AN INVESTIGATION OF THE NICKEL(II) AND COBALT(II) COMPLEXES EMPLOYING PENTADENTATE LIGANDS DERIVED FROM SALICYLALDEHYDE AND BIS(3,3'-AMINOPROPYL)ETHER OR SULFIDE

by

Anne King St. Clair

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APPROVED:

Chairman: Dr. Larry T. Taylor

Dr. James P. Wightman

Dr. Michael A. Ogliaruso

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This thesis is dedicated to the memory of my father

Otis Gardner King, Sr.
M.D.

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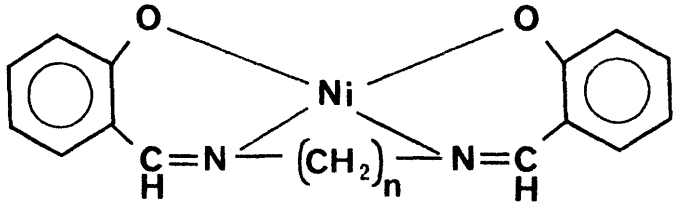
INTRODUCTION

In recent years, particular interest has been shown in the fields of coordination and bioinorganic chemistry concerning the transition metal ions nickel(II) and cobalt(II). Special attention has been given to complexes formed by the combination of these ions with linear polydentate Schiff base ligands. Many of the nickel(II) complexes have proved to be stereochemically interconvertible from the solid state to solution and some have been shown to be magnetically "anomalous."[1] The cobalt(II) complexes have been recognized as excellent oxygen carriers and models for vitamin B_{12} coenzyme[2] -- a compound of great necessity to the human body even though its biological and chemical roles are not understood. The purpose of this thesis is to examine some complexes of nickel(II) and cobalt(II) derived from potentially pentadentate ligands made from substituted salicylaldehydes and bis(3,3'-aminopropyl)ether or sulfide. Physical and chemical properties of these coordination compounds have been studied.

HISTORICAL

The coordination number of divalent nickel varies depending upon the surrounding ligands. The metal ion has a $3d^8$ valence electron configuration and is known to form compounds of square planar, tetrahedral, square pyramid, trigonal bipyramid and octahedral geometry.[3] The most common configuration of quadricoordinate Ni(II) is the square planar form. Of special interest are complexes of the type Ni-O_2N_2 derived from Schiff bases of salicylaldehyde[4] and diamines. These complexes have shown to be particularly representative of an intermediate situation in which there is a distribution between spin-free and spin-paired forms dependent upon the field strength produced by the four donor ligands. Holm[5] has conducted a study of the spectral and magnetic properties of some Ni-O_2N_2 compounds with special emphasis on ligand field strengths. This combination of ligands with an ethylene bridge (Structure Ia) produces a strong in-plane field and all such compounds are diamagnetic. The complexes are of C_{2v} symmetry with nearly planar stereochemistry around the metal. It has been found, however, that the ligand field strength of these compounds decreases significantly going from an ethylene (Structure Ia) to a trimethylene bridge (Structure Ib). In complexes of Ni(saltn) there is a red shift of 1700 cm^{-1} relative to the ethylene compound. Holm explains this decrease in field strength in terms



Ia. n = 2, Bis(salicylaldehyde)-ethylene-diimine Ni(salen)

Ib. n = 3, Bis-(salicylaldehyde)trimethylene-diimine Ni(saltn)

Structure I

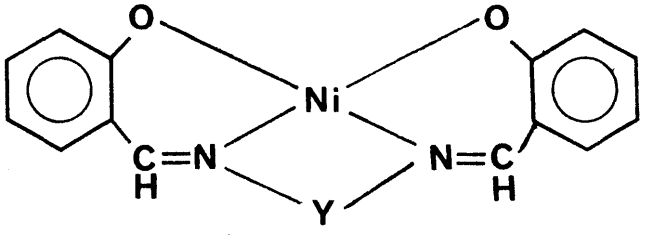
of rotational conformation. There are two conformations of the bridge in Ni-O_2N_2 that allow the compound to remain planar. The configuration in Figure 1a is strain-free where non-bonded

1a 1b

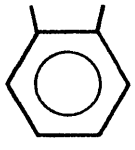
Figure 1

repulsions are at a minimum and the N-N distance is a normal 2.5 Å. However, 1b shows a rotation of 55° about the C-C bond where the N-N distance has increased to approximately 3.5 Å. The metal to nitrogen distances would thereby increase thus weakening the field. Holm found that the field is further weakened by increasing the chain to form a tetramethylene bridge.[5] Such a complex is diamagnetic but not strictly planar.[6]

Yamada and coworkers have reported on the ability of nickel(II) complexes (similar to those of Structure I) to adopt coordination numbers greater than four. This phenomenon should be governed by two factors: (1) electronic factor (includes the nature of the M-L bond, electronegativity of M and L, ligand field strength, (CFSE) and (2) steric factor (includes ligand shapes and crystal field packing). The behavior of Ni(salen) and Ni(saltn), Structure I, Ni(salpn) and Ni(salophen), Structure II, in solution was thought



Y = $-CH(CH_3)CH_2-$ for Ni(salpn)

Y =  for Ni(salophen)

Structure II

to depend on the above factors. Yamada found all to be diamagnetic and square planar in non-donor solvents. When dissolved in pyridine, however, the complex with the three-carbon chain Ni(saltn) coordinated two molecules of pyridine to form a six-coordinate complex.[7] Ni(salophen) in pyridine became partially paramagnetic, and Ni(salen) and Ni(salpn) remained nearly planar and diamagnetic.[7, 8] In-plane field strengths of these compounds can thus be represented in this order:

$$\text{Ni(salen), Ni(salpn)} > \text{Ni(salophen)} > \text{Ni(saltn)}.$$

Even though some may show a tendency toward higher coordination in donor solvents, all remain four-coordinate as solids.

