

THE PREPARATION AND CHARACTERIZATION
OF SEVERAL HEXAAZA MACROCYCLIC COMPOUNDS
OF COBALT(II), NICKEL(II), AND COPPER(II)

By

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To my wife and parents
for loving encouragement.

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KEY TO SYMBOLS AND ABBREVIATIONS

DAP	2,6-diacetylpyridine
PDC	2,6-pyridinedicarboxaldehyde
DAPH	2,6-pyridinediacetyldihydrazone
PDCH	2,6-pyridinedialdihydrazone
ketomacr	See Fig. 5a
aldomacr	See Fig. 5b
aldoketomacr	See Fig. 5c
monoglyme	1,2-dimethoxyethane
TMCD	6,12,19,25-tetramethyl-7,11:20,24-dinitrilodi- benzo [<u>b</u> , <u>m</u>][1,4,12,15] tetraazacyclodocosine
Λ	molar conductance, micromohs $M^{-1}cm^{-1}$
Λ_0	limiting conductance
χ_M'	corrected molar magnetic susceptibility

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THE PREPARATION AND CHARACTERIZATION
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OF COBALT(II), NICKEL(II), AND COPPER(II)

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Major Department: Chemistry

Ten new macrocyclic complexes containing the ligands, 2,5,11,14-tetramethyl-3,4,12,13,19,20-hexaazatricyclo[13.3.1.1^{6,10}]eicosa-1(19),2,4,6,8,10(20),11,13,15,17-decaene (ketomacr), 3,4,12,13,19,20-hexaazatricyclo[13.3.1.1^{6,10}]eicosa-1(19),2,4,6,8,10(20),11,13,15,17-decaene (aldomacr), and 2,14-dimethyl-3,4,12,13,19,20-hexaazatricyclo[13.3.1.1^{6,10}]eicosa-1(19),2,4,6,8,10(20),11,13,15,17-decaene (aldoketomacr), have been prepared via the template method. The complexes were produced with chloride and nitrate salts of cobalt(II), nickel(II), and copper(II) by a Schiff base condensation of 2,6-diacetylpyridine and 2,6-pyridinediacetyldihydrazone for ketomacr, 2,6-pyridinedicarboxaldehyde and 2,6-pyridinedialdihydrazone for aldomacr, and 2,6-pyridinedicarboxaldehyde and 2,6-pyridinediacetyldihydrazone for aldoketomacr. Isolation of the free

macrocyclic base could neither be accomplished by direct synthesis nor by removal of the complexes' metal ion.

The complexes were characterized by elemental analysis, infrared, ultraviolet, visible, and electron spin resonance spectra, conductance, and magnetic susceptibility determinations. The results of these studies support the formulation of each of the complexes as a metal ion surrounded by a planar, quadradentate ligand with water either very loosely held in the axial positions or present as part of the crystal lattice.

The nickel(II) chloride and nitrate complexes of ketomacr have above-normal room temperature magnetic moments which are reduced by 0.5 BM upon dehydration of the samples. The temperature dependent magnetic susceptibility data, obtained for $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{aldoketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, and $\text{Cu}(\text{ketomacr})(\text{NO}_3)_2$, followed the normal Curie-Weiss law.

INTRODUCTION

Metal template reactions have been defined as "ligand reactions which are dependent on, or can be significantly enhanced by, a particular geometrical orientation imposed by metal coordination" (1). A macrocyclic complex is one in which the metal ion is circumscribed by a ligand which is, itself, a closed ring. Review articles concerning various aspects of the coordination chemistry of macrocyclic ligands reflect the increased attention this class of compounds has received in the past fifteen years (1-12). The entire Volume 100 of Advances in Chemistry Series is dedicated to the biological involvement of metal complexes, many of which are macrocyclic complexes. Such macrocyclic complexes--in particular, those which have a planar arrangement of four nitrogen donor atoms--are related in varying degree to a number of biologically important molecules such as porphyrins (3) and corrins (4) (Figures 1 and 2). Metal complexes are involved in material transfer such as oxygen transport by hemoglobin, in material storage such as that of iron by ferritin and in energy transfer as performed by chlorophyll systems. Some workers have proposed that a macrocyclic complex is involved in natural nitrogen fixation (5).

In an attempt to more completely elucidate the behavior

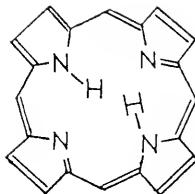


Fig. 1 Porphyrin skeleton

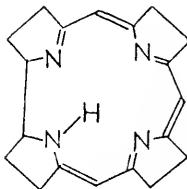


Fig. 2 Corrin skeleton

of metal ion-macrocyclic ligand systems, a study of model systems less complicated than the macrocyclic systems and complexes found in nature is reasonable; that is, knowledge of the properties and behavior of macrocyclic complexes is desirable for the understanding it may impart to biological behavior. Synthetic macrocyclic complexes prepared during the investigations reported herein are potential analogs of the natural systems and consequently are of use in model experiments (6).

One factor enhancing the stability of macrocyclic complexes is the chelate effect. This term means that a metal chelate complex is more stable than a related complex containing only monodentate ligands (13). For transition metal ions the chelate effect consists of an enthalpy and an entropy contribution.

Further stability may be gained by the formation of multiple metal-ligand bonds. Multiple bonding of this type may occur provided (14): (i) the metal contains electrons in the d_{xz} and d_{yz} orbitals (where the axis system is defined such that the organic macrocycle coordinated to the metal lies in the xy plane) and (ii) the ligand contains empty π -antibonding molecular orbitals of proper symmetry to which the contribution of the metal (π -donor) atom is finite. The satisfaction of these two requirements allows back donation of the d-electrons from the metal to the π -antibonding orbitals of the ligand imparting double bond character to the metal-ligand bond. The

C=N linkage, frequently occurring in natural systems, meets the criteria listed above; experiments have demonstrated that there appears to be considerable stabilization of the metal-ligand bond through partial double bond formation (15). It is likely that a combination of all the above effects results in the exceptional stability of macrocyclic complexes.

Many unsaturated macrocyclic complexes have been observed to be inert (16). This inertness has been attributed to very large dissociational activation energies. Because of the closed ring structure of the macrocycle, no simple dissociative step involving the metal ion or donor atom can occur. It is not possible to extend the metal-donor distance sufficiently to constitute bond breaking without either bond breaking within the ligand or extensive rearrangement within the coordination sphere.

Synthetic routes to the preparation of macrocyclic complexes can be divided into two broad categories. One is derived from a Schiff base condensation of carbonyl compounds with bis(diamine) complexes (11,16,17). Another is derived from the reaction of coordinated mercaptides with alkyl and aryl dihalides. Examples of the latter type of complexes have been prepared by Busch and co-workers (18,19).

Metal template reactions are almost mandatory for the synthesis of macrocyclic metal complexes (20). The metal ion coordinates to and orients the reactant species in such a way as to render the cyclization more probable than were

the metal ion absent. Reaction of the organic moieties in the absence of the metal ion either leads to oligomers and/or very low yields of the desired macrocycle. For a more complete discussion of this "template effect" the reader is referred to review articles by Busch et al. (2,10,21).

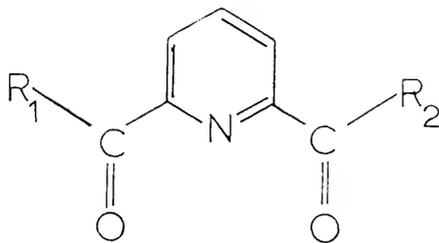
The design of a ligand must take into account the factors affecting the stability of metal complexes including the geometry of the molecular construction. The geometrical consideration can be grouped into four categories: (i) size of metal ion, (ii) type of donor atoms, (iii) "hole size" of the macrocycle, and (iv) other steric considerations relating to the periphery of the macrocyclic base.

Black and Hartshorn have compiled a review (22) of these features of ligand design and synthesis, with emphasis placed upon the nature of the ligands. Busch and co-workers have demonstrated (23) the relationship of metal ion radius and macrocyclic ring size to values of the ligand field parameter Δq^{XY} . They conclude that the metal-donor distance can have a profound effect on the strength of the metal-donor interaction.

Up until the last decade (10), few macrocyclic complexes with extended conjugation have been prepared. Certainly more stringent steric considerations have to be observed in the design and preparation of complexes of this type. Since many biologically important systems contain this extended conjugation within the macrocyclic ring, it was decided to attempt the preparation and characterization of complexes of this type via Schiff base condensations and metal template techniques.

The organic reactants chosen for the Schiff base condensations (Figs. 3, 4, and 5) were: DAP and DAPH, PDC and PDCH, and PDC and PDCH (see page ix for a list of symbols). Metal ions of the first row transition series were chosen for their known (24) tendency to promote metal template reactions involving systems similar to those listed above. Also metal ions of this type are catalysts in the sense that such Schiff base condensations are known to proceed by way of a nucleophilic attack by the amine nitrogen on the carbon of the carbonyl group to yield a carbinol-amine intermediate. Coordination of the carbonyl oxygen on DAP or PDC to a positive center--the metal ion--would favor the reaction by making the carbonyl carbon atom more susceptible to nucleophilic attack. The presence of the pyridine group between the carbonyl functions in DAP or PDC promotes initial tridentate chelation of the reactant (21). This chelation then activates the coordinated carbonyls toward reaction with the amine groups on DAPH or PDCH leading to the macrocyclic complex.

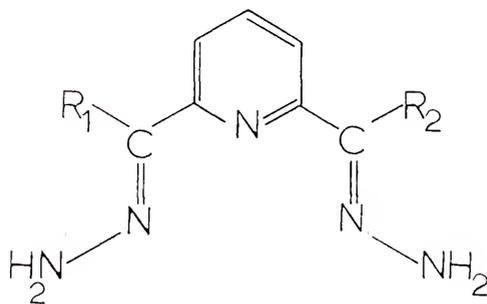
Work on this study was almost complete when, to this writer's consternation, a recent article by Goedken et al. (25) was discovered in the literature which reported the synthesis and structural characterization of iron(II) complexes of the ketomacrocyclic ligand. This discovery does take some of the novelty away from this work; but little overlap exists. Different solvent systems and a different approach to the template reaction were employed. Goedken did prepare the Co(II) derivative, but this is the only part where both works are



DAP - $R_1=R_2=CH_3$; 2,6-diacetylpyridine

PDC - $R_1=R_2=H$; 2,6-pyridinedicarboxaldehyde

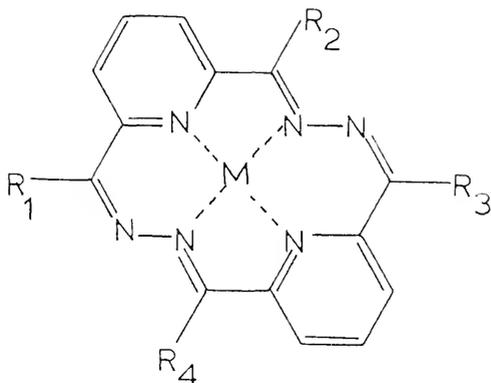
Fig. 3 Structural formula of DAP and PDC



DAPH - $R_1=R_2=CH_3$; 2,6-pyridinediacetyldihydrazone

PDCH - $R_1=R_2=H$; 2,6-pyridinedialdihydrazone

Fig. 4 Structural formula of DAPH and PDCH



- a) $R_1=R_2=R_3=R_4=CH_3$; 2,5,11,14-Tetramethyl-3,4,12,13,19,20-hexaazatricyclo[13.3.1.1^{6,10}]eicosa-1(19),2,4,6,8,10(20),-11,13,15,17-decaene.

Abbreviated as ketomacr.

- b) $R_1=R_2=R_3=R_4=H$; 3,4,12,13,19,20-Hexaazatricyclo-[13.3.1.1^{6,10}]eicosa-1(19),2,4,6,8,10(20),11,13,15,17-decaene.

Abbreviated as aldocr.

- c) $R_1=R_2=H$, $R_3=R_4=CH_3$; 2,14-Dimethyl-3,4,12,13,19,20-hexaazatricyclo[13.3.1.1^{6,10}]eicosa-1(19),2,4,6,8,10(20),-11,13,15,17-decaene.

Abbreviated as aldoketomacr.

*Fig. 5 Structural formulas of ketomacr, aldocr, and aldoketomacr.

*The symbol M placed within the structure of the macrocycle may represent Ni(II), Cu(II) or Co(II). Its presence here is to clarify sites of bonding.

identical. Further comparison to Goedken's work will follow in the discussion.

A different but novel type of system considered to be extremely interesting is represented in Fig. 6. This tridentate ligand would be expected to form complexes of mixed type, i.e., it would contain both M-N and M-C bonds. Indeed, preparation of the original ligand and complexes could be followed by cyclization to form novel macrocyclic complexes.

Such an investigation would include the study of the interactions of the metal-ligand bonds. Two configurations could exist (26) in this type of metal-ligand arrangement. The alkyne type would give rise to a typical acetylenic stretching vibration between 2000 and 2200 cm^{-1} (27, 28). The other type, the alkene type, would have associated with it an acetylenic stretching vibration around 1800 cm^{-1} (29).

The alkyne type would result from the donation of the electron density in an acetylene π -bonding orbital into an empty p - or d -orbital on the metal and back donation of the electron density from a filled d -orbital to an acetylene π -antibonding orbital.

The lowering of the energy of the acetylenic stretching vibration in the alkene type would be due to the reorganization of the electron density of the acetylene bond to give an olefin-like arrangement. As a result of this rearrangement two sigma bonds would be formed between the metal ion and the acetylene.

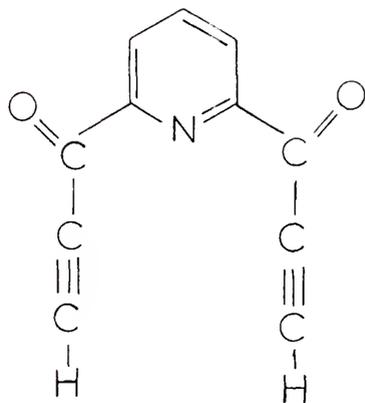


Fig. 6 2,6-Bis(propynone)pyridine

EXPERIMENTAL

Reagents

Unless otherwise specified all chemicals were commercially available as reagent grade and were used without further purification.

2,6-Pyridinedimethanol. This compound was purchased from Aldrich Chemical Co. and used without further purification: mp 113-114°.

2,6-Diacetylpyridine. This compound was purchased from Aldrich Chemical Co. and used without further purification: mp 78-79°.

Preparation of Starting Materials

2,6-Pyridinediacetyldihydrazone. A modification of the reported procedure of Curry et al. (30) was followed. Five grams (0.03 mole) of 2,6-diacetylpyridine were dissolved in 150 ml of absolute ethanol and this solution was added dropwise to a stirred solution of 7 ml (0.15 mole) of 99-100% hydrazine hydrate (Matheson, Coleman and Bell) kept at 5°C. Stirring was continued for six hours as the temperature slowly rose to room temperature. The crude white product was collected on a sintered glass funnel and recrystallized from hot absolute ethanol giving 5.2 g (85%) of the dihydrazone: mp 185-190° [lit. (31) mp 181°].

Repeated attempts to purify the product by recrystallization were unable to lower the melting point to the literature values of 181° . However, only one component was shown by thin layer chromatography.

Anal. Calcd for $C_9H_{13}N_5$: C, 56.53; H, 6.85; N, 36.62. Found: C, 56.50; H, 6.85; N, 36.65.

2,6-Pyridinedicarboxaldehyde. A modification of the method of Papadopoulos *et al.* (32) was employed. Seventy grams of freshly prepared manganese dioxide were suspended in 500 ml of chloroform containing 5.7 g of 2,6-pyridinedimethanol. The mixture was stirred at reflux for five hours, filtered with suction and the oxide washed with five 100 ml portions of ether. The filtrates were combined and evaporated under a stream of N_2 . The off-yellow residue was taken up in a minimum amount of solvent containing 80% benzene and 20% ethyl acetate. This was placed on a 3 cm X 55 cm silica gel (60-200 mesh, Matheson, Coleman and Bell) column and eluted with the same solvent mixture collecting the middle portion, 250 ml, in 50 ml fractions after discarding the first 150-200 ml. Flow rate of the column was 5 ml per minute. Each of the desired fractions was evaporated with a stream of N_2 and the melting points of the white crystalline residues were checked. The product fractions were combined giving 3.0 g (53%) of the dialdehyde: mp $120-122^{\circ}$ [lit. (33) mp 124°].

2,6-Pyridinedialdihydrazone. A modification of the method reported by Stoufer and Busch (34) was followed. Two grams of 2,6-pyridinedicarboxaldehyde (0.015 mole) in 35 ml of warm absolute ethanol were added dropwise to a solution of

5 g (0.1 mole) of 99-100% hydrazine hydrate (Matheson, Coleman and Bell) and 10 ml of absolute ethanol. Stirring was continued at room temperature for four hours. After 30 minutes a fine white crystalline solid formed. The product was stored in a freezer overnight, filtered on a glass sintered funnel and recrystallized from hot ethanol giving 1.7 g (70%) of the dihydrazone: mp 144-146° [lit. (35) mp 130-135°]. Further recrystallization did not lower the melting point and thin layer chromatography showed only one component.

Anal. Calcd for $C_7H_9N_5$: C, 51.47; H, 5.56; N, 42.89. Found: C, 51.44; H, 4.81; N, 43.64.

Freshly prepared MnO_2 . A modification of the method reported by Sondheimer et al. (36) was followed. A solution of 70 g (0.45 mole) of $KMnO_4$ and 700 ml water in a 2-liter beaker was made acidic with 25 ml of conc. H_2SO_4 . To this hot, stirred solution of $KMnO_4$ was added slowly a solution of 100 g (0.60 mole) $MnSO_4 \cdot H_2O$ in 400 ml of water. After adding the $MnSO_4$ solution, excess $KMnO_4$ was added until the intense purple color was obvious. Stirring was continued for six hours.

The brown MnO_2 product was filtered with suction and washed as many times as necessary to remove any excess permanganate ion. The product was then dried 24 hours at 130°, ground to a fine powder giving 90 g (93%) of oxide and stored over P_4O_{10} .

Procedures

Ni(ketomacr)Cl₂·4H₂O. A solution of 0.951 g (0.004 mole) of nickel(II)chloride hexahydrate and 0.653 g (0.004 mole) of 2,6-diacetylpyridine in 300 ml absolute ethanol was brought to reflux at which point two drops of concentrated hydrochloric acid were added. A solution of 0.765 g (0.004 mole) 2,6-pyridinediacetyldihydrazone in 200 ml warm absolute ethanol was added dropwise with stirring over a period of one hour to the above solution. The mixture was refluxed for an additional 18 hours. The initial yellow-green solution turned to a yellow-brown and finally to a green-brown heterogeneous mixture. Two hundred milliliters of solvent were stripped off the heterogeneous mixture and 300 ml of diethyl ether were added to precipitate additional product. The green product, filtered with suction through a medium frit glass sintered funnel, was washed via a Soxhlet extractor with refluxing methanol. The remaining grey-green solid was dried in vacuo over P₄O₁₀ giving 1.913 g (92%) of product.

Upon drying in an oven at 120°C for 24 hours a water loss of four moles of water per mole of complex was observed.

After allowing the dried product to remain in contact with atmospheric moisture, the four moles of water per mole of complex were reabsorbed.

Anal. Calcd for Ni(C₁₈H₁₈N₆)Cl₂·4H₂O: C, 41.57, H, 5.04; N, 16.16; Ni, 11.29; Cl, 13.63. Found: C, 41.23; H, 5.21; N, 16.03; Ni, 11.45; Cl, 13.23.

Ni(aldomacr)Cl₂·4H₂O. A procedure similar to that reported for the Ni(ketomacr)Cl₂·4H₂O preparation was followed using a solution of 0.540 g (0.004 mole) 2,6-pyridinedicarboxaldehyde and 0.951 g (0.004 mole) nickel(II) chloride hexahydrate in 300 ml of absolute ethanol. This solution was brought to reflux and two drops of concentrated hydrochloric acid were added to the above solution. To this was added dropwise a solution of 0.653 g (0.004 mole) 2,6-pyridinedialdihydrazone in 200 ml absolute ethanol. The resulting brown-green solid was worked up as in the preceding preparations yielding 0.919 g (49%) of product.

