rather undergo partial decomposition than to cyclize. A possible explanation of this behavior might be that the terminal nitrogen is coordinated relatively strongly to the nickel atom. This attachment could prevent the amine from reacting at the oxygen site. In the dehydrogenated compound, the terminal nitrogen could still be coordinated to the nickel atom, and the ring thus formed could be further stabilized by election delocalization over a pseudo conjugated system.

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*Private communication.

Reactivity of Coordinated CO Groups

The reactivity of the coordinated CO groups of NiMMK toward aliphatic amines is somewhat unusual for a carbon-oxygen-metal bond. Other authors[6, 7, 9, 21, 22, 23] who have attempted to cyclize tetradentate cis-N_2O_2 type ligands with aliphatic amines have been unsuccessful in cases where a β (meso) carbonyl substituent was absent. Coordinated carbonyl groups have been shown to react readily with mono- or di-amine compounds, i.e., reactions of salicylaldehyde,[1] but these reactions normally stop short of macrocycle formation and that adds significance to the results of this project. For this reason the factors which appear to be involved in these reactions will be recounted here.

Thus far these reactions have not been observed to take place in the presence of a solvent; they appear to occur best in dry amines, at room temperature for the diamines, but only at an elevated temperature for ethylamine. Another point is that the amines, especially the diamines, form very stable hydrated species which may serve to remove the water molecules formed in the condensation reactions from the reaction and perhaps to act as a Le Chatelier stress on an equilibrium which may occur. Also one oxygen atom of the ketazine appears to be more available for reaction than the other which is identical before the first amine condensation reaction; this

suggests that changing a Ni-O-C bonding system to a Ni-N-C system makes the second Ni-O-C bonding system stronger. Framework models show that the nickel ion in the nickel ketazines would have vacant axial sites available for possible further coordination and the preliminary studies of NiApSo suggest that an amine group is coordinated in one of these axial sites. However, attempts to form adducts with donor ligands such as pyridine have so far been unsuccessful. It seems that for 1,2 diaminoethane and 1,2 diaminopropane that the macrocyclic compounds are both kinetically and thermodynamically favored, as the same main product results at ambient or reflux temperatures. For 1,3 diaminopropane it seems that the products obtained are the kinetically favored products. NiApSo is formed at ambient temperature or 100°, but not at reflux temperature and the macrocycle which appeared to be formed at 100° hydrolyzed on an alumina column due only to adsorbed water on the alumina. Similarly for NiESo, it was only obtained from reactions at 100° and hydrolyzed readily to NiMMK due to adsorbed water on an alumina column. For NiESo this seems to indicate a large barrier to its formation, but a small barrier to decomposition. The NiESo compound potentially is a key to further understanding of the mechanism(s) involved in these reactions as its ultraviolet-visible spectrum is intermediate to

those of NiMMK, Ni H cyclo 13, and NiApSo, a fact which may be useful to spectroscopic studies of the kinetics of these reactions.

Several attempts were made to incorporate o-phenylenediamine into a nickel cyclo 13 type of compound, however, all of these attempts were unsuccessful. This diamine had been used by Jager[6, 21] to synthesize macrocyclic compounds from cis N_2O_2 compounds similar to the nickel ketazines.

The reactivity of NiMMK towards ammonia, aniline, and 3,3' iminobispropylamine was also investigated. In all three cases for reactions at or below room temperature the starting material NiMMK was recovered from the reaction mixture. Only 3,3' iminobispropylamine was allowed to react with NiMMK at about 100° and the product of this reaction was a red oil which could not be crystallized nor characterized. This oil might have been a polymeric material as the carbon chain between terminal amine groups was relatively long and polymeric materials have been previously reported in similar cyclization reactions.[21]

Also in the course of this project, evidence was obtained which indicated that another product was formed in the room temperature reaction of NiMMK with 1,2 diaminoethane. In the mass spectrum of an unrecrystallized product of one of these reactions, a peak was observed at 18 mass units above the parent ion. This peak probably