By far the most popular coordination numbers of transition metals are four and six. Five-coordinate compounds are few in number. Ligand systems best documented for forming pentacoordinated complexes are (1) Schiff base ligands made from salicylaldehyde and N,N-dialkylethylenediamine,[9] (2) salicylaldehyde with methylamine[10] (3) ligands containing highly polarizable atoms such as phosphorus and arsenic,[11] (4) and alkylated polydentate amines.[12-15] These ligands are bulky and therefore suited for filling all the space around the metal. Steric hindrance prevents any coordination in the sixth position. Structural types of pentadentate ligands include the linear open-chain, branched chain,[16] tetradentate macrocyclic where a side chain contains the fifth donor atom (as in coenzyme B_{12}),[2] macrocyclic with the five donors in a ring,[17, 18]

and a "basket-like" macrocyclic ligand[19] represented respectively in Figure 2.

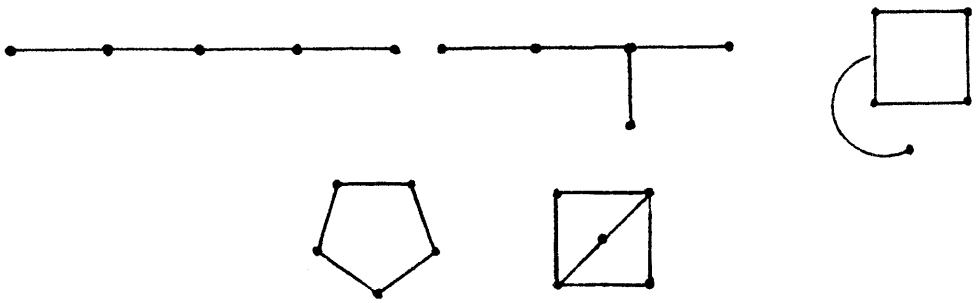
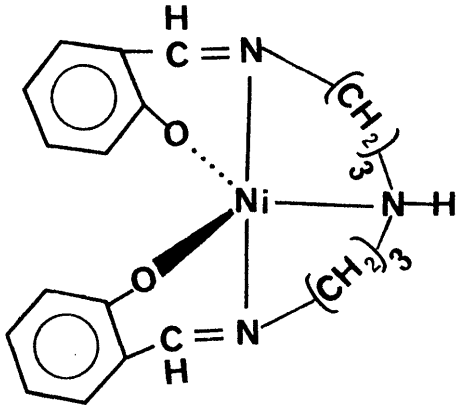


Figure 2 - Pentadentate ligands

Sacconi[20] synthesized the first five-coordinated complexes of 3d metals with a single pentadentate ligand. The high-spin nickel species, Structure III, derived from salicylaldehyde and 3,3'-bis(aminopropyl)amine assumes an unusual geometry intermediate between a trigonal bipyramid and square pyramidal configuration.



Structure III - Ni(SalDPT)

Assignment of geometry to five-coordinate complexes has proved to be a very risky task. Most prominent are the trigonal

bipyramid and "square pyramid" where the metal is at a 10° angle above the inplane field. Sacconi's M(SalDPT) complexes fall in between these two configurations. The energy difference between square pyramid and trigonal bipyramidal configurations is not very large[21] (Figure 3). The difference in the two configurations calculated from d-orbital splitting diagrams is estimated at 3.74 Dq for high-spin and 4.12 Dq for low-spin compounds.[22]

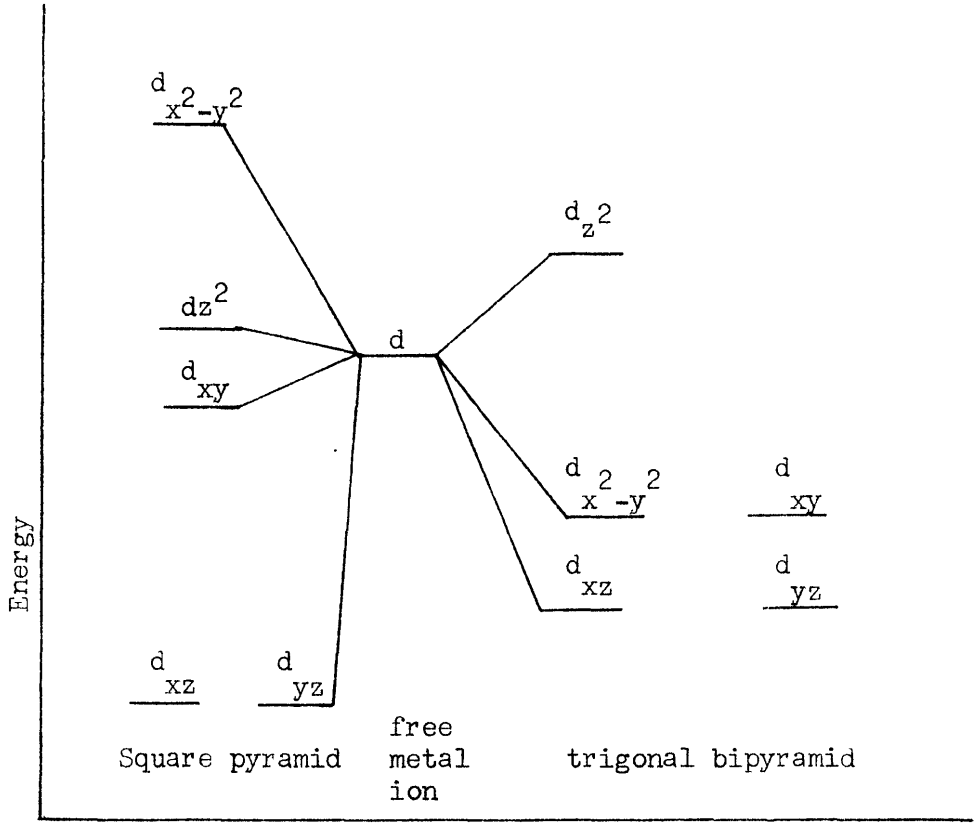
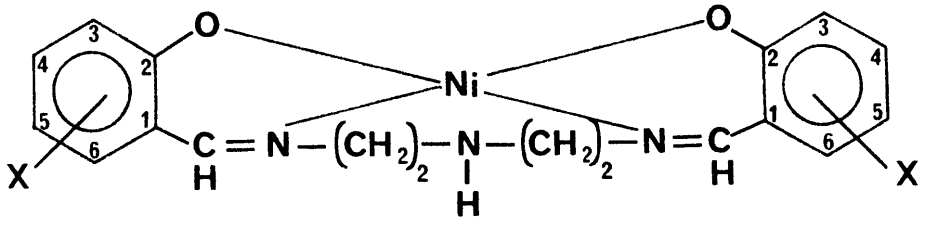