Upon drying in an oven at 120°C for 24 hours a water loss of four moles of water per mole of complex was observed. After allowing the dried product to remain in contact with atmospheric moisture, the four moles of water per mole of complex were reabsorbed.

Anal. Calcd for Ni(C₁₄H₁₀N₆)Cl₂·4H₂O: C, 36.21; H, 3.91; N, 18.12; Ni, 12.65; Cl, 15.28. Found: C, 36.50; H, 3.43; N, 18.68; Ni, 13.0; Cl, 15.12.

Ni(ketomacr)(NO₃)₂·6H₂O. A procedure similar to that reported for the Ni(ketomacr)Cl₂·4H₂O preparation was followed using a solution of 1.163 g (0.004 mole) nickel(II) nitrate hexahydrate and 0.653 g (0.004 mole) 2,6-diacetylpyridine in 300 ml of absolute ethanol. This solution was brought to reflux at which point two drops of concentrated nitric acid were added. A solution of 0.765 g (0.004 mole) 2,6-pyridinediacetyldihydrazone in 200 ml absolute ethanol was added dropwise. The resulting light green solid was worked up as in the preceding preparations yielding 0.651 g (32.5%) of product.

Upon drying in an oven at 120°C for 24 hours a water loss

of six moles of water per mole of complex was observed. After allowing the dried product to remain in contact with atmospheric moisture, the six moles of water per mole of complex were reabsorbed.

Anal. Calcd for $\text{Ni}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: C, 35.48; H, 4.96; N, 18.39; Ni, 9.64. Found: C, 35.31; H, 4.92; N, 18.38; Ni, 9.48.

Ni(aldoketomacr)Cl₂·4H₂O. A procedure similar to that reported for the preparation of $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ was followed using a solution of 0.951 g (0.004 mole) nickel(II) chloride hexahydrate and 0.540 g (0.004 mole) 2,6-pyridinedicarboxaldehyde in 300 ml 95% ethanol. When the solution was brought to reflux, five drops of concentrated hydrochloric acid were added. A solution of 0.765 g (0.004 mole) 2,6-pyridinediacetyldihydrazone was added dropwise over a period of one hour. The light yellow-green solution turned dark green as reflux was continued for 20 hours. A volume of 200 ml of solvent was stripped off and petroleum ether was added to precipitate the product. The product was worked up as in the preceding preparations giving 0.901 g (46%) of a brown-green solid.

Anal. Calcd for $\text{Ni}(\text{C}_{16}\text{H}_{14}\text{N}_6)\text{Cl}_2 \cdot 4\text{H}_2\text{O}$: C, 39.06; H, 2.87; N, 17.08; Ni, 11.9. Found: C, 39.53; H, 3.01; N, 17.43; Ni, 12.3.

Co(ketomacr)Cl₂·4H₂O. A solution of 0.653 g (0.004 mole) 2,6-diacetylpyridine and 0.952 g (0.004 mole) cobalt(II)

chloride hexahydrate in 300 ml 95% ethanol was brought to reflux. Two to three drops of concentrated hydrochloric acid were then added. A solution of 0.765 g (0.004 mole) 2,6-pyridinediacetyldihydrazone in 200 ml warm absolute ethanol was added dropwise over a period of one hour with stirring. The mixture was then refluxed for an additional 20 hours during which time the royal blue solution turned black. Approximately 150 ml of solvent were removed by distillation and 300 ml of petroleum ether were added to precipitate the product. The dark black-green precipitate was filtered with suction, washed with refluxing methanol in a Soxhlet extractor and dried in vacuo over P_4O_{10} giving 1.569 g (75%) of the desired product.

Anal. Calcd for $Co(C_{18}H_{18}N_6)Cl_2 \cdot 4H_2O$: C, 41.55; H, 5.04; N, 16.15; Co, 11.33. Found: C, 41.13; H, 5.38; N, 16.40; Co, 11.1.

Co(aldomacr)Cl₂·4H₂O. A procedure similar to that reported for the $Co(ketomacr)Cl_2 \cdot 4H_2O$ preparation was followed using a solution of 0.952 g (0.004 mole) cobalt(II) chloride hexahydrate and 0.540 g (0.004 mole) 2,6-pyridine-dicarboxaldehyde in 300 ml 95% ethanol at reflux to which had been added two drops of concentrated hydrochloric acid. A solution of 0.653 g (0.004 mole) 2,6-pyridinedialdihydrazone and 200 ml absolute ethanol was added dropwise over a period of one hour. The black-green product was precipitated with ether and worked up as in the preceding preparations giving

1.657 g (89%) of a black powder.

Anal. Calcd for $\text{Co}(\text{C}_{14}\text{H}_{10}\text{N}_6)\text{Cl}_2 \cdot 4\text{H}_2\text{O}$: C, 36.23; H, 3.91; N, 18.12; Co, 12.70. Found: C, 36.45; H, 3.61; N, 17.91; Co, 12.40.

Co(ketomacr)(NO₃)₂·4H₂O. A procedure similar to that reported for the preparation of $\text{Co}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ was followed using a solution of 2.911 g (0.01 mole) cobalt(II) nitrate hexahydrate and 1.633 g (0.01 mole) 2,6-diacetylpyridine in 500 ml absolute ethanol with two drops of concentrated nitric acid. A warm solution of 250 ml absolute ethanol and 1.91 g (0.01 mole) 2,6-pyridinediacetyldihydrazone was added dropwise to the above refluxing solution. After the reaction was complete, 400 ml of solvent were stripped off and ether was added to precipitate the product. The product was worked up as in the preceding preparations giving 1.337 g (23%) of a brown solid.

Anal. Calcd for $\text{Co}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$: C, 37.71; H, 4.57; N, 19.54; Co, 10.28. Found: C, 38.04; H, 4.34; N, 19.82; Co, 10.4.

Cu(aldomacr)Cl₂·4H₂O. A solution of 0.682 g (0.004 mole) copper(II) chloride dihydrate and 0.540 g (0.004 mole) 2,6-pyridinedicarboxaldehyde in 300 ml 95% ethanol was brought to reflux. To this bright green solution were added two drops of concentrated hydrochloric acid. A solution of 0.653 g (0.004 mole) 2,6-pyridinedialdihydrazone in 200 ml absolute ethanol was then added dropwise over a period of two hours.

The reaction mixture turned dark green-brown and was refluxed an additional 18 hours.

Two hundred and fifty milliliters of solvent were removed by distillation. Ether was added to precipitate the product. The black solid was filtered with suction, washed with refluxing methanol in an extractor and dried in vacuo giving 1.277 g (68%) of a fine brown-black powder.

Anal. Calcd for $\text{Cu}(\text{C}_{14}\text{H}_{10}\text{N}_6)\text{Cl}_2 \cdot 4\text{H}_2\text{O}$: C, 35.87; H, 3.87; N, 17.93; Cu, 13.55. Found: C, 35.45; H, 3.41; N, 17.41; Cu, 13.9.

$\text{Cu}(\text{ketomacr})(\text{NO}_3)_2$. A procedure similar to that reported for the preparation of $\text{Cu}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ was followed using a solution of 0.653 g (0.004 mole) 2,6-diacetylpyridine and 0.966 g (0.004 mole) copper(II) nitrate hexahydrate in 300 ml 95% ethanol. This solution was brought to reflux and two drops of concentrated nitric acid were added. A solution of 0.765 g (0.004 mole) 2,6-pyridinediacetyldihydrazone in 200 ml warm absolute ethanol was added dropwise over a period of 90 minutes. The mixture was refluxed for 20 hours. The product was worked up as in the preceding preparations giving 1.416 g (70%) of a black powder.

Anal. Calcd for $\text{Cu}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{NO}_3)_2$: C, 42.73; H, 3.59; N, 22.15; Cu, 12.60. Found: C, 43.19; H, 3.40; N, 21.83; Cu, 12.7.

$\text{Cu}(\text{aldoketomacr})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. A procedure similar to that reported for the preparation of $\text{Cu}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ was followed using a solution of 0.540 g (0.004 mole) 2,6-pyridine-

dicarboxaldehyde and 0.682 g (0.004 mole) copper(II) chloride dihydrate in 300 ml absolute ethanol. Two drops of concentrated hydrochloric acid were added to this refluxing solution. A solution of 0.765 g (0.004 mole) 2,6-pyridine-diacetyldihydrazone in 200 ml warm absolute ethanol was then added dropwise over a period of one hour. The reaction mixture was refluxed for 18 hours. Approximately 250 ml of solvent were removed and 300 ml ether were added to precipitate the product. The green-brown solid was worked up as in the preceding preparations giving 1.216 g (66%) of product.

Anal. Calcd for $\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_6)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: C, 41.71; H, 3.93; N, 18.24; Cu, 13.79. Found: C, 41.62; H, 3.73; N, 18.33; Cu, 14.2.

Attempted preparation of the ketomacr ligand. In a one-liter round bottom flask 0.653 g (0.004 mole) 2,6-diacetylpyridine was dissolved in 350 ml of absolute ethanol. This solution was brought to reflux and one drop of concentrated hydrochloric acid was added. To this clear colorless solution a solution of 0.765 g (0.004 mole) 2,6-pyridinediacetyldihydrazone in 175 ml absolute ethanol was added dropwise over a period of one hour. The reaction mixture immediately turned lemon-yellow. Reflux was continued for 18 hours during which time a yellow solid formed.

The yellow product was filtered with suction, washed with hot ethanol and dried over P_{40}_{10} for 2 days. The product did not melt up to a temperature of 300°C .

Anal. Calcd for $C_{18}H_{18}N_6$: C, 67.91; H, 5.70; N, 26.39.
Found: C, 66.56; H, 5.91; N, 25.52.

Attempted preparation of the aldocr ligand. A solution of 0.135 g (0.001 mole) 2,6-pyridinedicarboxaldehyde in 250 ml absolute ethanol was brought to reflux and one drop of concentrated hydrochloric acid was added. To this reaction mixture a solution of 0.163 g (0.001 mole) 2,6-pyridine-dialdihydrazone in 250 ml absolute ethanol was added dropwise over a period of 45 minutes. The colorless solution turned yellow with the first drop of dihydrazone. Reflux was continued for 20 hours. A yellow precipitate had formed by this time and was filtered with suction, washed with ethanol, and dried over P_4O_{10} in vacuo. The product did not melt up to a temperature of $300^{\circ}C$.

Anal. Calcd for $C_{14}H_{10}N_6$: C, 64.11; H, 3.84; N, 32.04.
Found: C, 62.63; H, 4.22; N, 29.02.

Attempted preparation of $Cu(ketomacr)Cl_2$. A solution of 1.306 g (0.008 mole) 2,6-diacetylpyridine and 1.802 g (0.008 mole) copper(II) chloride dihydrate in 250 ml methanol was brought to reflux and two drops of concentrated hydrochloric acid were added. To this solution was added dropwise over a period of one hour a solution of 1.530 g (0.008 mole) 2,6-pyridinediacetyldihydrazone in 350 ml methanol. Reflux was continued for 24 hours and the lime-green reaction mixture turned dark green.

The reaction mixture was concentrated to a volume of 100 ml and a volume of 500 ml of ether was added to precipitate the dark green product. The product was filtered, washed with

ether and dried over P_4O_{10} in vacuo giving 2.575 g of green solid.

Anal. Calcd for $Cu(C_{13}H_{18}N_6)Cl_2$; C, 47.74; H, 4.01; N, 18.56; Cu, 14.03; Cl, 15.66. Found: C, 43.39; H, 4.10; N, 15.91; Cu, 15.20; Cl, 13.92.

Attempted preparation of $Zn(ketomacr)Cl_2$. A solution of 1.306 g (0.008 mole) 2,6-diacetylpyridine and 1.090 g (0.008 mole) zinc(II) chloride in 250 ml methanol was brought to reflux and one drop of concentrated hydrochloric acid was added. To this was added dropwise a solution of 1.530 g (0.008 mole) 2,6-pyridinediacetyldihydrazone in 350 ml methanol over a period of one hour. Reflux was continued for 24 hours during which time the reaction mixture had turned lemon yellow.

A volume of 200 ml of methanol was distilled off and the remainder of the solution was further concentrated using a flow of N_2 gas to a final volume of 100 ml. The yellow solid was filtered with suction, washed with ether and dried over P_4O_{10} in vacuo giving 1.859 g of product.

Anal. Calcd for $Zn(C_{18}H_{18}N_6)Cl_2$: C, 47.55; H, 3.99; N, 18.48; Zn, 14.38; Cl, 15.60. Found: C, 57.71; H, 5.15; N, 21.02; Zn, 3.26; Cl, 7.25.

Attempted preparation of $Mn(ketomacr)(ClO_4)_3$. A lavender solution of 2.855 g (0.004 mole) hexaureamanganese(III) perchlorate in 250 ml absolute ethanol, to which had been added two drops of concentrated perchloric acid, was added to

0.653 g (0.004 mole) 2,6-diacetylpyridine. The now red-violet solution was brought to reflux and a solution of 0.765 g (0.004 mole) 2,6-pyridinediacetyldihydrazone in 200 ml absolute ethanol was added dropwise. The red solution turned yellow immediately. Reflux was continued overnight and a yellow-orange solid was filtered, washed with ethanol and dried in vacuo over P_4O_{10} giving 1.230 g of product.

Anal. Calcd for $Mn(C_{18}H_{18}N_6)(ClO_4)_3$: C, 32.19; H, 2.70; N, 12.51; Cl, 15.84. Found: C, 58.41; H, 5.26; N, 22.76; Cl, 3.97.

Attempted preparation of $Mn(ketomacr)Cl_2$. A solution of 1.306 g (0.008 mole) 2,6-diacetylpyridine and 1.583 g (0.008 mole) manganese(II) chloride tetrahydrate in 250 ml methanol was brought to reflux and two drops of concentrated hydrochloric acid were added. A solution of 1.530 g (0.008 mole) 2,6-pyridinediacetyldihydrazone in 350 ml methanol was added dropwise over a period of one hour. Reflux was continued for 24 hours with the reaction mixture turning a dirty yellow color during this time. The yellow-orange solid that had formed was filtered with suction, washed with ether and dried over P_4O_{10} in vacuo giving 2.421 g of product.

Anal. Calcd for $Mn(C_{18}H_{18}N_6)Cl_2$: C, 48.67; H, 4.08; N, 18.92; Mn, 12.37; Cl, 15.96. Found: C, 65.56; H, 5.42; N, 23.51; Mn, 1.78; Cl, 2.14.

Attempted preparation of $Hg(ketomacr)(NO_3)_2$. A solution of 0.653 g (0.004 mole) 2,6-diacetylpyridine and 1.370 g

(0.004 mole) mercury(II) nitrate monohydrate in 200 ml absolute ethanol was brought to reflux and a pinch of NH_4NO_3 solid was added. To this solution was added dropwise a solution of 0.765 g (0.004 mole) 2,6-pyridinediacetyldihydrazone in 250 ml absolute ethanol. The white cloudy reaction mixture turned yellow as the hydrazone was added. Reflux was continued for 24 hours. Free mercury was observed in the bottom of the reaction flask at the conclusion of the reaction.

The reaction mixture was filtered with suction and a yellow-orange solid was recovered. The product was washed three times with ethanol and twice with ether and then dried in vacuo over P_4O_{10} .

Anal. Calcd for $\text{Hg}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{NO}_3)_2$: C, 33.61; H, 2.80; N, 17.42; Hg, 31.21. Found: C, 38.57; H, 3.44; N, 16.95; Hg, 30.65.

Sodium acetylide. A method similar to that of Rutledge (37) was followed using a suspension of sodium dispersion in hexane. Acetylene gas was purified by passing it through a dry ice-acetone trap and concentrated sulfuric acid to remove any acetone.

The sodium dispersion was prepared by dissolving six grams of metallic sodium in 150 ml of liquid NH_3 . Precooled hexane was then added to the blue solution of Na and NH_3 . The NH_3 was allowed to evaporate at room temperature with stirring resulting in a fine dispersion of sodium metal in hexane.

The purified acetylene was bubbled into the sodium dispersion at the boiling point of hexane (69°C) for 3-5 hours. The greyish sodium dispersion became beige in color at the completion of the conversion of the sodium metal to the acetylide.

The hexane was removed under reduced pressure. A pale yellow solid was recovered. The monosodium acetylide product was identified based upon the results of acid-base titrations.

2,6-pyridinedicarboxylic acid chloride. A sample of 16.8 g (0.1 mole) 2,6-pyridinedicarboxylic acid was placed in a 250 ml three-neck round bottom flask fitted with a water cooled reflux condenser and magnetic stirring bar. A volume of 100 ml thionyl chloride was added and the mixture was refluxed for 24 hours. The solid acid dissolved and a yellow-orange solution resulted. The excess thionyl chloride was removed with reduced pressure and a pink solid remained.

The product was purified by sublimation giving 16.9 g (81%) of the pure white crystalline acid chloride; mp 58-60° [lit. (38) mp 56-58°].

Attempted reaction of 2,6-pyridinedicarboxylic acid chloride with sodium acetylide. In trying to prepare the acetylene derivative of 2,6-pyridinedicarboxylic acid chloride, (Fig. 6). Attempts were made to carry out this reaction in various solvent systems: diethyl ether, 1,4-dioxane, tetrahydrofuran, liquid SO₂ and benzene. Care was taken to dry each solvent. The organic solvents were observed to become warm or to boil upon the addition of solid sodium acetylide to a

solution of 2,6-pyridinedicarboxylic acid chloride.

A violent reaction was observed at the mouth of the flask when sodium acetylide was added to a solution of the acid chloride in liquid SO_2 . A yellow-orange flame resulted each time.

The two solids, sodium acetylide and 2,6-pyridinedicarboxylic acid chloride, were mixed together under a N_2 atmosphere resulting in a violent reaction evolving heat and smoke. Charring of the solids resulted. In each case product isolation was attempted with no success. Either the acid chloride or the parent acid was recovered.

APPARATUS

Spectrometers. Solution spectra in the visible and ultraviolet regions were obtained using a Cary Model 15 recording spectrophotometer. The solid state diffuse reflectance spectra were obtained using a Cary Model 1411 Diffuse Reflectance Accessory in conjunction with a Cary Model 14 recording spectrophotometer. Magnesium carbonate was employed as reference material.

Infrared spectra were obtained using a Perkin-Elmer Model 137 NaCl prism and 237B grating spectrophotometers; also employed was a Beckman Model IR-10 grating spectrophotometer. All spectra were calibrated with polystyrene. The pressed KBr pellet technique was used.

Electron spin resonance spectra were obtained on finely ground samples using the Varian Associates Model E-3 recording spectrometer.

Mass spectra were obtained on AEI Scientific Apparatus Model MS-30 double-beam, double focusing mass spectrometer equipped with a DS-30 data system. Each solid sample was run by direct introduction probe. Probe temperature ranged from 200^o to 340^oC.

¹H nmr spectra were measured on Varian Associates Model A60-A and XL-100 nuclear magnetic resonance spectrometers.

Conductance apparatus. Conductances were measured using an Industrial Instruments, Inc., Model RC-18 Conductivity Bridge and a cell of constant $1.431 \pm 0.006 \text{ cm}^{-1}$ at constant temperature of $25.0^\circ\text{C} \pm 0.01^\circ$, maintained by the use of a water bath.

Melting point apparatus. A Thomas Hoover "Uni-melt" capillary melting point apparatus was employed; the temperatures are uncorrected.

Analyses. Carbon, hydrogen, nitrogen, and halogen analyses were performed by Galbraith Laboratories, Inc., Penninsular Chem. Research, Inc., and Atlantic Microlab, Inc. Although the metal analyses reported herein were performed by Galbraith Laboratories, Inc., they were initially obtained by using a Perkin-Elmer Model 290B atomic absorption spectrometer. All samples were analyzed in aqueous solutions after digesting the complex almost to dryness in 20 ml of a 1:1 mixture of concentrated nitric and perchloric acids.

Gouy apparatus. Magnetic susceptibilities were determined by the Gouy method using equipment described previously in greater detail (39). The maximum field strength attained was 6620 oersteds. The magnetic field was calibrated using mercury(II) tetrathiocyanatocobaltate(II) (40). The cryostat and temperature control apparatus used were of the basic design of Figgis and Nyholm (41). Temperatures between 115° and 400°K could be maintained within $\pm 0.1^\circ$ as determined by a platinum resistance thermometer. The sample tube was made of a cylindrical piece of quartz, approximately 3.0 mm inside diameter and 16 cm in length which was sealed at one end.