*$HN(CH_2CH_2CH_2NH_2)_2$

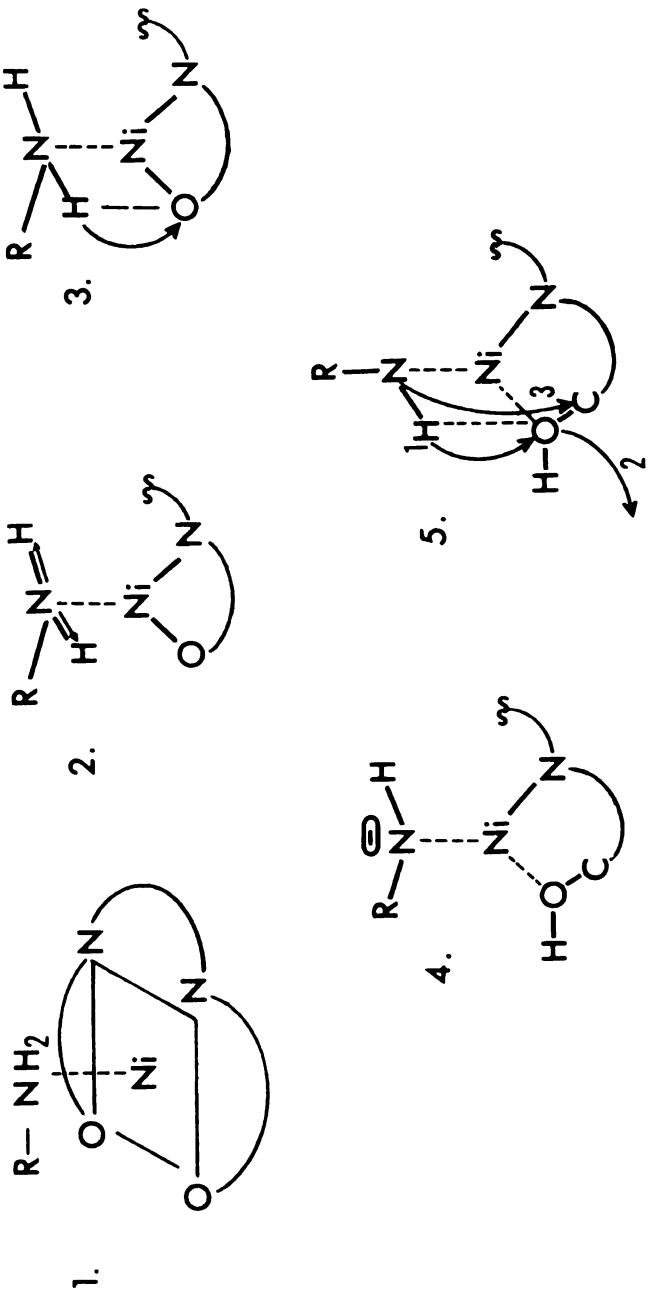
represented a compound intermediate between the nickel ketazines and the nickel macrocycles. Several possible structural explanations for this peak were examined of which the following three seemed most likely: one possibility was a compound similar to that formed in the reaction of NiMMK with 1,3 diaminopropane (vide supra); a second was a compound in which one amine group had displaced an oxygen, but the other had only proceeded halfway in the displacement reaction, leaving O-H and N-H groups, possibly hydrogen bonded together, in this compound; a third possibility was that the peak represented a Ni H cyclo 13 molecule with a water molecule attached to it in some way. This last possibility was discounted because it seemed unlikely for a water molecule to remain attached for a sufficient length of time to be observed by the mass spectrometer at 250° and under the vacuum present in the instrument. The only other data obtained on this compound was that it was more soluble than Ni H cyclo 13, but this does not confirm any of the possibilities.

Mechanism of the Reaction of NiMMK With Amines

The ideas presented in this section are somewhat speculative, but an attempt has been made to link together the information which is known into a coherent and consistent pattern. There are other possible explanations, but only the ones which appear to be most likely will be discussed here.