Figure 3 - d-orbital energy diagram

A very recent study of nickel complexes with pentadentate ligands by Coleman[23] affords a very interesting example of a magnetic phenomenon sometimes found in nickel(II) species.[10] Coleman's series of nickel complexes[23] were prepared from Schiff base ligands using substituted salicylaldehydes with diethylene-triamines (Structure IV). The complexes were found to be pseudo-



X = 5-H, 5-Br, 5-CH_3, 3-CH_3O, 3-$(CH_3)_2CH$

Structure IV - Ni(X-SalDIEN)

square planar with anomalous magnetic moments around 1.2 B.M. This phenomenon is thought to arise from either the coexistence of nonreadily interconvertible high- and low-spin complexes in the solid form or an equilibrium between singlet and triplet spin states due to a weakened inplane field.[24] The latter is quite probable since the complexes are believed to be near the "magnetic cross over point" where two energy levels are within

kT of each other. Population of both states is very possible.[23] This may be rationalized as follows. The complexes in Structure IV possess a five atom bridge between the imine nitrogens which would appear to weaken the inplane field to an even greater extent than Structures I and II. The secondary nitrogen may to some extent decrease the field strength due to a slight axial perturbation. The same argument can be applied to Structure III where a seven atom chain gives a five-coordinate high-spin complex. The d-orbital energy difference, Δ , decreases going from a strong inplane field to a weak inplane field or to one with axial perturbation[23] (Figure 4).

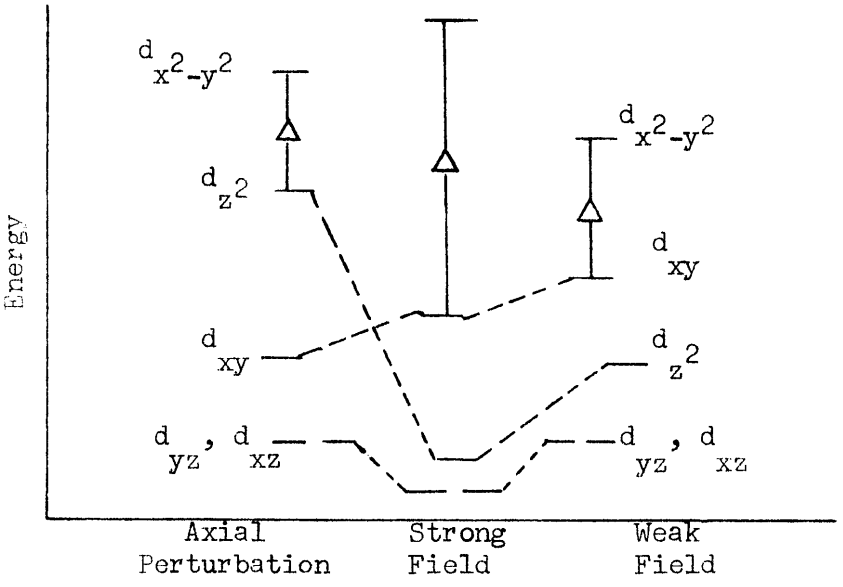
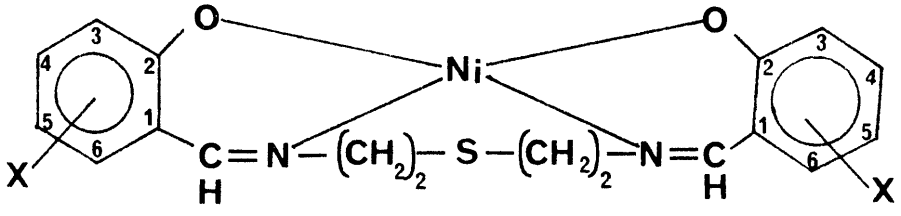


Figure 4 - d-orbital energies for square planar Ni(II)

Another type Ni(II) complex reported by Coleman[25] employs a sulfur atom as a potential fifth donor. Ni(X-SalDAES), Structure V, represents a series of compounds with magnetic properties very



X = 5-H, 5-Br, 5-CH_3, 3-CH_3O and 3-$(CH_3)_2CH$

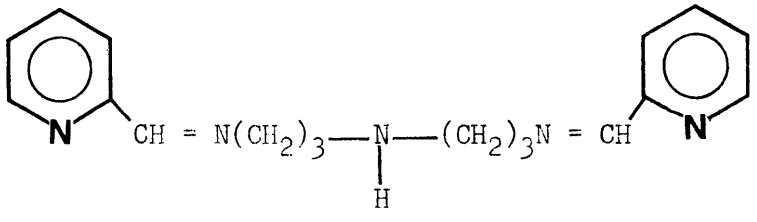
Structure V - Ni(X-SalDAES)

similar to those of Ni(X-SalDIEN). Magnetic moments for the Ni-O_2N_2S complexes were anomalous possibly due to a spin state isomerism between singlet and triplet states for a distorted five-coordinate complex. Either the formation of a metal-sulfur bond is complete resulting in a fully five-coordinate species, or the sulfur is only perturbing excited states of the metal ion and no bond is formed between the nickel and sulfur atoms. Ni(X-SalDAES) might ideally have one of the two structures shown in Figure 5.[25] Although the square pyramidal configuration is possible, the trigonal bipyramid structure is preferred by an analogous ligand.[20] No matter what structure is actually obtained, the SalDAES ligand must undergo great strain for the sulfur atom to reach coordination range.