Approximately 15 cm was used for containing the sample volume. It was suspended in the cryostat from a semi-micro balance by a gold chain attached to a tapered Teflon plug. The diamagnetic correction for the tube was measured as a function of temperature. A Mettler Model B-6 semi-micro balance of 0.01 mg sensitivity was used to measure the force exerted by the magnetic field upon the sample.

Polarograph. A Sargent Model XVI Polarograph was used in conjunction with a dropping mercury electrode for obtaining the polarogram of the $\text{Ni}(\text{ketomacr})\text{Cl}_2$ complex. A drop rate of one drop per two seconds was employed. Water, used as solvent, was deoxygenated by passing a stream of N_2 gas through the water for 15 minutes. The supporting electrolytes used were 0.1 M KCl and 0.1 M tetraethylammonium bromide. A $1 \times 10^{-3}\%$ solution of Triton X-100 was used to suppress maxima. A N_2 blanket was kept over the solution under study to prevent redissolution of oxygen.

Electrolysis Cell. A mercury cathode cell was prepared using the design of A.D. Meloven described by Willard, Merritt and Dean (42). A platinum spiral was used as the anode. The cell, 7 cm in diameter by 14 cm high, was fitted with a three-way stopcock. One arm of the stopcock was connected to the leveling bulb of mercury. The other arm permitted removal of the electrolyte. A d.c. power supply was used to supply the current.

RESULTS AND DISCUSSION

General

The macrocyclic complexes containing Ni(II) ion proved to be more easily prepared than those of Co(II) or Cu(II). The preparation of Ni(ketomacr)Cl₂ was attempted first because of the availability of DAP and DAPH, the precursors of the macrocyclic ligand. The preparation of Ni(ketomacr)Cl₂ had been claimed previously (43) but its characterization was incomplete. Although the infrared spectrum and analytical data are identical (within experimental error) to those obtained for the product isolated during the course of these investigations, the room temperature magnetic susceptibility obtained by this writer differs markedly from that reported previously. A more extensive comparison will be made later.

It was anticipated that a successful synthetic technique developed for this complex could be applied to the preparation of other complexes employing similar ligand types, i.e., PDC and PDCH or PDC and DAPH.

The "template reaction" method was employed first because a vast majority of the successful syntheses of complexes which incorporate a macrocyclic ring circumscribing a central metal ion have only been possible using the template technique (vide supra). It was observed that the dropwise addition of a solution

DAPH in ethanol to a refluxing solution of DAP and NiCl_2 in ethanol (containing a few drops of concentrated hydrochloric acid as catalyst) produced the desired macrocyclic complex after about 18 to 24 hours of reflux.

Attempts were made to prepare $\text{Ni}(\text{ketomacr})\text{Cl}_2$ by changing the sequence of the addition of reactants. An ethanolic solution of DAP and DAPH were added simultaneously to NiCl_2 . Neither of these two variations proved to produce the desired complex as evidenced by poor elemental analysis; thus, these two methods were not used. Goedken (25) failed in attempts to prepare any nickel macrocyclic complex. But the order of addition of hydrazine and DAP he employed is different from that reported in this work; i.e., he added hydrazine directly into an acetonitrile solution of a Ni(II) salt and DAP.

The green, hydrated $\text{Ni}(\text{ketomacr})\text{Cl}_2$ was precipitated, after distilling off approximately half of the solvent, by adding diethyl ether. The light green product, after being filtered and dried at room temperature over P_4O_{10} in vacuo, corresponded to a tetrahydrate. The nitrate salt, prepared in a similar manner, was isolated as a hexahydrate. The complexes $\text{Ni}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{aldoketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ were prepared in a similar manner; both complexes analyzed as tetrahydrates. The $\text{Ni}(\text{aldoketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ was a brown-green powder; the $\text{Ni}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ was a darker brown-green powder. Inspection of the complexes under a microscope revealed the complexes to be homogeneous, amorphous solids.

The macrocyclic complexes of cobalt and copper were prepared using similar techniques and are described in the Experimental section. The three cobalt complexes $\text{Co}(\text{ketomacr})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{aldoketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ all analyzed as tetrahydrates. No color change was observed for the cobalt complexes as the water was driven off with heat. The three copper complexes prepared and characterized are $\text{Cu}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{aldoketomacr})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{Cu}(\text{ketomacr})(\text{NO}_3)_2$. Again no color change was observed with water loss. The reason that $\text{Cu}(\text{ketomacr})(\text{NO}_3)_2$ should be isolated as the only anhydrous complex is not apparent. It is also noted that even though several attempts were made to prepare $\text{Cu}(\text{ketomacr})\text{Cl}_2$, no pure product was isolated.

It was observed that the waters of hydration could be removed by drying the samples overnight in an oven set at 120°C . The waters of hydration were subsequently readsorbed when the complexes were allowed to remain in the atmosphere a few days. The gain and loss of water was accompanied by a barely perceptible, reversible color change for the nickel complexes only, i.e., from a yellow-green characteristic of the anhydrous nickel complex to the light green color of the hydrate.

The character of this water is uncertain; but three possibilities exist: lattice water, coordinated water, and solvolytic water, i.e., water contained in the form of a carbinol-amine (44). A combination of these three can not be excluded a priori, either. Because there is, effectively, no color change when the complexes are dried, it is concluded that the water present is not in the coordination sphere of the metal ions. The

removal of a coordinated species from a metal ion changes the ligand field about that metal ion and accordingly, the relative energies of the spectroscopic terms. Familiar examples of this phenomenon include the conversion of the red, hexaaquocobalt(II) chloride to the blue, anhydrous cobalt(II) chloride.

For the water to be present as a carbinol-amine, the formation of the complex must stop at an intermediate stage in the Schiff base condensation reaction on one end and reverse itself one step on the other. Since two of the C=N bonds have already been formed in the DAPH, it would seem unlikely that such a reversal would occur if the ring was not puckered. However, if the ring was puckered, the C=N would be very susceptible to nucleophilic attack to form the carbinol-amine (45). The presence of four C=N bonds in each macrocycle would correlate with four H₂O molecules included as carbinol-amines, but would not account for the presence of six H₂O groups in Ni(ketomacr)-(NO₃)₂·6H₂O, the two H₂O groups in Cu(anketomacr)Cl₂·2H₂O, or the anhydrous nature of Cu(ketomacr)(NO₃)₂. The problem could not be resolved by infrared spectroscopy because of the extreme broadness of the characteristic absorptions.

Goedken et al. (25) have reported the preparation and crystal structure of iron(II) and cobalt(II) complexes of ketomacrocycle. The crystal structure of Fe(ketomacr)-(CH₃CN)₂(ClO₄)₂ showed the nitrogen atoms in the macrocyclic ring to be coplanar with the iron(II) ion. The axial ligands, acetonitrile, were above and below this plane. Therefore, because there is no structural evidence for puckering of the ring, it is concluded that the water, contained in the macrocyclic

complexes prepared in this study, does not result from solvolysis of the C=N linkages.

It was found that if a small excess of DAP was used in the synthesis, the product gave a consistently better analysis. The method whereby the hydrazone was added dropwise to a solution of the metal ion and DAP or PDC was used exclusively. When the products did not give the expected elemental analysis, because of apparent excess organic material, it was found that the solid product could be extracted with absolute methanol in a Soxhlet extractor to produce a product which gave the expected analysis. This Soxhlet extraction technique was used on all of the complexes except for $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for which it was unnecessary.

Recrystallization to improve the purity of a particular complex usually proved to be ineffective because of its limited solubility in either water or ethanol. Although other solvents were tried, the complexes were found to be more soluble in either water or ethanol. Saturated solutions of the complexes in water ranged from 10^{-2}M to 10^{-4}M ; thus recrystallization on a large scale was not feasible.

Infrared Spectra

The infrared spectra of the nickel, cobalt, and copper complexes, Figures 7, 8, 9, and 10, contain a recurrent absorption near 3350cm^{-1} , which is customarily assigned to OH or NH stretching vibrations. Incorporation of adsorbed water was assigned as the source of this band as a result of the previous considerations. Also the intensity of this band could be reduced, but

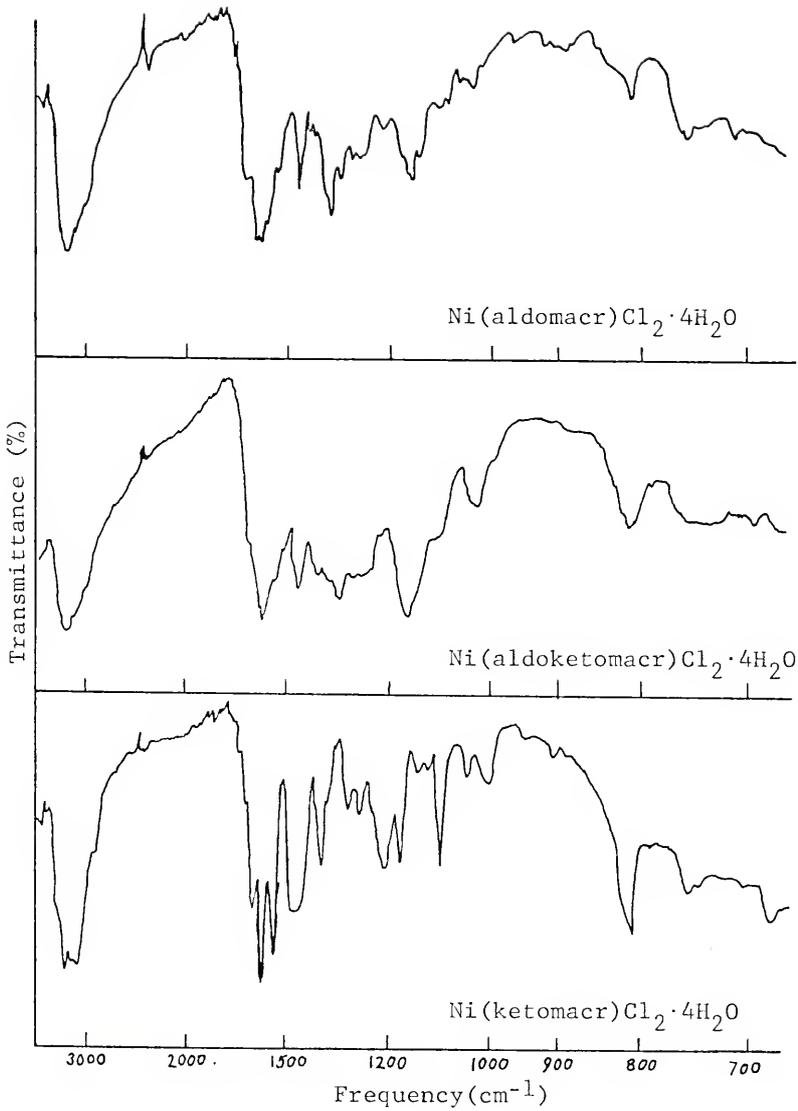


Fig. 7 Infrared spectra of Ni(aldomacr)Cl₂·4H₂O, Ni(aldoketomacr)Cl₂·4H₂O, and Ni(ketomacr)Cl₂·4H₂O.

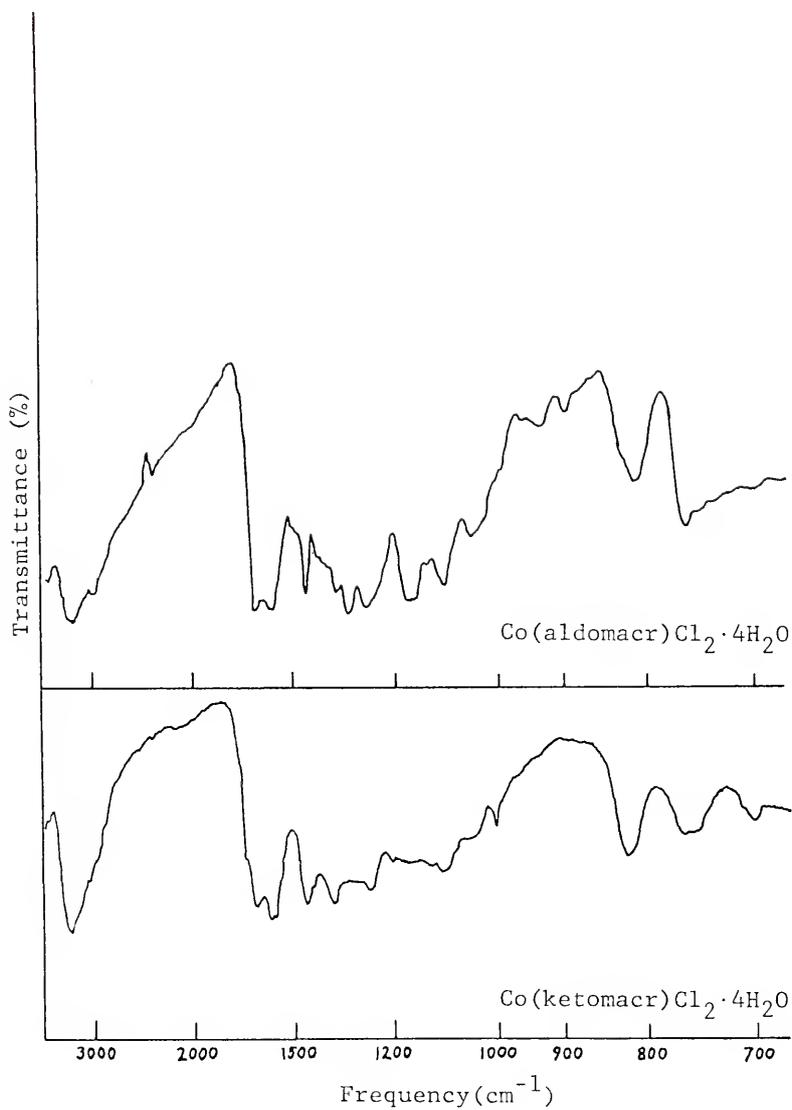


Fig. 8 Infrared spectra of $\text{Cl(aldomacr)Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co(ketomacr)Cl}_2 \cdot 4\text{H}_2\text{O}$.

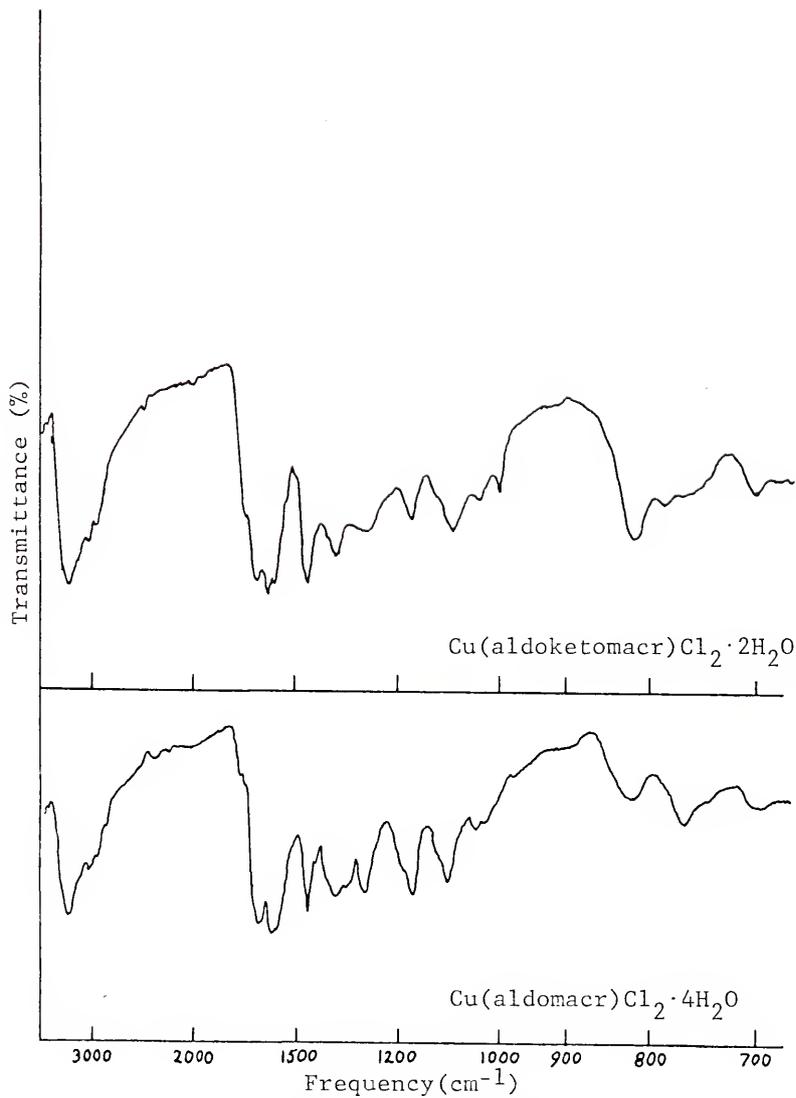


Fig. 9 Infrared spectra of Cu(aldoketomacr)Cl2·2H2O and Cu(aldomacr)Cl2·4H2O.

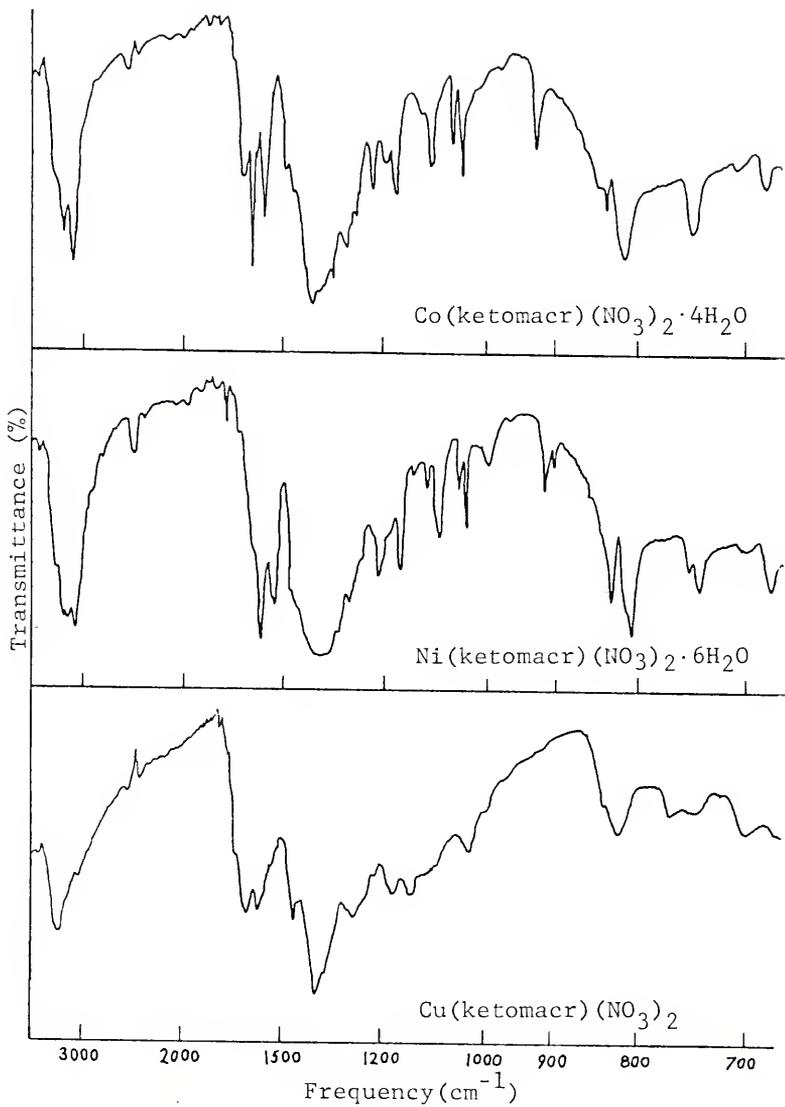


Fig. 10 Infrared spectra of $\text{Co(ketomacr)(NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni(ketomacr)(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cu(ketomacr)(NO}_3)_2$.

not entirely removed, by carefully drying the complex and preparing the KBr pellet under a dry nitrogen atmosphere. These spectra were presented because of their convenient size. The spectra of the same compounds were obtained using a Beckman Model IR-10 grating spectrophotometer; however, these IR-10 spectra contained no absorptions which were not identifiable in the spectra presented herein.