The mechanism which appears to be most likely is as follows: (1) an amine group coordinates to the nickel ion in an axial site; (2) as a result of this the N-H bonds become weaker; and (3) a Ni-O bond may be weakened, but whether or not this occurs, the oxygen is close to the amine hydrogens and hydrogen transfer can occur giving an $-N\bar{-}H$ —— -O-H type of intermediate; (4) the -O-H group is now less firmly coordinated to the nickel and the $-N\bar{-}H$ may be more strongly coordinated; (5) now the second amine hydrogen is transferred to the O-H group, perhaps through a hydrogen bonded intermediate or through nickel ion catalysis, as a result a water molecule is eliminated and the nitrogen, now firmly bonded to the nickel ion moves in to replace the departing oxygen; (6) a similar process could then take place for the replacement of the second oxygen atom, but now assisted by the "template effect" which holds the reactive species in close proximity. For the 1,2 diamines it appears there would be some strain introduced into the molecule on coordination of the second amine group to the nickel ion and perhaps this compensates for the apparent greater strength of the second Ni-O bond. In the 1,3 diamine case, the chain length is such that little or no strain would be introduced and the coordination of the amine together with a stronger Ni-O bond could be strong enough to stop the reaction at this five coordinate species. For ethylamine the same mechanism could apply,

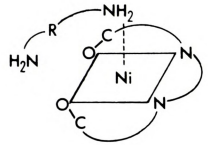
MECHANISM 1.

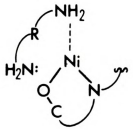


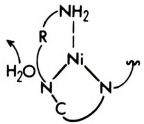
only in this case there would be no template effect and by the same token, a 50% lower probability of reaction due to the presence of only one reactive group per molecule. The latter point could account for the higher temperatures needed to observe a reaction, then the stronger Ni-O-C bonding could inhibit further reaction unless the temperature were raised. One advantage of this proposal is that only one reaction mechanism could account for all of the reactions observed. A question which this mechanism does not answer is "if the amines are forming five coordinate species, why could not pyridine adducts of NiMMK be observed by UV-Visible spectroscopy?"

A second mechanism which cannot be entirely discounted is as follows: (1) an amine group coordinates in an axial site of the nickel; (2) the initial reaction involves a nucleophilic attack by the lone pair of electrons on the nitrogen of the second NH_2 group on the carbon atom of the C-O group; (3) this results in the displacement of a water molecule and the replacement of the oxygen atom by a nitrogen; (4) this condensation can introduce strain into the ring containing the axially coordinated amine group which would lead to cyclization by a mechanism similar to "1" above. This mechanism fits well for the 1,2 diamine compounds. For the 1,3 diamine the reaction could stop at step 3 due to the formation of a stable species as the ring containing the axially coordinated amine group is

MECHANISM 2.

1. 

2. 

3. 

4. See Mechanism 1.

not strained and the second oxygen may be less reactive due to a different mechanism for reaction than the first oxygen. For ethylamine only a mechanism similar to "1" or one not involving the nickel ion at all is available. The fact that NiESo forms only at 100° could be explained by having this reaction take place according to the second part of Mechanism 2 (similar to "1"). The apparent lower reactivity of the C-O-Ni bonding system, by this mechanism, requires higher temperatures for the elimination to occur. One disadvantage of Mechanism 2 is that it is complicated and perhaps over-specific in requiring modification for each new species investigated. A second question which remains is "why doesn't a second ethylamine molecule react with NiESo to give a NiN_4 type compound similar to Ni H cyclo 13?"

Another mechanistic proposal of note involves transfer of an amine hydrogen to an oxygen and then a keto-enol rearrangement could take place. The carbonyl group could then become uncoordinated and the nitrogen would move in to transfer a second hydrogen and displace the new O-H group. The bonds would then rearrange to their former array and the hydrogen ion would be released into the solution. An advantage here would be an uncoordinated C=O group which Jager[6] and Bamfield[7] have suggested is important in this type of reaction. This mechanism does not necessarily require the use of the nickel ion which

does appear to play a role in these reactions. Also this mechanism requires a rather flexible ligand for which evidence is lacking.