The Ni(II) complexes discussed thus far have been neutral species containing dinegatively charged ligands. Spencer,[26]

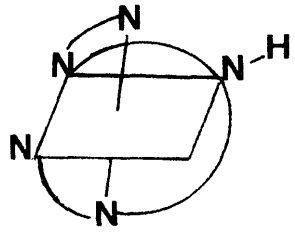
Figure 5

however, has reported some cationic nickel(II) complexes, derived from 2-pyridinecarboxaldehyde and bis(3,3'-aminopropyl)amine (pyDPT) (Structure VI). Complexes of the general formula



Structure VI

$(Ni(pyDPT)X)X$ and $(Ni(pyDPT)Y)PF_6$, where X^- = Cl^-, Br^-, I^-, NO_3^-, SCN^- and Y^- = Cl^-, Br^-, NO_3^-, SCN^-, have been prepared and found to be high-spin with a pseudo-octahedral environment about the Ni(II) ion. Five coordinate positions are filled by the pyDPT ligand and the sixth position is occupied by an anion or solvent molecule. The pyDPT ligand must experience somewhat of a strain at the azomethine linkages if it is to function as a pentadentate ligand. Structure VII has been speculated as the most favorable



Structure VII

arrangement of the ligand around the metal ion. This octahedral configuration offers the minimum steric strain on the ligand and is easily achievable with stereomodels.

Unlike nickel(II), the cobalt(II) ion has seven d electrons and is best known in stereochemistries of four-coordinate tetrahedral and six-coordinate octahedral.[27] It has been shown, however, that quadri-coordinate bis(salicylaldehydeethylenediimine)-cobalt(II) (CoSalen) assumes a square-planar configuration* having only one unpaired electron.[30] As with nickel(II), there has been

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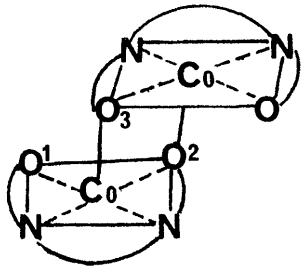
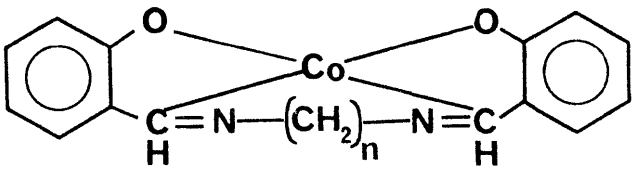
*CoSalen complex is a dimeric structure with oxygen bridges wherein each cobalt atom occupies a pseudo-square planar environment.[28] Co_2 $(Salen)_2$ is shown in Figure 6.



Co - O_1 = 1.88 Å
Co - O_2 = 1.95 Å
Co - O_3 = 2.25 Å

Figure 6 - $Co_2(Salen)_2$[29]

much interest in lengthening the methylene chain on this cobalt complex (Structure VIII) to see what effect it would have on the



Structure VIII

structure. West[31] found that by increasing the diimine bridge of the ligand to seven or greater, a distorted tetrahedral symmetry was acquired. Increasing the chain from two to seven should provide the desired flexibility to obtain such a shape. Steric requirements of the ligand force Co(Salen) into a square-planar configuration, but in the absence of these steric factors the lowest energy state attainable for Co(II) is tetrahedral. Similar compounds have been prepared by Urbach[32, 33] and coworkers where n = 3-6 for Structure VIII. Like West, they found the cobalt complexes with four to six methylene groups to be pseudo-tetrahedral thus relieving the steric interactions of the polymethylene bridge. The trimethylene derivative, however, possessed different spectral properties from the higher homologs. When n = 3, the ligand does not have enough flexibility to occupy tetrahedral positions. The stereochemistry of the trimethylene complex can only be postulated as a flattened tetrahedral structure, although possibilities for a five-coordinate complex cannot be completely discounted.[32]

Five-coordination for cobalt(II) is uncommon and very little is known on the subject. It has been reported that cobalt(II) derivatives of Schiff bases can act as oxygen-carriers.[34] It is hoped that the oxygenation of such Co(II) complexes will shed much light on factors governing the reversible uptake of O_2 by 3d metal complexes.[35] Also important in a biochemical sense are the pentadentate cobalt(II) models[36] of vitamin B_{12} coenzyme. Co(SalDPT), the cobalt derivative of Structure III prepared by Sacconi,[20] was found to be not only a reversible oxygen-carrier but a precursor for a new vitamin B_{12} model sigma-bonded cobalt-carbon complex. Derivatives of R-Co(SalDPT),[37] where R = a primary alkyl group, are reported as highly stable complexes adopting a six-coordinate pseudo-octahedral structure in the solid state.

Analogous to Sacconi's Co(SalDPT) are some cationic Co(II) complexes of pyDPT (Structure VI) prepared by Spencer.[38] Complexes of $\left(Co(pyDPT)X\right)X\cdot H_2O$ where X = Cl^-, Br^-, I^-, NO_3^-, and SCN^-; $\left(Co(pyDPT)\right)(PF_6)_2$ and $\left(Co(pyDPT)(SeCN)\right)$ SeCN have been synthesized and characterized. The chloride, bromide, and nitrate complexes are inclined to be extremely hygroscopic. Magnetic moments on these compounds are a function of the extent of hydration; as H_2O is absorbed the moment is reduced. The thiocyanate and selenocyanate derivatives possess intermediate anomalous magnetic moments in the solid state most probably due to a doublet-quartet spin state equilibrium. All five of these compounds are postulated as six-coordinate pseudo-octahedral species where an anion or water molecule occupies the sixth position. The weaker iodide and

hexafluorophosphate ligands, however, show typical low-spin moments and are speculated as five-coordinate.

The various coordination states of nickel(II) and cobalt(II) have been reviewed. It has been shown that lengthening the chain of atoms between imine nitrogens of Salen derived nickel and cobalt(II) complexes greatly affects the strength of the inplane ligand field. When a fifth donor atom is available, there is a certain degree of axial perturbation on the field depending upon the type of donor. Geometry has been shown to depend upon the size of the ligand and shape it can accomplish. At any extent, substitutions made on the salicylaldehyde ring have had little effect on the shape or behavior of the complex when compared to the length of the imine bridge. Both steric and electronic requirements of the complex ligands have proved essential in determining configurations of the compounds. It is of special interest at this point to investigate the properties of some new nickel(II) and cobalt(II) complexes where oxygen and sulfur atoms act as the fifth potential donors in salicylaldehyde derived pentadentate ligands.