The infrared spectra of the metal complexes tend to be very broad and poorly resolved as is characteristic of many highly conjugated macrocyclic complexes (46). Following the approach of Nakamoto (46), the infrared spectra of the complexes might be expected to be a composite of the spectra of the corresponding precursors: DAP and DAPH, PDC and PDCH, PDC and DAPH. Similarities are found except for the absence of the relatively sharp primary amine and carbonyl stretching absorptions.

The C=N absorption in conjugated systems interact to a large extent with other double bonds in the compound and thus it is frequently difficult to assign a definite position to this group. Busch (17), however, has reported the imine absorption of a related macrocyclic system to occur at 1570 cm^{-1} . Other studies (47) have reported complexed imine absorptions between 1610 and 1615 cm^{-1} . Bellamy (48) has reported C=N stretching vibrations as high as 1690 cm^{-1} . The profusion of bands in the 1600 cm^{-1} region arising from the C=N grouping and the pyridine ring absorptions made absolute assignment of bands in this region difficult. To complicate matters even more, the OH deformation vibrations are also found in the 1600 cm^{-1} region. The C=N vibrations could be strongly coupled with the ring

vibrations in which case, it would be impossible to make an unequivocal assignment. However, it is still very tempting to try to make some assignment of the C=N absorption to the 1600 cm^{-1} region. Tables A-1, A-2, and A-3 of the Appendix list selected absorptions and their corresponding assignments.

All four nickel complexes show a broad, intense band ca. 1585 cm^{-1} which contains several weak shoulders. This band is attributed to a composite of ring vibrations (Bands I and II) and C=N stretching vibrations. The C=N band is better resolved in the spectra of Ni(ketomacr)⁺² salts. The very strong, broad absorption in the spectrum of Ni(ketomacr)(NO₃)₂·6H₂O lying in the $1400\text{-}1350\text{ cm}^{-1}$ region is assigned to an ionic NO₃⁻ stretching vibration (46). Coordinated nitrate complexes have NO₂ anti-symmetric and symmetric stretching vibrations in the $1531\text{-}1481\text{ cm}^{-1}$ and $1290\text{-}1253\text{ cm}^{-1}$ regions respectively (49).

The infrared spectra of the cobalt complexes also contain the broad undefined absorptions in the $1650\text{-}1575\text{ cm}^{-1}$ region which can be assigned to a combination of acyclic C=N and ring vibrations. The spectrum of Co(ketomacr)(NO₃)₂·4H₂O is better resolved in this region, exhibiting three strong peaks at 1645 , 1600 , and 1550 cm^{-1} . The band at 1600 cm^{-1} is attributed to the C=N stretching vibration. The broad band centered on 1380 cm^{-1} is assigned to an ionic NO₃⁻ stretching vibration (46).

The infrared spectra of the copper complexes are very similar to those of the nickel and cobalt complexes. Broad unresolved bands are again observed. The broad band in the $1640\text{-}1560\text{ cm}^{-1}$ region is present and is attributed to a combin-

ation of ring and acyclic C=N stretching vibrations. The NO_3^- stretching vibration is observed at 1380 cm^{-1} in the spectrum of $\text{Cu}(\text{ketomacr})(\text{NO}_3)_2$.

The infrared spectra of the complexes prepared support the assertion that a Schiff base condensation has occurred, i.e., there are neither characteristic C=O nor NH_2 stretching vibrations observed; but it is not possible to make an unequivocal assignment of the C=N stretching vibration. Nor is it possible to conclude on the basis of these data that the ligand exists in an imine form.

Electronic Spectra

A study of the ultraviolet-visible absorption spectra of the complexes was undertaken to ascertain the coordination geometry present in the macrocyclic compounds. As mentioned previously, the solubilities of the complexes limited the choice of solvents; but, even then, the solute concentrations of all but $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were less than 10^{-3}M . However, the large molar absorptivity coefficients of the complexes permitted a characterization under the very dilute conditions dictated. The λ_{max} and molar absorptivity coefficients are listed in Table 1 together with the absorptions observed in the diffuse reflectance spectra.

The spectra of aqueous solutions of both $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ contained absorptions at 267 and 340 nm with molar absorptivity coefficients of magnitude $10^4 \text{ M}^{-1}\text{cm}^{-1}$. The complexes $\text{Ni}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{aldoketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ showed three absorptions at 265, 320, and 450 nm with molar absorptivity coefficients of similar magnitude. There was no

Table 1. Electronic spectral data

Compound	λ (nm)	$\text{cm}^{-1} \times 10^{-3}$	$\epsilon \times 10^{-3} (\text{M}^{-1} \text{cm}^{-1})$
Ni(ketomacr) $\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	267	37.4	29.4
	340	29.4	1.16
	365*	27.4	7.16
Ni(ketomacr)(NO_3) $_2 \cdot 4\text{H}_2\text{O}$	267	37.4	32.5
	340	29.3	6.85
	360*	27.8	---
	900*	11.1	---
Ni(aldoketomacr) $\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	265	37.7	7.57
	320	31.2	3.6 ^o
	450	22.2	0.874
Ni(aldomacr) $\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	265	37.7	5.97
	320	31.1	3.88
	450	22.2	1.07
	375*	26.7	---
	455*	22.0	---
	565*	17.7	---
	630*	15.9	---
Co(ketomacr) $\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	273	36.6	1.17
	330	30.3	0.535
	400*	25.0	---
Co(ketomacr)(NO_3) $\cdot 4\text{H}_2\text{O}$	273	36.6	31.6
	335	29.9	9.74
	475	21.0	1.45
	505	19.8	0.963
	375*	26.7	---
Co(aldomacr) $\text{Cl}_2 \cdot 4\text{H}_2\text{O}^\ddagger$	265	37.7	1.49
	325	30.8	1.47
	545	18.3	0.752
Cu(aldoketomacr) $\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	245	40.8	1.81
	295	33.9	1.07
	335	29.8	0.617
	450*	22.2	---
Cu(aldomacr) $\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	255	39.2	12.4
	320	31.2	10.5
	450	22.2	2.38
	375*	26.7	---

Table 1. Continued

Compound	λ (nm)	$\text{cm}^{-1} \times 10^{-3}$	$\epsilon \times 10^{-3} (\text{M}^{-1} \text{cm}^{-1})$
Cu(ketomacr)(NO ₃) ₂	255	39.2	4.16
	320	31.2	2.83
	450	22.2	0.42
	375*	26.7	---

*Diffuse reflectance absorption

†Diffuse reflectance spectrum contains no absorption maxima

change in the solution spectra of the complexes upon standing for several days. The diffuse reflectance spectra of $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fig. 11) contain absorptions at 360 nm which can be considered to be the same one arising at 340 nm in the solution spectra.

The solution spectra of $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ contained no well-defined absorptions in the visible region. The observation is not surprising if one expects to see d-d transitions at the concentrations required. The spectra of $\text{Ni}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{aldoketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ do show a band in the visible region of the solution spectra at 450 nm and the diffuse reflectance spectrum of $\text{Ni}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ shows a weak shoulder at 455 nm. The diffuse reflectance spectrum, obtained by spreading the powdered sample on 3M masking tape, of $\text{Ni}(\text{aldoketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ is a straight line. Only the spectra of five of the complexes are illustrated because of the lack of characteristic features in the spectra of the other complexes.

The solution electronic spectra of the cobalt and copper complexes also contain the two characteristic bands in the ultraviolet region, viz., at 260 and 330 nm. The diffuse reflectance spectra (Figures 12 and 13) contain broad bands around 350-450 nm, except for the spectrum of $\text{Co}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ which is a straight line. However, the molar absorptivity coefficients of the complexes in this region are too large to result from d-d transitions (14); rather, they are

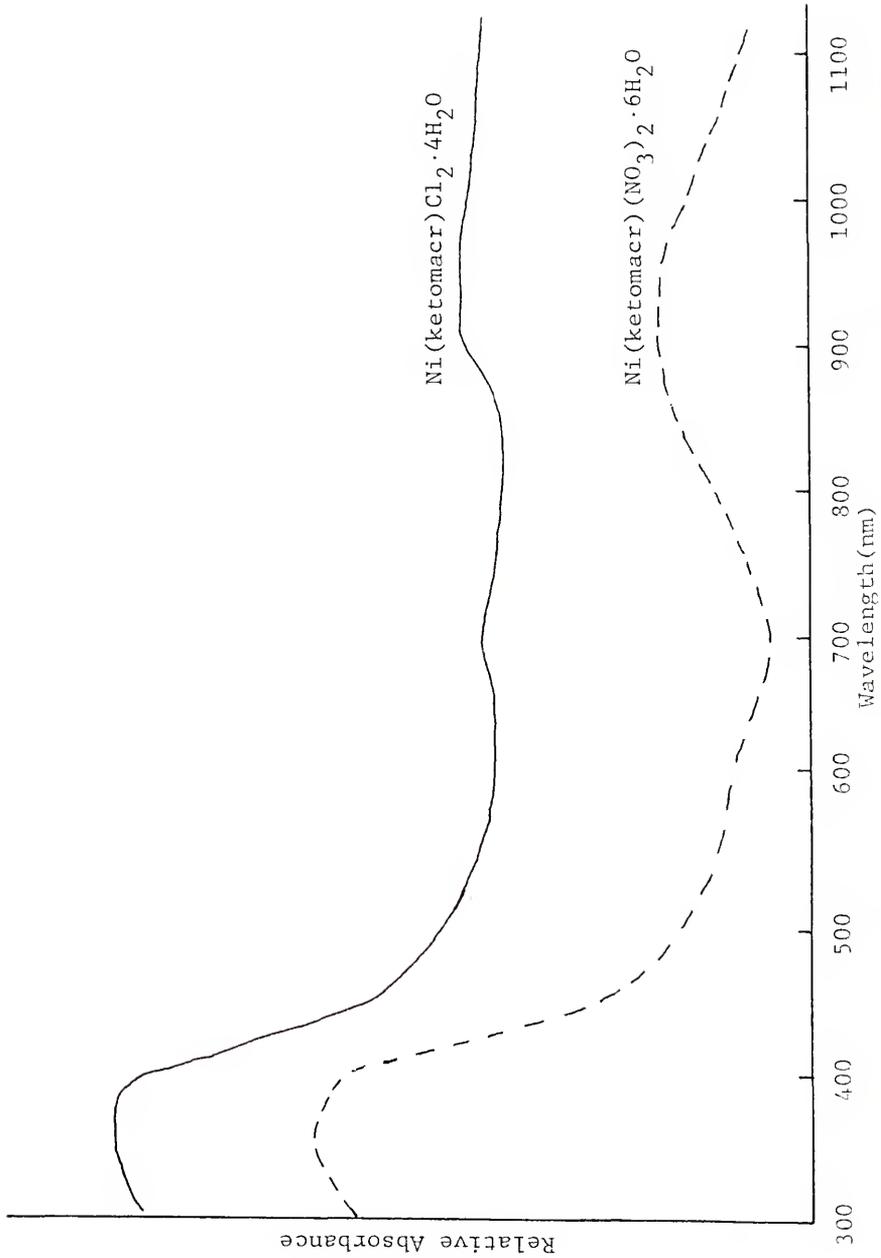


Fig. 11 Diffuse reflectance spectra of Ni(ketomacr)Cl₂·4H₂O and Ni(ketomacr)(NO₃)₂·6H₂O

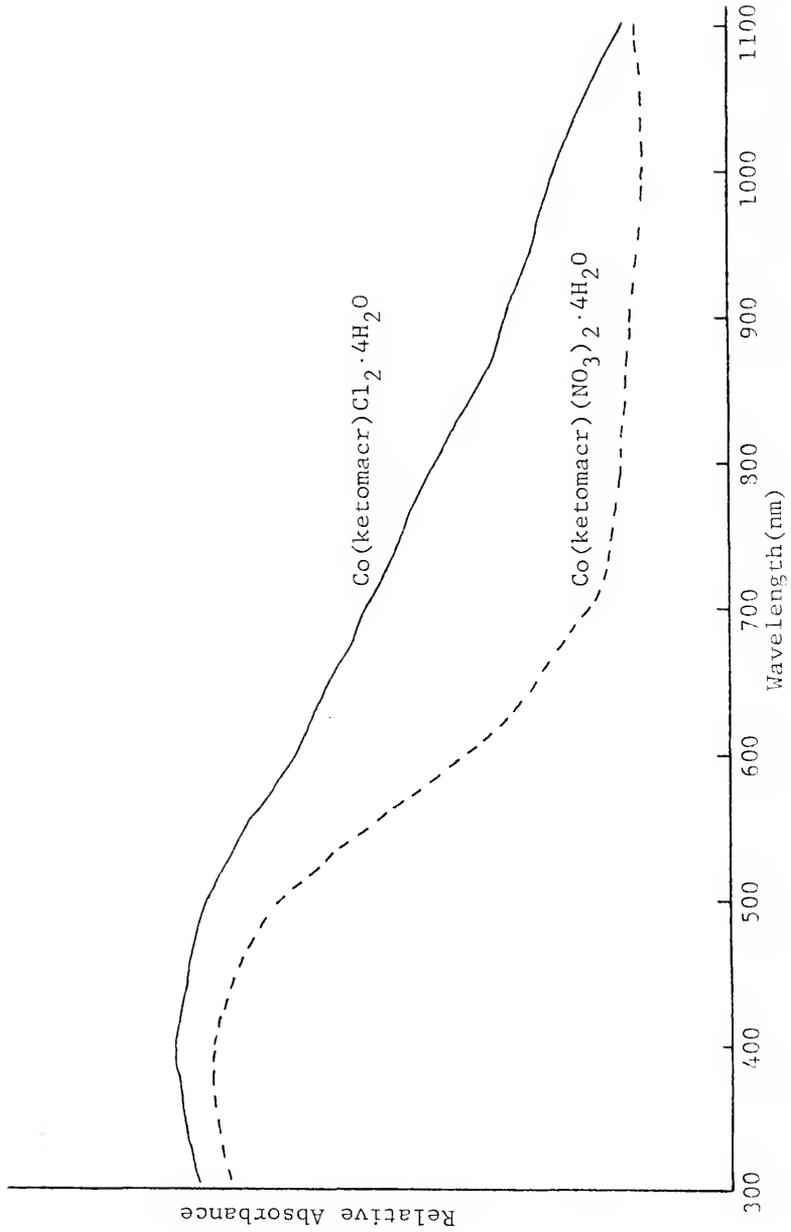


Fig. 12 Diffuse reflectance spectra of $\text{Co(ketomacr)Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co(ketomacr)(NO}_3)_2 \cdot 4\text{H}_2\text{O}$

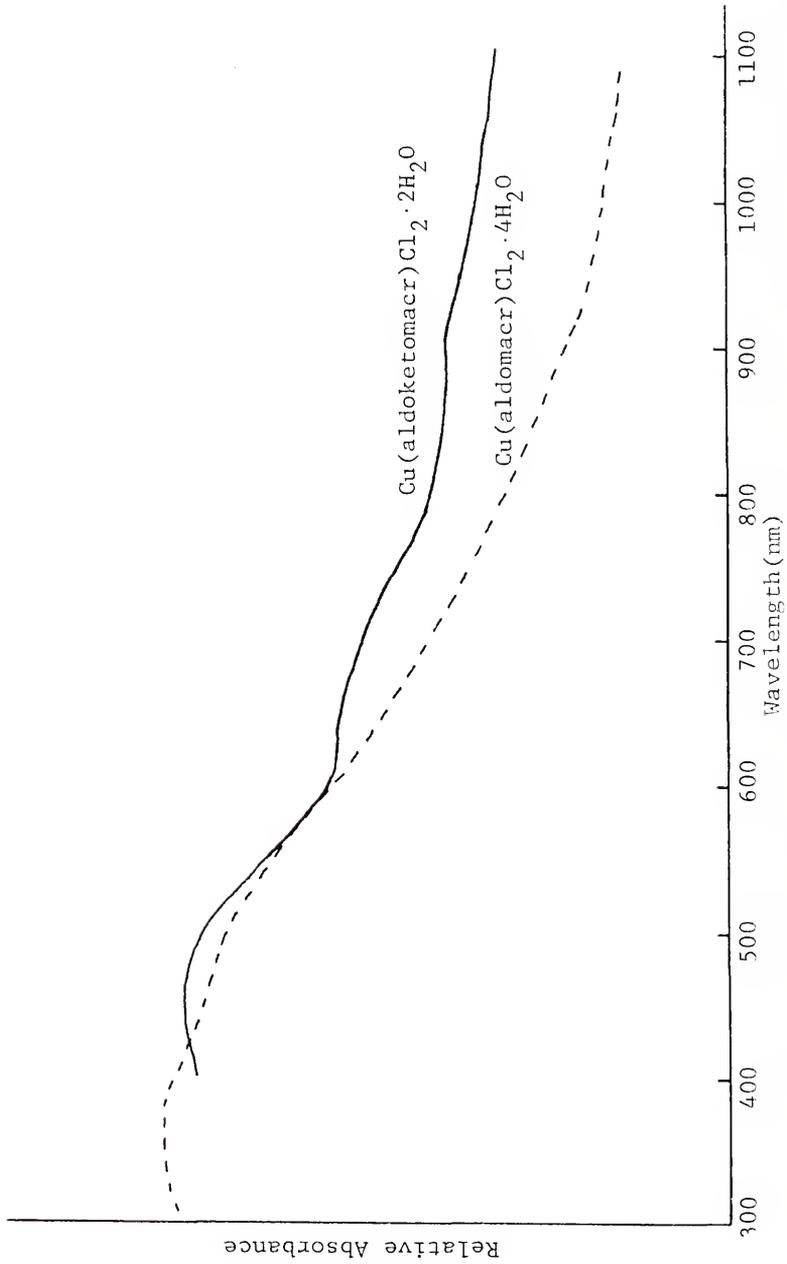


Fig. 13 Diffuse reflectance spectra of $\text{Cu(aldoketomacr)Cl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu(aldomacr)Cl}_2 \cdot 4\text{H}_2\text{O}$

attributed to charge transfer bands. The charge transfer bands may vary in position and intensity from one system to another. The band observed near 320 nm in the solution spectra may be present in the reflectance spectra; but it is so poorly resolved as to escape detection. Comparison of the solution electronic spectra with the diffuse reflectance spectra failed to reveal additional similarities.

The transitions in the ultraviolet region of the spectra are assigned to charge transfer absorptions localized upon the (aromatic) ligands. The lower energy (visible) transitions are attributed to charge transfer bands to the complex. Thus, the coordination geometry cannot be inferred from either the solution electronic spectra or the diffuse reflectance spectra of the complexes.

Conductance

The conductance of an aqueous solution of each of the macrocyclic complexes was obtained in order to infer whether or not anion coordination is present. The molar conductances for the complexes at selected concentrations are reported in Table 2. The slight solubility of several of the complexes prevents a straightforward comparison of the molar conductance at the same concentration; however, trends are apparent. Several electrolyte types, i.e., 1:1, 1:2, 2:1, 1:3, 3:1, and 1:4, and their molar conductance in water for $1 \times 10^{-3} M$ solutions are listed in Table 3. The values obtained for the complexes lie in the range of 2:1 electrolytes. Therefore, it is concluded that coordination with the anion is unimportant. A standard curve for a 2:1 electrolyte (Fig. 14) was prepared using

Table 2. Selected molar conductance and limiting conductance of prepared complexes in H₂O at 25.0°C.

Complex	Molar Concentration	Λ (ohm ⁻¹ cm ⁻¹)	Λ_0
Ni(ketomacr)Cl ₂ ·4H ₂ O	9.84x10 ⁻⁴	332	392
Ni(ketomacr)(NO ₃) ₂ ·6H ₂ O	1.00x10 ⁻³	242	327
Ni(aldoketomacr)Cl ₂ ·4H ₂ O	2.2 x10 ⁻⁴	367	392
Ni(aldomacr)Cl ₂ ·4H ₂ O	4.48x10 ⁻⁴	328	357
Co(ketomacr)Cl ₂ ·4H ₂ O	1.71x10 ⁻⁴	244	298
Co(ketomacr)(NO ₃) ₂ ·4H ₂ O	4.31x10 ⁻⁴	224	264
Co(aldomacr)Cl ₂ ·4H ₂ O	3.06x10 ⁻⁴	281	389
Cu(ketomacr)(NO ₃) ₂	1.66x10 ⁻⁴	348	394
Cu(aldoketomacr)Cl ₂ ·2H ₂ O	2.43x10 ⁻⁴	322	337
Cu(aldomacr)Cl ₂ ·4H ₂ O	2.52x10 ⁻⁴	245	312
BaCl ₂ (experimental)	5.0 x10 ⁻⁴	265	340
BaCl ₂ (literature)(50)	5.0 x10 ⁻⁴	272	280

Table 3. Known electrolyte types and their molar conductivity.