Mechanism 1 seems to account for the known data better than the other mechanisms examined, and it offers the advantage of simplicity. However, it appears that further work in this area will be necessary to confirm any proposed mechanism. One of the most promising avenues for further research would be to find a solvent in which these cyclization reactions would occur. If these reactions were to occur in a solution, the progress of the reaction could be followed spectroscopically and more data about the reaction mechanism might be obtained. Preliminary evidence indicates that the cyclization reaction may occur in 1,2 dichloroethane followed, however, by decomposition. Several attempts to find a solvent for these reactions have been unsuccessful. When a slight excess of 1,2 diamino-ethane was refluxed with NiMMK in n-butanol, the NiMMK was recovered in better than 90% yield. In another attempt, a series of solutions of 1,2 diaminopropane and NiMMK, and 1,3 diaminopropane and NiMMK were prepared in chloroform with molar ratios of 25-1 or 120-1 of diamine to NiMMK. The ultraviolet visible spectra of these solutions were run after allowing the solutions to sit in the dark for seven days; the spectra did not indicate the presence of species other than NiMMK, but in each case violet crystals

had formed in the flask probably indicating the decomposition of NiMMK to nickel amine complexes.

Suggestions for Future Work

In addition to the search for a solvent in which these reactions will take place, there are several other areas of this project which might be profitably investigated by future workers. Some of these areas are described briefly here along with a summary of the work which has been done in these areas already.

One area which might benefit by further investigations would be a correlation of the aqueous pK values for the amines and their reactivity towards NiMMK. Other authors[7, 8] have noted that the basicity of amines seems to be related to their reactivities with Schiff's base type complexes. The amines which have been shown to react with NiMMK have pKa_1 values between about 9.7 and 10.7, and pKa_2 values of about 6.7 to 7. At this time, a reasonable explanation for this apparent correlation is not available and it may be only a coincidence. However, other amines with a wide range of pKa values are available and their reactivity toward NiMMK might be investigated to confirm or deny these preliminary indications. If a correlation does exist, it could be a step toward a better understanding of other similar reactions.

If ketazine type complexes could be synthesized with paramagnetic metal ions, it might be possible to learn

something about the extent of electron delocalization in the compound. Similar information about electron delocalization in the macrocyclic complexes could also be useful. Unfortunately, all attempts to synthesize ketazine complexes with other metal ions were unsuccessful; it may be possible to accomplish this goal by varying the synthetic procedure, but this does not appear very probable. For the macrocycles, it may be possible to precipitate the nickel out of a complex with cyanide or sulfide ions and then replace it with another metal; this has not been attempted as yet.

It may be possible to synthesize the cyclo 13 type ligands in the absence of metal ions, or even to synthesize the linked benzil monohydrazone residue portion of the ligand, coordinate it to a metal ion, and then react it with a ketone to complete the ring. Either of these methods might yield a macrocyclic complex of another metal ion. Some preliminary reaction routes have been investigated. As a first step toward the synthesis of the cyclo 13 ligand, benzil monohydrazone was allowed to react with 1,2 diaminoethane both in a solvent and neat. No reaction appeared to take place in solution, but in the neat reaction, 2,3 diphenyl 1,4 diazine was formed. A similar compound, 2,3 diphenyl quinoxaline, was formed when benzil monohydrazone was allowed to react with o-phenylenediamine in solution. Apparently these heterocyclic compounds form

preferentially to the desired compound which would have two benzil monohydrazone residues linked through the former oxygen sites by the diamine. It may be possible to synthesis this compound by starting with benzil and blocking one oxygen by acetylation, then reacting it with the diamine, followed by hydrolysis and a reaction with hydrazine; however, this synthesis was not attempted.

Attempts were also made to form a cyclo 13 type compound by a template type synthesis wherein benzil monohydrazone, nickel acetate, acetone, and 1,2 diamino-ethane or o-phenylendiamine were placed in solution together and allowed to react. The products obtained from these reactions appeared to be nickel complexes of the diamine employed.

VI. CONCLUSIONS

In summary, a series of nickel ketazine compounds have been synthesized and characterized. The reactions of one of these ketazines with some mono- and di-amine compounds have been investigated and two new types of compounds, the macrocyclic NiN_4 and the non-cyclic NiN_3O, have been characterized. Also a mechanism has been proposed for the reaction of the coordinated carbonyl group of NiMMK with amine compounds.

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