EXPERIMENTAL

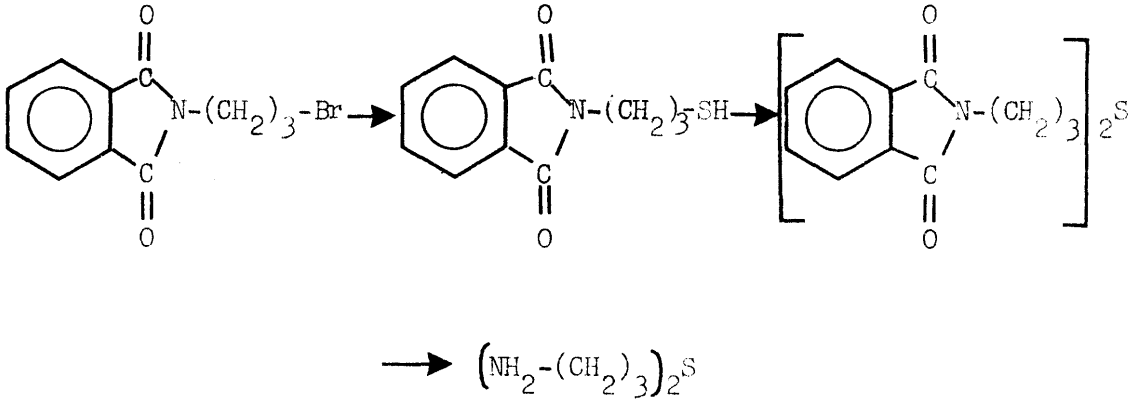
Materials

Salicylaldehyde, cobalt(II) acetate·4-hydrate, and nickel(II) acetate·4-hydrate were obtained from Fisher Scientific Company, Fair Lawn, New Jersey. N-(3-Bromopropyl)phthalimide was provided by Columbia Organic Chemicals Company, Inc., Columbia, South Carolina. Bis(2,2'-cyanoethyl)ether was obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. Raney Active Nickel Catalyst No. 28 was obtained from W.R. Grace & Company, Chattanooga, Tennessee. These chemicals were used directly without further purification. Technical grade 3-methoxysalicylaldehyde (o-vanillin), furnished by Aldrich Chemical Company, was recrystallized twice from 95 per cent ethanol with the addition of Norit decolorizing carbon prior to filtration. Certified spectroanalyzed pyridine and methanol were obtained from Fisher Scientific Company. All other chemicals and solvents were of reagent grade or equivalent.

Bis(3,3'-aminopropyl)ether (DAPE) was prepared by a catalytic hydrogenation method similar to that proposed by Modest et.al.[39] Bis(2,2'-cyanoethyl)ether (13 g) was dissolved in 150 ml of absolute ethanol and placed in a Paar hydrogenation bottle. Anhydrous ammonia was bubbled through the solution for 20 minutes to prevent any formation of secondary amines during the hydrogenation. Approximately 10 ml of Raney nickel catalyst under water was added to the reaction bottle. The dinitrile was promptly hydrogenated at room temperature for 17 hours at a pressure of four atmospheres. The catalyst was then separated from the mixture by filtration, and the ethanol and

ammonia were removed by means of a flash evaporator. The remaining pale green solution was vacuum distilled at 5 mm Hg pressure; and the desired colorless product was collected at 85°C. The ether prepared by a similar procedure[40] was reported to have a boiling point of 81-82°C at 4 mm Hg. The product was further characterized by its infrared spectrum showing expected bands in the N-H and C-O-C stretching frequencies. Another product, γ-aminopropanol,[41] has been known to result from the hydrogenation described above. The alcohol has a slightly lower boiling point than DAPE, but nearly the same refractive index.[40] Product containing the alcohol, however, was found to be insoluble in 1,1,2-trichlorotrifluoroethane whereas pure DAPE dissolved in this solvent. The alcohol was further distinguished from DAPE by its broad OH stretch in the infrared. The percent of γ-aminopropanol present in the reaction product varied according to the amount and age of the nickel catalyst used and the duration of hydrogenation.

Bis(3,3'-aminopropyl)sulfide (DAPS) was made according to a multi-step procedure[42] involving preparations of N-(3-mercaptopropyl)phthalimide and bis(N,n-propylphthalimido)sulfide using



N-(3-bromopropyl)phthalimide as a starting material.

Potassium hydroxide (8.4 g) was dissolved in 250 ml of absolute ethanol, saturated with H_2S for 15 minutes, and placed in a glass bomb. To the resulting KHS solution was added a clear solution of N-(3-bromopropyl)phthalimide (40.2 g) dissolved in 300 ml of ethanol. There was an immediate precipitation of white solid which was probably KBr. The bomb was sealed and placed in a steam cone for one hour. The bomb was then cooled to room temperature and opened. A total of 600 ml distilled water was added to the solution to separate the desired product and KBr. The mixture turned milky with white crystals being produced in the bottom of the container. The product was allowed to digest in a cold room overnight and was filtered by suction. The N-(3-mercaptopropyl)-phthalimide preparation just described was repeated several times.

To a stirred solution of N-(3-mercaptopropyl)phthalimide (15.0 g) dissolved in 30 ml of absolute ethanol was added dropwise a solution prepared by dissolving sodium (1.88 g) in 35 ml ethanol. A solution of N-(3-bromopropyl)phthalimide (18.0 g) dissolved in 75 ml of ethanol was heated to boiling and added dropwise to the mercapto solution producing a white precipitate. The mixture was refluxed for 45 minutes and then cooled by refrigeration. The product was filtered and dried in vacuo at room temperature.