Electrolyte	Molar Conductivity*
<u>1:1</u>	
$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$	96.8
$\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$	106.8
NaCl	123.7
<u>1:2 & 2:1</u>	
CaCl_2	260.8
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	261.3
$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$	257.6
$[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	260.2
$[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Br}_2$	280.1
$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$	228.9
$\text{K}_2[\text{PtCl}_6]$	256.8
<u>1:3 & 3:1</u>	
LaCl_3	393.5
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	431.6
$[\text{Co}(\text{NH}_3)_6]\text{Br}_3$	426.9
$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$	441.7
$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$	404.0
<u>1:4</u>	
$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	522.9

* 1×10^{-3} M solutions in H_2O at 25.0°C (51).

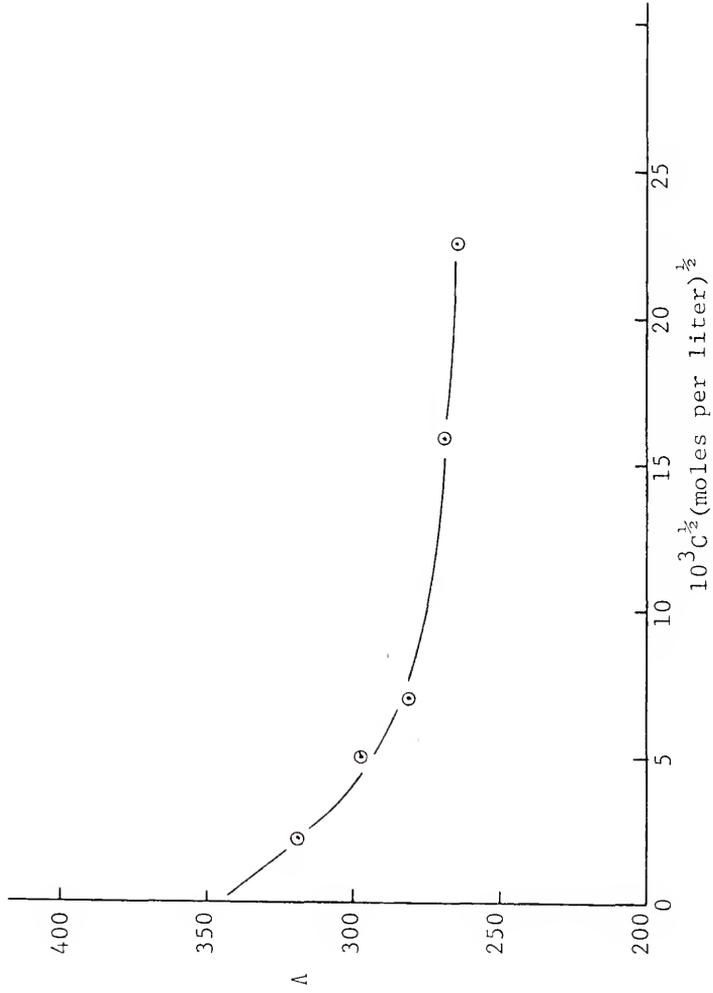


Fig. 14 Molar Conductance vs. $C^{1/2}$ for BaCl_2 .

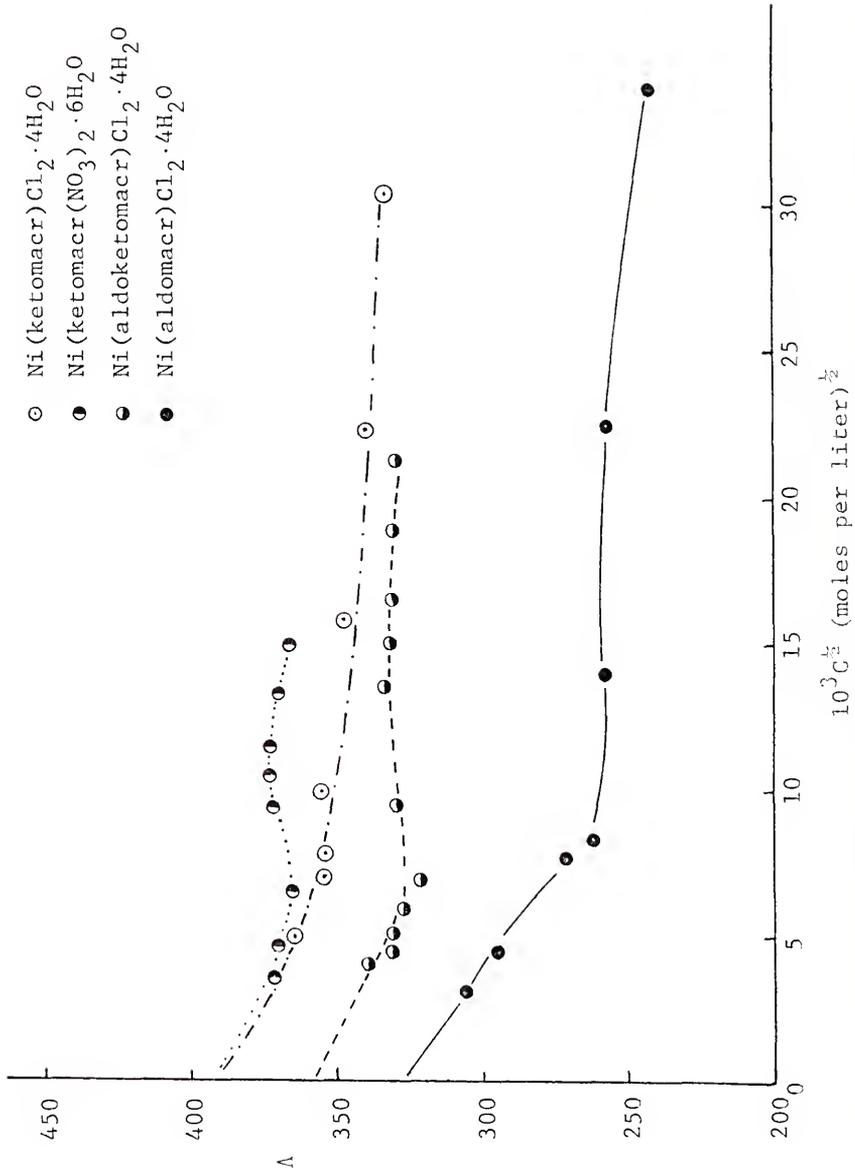


Fig. 15 Molar Conductance vs. $C^{1/2}$ for Ni(ketomacr)Cl₂·4H₂O, Ni(ketomacr)(NO₃)₂·6H₂O, Ni(aldo ketomacr)Cl₂·4H₂O, and Ni(aldomacr)Cl₂·4H₂O

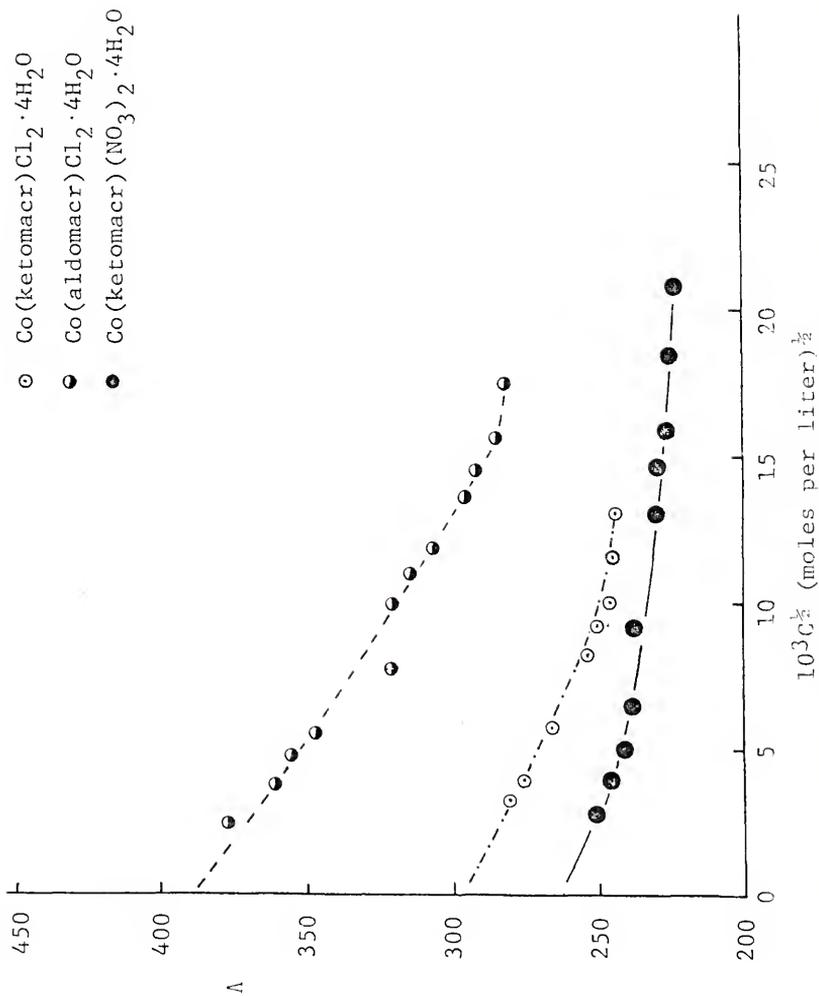


Fig. 16 Molar conductance vs. $C^{1/2}$ for Co(ketomacr)Cl₂·4H₂O, Co(aldomacr)Cl₂·4H₂O, and Co(ketomacr)(NO₃)₂·4H₂O.

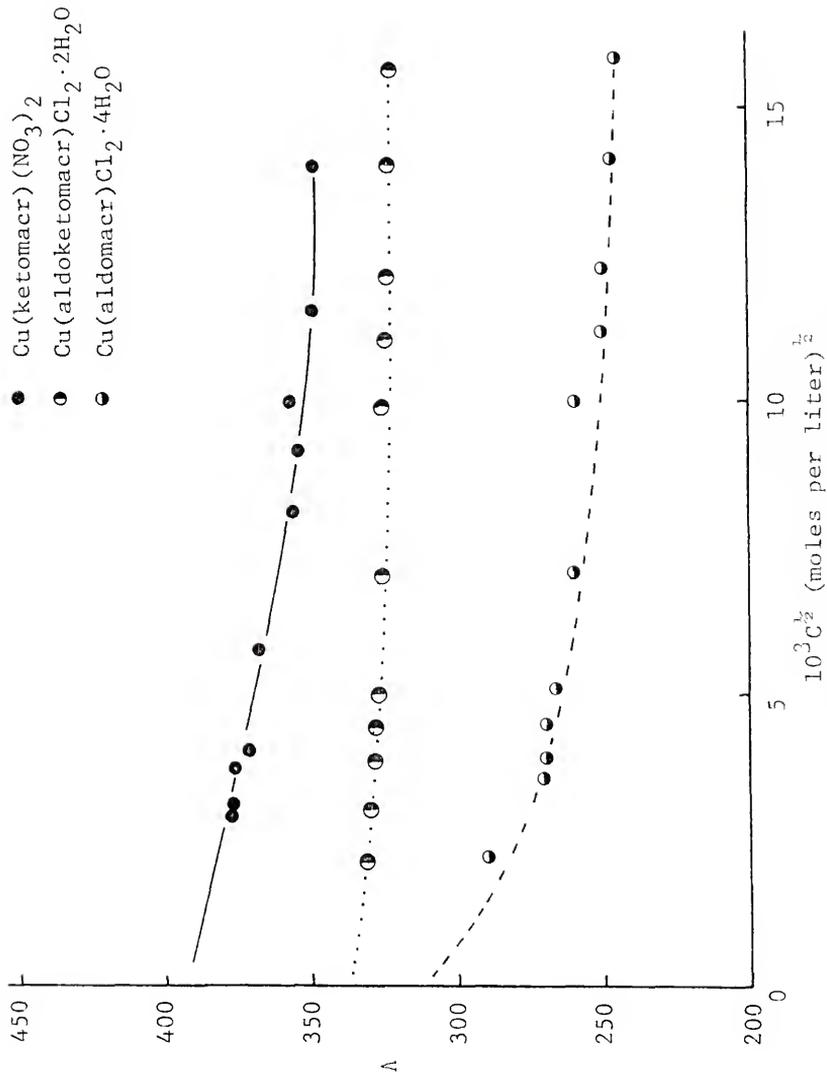


Fig. 17 Molar conductance vs. $C^{1/2}$ for Cu(ketomacr) (NO₃)₂, Cu(aldoketomacr) Cl₂ · 2H₂O, and Cu(aldomacr) Cl₂ · 4H₂O.

standard solutions of BaCl_2 . The plots of molar conductance versus the square root of concentrations of all the complexes (Figs. 15, 16, and 17) and the standard curve for BaCl_2 are similar. At concentrations larger than 10^{-4}M there is a linear portion of the curve which then breaks upward into a steeper slope at the lower concentrations. The limiting conductance of each of the complexes is comparable to that observed for BaCl_2 . The limiting conductance was obtained by linear extrapolation of the straight portions of the molar conductance versus square root of concentration curve (52). These values are reported in Table 2. The limiting conductance for a $5.0 \times 10^{-4}\text{M}$ solution of BaCl_2 was found to be $340(\text{ohm M cm})^{-1}$. Those of the complexes are listed in Table 2.

Magnetic Susceptibility

The magnetic susceptibilities of the complexes were determined using the Gouy method, except for $\text{Cu}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ in which case the nmr technique was used. The magnetic data for the macrocyclic complexes, discussed herein, are listed in Table 4.

The room temperature magnetic moments for $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were found to be 3.89 and 3.77 BM respectively. These moments are considered to be high for high-spin octahedral nickel(II) ion (53); but they fall within the range of values reported for either high-spin tetrahedral or some five-coordinate nickel(II) ions. Effective magnetic moments from 3.69 to 3.85 BM have been reported (54) for five-coordinate nickel(II) complexes. Complexes of

Table 4. Magnetic data

Complex	$\chi_M' \times 10^3$ (cgs units)	T(°K)	θ°	μ_{eff} (BH)
Ni(ketomacr)Cl ₂ ·4H ₂ O	6.273	300	-6	3.89
	4.610	308		3.88(nmr) 3.40 (anhydrous) 3.85(TI)
Ni(ketomacr)(NO ₃) ₂ ·6H ₂ O	5.976	302	-10	3.77 3.74 3.75(TI)
Ni(aldoketomacr)Cl ₂ ·4H ₂ O	1.777	301	--	2.08
Ni(aldomacr)Cl ₂ ·4H ₂ O	2.822	300	--	2.62
Co(ketomacr)Cl ₂ ·4H ₂ O	3.383	300	-20	2.86 2.75(TI)
Co(ketomacr)(NO ₃) ₂ ·4H ₂ O	9.418	300	--	4.73
Co(aldomacr)Cl ₂ ·4H ₂ O	2.599	300	-30	2.51 2.37(TI)
Cu(aldomacr)Cl ₂ ·4H ₂ O	--	308	--	1.19(nmr)
Cu(aldoketomacr)Cl ₂ ·2H ₂ O	1.351	301	--	1.81
Cu(ketomacr)(NO ₃) ₂	0.934	299	-14	1.50 1.46(TI)

*TI = Temperature Independent Moment

nickel(II) with N-methyldabconium ion (L^+), H_2O or NH_3 , and halide ion were prepared (55), $NiL(H_2O)Cl_3$, and found to be nonionic. The magnetic data for these five-coordinate complexes are consistent with either a trigonal bipyramidal structure or a square pyramidal structure. Based upon the electronic spectra obtained, the authors concluded that the structures were trigonal bipyramidal.

A sample of $Ni(ketomacr)Cl_2 \cdot 4H_2O$ was dried to determine what effect the presence of the water has on the magnetic susceptibility. The room temperature moment of the anhydrous product observed was 3.40 BM, about 0.5 BM less than that found for the hydrated complex. This change is considered to be significant because the moment of the anhydrous complex lies in the range of high-spin octahedral nickel(II) ions (14, 53). There is some definite interaction of the water molecules with the paramagnetic center of the complex as evidenced by the change in the magnetic moment. The type of interaction involved is not fully understood. Weller (43) reported the preparation of $Ni(ketomacr)Cl_2$; but his product is not the same as that prepared during the course of this study. For example, he reported a magnetic moment of 1.03 BM; but, using the separation techniques reported herein, an anhydrous product having a room temperature moment of 3.40 BM was isolated. The differences in separation techniques are considered to be the major factor governing the lack of correspondence.

Most transition metal compounds are magnetically dilute.

i.e., their paramagnetic centers are isolated from each other by inert ligand molecules. In such compounds the paramagnetic ions act independently of each other. In these cases the idealized behavior for the variation of magnetic susceptibility with temperature is the Curie law, $\chi'_m = C/T$, where χ'_m is the susceptibility per mole of paramagnetic material corrected for the diamagnetism of the constituent atoms, C is the Curie constant and T the absolute temperature. However, the majority of the paramagnetic substances do not obey this law but a modified version called the Curie-Weiss law, $\chi'_m = C/(T+\theta)$, in which θ is an empirical quantity and is a measure of the deviation from the idealized Curie law description. This parameter is determined by plotting $1/\chi'_m$ versus T and determining the intercept at $1/\chi'_m = 0$. For magnetically dilute paramagnetics, θ is usually a small quantity.

The data obtained from temperature-dependent magnetic susceptibility studies of $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, and $\text{Cu}(\text{ketomacr})(\text{NO}_3)_2$ are given in Tables 5-9 and represented graphically in Figs. 18-22. All the complexes measured followed the Curie-Weiss law with small θ values listed with the temperature-dependent data.

Because the effective moments for the $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were considered to be large for a high-spin d^8 ion in an octahedral or tetrahedral field, the moments were checked using an nmr technique (56). This nmr technique allows one to determine the paramagnetic moment of a

Table 5. Temperature-dependent magnetic susceptibility of $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$.

Temperature, $^{\circ}\text{K}$	$\chi'_M \times 10^3$
260	7.20
240	7.78
220	8.47
200	9.54
180	10.56
160	11.90
150	12.60
140	13.50
130	14.41
120	15.52

$\theta = -6^{\circ}$, Curie constant

$$\chi_{\text{dia}} = 0.261 \times 10^{-3}$$

χ'_M = corrected molar magnetic susceptibility

Table 6. Temperature-dependent magnetic susceptibility of $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Temperature, °K	$\chi_M' \times 10^3$
260	6.74
240	7.31
220	7.93
200	8.77
180	9.69
160	10.88
150	11.46
140	12.25
130	12.98
120	13.89

$$\theta = -10^0$$

$$\chi_{\text{dia}} = 0.275 \times 10^{-3}$$

Table 7. Temperature-dependent magnetic susceptibility of $\text{Co}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$.

Temperature, $^{\circ}\text{K}$	$\chi_M' \times 10^3$
260	3.82
240	4.05
222	4.44
200	4.88
180	5.35
160	6.02
150	6.35
140	6.77
127	7.32

$$\theta = -20^{\circ}$$

$$\chi_{\text{dia}} = -0.261 \times 10^{-3}$$

Table 8. Temperature-dependent magnetic susceptibility of $\text{Co}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$.

Temperature, $^{\circ}\text{K}$	$\chi'_M \times 10^3$
260	2.93
240	3.09
220	3.33
200	3.65
180	3.96
160	4.40
150	4.63
140	4.92
128	5.27

$$\theta = -30^{\circ}$$

$$\chi_{\text{dia}} = -0.214 \times 10^{-3}$$

Table 9. Temperature-dependent magnetic susceptibility of $\text{Cu}(\text{ketomacr})(\text{NO}_3)_2$.

Temperature, $^{\circ}\text{K}$	$\chi_M' \times 10^3$
260	1.40
240	1.52
220	1.62
200	1.79
180	1.94
160	2.19
150	2.37
140	2.52
129	2.68

$$\theta = -14^{\circ}$$

$$\chi_{\text{dia}} = -0.196 \times 10^{-3}$$

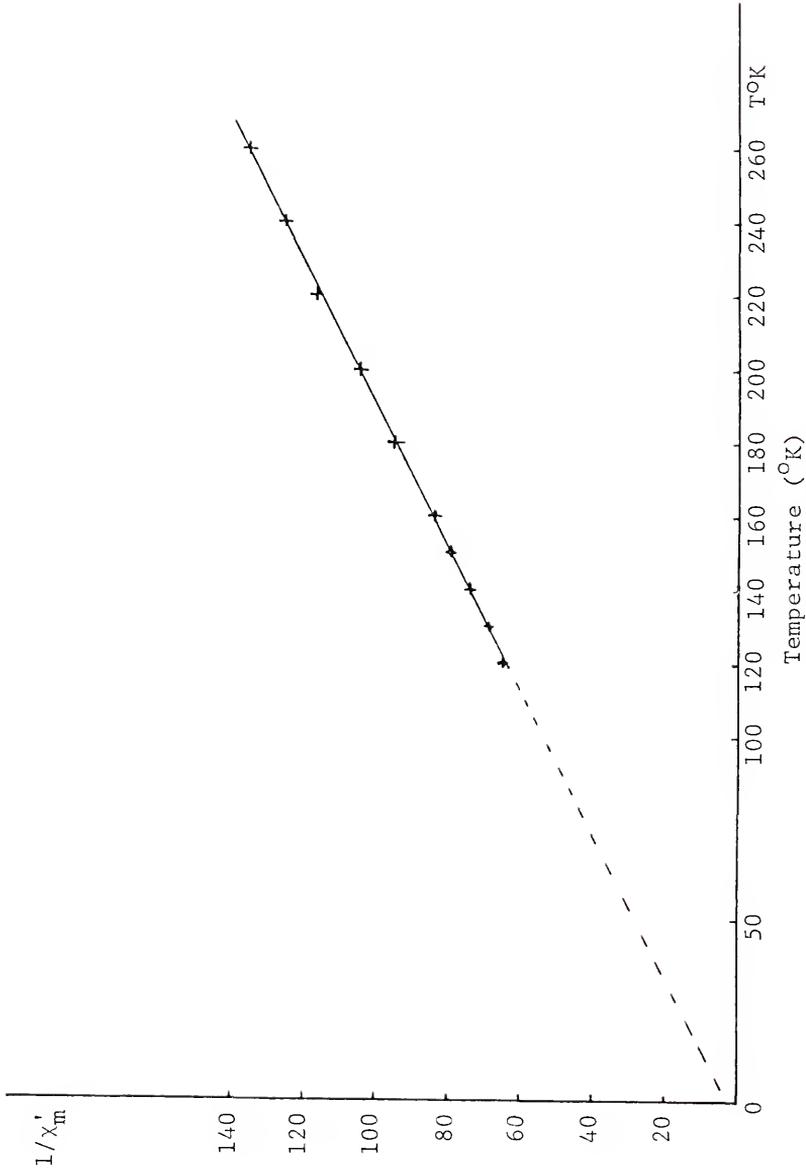


Fig. 13 Temperature dependence of inverse magnetic susceptibility for $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$.

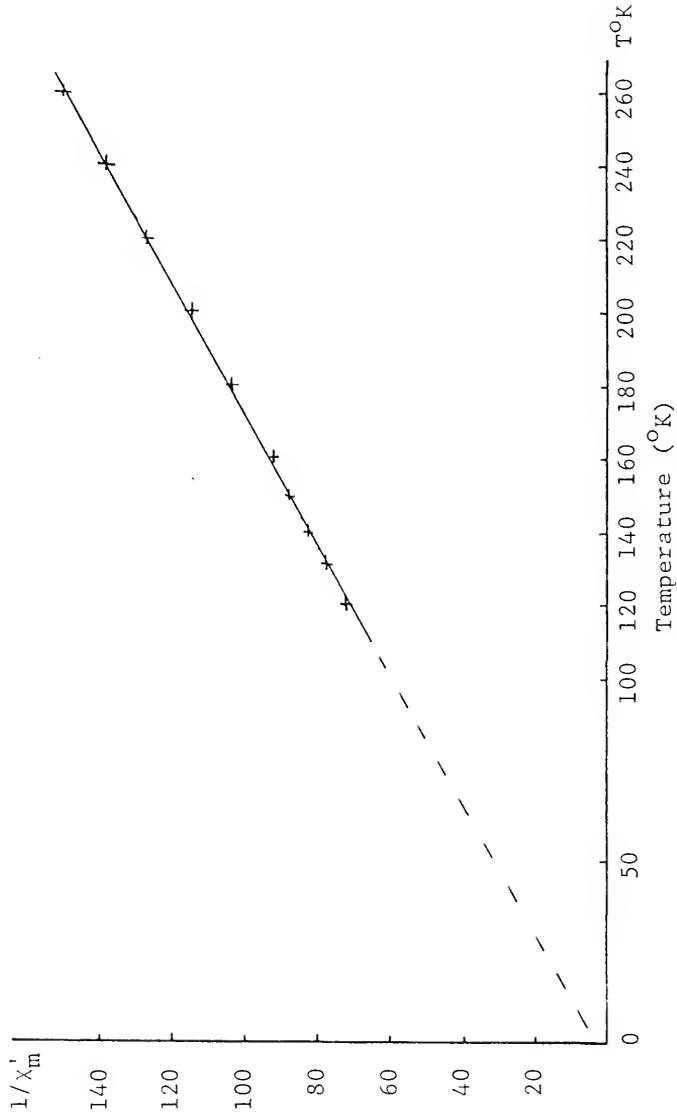


Fig. 19 Temperature dependence of inverse magnetic susceptibility for $\text{Ni}(\text{ketomac})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

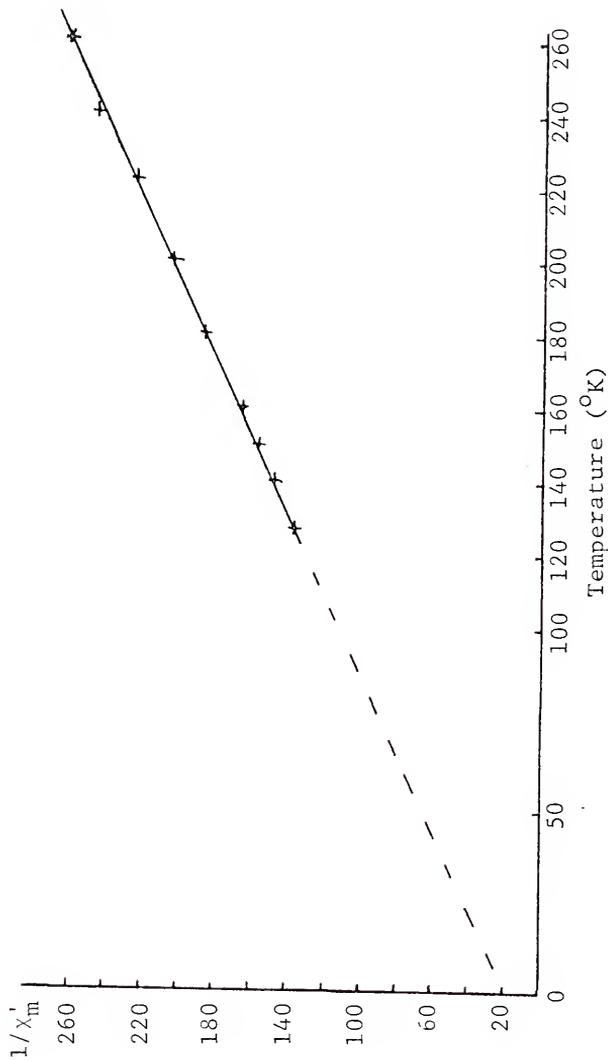


Fig. 20 Temperature dependence of inverse magnetic susceptibility for $\text{Co}(\text{ketomac})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$.

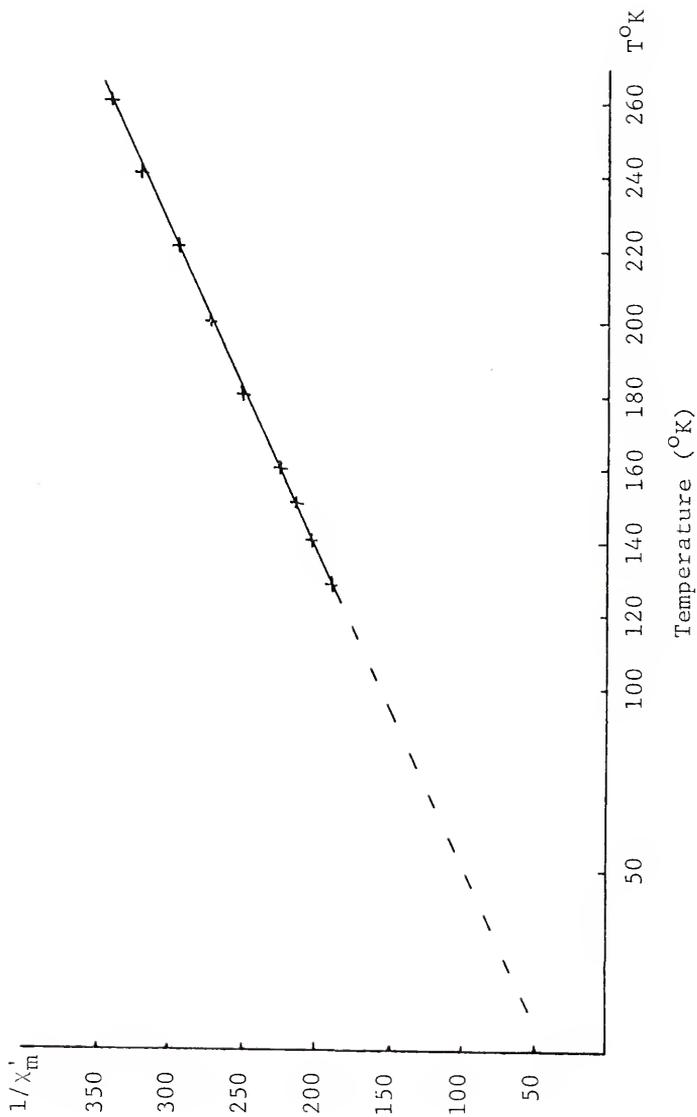


Fig. 21 Temperature dependence of inverse magnetic susceptibility for $\text{Co}(\text{aldoketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$.

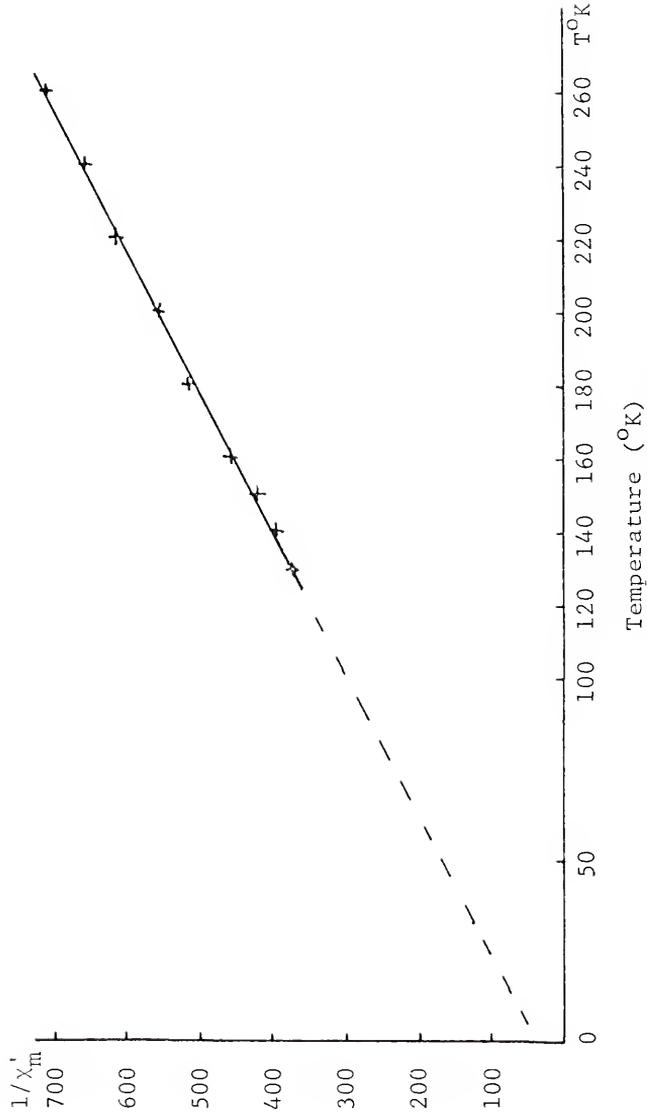


Fig. 22 Temperature dependence of inverse magnetic susceptibility for $\text{Cu}(\text{ketomacr})(\text{NO}_3)_2$.

solution of the complex under study by measuring the shift difference of the nuclei (^1H) of an indicator (\underline{t} -butanol) in two compartments of the nmr tube. A capillary melting point tube was half filled with a 2.99×10^{-6} mole/ml solution of $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ in 2% aqueous \underline{t} -butanol and sealed. This capillary tube was placed in a standard nmr tube which was filled just to the top of the capillary tube with a 2% solution of \underline{t} -butanol. An nmr spectrum was run on a 60 MHz instrument and two resonances due to the shift difference in the methyl protons on the \underline{t} -butanol were observed, one from the unshielded solution of \underline{t} -butanol (outer compartment) and the other (less intense) from the shielded protons (inner compartment). The methyl protons in the inner compartment, shielded by the paramagnetic nickel ion of the complex, were shifted upfield from the unshielded methyl protons of the reference.

The shift difference of the absorption signals of the \underline{t} -butanol protons in the two compartments is related to the volume susceptibility of the two solutions and, therefore, to the molar susceptibility and magnetic moment of the paramagnetic substance in the inner tube. The magnetic moment is related to the shift difference by the equation $\mu = a(\Delta\nu/C^*)^{\frac{1}{2}}$ where $a = 2.522 \times 10^{-4}$ ($\text{mole } ^\circ\text{K}^{-1} \text{ ml}^{-1} \text{ Hz}^{-1}$) $^{\frac{1}{2}}$, T = absolute temperature, C^* = concentration of complex in mole/ml, and $\Delta\nu$ is the frequency difference in Hz of the two signals of the \underline{t} -butanol.

This technique was used with both $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ complexes and the magnetic moments were determined to be 3.88 and 3.74 BM respectively. These values

agree, to within experimental error, with those values obtained by the Gouy method. It is concluded that the paramagnetic center which gives rise to the observed magnetic moment is the same in the solid state and in aqueous solution. Based on the information gathered from the conductance studies, one must discount the presence of a five-coordinate species in solution in which the fifth ligand is a coordinating anion. However, interaction of solvent molecules cannot be discounted. This interaction is considered to be finite because the moments which are the same for both the hydrated solid solution states differ from that of the anhydrous solid.

The room temperature magnetic moments for $\text{Ni}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{aldoketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ were found to be 2.62 and 2.08 BM respectively. Both are considered to be too low for simple high-spin nickel(II) (14,53). Nor are the data presented in keeping with the expected square-planar arrangement about the nickel ion. The majority of square complexes of nickel involving unsaturated ligands containing N-donors are diamagnetic (53). It is difficult to rationalize these intermediate moments. The presence of inequivalent nickel ions, a folded ligand, or a conformational equilibrium of the complex are possible contributors to the unusual magnetic moments. Further investigation is needed; but it was considered to lie beyond the scope of this work.

The room temperature magnetic moments for $\text{Co}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, and $\text{Co}(\text{ketomacr})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were observed to be 2.36, 2.51, and 4.73 BM respectively. Square planar cobalt(II) complexes are not numerous but have been found

to invariably give magnetic moments in the range of 2.1-2.8 BM (53). Tetrahedral complexes of cobalt(II) fall in the range of 4.4-4.8 BM. The room temperature moments for $\text{Co}(\text{ketomacr})\text{-Cl}_2\cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{aldomacr})\text{Cl}_2\cdot 4\text{H}_2\text{O}$ both lie in the range observed for square planar cobalt(II). These moments are too large for a low-spin d^7 ion in an octahedral environment for which the spin-free moment would be 1.73 BM. Thus, these two complexes are considered to be of square planar geometry.

The square planar arrangement about the metal ion has been demonstrated with the ketomacrocylic complex of iron(II) and inferred for cobalt(II) which were prepared by Goedken et al. (25). The crystal structure presented for the iron(II) complex illustrates that the macrocylic ligand lies in a planar arrangement around iron(II) ion as depicted in Fig. 5. However, their complexes are approximately of octahedral geometry because of the two axial ligands present and would not necessarily exhibit the same properties as those complexes prepared in this study. Two types of geometry that could be considered are octahedral and square planar, in which a tetragonal distortion is considered to be an extension of the square planar geometry.

Goedken et al. (25) report the preparation of a low-spin cobalt(II) complex with the ketomacrocylic ligand. This octahedral complex has a reported magnetic moment of 1.83 BM. Unfortunately, Goedken has not reported any additional characterization of the cobalt complex. The magnetic data of the cobalt complexes discussed herein are listed in Table 4 and

the Curie-Weiss plots for $\text{Co}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ are illustrated in Figures 20 and 21.

Spin-free octahedral cobalt(II) complexes customarily have magnetic moments between 4.50 and 5.20 BM and values of θ between -9° and 30° (41, 53). In octahedral complexes one does not observe magnetic moments as low as the "spin-only" moment of 3.89 BM. High-spin octahedral cobalt(II) compounds reflect an unusually large orbital contributions to the magnetic moments. Considerable orbital contribution is seen in $\text{Co}(\text{ketomacr})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ as evidenced by a magnetic moment of 4.73 BM at room temperature. Although this moment is on the low end of the range expected for octahedral or distorted octahedral cobalt(II) complexes (53), the complex is considered to have octahedral geometry.

The magnetic properties of copper(II) complexes fall into two broad classes (57). First, there are those having essentially temperature-independent magnetic moments in the range 1.75-2.20 BM. The complexes exhibiting such moments are mononuclear complexes, i.e., having no major interaction between unpaired electrons in different copper ions. The second class (58), in which the moments are substantially below the spin-only value and markedly temperature-dependent, is composed of complexes in which pairs of copper(II) ions are held close together, usually by carboxylate anions.

The magnetic moments of the macrocyclic copper(II) complexes are listed in Table 4. The temperature-dependence of the magnetic susceptibility of $\text{Cu}(\text{ketomacr})(\text{NO}_3)_2$ was found to follow Curie-Weiss law and is illustrated in Fig. 22. The room temper-

ature moments of all the copper complexes tend to be on the low side of the expected value. The moment reported for $\text{Cu}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ was obtained using the nmr techniques. The use of this method was necessitated by the small quantity of sample available which also precluded obtaining temperature-dependent data for the complex.

Because the moments for the copper complexes are less than expected for spin-free copper(II) ion, it is tempting to incorporate some sort of Cu-Cu interaction which is known (59,60) to reduce the observed moment. This Cu-Cu interaction could be a direct interaction of the copper atoms within the crystal or it could be indirect, i.e., through a bridging atom of the complex such as the N atom. However, there are no data which would lead to the conclusion that the complex is binuclear. Although the Cu-Cu interaction is expected to be more probable in the solid state than in solution, it is the solution moment of $\text{Cu}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ that is smallest ($\mu_{\text{eff}} = 1.19 \text{ BM}$). A clear-cut explanation is not possible with the available data.