To a refluxing solution of bis(N,n-propylphthalimido)sulfide (75.4 g) dissolved in 600 ml of absolute ethanol was added hydrazine hydrate (65.9 g). A thick white precipitate was present, and the mixture was refluxed for two hours. To this pale green solution

was added dropwise 78 ml of concentrated HCl and refluxing was resumed for 40 minutes. Approximately 500 ml of the ethanol was removed by distillation. Distilled water was added, and the liquid was separated from the white solid by filtration. The remaining ethanol was removed from the filtrate by distillation. As the hot filtrate cooled, a white precipitate emerged and this was removed also by filtration. Solid sodium hydroxide was added to the solution until a pH of 10 was reached using litmus paper as a reference. A precipitate was present giving the solution a milky mint green appearance. This mixture was extracted four times with 100 ml portions of diethyl ether. The ether solutions were combined and dried over anhydrous sodium sulfate overnight. The solution was filtered and distilled to remove the ether. The remaining 25 ml of pale green liquid was vacuum distilled at 8-10 mm Hg pressure. The colorless product was collected over a temperature range of 154-162°C depending on the change in pressure. DAPS was further identified by its infrared spectrum.

5-Bromosalicylaldehyde was prepared by dissolving salicylaldehyde (122.1 g, 1.0 mole) in 250 ml of glacial acetic acid. The colorless solution was then cooled in an ice bath and stirred. To this mixture, Br_2 (80.0 g, 0.05 mole) dissolved in 150 ml glacial acetic acid was added dropwise through a separatory funnel. Upon addition of the bromine the solution turned orange with precipitation of yellow crystals on cooling. A liter of distilled H_2O was added to the flask and the solution was stirred and filtered. The light

solid was washed several times with H_2O to give white crystals of 5-bromosalicylaldehyde which were dried in vacuo at room temperature.

3-Isopropylsalicylaldehyde was made according to the procedure described in the Duff Reaction.[43] To a 2000 ml, triple-neck flask fitted with a mechanical stirrer, was added 480 ml (600 g) of glycerin and boric acid (141 g). The solution was stirred and heated to 170°C with a Fisher burner and held at that temperature for 30 minutes to dehydrate the mixture. The solution was then cooled to 135°C by running cool H_2O over the outside to the flask. To this colorless mixture was added hexamethylenetetramine (100 g) and 2-isopropylphenol (100 g) slowly with portions of each added alternately. The resulting reddish colored mixture was reheated to 143°C. Heating was stopped immediately at the onset of the exotherm evident by a color change to dark red-brown. The temperature of the reaction mixture was maintained at 150-160°C for seven minutes and the flask cooled to 100°C with ice water. When the temperature was stable at 110°C, a solution of 90 ml concentrated H_2SO_4 and 300 ml distilled H_2O was added to the reaction vessel. A steam bubbler, two condensors, and receiver were attached immediately and the mixture was steam distilled with gentle heating over a period of four hours. The distillate appeared cloudy with the product in the form of pale yellow oil droplets. The reaction was stopped at the first appearance of solid material in the condensors. A total of 1100 ml distillate was collected. Three parts of the water solution were extracted twice with 150 ml portions of diethyl

ether. The ether solution was dried over anhydrous sodium sulfate (100 g) for 16 hours and filtered by gravity. The operation was completed by distillation of the ether from the mixture leaving a clear yellow liquid, 3-isopropylsalicylaldehyde. Any solid material present in the product was removed by filtration.

Bis(3-methoxysalicylaldehyde)nickel(II) 2-hydrate was prepared according to Holm[44] by dissolving 3-methoxysalicylaldehyde (30.4 g, 0.02 mole) with 600 ml absolute ethanol in a 1,000 ml flask. The solution was stirred and refluxed. In solid form, $Ni(OAc)_2 \cdot 4H_2O$ (28.4 g, 0.1 mole) was added slowly to the reaction vessel. A bright yellow-green precipitate formed which was filtered from the solution, washed with ethanol and dried in vacuo at room temperature. The product was referred to as $Ni(3\text{-}CH_3O\text{-}Sal)_2 \cdot 2H_2O$.

All ligands obtained from substituted salicylaldehydes and bis(3,3'-aminopropyl)ether (DAPE), or bis(3,3'-aminopropyl)sulfide (DAPS) will be hereafter referred to as X-SALDAPE and X-SALDAPS respectively. The procedures for preparing these compounds are described below.

Preparation of H-SALDAPE

To a stirred solution of salicylaldehyde (26.2 g) dissolved in 20 ml of petroleum ether was added DAPE (14.4 g) dropwise from a separatory funnel. The mixture was stirred for 10 minutes after the addition of the diamine. The solution contained a yellow oil from

which crystals formed as the mixture was cooled. Yellow crystals of H-SALDAPE were filtered by suction and recrystallized from 95% ethanol.

Preparation of 5-BrSALDAPE

5-Bromosalicylaldehyde (29.6 g, 0.148 mole) dissolved in 55 ml of 95% ethanol was stirred and refluxed. To this solution was added DAPE (9.77 g, 0.074 mole) dropwise. Upon addition of the DAPE, the solution turned yellow in color. The reaction mixture was cooled overnight to produce a yellow crystalline product which was filtered, washed with diethyl ether and dried in vacuo at room temperature.

Preparation of H-SALDAPS

To a stirred solution of salicylaldehyde (35.9 g, 0.294 mole) dissolved in 250 ml of petroleum ether was added dropwise DAPS (21.8 g, 0.147 mole). A yellow oil formed immediately. The solution was cooled in an ice bath causing the formation of yellow crystals from the oil. The crystals were collected by filtration and recrystallized from 95% ethanol.

Preparation of 5-BrSALDAPS

To a stirred solution of 5-bromosalicylaldehyde (8.16 g, 0.04 mole) dissolved in 100 ml of 95% ethanol was added dropwise DAPS (2.96 g, 0.02 mole) dissolved in 10 ml 95% ethanol. Upon addition of the DAPS, the solution changed from colorless to a

dark orange color with the formation of a yellow precipitate. The yellow material was filtered by suction and recrystallized from 95% ethanol. Bright yellow crystals were obtained as a product.