Electron Spin Resonance

For an electron of spin $s = \frac{1}{2}$, the spin angular momentum quantum number can have values of $m_s = \pm\frac{1}{2}$, which, in the absence of a magnetic field, leads to a doubly degenerate spin state. When a magnetic field is applied, the degeneracy is resolved as represented in Fig. 23. In an electron spin resonance experiment a transition from the $M'_S = -\frac{1}{2}$ to the $M'_S = +\frac{1}{2}$ state occurs upon absorption of a quantum of radiation. The spectroscopic splitting factor, g , is inversely proportional to the field strength at which the resonance is observed, i.e., $E = g\beta H$, where H is the field strength and β is the Bohr magneton. For

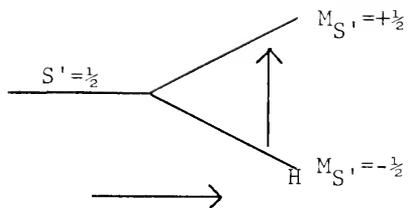


Fig. 23a Splitting diagram for a single electron.

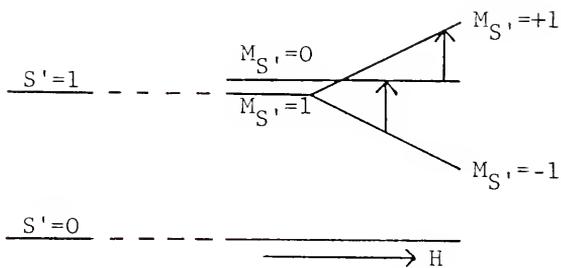


Fig. 23b Zero-field splitting diagram.

a free electron g has the value of 2.0023. In general, the magnitude of g depends upon the orientation of the molecule containing the unpaired electron with respect to the magnetic field (61) and the spin and orbital angular momenta.

The electron spin resonance spectra were obtained for the nickel complexes at liquid nitrogen temperatures (77°K). The esr data are listed in Table 10. The room temperature spectra were attempted but no resonances were observed. The spectra of $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ both showed a single, very broad and unsymmetric resonance approximately 5000 gauss wide. Indeed, it is so broad that no g value can be determined. The spectra of $\text{Ni}(\text{aldoketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ also gave extremely broad spectra but with a relatively narrow resonance superimposed upon the broad absorption at g values of 2.00 and 1.99, respectively. In hexaaquonickel(II), it is found experimentally that $g = 2,25$ (61). The difference from a g value of 2.00 is attributed to spin-orbit coupling. The broad resonances are typical of most nickel(II) complexes (62, 63).

The esr spectra of the cobalt complexes were obtained at both room temperature and liquid nitrogen temperature. The g values, listed in Table 10, fall in the range of 2.0 to 2.2. The spectrum of $\text{Co}(\text{ketomacr})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (the only high-spin complex prepared) at liquid nitrogen temperatures contains an eight-line hyperfine structure with coupling constants of about 78 gauss. Such hyperfine structure can be ascribed to the interaction of unpaired electrons with the cobalt ion nucleus (62, 64) which possesses a nuclear spin of 7/2.

Table 10. ESR data

Compound	g (RT)	LW(gauss)	g (77°K)	LW(gauss)
Ni(aldomacr)Cl ₂ ·4H ₂ O	---	---	1.996	30
Ni(aldoketomacr)Cl ₂ ·4H ₂ O	---	---	2.000	1100
Ni(ketomacr)Cl ₂ ·4H ₂ O	---	---	---	--
Ni(ketomacr)(NO ₃) ₂ ·6H ₂ O	---	---	---	--
Co(aldomacr)Cl ₂ ·4H ₂ O	2.000	35	2.001	25
Co(ketomacr)Cl ₂ ·4H ₂ O	2.003 2.186	25 300	2.206	275
Co(ketomacr)(NO ₃) ₂ ·4H ₂ O	2.204	375	2.221*	550
Cu(aldomacr)Cl ₂ ·4H ₂ O	2.101	260	2.099	160
Cu(aldoketomacr)Cl ₂ ·2H ₂ O	2.126	195	2.199	150
Cu(ketomacr)(NO ₃) ₂	2.078	170	2.078	140

LW = line width

*center of gravity of 8 line hyperfine split.

Low-spin cobalt(II) complexes with planar, four N or two N and two O, coordinating ligands show esr spectra with g_{\parallel} values of 2.0 and g_{\perp} values of 2.2-2.9 (65). The spectrum of cobalt(II) ion in the cubic field of a MgO host lattice has been analyzed by Low (66) and by Bleaney and Hayes (67). The results showed a g value of 4.2. No g_{\perp} value near 4.0 was observed for any of the macrocyclic complexes. The spectra, similar to those of the nickel complexes, had narrow resonances superimposed upon a very broad resonance; therefore, it was not possible to ascertain the g value for the broader absorptions. Presumably this broadening arose from a decrease in the spin-lattice relaxation time which accompanies either an increase in temperature or an increase in orbital contribution to the magnetic susceptibility (68).

Although, based upon the esr spectra data, little insight can be gained concerning the structure of the nickel and cobalt complexes, the esr spectra of the copper complexes were more ideal. Single resonances were observed at g values of approximately 2.1 at room and liquid nitrogen temperatures. The spectra exhibited level base lines. The g values listed in Table 10 are typical of both octahedral and planar copper(II) complexes (57, 69, 70).

It is noted that for the nickel complexes which exhibit the large magnetic moments no esr signal was observed. For those having the smaller magnetic moments an esr signal was observed. Thus, there must be two different types of nickel in these complexes.

Ligands

Standard procedures were followed (2, 10, 19, 27) in attempting to synthesize the uncoordinated ketomacrocycle and aldolmacrocycle by direct reaction of precursors. The procedure presented in the experimental section is to be considered representative of a number of attempted syntheses. The attempted syntheses of the ketomacrocycle differed according to changes in the variables related to solvent, catalyst, reactant ratios, and concentrations of the reactants.

The solvents used were: 95% ethanol, methanol, n-butanol, acetone, and 2,2-dimethoxypropane was chosen to effect the removal of H₂O produced by the Schiff base condensation thus enhancing the condensation.

Schiff base condensations are frequently acid catalyzed; thus, it was expected that a few drops of a strong acid would be needed to promote the condensation reaction. None the less, one attempt was made to prepare the macrocyclic ligand in the absence of added acid to decrease the number of system components. For each solvent system employed, the solutions of reactants were colorless as, subsequently, were the combined solutions. And no solid was produced. Because acyclic aldazines are known to be yellow in color (71) and the expected oligomeric or macrocyclic products sparingly soluble (59), it was concluded that no desired condensation had occurred. But, if a few drops of either concentrated sulfuric acid or concentrated hydrochloric acid were added as catalyst to the reaction mixture of DAP, the reaction mixture became yellow as the addition of the solution of DAP proceeded: upon refluxing for several hours, a yellow

solid began to form. The appearance of the yellow product was the same whether sulfuric or hydrochloric acid was used as evidenced by similar infrared spectra.

Other attempts to alter the condensation reaction included changing of both the mole ratios of DAP to DAPH, by adding a solution of DAPH to an excess of DAP, and the concentrations of reactant solutions within the range of 10^{-3} to 10^{-6} M (to prevent or, at least, to minimize the formation of oligomers). However, these variations proved to be ineffective as were all of the previous attempts, i.e., each preparation resulted in the formation of the same lemon-yellow solid as evidenced by their insolubility in numerous organic solvents, their relatively high melting point ($>300^{\circ}\text{C}$), and the elemental analysis which are inconsistent with those expected for the macrocyclic products.

Attempts were made to separate ketomacrocyclic from the yellow solids described above. These attempts, motivated by mass spectral data (vide infra), included sublimation and an in situ reaction of the oligomeric solid with nickel(II) chloride. It was impossible to recrystallize any of the yellow solids formed since none was soluble in any of the solvents used even though differences in solubility have been reported for at least one macrocycle (TMCD) and an oligomeric side product (59). Attempted sublimation of the various condensates was unsuccessful, i.e., no solid was collected on the cold finger of the sublimator although the temperature was slowly

raised to 230°C and the pressure was reduced to 10^{-5} torr.

It would be reasonable to expect Ni(II) ion to preferentially complex with the oligomeric condensate rather than the macrocycle. As discussed previously in the Introduction, a step-wise replacement of coordinated solvent molecules on the Ni(II) ion is possible with non-cyclized ligands similar to the oligomeric condensate; whereas, reaction of Ni(II) ion with the macrocycle would require that all of the solvent molecules of the Ni(II) ion be removed prior to coordination so that the Ni(II) ion would "fit" into the central hole of the macrocycle. The step-wise process has a smaller entropy requirement associated with it than does the latter process, thus making energy requirements smaller for the step-wise reaction. If the condensate were more soluble than the macrocycle, the step-wise complexation reaction could occur without any competition from the macrocycle. On the other hand, if the macrocycle were the more soluble, the activation energy requirements might be too large for the Ni(II) ion to react directly with the macrocycle regardless of solubility. Thus, this technique might also be ineffective in removing or separating the free ketomacrocycle.

The attempt to remove any free ketomacrocycle from the yellow condensate by reacting the yellow product in situ with a refluxing ethanolic solution of nickel(II) chloride also proved to be ineffective, as evidenced by the lack of any color change of the mixture. Experience has shown that formation of $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ is associated with a color change of yellow-green to a dark green or brown-green color. The yellow condensate was still suspended in the yellow-green solution

of nickel(II) chloride and ethanol. It is concluded that neither the oligomeric condensate nor the ketomacrocycle complexed with the Ni(II) ion.

To provide direction in the preparation and isolation of the free macrocycle the yellow products produced were characterized by mass spectra, infrared spectra, and elemental analysis.

Mass spectral data for the product isolated in the attempted synthesis of the ketomacrocycle, obtained under relatively extreme conditions, are contained in Table A-6 of the Appendix. It was difficult to obtain a good mass spectrum; the probe temperature had to be set at its maximum of 350°C to achieve reasonable intensity, attesting to the stability and nonvolatile nature of this product.

The peak corresponding to the greatest mass was weak (m/e equal 624; relative intensity of 1.5%); its mass was ca. twice the mass of the desired macrocycle. This peak could correspond to a condensate consisting of four units of DAP to three units of hydrazine. A weak peak corresponding to the parent ion was observed at m/e 318. Although the presence of this peak would normally lead one to expect that some of the free ketomacrocycle was present in the sample, little credence was placed in this peak because the mass spectrum had the general appearance of a "picket fence" and about any peak $m/e \leq 479$ could be found. Peaks of lesser m/e could correspond to fragments of the particle that gives rise to the peak m/e 624. A systematic cracking pattern can be followed by

beginning at the larger values of m/e and proceeding to the lesser values of m/e . This cracking pattern can be achieved by subtracting appropriate atoms and/or groups to form the next fragment.

The infrared spectra of the condensate, DAP, and DAPH are presented in Fig. 24. In general the spectrum of the condensate had the appearance of a composite of the spectra of DAP and DAPH with the major exceptions of the C=O and N-H vibrations. The spectrum contained characteristic absorptions at 1700 and 1610 cm^{-1} which were assigned to a carbonyl stretching vibration and an acyclic C=N stretching vibration, respectively (44, 47). The presence of the carbonyl band was not unexpected because other evidence indicated that not all of the product was macrocycle. The relative intensity of the C=O absorption is less than that observed in the spectrum of DAP which is consistent with a terminal carbonyl. The high energy band associated with the ring vibrations (Band I-ring) is absent in the spectra DAP and DAPH but can be found in the spectra of PDC and PDCH at 1580 cm^{-1} . Because of the numerous bands between 1580 and 1200 cm^{-1} , there was no attempt to make these assignments.

The spectrum of the condensate lacked the absorptions at 3300 and 3150 cm^{-1} observed in the spectrum of DAPH and assigned to the antisymmetric and symmetric stretching vibrations of the NH_2 group. Nor was the NH_2 deformation mode, observed at 1640 cm^{-1} in the spectrum of DAPH present in the spectrum

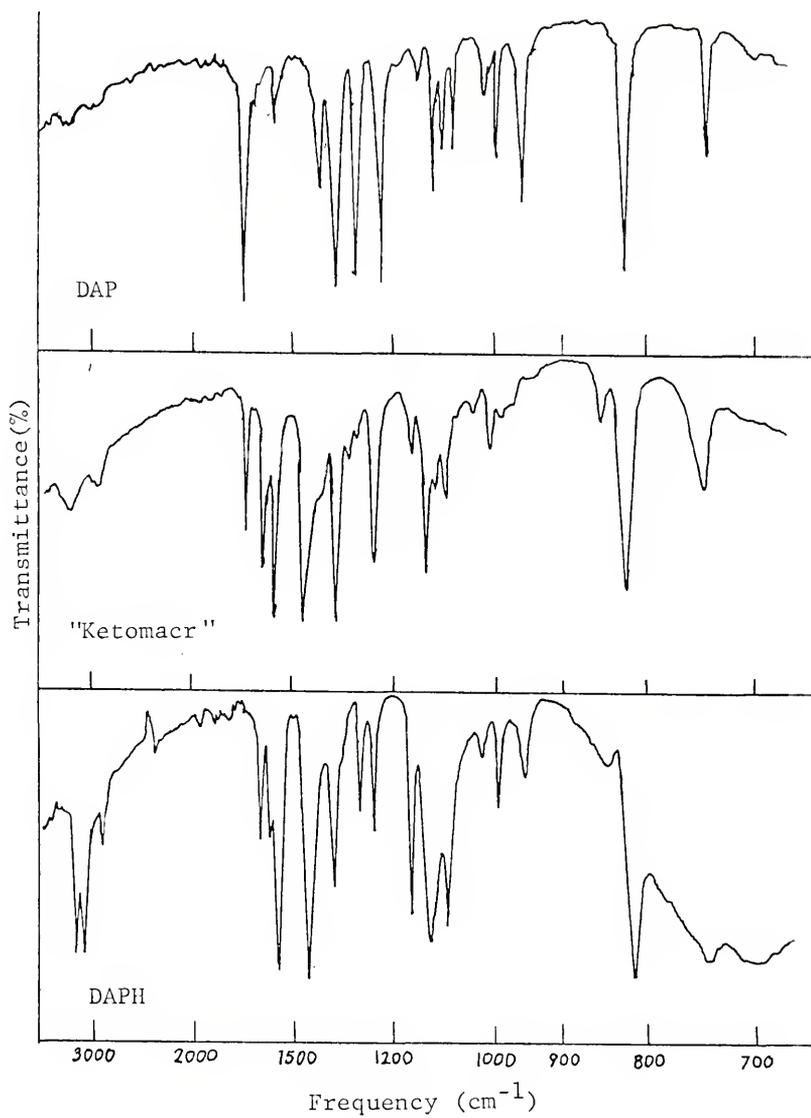


Fig. 24 Infrared spectra of "ketomacr" and its precursors.

of the condensate. The absorptions present at 1560, 1450, and 1425 cm^{-1} generally can be assigned to ring vibrations. The assignment of absorptions are presented in Table A-4 of the Appendix.

It is concluded on the basis of the infrared spectral data that the yellow solid is an acyclic product, terminated on at least one end with a carbonyl function. The presence of any unreacted DAP in the product is precluded by the good solubility of DAP in the solvents that were used to wash the product. Therefore, any similarities in the spectrum of the condensate to that of DAP must be assigned to functional groups bound to the product, a conclusion consistent with the mass spectra data.

The sum of the weight percentages of C, H, and N from the elemental analysis is 98%. The 2% difference is attributed to the presence of oxygen arising either from the oxygen in water or the oxygen of a carbonyl group. Based upon the infrared spectrum, it is proposed that the oxygen is a carbonyl oxygen. Also, since the product was dried in vacuo over P_4O_{10} for 24 hours at 100°C prior to analysis and no gain in weight was observed when the solid was allowed to stand overnight in atmospheric moisture, it is unlikely that any water was present prior to the analysis. The CHN ratio approximates a moiety containing a linear arrangement of two units of macrocycle terminated on one end by a carbonyl, i.e., $\text{C}_{36}\text{H}_{36}\text{N}_{12}\text{O}$, (Calcd: C, 66.24; H, 5.56; N, 25.75. Found: C, 66.56; H, 5.91; N, 25.52). Thus it is concluded, on the basis of mass spectral data, infrared data, and elemental analysis, that oligomerization occurred instead of the desired cyclization.

Because all of the attempts to prepare the ketomacrocycle were unsuccessful, alternate methods were considered. The most logical alternative was to separate the free base from a complex of the ketomacrocylic ligand (vide infra). The complex $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ was chosen as the reactant species because the complex is the most easily prepared of all the other complexes and is reasonably soluble in polar solvents. Methods which might be expected to remove the Ni(II) ion from the macrocycle would include: electrochemical reduction of the metal, chemical reduction of the metal, precipitation of Ni(II) ion with sulfide ion or complexation of Ni(II) ion with cyanide ion (16).

Before alternate methods of preparation of the free ketomacrocycle were considered, it was necessary to settle the question: "Why bother with preparing free ligand when the complexes are easier to prepare?" The evidence for the preparation of the macrocylic complexes is good (vide supra), but more information might be gained about metal-donor interactions, for example, if the free ligand were available for comparison studies. It would also be informative to be able to prepare the complexes from two different synthetic routes and compare the products. The ligand would, of course, be fully characterized and possibly reveal properties suggesting further study.

To assess the optimum conditions for electrochemical reduction, a polarogram of $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ was taken. It was anticipated that electrochemical reduction would preferentially reduce the metal within the complex allowing the metal

to "pop" out of the central hole of macrocycle. Indeed, it was also anticipated that the polarogram might give some information about the coordinated macrocycle itself. The Sargent Model XVI Polarograph employed had the capability to measure current changes within the voltage range of ± 3 volts using a saturated calomel electrode as the reference electrode. After obtaining a half-wave potential, $E_{1/2}$, of -12.5 volts of a standard 0.01 M solution of Ni(II) ion [lit. (72) $E_{1/2} = -1.1$ volts] in 1.0 M KCl solution, the polarogram of the complex was attempted. Various voltage settings, concentrations of complex (10^{-2} to 10^{-5} M), and type of supporting electrolyte were tried. However, no polarographic wave of any kind, except that of the supporting electrolyte, could be observed for the several solutions of the complex. It was concluded that the complex was too stable, i.e., the voltage range of the instrument was not sufficiently large. It is known (73) that the half-wave potential for the reduction of a metal complex is generally more negative than that for the corresponding simple metal ion. Thus, it would be anticipated that a more negative potential would be required to reduce the metal from the complex than could be achieved by the polarograph.

A mercury cathode cell described in the Experimental section was used in the subsequent attempt to reduce the complexed Ni(II) ion under more stringent conditions using electrolysis. This particular cell was chosen because of two factors (42). Many metals depositing on mercury can form an alloy (amalgam) with the mercury. The deposition potentials of these metals

on the mercury are now displaced from their value in the positive direction with respect to reduction potentials. The deposition is also aided by the fact that the hydrogen over-voltage on mercury is particularly large.

A saturated solution, 10^{-2} M, containing suspended solid of $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ together with a supporting electrolyte to 0.1 M sodium perchlorate was placed in the cell. A potential was applied to the cell but no reaction was observed until the potential was increased to 3.0 volts at which point gas evolution was observed at both the platinum and mercury electrodes. Increasing the potential to 20.0 volts only served to increase, linearly, the current from 0.00 to 1.00 amp. Most of the suspended solid rose to the top of the cell because of the stirring action of the bubbles.

Even though it was concluded that no reduction had taken place, a control experiment was performed to provide additional basis for this conclusion. Accordingly, a solution of 0.1 M sodium perchlorate, the supporting electrolyte, was electrolyzed in an identical manner. No current flow was observed until the potential had been increased to 3.0 volts; at 5.0 volts both solutions, the control and complex, had a corresponding current of 0.15 amp passing through them. A solution containing 0.02 M Ni(II) ion in 0.1 M NaClO_4 deposited metallic nickel on the mercury electrode at 3.0 volts (current 0.05 amp) as evidenced by a blackish coloration of the mercury pool. Gas evolution was noted at 3.0 volts in all three cases. Had there

been any reductive processes occurring at the mercury cathode before or after the reduction of water began, a non-linear increase in current would have been observed. Since no such increase was observed in comparing the electrolysis of the supporting electrolyte to that of the electrolysis of the complex, it is concluded that no reduction of Ni(II) ion out of the complex was achieved and that only water was electrolyzed to H_2 and O_2 .

Chemical reduction of the metal from the macrocycle was attempted using sodium-potassium alloy. The sodium-potassium alloy has been used as a rich source of electrons for reactions requiring a powerful reducing agent (74), e.g., reduction of bis(trimethylamine)-boronium iodide in 1,2-dimethoxyethane to produce 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diborallocyclopentane ($B_2N_2C_5H_{18}$). The utility of this alloy is enhanced because it is a liquid at room temperature when prepared as a mixture of 25% sodium and 75% potassium by weight. The use of the alloy as a source of electrons is known (75); but, the alloy is not widely used because of its high reactivity toward any easily reduced material. It was expected that solvated electrons might reduce the complexed Ni(II) ion of the macrocycle and, thereby, promote its removal from the complex. Alternatively, the ligand could be reduced preferentially allowing the reduced form of the macrocycle to be more easily separated from the metal ion. The application of the alloy for such a purpose as this was considered to be both novel and reasonable.

The sodium-potassium alloy, when added to and stirred vigorously with monoglyme under N_2 , produces a system of solvated electrons as evidenced by the blue color of the solution; however, upon cessation of stirring, the blue color is lost within a few seconds. Thus, while a solution is stirred there is good contact of "free" electrons with any material that would be present in the solvent.

In the application of this technique, a one-half gram sample of the sodium-potassium alloy (equivalent to 15 mmoles of electrons) was added under N_2 to a 25 ml yellow-green monoglyme suspension containing 0.5 g (1.0 mmole) $Ni(ketomacr) \cdot 4H_2O$. Vigorous stirring with a glass-encased magnetic stir-bar caused the suspension to become blue-green in color. No change in color was noted after seven hours of stirring; the mercury-like alloy was still present. The reaction was decanted off the alloy leaving a yellow-green suspension of the macrocyclic complex in monoglyme. The yellow-green suspension was filtered under N_2 . The clear, colorless filtrate was evaporated under a stream of N_2 ; but, no residue formed. The green solid collected on the filter was washed several times with diethyl ether and the combined washings evaporated; no non-volatile product remained. Because neither nickel(II) chloride (anhydrous or hydrated) nor the oligomeric condensate are soluble in monoglyme or ether, the separation of the free ligand was dependent upon its solubility in these solvents. The ligand is expected to be yellow in color and since no increase in yellow color was noted in the suspension

after the alloy had been removed, it is concluded that no free ligand was produced. However, the lack of solubility of the free macrocycle may be the reason that none was separated. It must be noted, however, that the macrocyclic complex itself was still intact, suggesting significant stability to a highly reducing environment.

The attempt to remove Ni(II) ion from $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ by precipitation was carried out by bubbling hydrogen sulfide into 20 ml of a 0.01 M solution of the complex in absolute ethanol to which had been added one milliliter of concentrated ammonia. A color change of transparent green to an opaque black was observed within ca. 30 seconds of the introduction of H_2S into the solution of complex. No color change had been observed with the addition of ammonia. The solution was filtered and a black solid was recovered. The brown filtrate was acidified with several drops of hydrochloric acid, the solution turned green and the solvent was removed with a stream of N_2 . As the solution became more concentrated, it became deep in color and finally a grey-green solid containing NH_4Cl and an unknown product remained. The grey-green solid was washed with ether and the combined washings evaporated under a stream of N_2 . After removal of solvent no non-volatile residue remained. Here again the free ketomacrocycle was assumed to be soluble in ether and ethanol. Water was added to the grey-green solid which dissolved completely, the resulting solution having the appearance of a solution of the original complex.

A solution of nickel(II) chloride was treated in the manner described above. A black precipitate of NiS formed and was filtered. The filtrate was colorless and the black precipitate was insoluble in concentrated hydrochloric acid. The differences in the results of the complex and NiCl₂ solutions indicate that the black solid produced from the complex solution was a sulfide or hydrogen sulfide adduct of the complex which was more insoluble than the chloride salt in ethanol but which was soluble in concentrated hydrochloric acid. Because NiS is insoluble ($K_{sp}=1.4 \times 10^{-24}$ (76)), it was expected that any NiS formed would be in the precipitate and insoluble in strong acid but none was recovered.

Less effort was expended in attempts to prepare the aldomacrocycle because the availability of the precursors PDC and PDCH was limited. Only the preparation discussed in the Experimental section of this work was attempted.

The results of the attempt to prepare the aldomacrocycle by direct synthesis were similar to those of the ketomacrocycle. So similar that a repetition of the previous work with the ketomacrocycle was expected so there was no need to pursue any extensive work-up of the aldomacrocycle. The Schiff base condensation of PDC with PDCH produced a yellow solid, insoluble in various organic solvents, of melting point greater than 300°C, and giving elemental analysis inconsistent with the expected macrocyclic product.

Attempts to isolate the pure aldomacrocycle from the yellow

condensate were carried out under the same condition as were those of the ketomacrocycle. Sublimation produced no product on the cold finger of the sublimator and an in situ reaction of NiCl_2 in ethanol with the condensate produced no complex.

The infrared spectra of the condensate, PDC, and PDCH are presented in Fig. 25. The general appearance of the spectrum of the condensate is that of a composite of the spectra of PDC and PDCH and has the same general features of the spectrum of the ketomacrocycle except where noted. The carbonyl stretching vibration is present at 1730 cm^{-1} but is very weak compared to that found in the spectrum of the ketomacrocycle. The acyclic C=N stretching vibration is assigned to the absorption at 1590 cm^{-1} . A comparison of absorption and assignments made can be found in Table A-5 of the Appendix.

The mass spectral data of the aldomacrocycle are presented in Table A-7 of the Appendix. A probe temperature of 340°C was necessary to achieve a resolved spectrum. The highest observed peak was m/e 338 (relative intensity of 0.1%). The peak corresponding to the parent ion was weak ($m/e = 262$; relative intensity - 0.3%). The general appearance of the mass spectrum is such that any peak below 282 m/e can be found.

The sum of the weight percentages of the C, H, and N from the elemental analysis equaled 95.88%. The 4.12% difference is attributed to the presence of oxygen. The CHNO ratios were calculated to be $\text{C}_{20}\text{H}_{16}\text{N}_8\text{O}$. It is not possible to formulate a product which would conform to a reasonable compound based on the empirical formula.

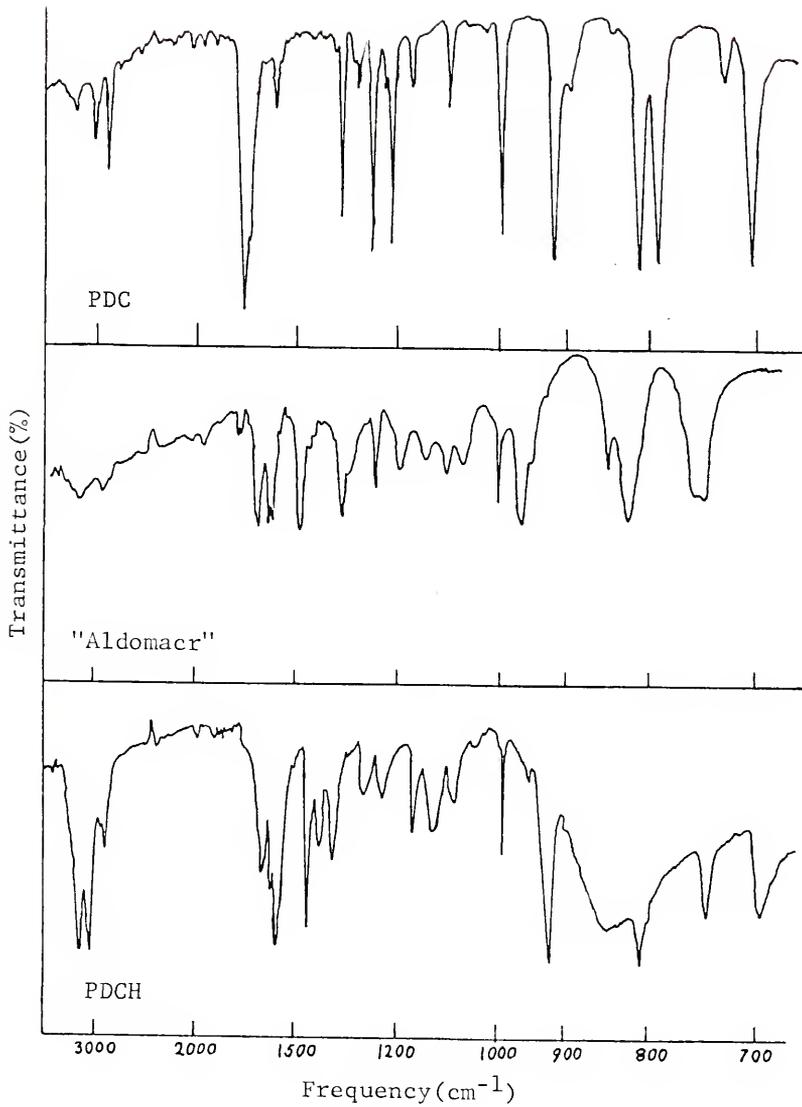


Fig. 25 Infrared spectra of "aldomacr" and its precursors.

As in the case of the ketomacrocycle, based upon infrared spectra, mass spectra data, elemental analysis, and the results of the attempts to isolate the free aldmacrocycle, it is suggested that for the aldmacrocycle no cyclization of the macrocycle occurred and that some type of oligomer was formed.

SUMMARY

The preparation of ten macrocyclic complexes of Co(II), Ni(II), and Cu(II) was accomplished by the Schiff base condensation of either DAP or PDC with either DAPH or PDCH in the presence of the appropriate metal salt. Preparation of the free ligands and attempts to isolate free macrocyclic base from the complexes were unsuccessful. Attempts to prepare the free ligands by direct synthesis resulted in oligomerization with the possible formation of the macrocycle as a very minor product -- as evidenced by mass spectral data.

The complexes prepared were characterized by elemental analysis, infrared, ultraviolet, visible and electron spin resonance spectra, conductance and magnetic susceptibility determinations.

The infrared spectra, although providing evidence for the formation of Schiff base linkages as well as for the disappearance of amine and carbonyl groups, are not totally definitive. A number of assignments have been made, however.

The electronic spectrum of each of these complexes contained one characteristic absorption in the ultraviolet region attributable to the aromatic, heterocyclic base. In contrast, the visible region of the spectrum contained no characteristic absorptions even though the majority of the

complexes absorbed so strongly in this region that the d-d transitions which might have been present would have been masked.

The esr and average magnetic susceptibility data, taken in conjunction with those obtained from other kinds of measurements, provide evidence of low-spin cobalt(II) species and of inequivalent nickel ions in some of the complexes prepared. In general, the complexes are considered to be essentially square planar with sufficient axial interaction by solvent (e.g., water) to produce a distorted octahedral symmetry in a certain few of the complexes. Above normal room temperature magnetic moments were observed for $\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Subnormal moments were observed for $\text{Cu}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{aldoketomacr})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. Temperature-dependent magnetic susceptibility data were obtained and normal Curie-Weiss plots were observed. The above normal magnetic moments were reduced by 0.5 BM upon drying the complexes, demonstrating significant effect of water molecules upon the paramagnetic center.

Conductance data were interpreted to indicate the existence of dipositive macrocyclic cations and uninegative anions in aqueous solution: they preclude coordination of the anions to the metal ions.

The results of these investigations support the formulation of each of the complexes as a metal ion surrounded by a planar, quadridentate ligand with water either loosely held in the axial positions or present as part of the crystal lattice. Thus, the data provide strong support for the conclusion that the

macrocyclic complexes sought were actually prepared.

APPENDIX

Table A-1. Selected Infrared absorption bands (cm^{-1}) for Ni(II) macrocyclic complexes.

Assignment	$[\text{Ni}(\text{ketomacr})(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$	$[\text{Ni}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}]$
H_2O	3450-3100b	3350-3100
?	1640(sh)	--
?	1625(sh)	1630w
C=N st (acyclic)	1600(sh)	--
Bond(I) ring	1580s	1590s
Bond(II) ring	1540(sh)	1540s
?	1530m	--
?	--	1460s
NO_3^- st	1400-1350s(b)	--
?	1220m	1210m
CH d or ring	1185m	1170m
?	1080m	1085s
?	1035m	1035w
CH d	815s	810m
?	750w(sh)	750w
?	740w	740w(sh)

Table A-1 Continued

Assignment	[Ni(aldoketomacr)Cl ₂ ·4H ₂ O]	[Ni(aldomacr)Cl ₂ ·4H ₂ O]
H ₂ O	3300b	3350b
?	1650(sh)	1650(sh)
?	1625(sh)	1620s
C=N st (acyclic)	1600(sh)	1610s
Bond(I) ring	1590s	1580w
Bond(II) ring	1550(sh)	1550(sh)
?	-- (sh)	1530(sh)
?	1480m	1470m
NO ₃ ⁻ st	--	--
?	--	1220w
CH d or ring	1180m(b)	1160m(b)
?	1085m	1080w
?	1040m	1035w
CH d	820m(b)	820w
?	--	755w
?	--	--

(st = stretch, d = deformation, s = strong, w = weak,
m = medium, sh = shoulder, b = broad.)

Table A-2. Selected infrared absorption bands (cm^{-1}) for Co(II) macrocyclic complexes.			
Assignment	$\text{Co}(\text{aldomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	$\text{Co}(\text{ketomacr})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	$\text{Co}(\text{ketomacr})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
H_2O	3300	3350	3150
	3000(sh)	3050(sh)	
C=N st (acyclic)	1650	1650	1645
Band I (ring)	1575	1580	1600
?	1460	1460	1550
NO_3^-	--	--	1450(sh)
?	1360	1360	1380
?	1320	--	--
?	1280	--	1320
?	--	--	1280(sh)
CH d	1170	1260	--
Ring	--	--	1160
?	1040	1090	1090
			1050

Table A-2 Continued

Assignment	Co(aldomacr)Cl ₂ ·4H ₂ O	Co(ketomacr)Cl ₂ ·4H ₂ O	Co(ketomacr)(NO ₃)·4H ₂ O
?	930	--	920
CH d	810	820	810
?	760	760	760

(st = stretch, d = deformation, s = strong, w = weak, m = medium, sh = shoulder,
b = broad)

Table A-3. Selected infrared absorption bands (cm^{-1}) for Cu(II) macrocyclic complexes.

Assignment	Cu(aldomacr) $\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	Cu(aldoketomacr) $\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	Cu(ketomacr) $(\text{NO}_3)_2$
H_2O	3350s	3350s	3400m
	3000s	3000s	3000m
?	1640	1640	1640
C=N st (acyclic)	1590	1595	1580
Band I (ring)	1560(sh)	1560(sh)	1565(sh)
?	1450	1440	1450
NO_3^-	--	--	1380
?	1360	1360	1350(sh)
?	--	1320(sh)	--
?	1275	1270	1265
Ch d or Ring	1165	1165	1170
?	1090	1085	--
?	1040	1030	1020
?	995(sh)	995	995(sh)

Table A-3 Continued

Assignment	Cu(aldomacr)Cl ₂ ·4H ₂ O	Cu(aldoketomacr)Cl ₂ ·2H ₂ O	Cu(ketomacr)(NO ₃) ₂
Ch d	820	815	820
?	765	--	765
?	700	700	700

(st = stretch, d = deformation, s = strong, w = weak, m = medium, sh = shoulder,
b = broad)

Table A-4. Selected infrared absorption bands (cm^{-1}) for "ketomacr" and its precursors.

Assignment	DAP	DAPH	"Ketomacr"
NH_2 st-a	--	3300	--
NH_2 st-sym	--	3150	--
CH st	--	2850	2900
C=O st	1700	--	1700
NH_2 d	--	1640	--
C=N st (acyclic)	--	1595	1610
Band II (ring)	1570	1570	1560
Band III (ring)	1430	1450	1450
Band IV (ring)	1405	1425(sh)	1425(sh)
CH or Ring	--	1160	1150
CH d	820	810	820

(st = stretch, st-a = antisymmetric stretch,
d = deformation, s = strong, m = medium, w = weak,
sh = shoulder)

Table A-5. Selected infrared absorption bands (cm⁻¹) for "aldomacr" and its precursors.

Assignment	PDC	PDCH	"Aldomacr"
NH ₂ st-asym	--	3250m	--
NH ₂ st-asym	--	3100m	--
	3010m	--	--
CH st	2980sh	2890w	2950w(b)
	2810m	--	--
C=O st	1720	--	1740
	1695sh	--	1720
NH ₂ d	--	1640m	1640
C=N st (acyclic)	--	1600m	1590m
Band I (ring)	1580m	1580vs	1560
Band II (ring)	1560sh	1560sh	1535sh
Band III (ring)	--	1460vs	1480
Band IV (ring)	--	1420m	--
CH d	1165m	1160m	1165m
CH d	810s	810m	815s
CH d	790	--	--

(st = stretch, st-asym = antisymmetric stretch,
d = deformation, s = strong, m = medium, w = weak,
sh = shoulder)

Table A-6. Mass spectral cracking pattern for the condensate of DAP and DAPH

m/e	% relative intensity	Fragment
624	1.5	$-(C-(CH_3)-py-C-(CH_3)N_2)_3-C(CH_3)py$
477	1.4	$(NC-py-CN)_3-C(CH_3)O$
465	3.6	624 or less $C-(CH_3)-py-C(CH_3)N_2$
449	4.8	465 less 0
437	1.7	
423	1.7	
406	1.3	
394	1.0	
379	1.0	
360	3.6	$O[(CH_3)C-py-C(CH_3)N_2]_2-C(CH_3)$
344	2.5	
331	1.5	
318	3.2	Parent ion
319	15.	
306	36.	360 less $N_2C(CH_3)$
291	19.	306 less CH_3
278	16.	
263	16.	
250	10.	
235	7.8	
221	6.6	
201	18.	
188	6.5	
173	17.6	
162	23.	$NC(CH_3)-py-C(CH_3)N$
146	36.	
131	27.	
121	100.	$py-C(CH_3)O$
104	73	

Table A-6 Continued

m/e	% relative intensity	Fragment
93	55.	
72	64.	
65	27.	
52	40.	C-N-N-C
42	90	
28	73	

Only m/e peaks of relative intensity greater than 10% were reported except where noted.

Spectrum run at 70eV and 350°C.

Table A-7. Mass spectral cracking pattern for the condensate of PDC and PDCH.

m/e	% relative intensity	Fragment
339	0.1	HC[-py-C(H)N ₂ -CH] ₂ -py-CH
326	0.1	339 less CH
311	0.2	
295	0.2	
280	0.2	
266	1.2	
264	1.2	235 plus HCO
262	0.3	339 less py-CH
249	1.0	
248	0.7	235 plus CH
238	2.2	
236	3.3	
235	2.5	NC(H)-py-C(H)N ₂ -C(H)-py
232	7.3	
221	5.4	235 less N
208	2.4	
206	3.1	
194	1.5	
181	2.0	
164	2.1	
154	3.3	
144	3.2	
135	23.7	NC(H)-py-C(H)O
133	11.6	
129	12.9	N-C-py-C-N
113	10.0	
107	14.2	
106	36.5	
105	25.9	

Table A-7 Continued

m/e	% relative intensity	Fragment
104	69.4	
103	36.4	HC-py-CH
101	17.4	
93	11.5	
91	13.9	
79	30.6	
78	26.2	
77	40.0	py = C ₅ H ₃ N
76	24.0	
75	33.1	
65	12.0	
64	13.9	
63	10.9	
53	10.7	
52	30.1	
51	29.1	
50	19.7	
47	30.8	
45	10.1	
44	100.	

Only m/e peaks of relative intensity greater than 10% were reported except where noted.

Spectrum run at 70 eV and 340°C.

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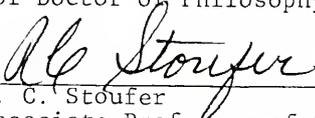
BIOGRAPHICAL SKETCH

Frederick Felder Myers, Jr. was born June 4, 1948 at Hattiesburg, Mississippi. In May, 1966 he was graduated from New Augusta High School in New Augusta, Mississippi. In May, 1970 he was awarded the degree of Bachelor of Science from Mississippi State University with a major in chemistry. In September of 1970, he enrolled in the Graduate School of the University of Florida. He worked as a graduate assistant in the Department of Chemistry until June, 1975. In June, 1972 he received his commission as a Second Lieutenant in the United States Air Force through the ROTC program at the University of Florida.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



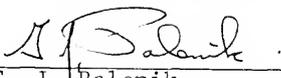
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December, 1975



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