PREPARATION OF THE COMPLEXES

Preparation of Ni(H-SALDAPE)

H-SALDAPE (3.40 g, 0.01 mole) was dissolved in 50 ml of absolute ethanol. The yellow solution was stirred and refluxed for 10 minutes. Simultaneously, $Ni(OAc)_2 \cdot 4H_2O$ (2.49 g, 0.01 mole) was dissolved in 140 ml absolute ethanol, stirred and heated. The hot nickel solution was added dropwise to the ligand very slowly, and the reaction mixture began to darken. The nickel acetate was added over a period of one hour after which the heating was stopped. An olive green precipitate was present in the dark olive solution. The reaction vessel was allowed to cool to room temperature; the green solid was filtered and washed with absolute ethanol. The Ni(H-SALDAPE) was dried *in vacuo* at room temperature and later at 100°C.

Preparation of Ni(5-BrSALDAPE)

To a stirred refluxed solution of 5-BrSALDAPE (4.96 g, 0.01 mole) dissolved in 50 ml of absolute ethanol was added dropwise $Ni(OAc)_2 \cdot 4H_2O$ (2.49 g, 0.01 mole) dissolved in 140 ml ethanol. As the metal and yellow ligand reacted the solution turned greenish-brown with the formation of an olive green precipitate. The solid

began sticking to the walls of the flask and was on the verge of tarring several times. The situation was remedied by slowing the rate of addition of the nickel. This same phenomenon had previously been observed by Holm[44] in his preparation of bis(alkylsalicylaldehydo)nickel(II) 2-hydrate complexes. After 2 and 1/2 hours of refluxing, the mixture was brought to room temperature. The green powder was filtered, washed with ethanol, and dried *in vacuo* both at room temperature and at 100°C.

Preparation of Ni(3-$(CH_3)_2$CH-SALDAPE)

3-Isopropylsalicylaldehyde (4.92 g, 0.03 mole) was dissolved in 25 ml of absolute ethanol. To the stirring solution was added dropwise from a separatory funnel DAPE (1.98 g, 0.015 mole) dissolved in 25 ml ethanol. The orange-yellow solution was heated and combined with triethylorthoformate (4.45 g, 0.03 mole) and triethylamine (3.04 g, 0.03 mole) to produce a reddish-orange color. $Ni(OAc)_2 \cdot 4H_2O$ (3.73 g, 0.015 mole) was dissolved in 200 ml ethanol and added dropwise to the refluxing ligand mixture. Upon addition of the metal, the solution darkened to give a green color, but there was no sign of a precipitate after four hours reflux time. The clear green solution was left stirring with the heat just below the reflux point for three more hours. While stirring, the reaction solution was brought to room temperature, submitted to an ice bath with the volume reduced by one third. Still no solid material had formed and the flask was stored overnight in

a freezer. Distilled water was added to the solution to induce precipitation. A light green solid immediately precipitated from the solution, was filtered, and washed with 95% ethanol. The material was dried in vacuo at room temperature and at 50°C.

Preparation of Ni(H-SALDAPS)

To a stirred solution of H-SALDAPS (1.76 g, 0.005 mole) dissolved in 50 ml of n-butanol was added 3 ml triethylorthoformate. $Ni(OAc)_2 \cdot 4H_2O$ (1.25 g, 0.005 mole) dissolved in 70 ml of n-butanol was added dropwise to the refluxing ligand. An olive solid material formed in the dark olive green solution. The container was cooled to room temperature. The olive green powder was filtered leaving a dark brown filtrate. The substance was dried in vacuo at 140°C.

Preparation of Ni(5-BrSALDAPS)

To a stirred and heated solution of 5-BrSALDAPS (2.57 g, 0.005 mole) dissolved in 55 ml n-butanol was added dropwise $Ni(OAc)_2 \cdot 4H_2O$ (1.25 g, 0.005 mole) in 40 ml n-butanol. To this mixture was added 3 ml triethylorthoformate. An olive precipitate was present in the dark solution. The product was filtered and dried in vacuo at 140°C.

Preparation of Ni(3-$(CH_3)_2$CH-SALDAPS)

This complex was prepared by the procedure described for Ni(3-$(CH_3)_2$CH-SALDAPE) with a substitution of DAPS (2.22 g) for DAPE. The reaction provided a green solid material as product while refluxing for two hours after addition of the nickel acetate.

The reaction flask was cooled under running water and the green solid was filtered by suction. The product was dried *in vacuo* at room temperature.

Preparation of Ni(3-CH_3O-SALDAPS)

$Ni(3\text{-}CH_3O\text{-}SAL)_2 \cdot 2H_2O$ (3.97 g, 0.01 mole) was suspended in 200 ml of n-butanol, stirred and heated. When the solid had completely dissolved yielding a clear solution, 10 ml triethylorthoformate was added. To this mixture, was added at once a solution of DAPS (1.48 g, 0.01 mole) dissolved in 30 ml of n-butanol. An olive green precipitate appeared instantaneously and the heating was stopped at the first signs of tarring. The green powder was filtered and dried *in vacuo* at 100°C.

Preparation of Co(H-SALDAPE)

To a stirred and heated solution of salicylaldehyde (1.22g, 0.01 mole) in 50 ml of absolute ethanol was added dropwise DAPE (0.66 g, 0.005 mole) dissolved in 20 ml ethanol. The solution was flushed with N_2 and brought to reflux. Simultaneously, $Co(OAc)_2 \cdot 4H_2O$ (1.24 g, 0.005 mole) dissolved in 30 ml of distilled H_2O was heated and flushed with N_2. The purple cobalt solution was added dropwise to the yellow ligand while both remained under nitrogen. The resulting red-brown solution was refluxed for one hour after the addition of the metal. The reaction flask was brought to room temperature and the sides of the flask were scratched with no results. The solution was placed in a cold room overnight to produce a light

golden precipitate. The complex was filtered in an inert atmosphere where it appeared to blacken toward the center of the filter paper. This darker material was probably due to the presence of a small amount of oxygen. The bright gold portion of the precipitate, however, was collected as Co(H-SALDAPE) for further analysis. The product was dried in vacuo at room temperature.

Preparation of Co(H-SALDAPS)

H-SALDAPS (3.56 g, 0.01 mole) was dissolved in 100 ml of absolute ethanol and the mixture stirred, heated, and flushed with N_2. To this was added triethylamine (2.02 g, 0.01 mole) dissolved in a minimum amount of ethanol and 4-5 ml of triethylorthoformate. The solution was refluxed 1/2 hour. $Co(OAc)_2 \cdot 4H_2O$ (2.49 g, 0.01 mole) was combined with 60 ml of methanol (containing only 0.05% H_2O) and several milliliters of triethylorthoformate. The clear purple cobalt solution was flushed with N_2 and added dropwise to the reaction flask. A thick tar formed around the nitrogen bubbler and on the bottom of the flask. Approximately 20 ml of N,N-dimethylformamide was added to the mixture which dissolved the tar and precipitated a fine orange solid. The solution was allowed to cool to room temperature, but the precipitate turned to tar. The flask was reheated, more N,N-dimethylformamide added, and the tar redissolved. The orange precipitate reappeared and was filtered while hot in an inert atmosphere.

After filtration the solid was reddish-brown in color. It was dried *in vacuo* at room temperature and at 100°C.

Preparation of Co(3-$(CH_3)_2$CH-SALDAPS)

To a stirred solution of 3-isopropylsalicylaldehyde (1.64 g, 0.01 mole) dissolved in 20 ml absolute ethanol was added at once DAPS (0.74 g, 0.005 mole) dissolved in 15 ml ethanol which contained triethylamine (1.10 g). The solution was flushed with N_2, heated to reflux, and 4 ml triethylorthoformate was added. Cobalt acetate (1.24 g, 0.005 mole) dissolved in 30 ml methanol and was flushed with N_2 for 10 minutes and added dropwise under nitrogen to the ligand flask. The reaction solution became dark red in color as more and more cobalt was added. When addition of the metal was finished the dark solution was allowed to reflux 1 and 1/2 hours. Heating was stopped and a thick tar formed around the N_2 bubbler and on the sides of the flask. A small volume of N,N-dimethylformamide was added to the solution and heating was resumed. The tar dissolved, but there was no sign of a precipitate. The mixture was cooled very slowly to room temperature and a fine orange solid emerged on a dropwise addition of distilled water. The solution was refrigerated overnight and filtered in an inert atmosphere. The solid material turned a dark golden color on filtering and was dried *in vacuo* at room temperature and 100°C.

Physical Measurements

Elemental analyses were performed in these laboratories using a Perkin-Elmer Model 240 carbon, hydrogen, nitrogen analyzer.

Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-7 double-focusing mass spectrometer. Each sample was placed on a solid inlet probe and maintained at an appropriate temperature below the point of sample decomposition. The source temperature was held at approximately the same temperature as the solid probe. The analyzer tube and ion source were maintained at pressures less than 10^{-6} Torr. Perfluorokerosene was used to calibrate the mass to charge ratios.

Infrared spectra were obtained on a Perkin-Elmer Model 621 Grating Spectrophotometer and Beckman IR-5A recording spectrophotometer over the region 5000-400 cm^{-1}. Samples were prepared as Nujol mulls or solid melts between potassium bromide or sodium chloride windows.

Magnetic susceptibility data on solid samples were obtained by the Faraday method using a Varian electromagnet and a Cahn RG Electro-balance with a capacity of 2.5 grams and a sensitivity of 0.1 microgram. Susceptibilities were obtained at room temperature and at field strengths of 4,000-10,000 gauss. The system was calibrated using mercury(II) tetrathiocyanatocobaltate(II). Molar diamagnetic susceptibilities were calculated using Pascal's constants.[45]

Magnetic measurements of paramagnetic species in solution were

obtained according to an n.m.r. method proposed by Evans[46] using a C-60H NMR spectrometer constructed by Japan Electron Optics Laboratory Co., Ltd. (JEOLCO) with a proton JNM-C-60H variable temperature probe. Measurements were performed at temperatures ranging from 26°C to -11°C regulated by a JEOLCO JES-VT-3 temperature controller.* A special n.m.r. coaxial cell obtained from Wilmad Glass Company was used in the study. The inner capillary was filled with a solution of pyridine and tetramethylsilane as an inert reference; the outer tube contained a solution of pyridine, TMS, and sample. The frequency shift for TMS in the reference solvent and the sample solution was then measured. The mass susceptibility of the dissolved sample was calculated from the following equation:

$$Xg = \frac{3\Delta f}{2\pi fm} + X_o + \frac{X_o(d_o - d_s)}{m}$$

where

Δf = frequency shift between reference and sample in $\frac{\text{cycles}}{\text{sec.}}$

f = frequency of measurement in cycles/sec.

m = mass of sample in grams/ml of solution

X_o = bulk diamagnetic susceptibility of solvent

d_o = solvent density

d_s = solution density

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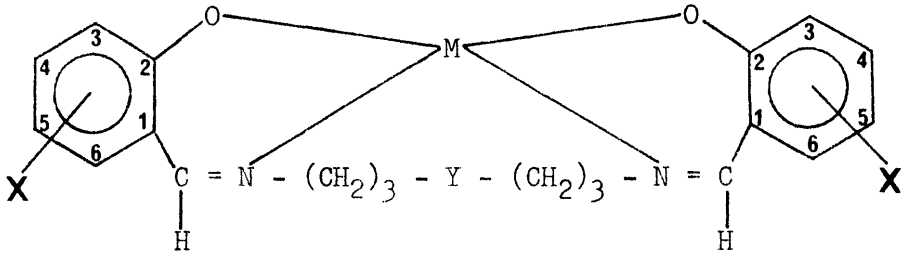
*Temperatures were determined using methanol as a calibrant.[47]

The last two terms of the equation were neglected in determining susceptibility values. Diamagnetic corrections were made using Pascal's constants.[45]

Ultraviolet-visible-near infrared spectra of solid materials and solutions were obtained with a Cary 14 recording spectrophotometer. Diffuse transmittance spectra of solids were obtained as Nujol mulls placed directly on Whatman No. 1 filter paper.[48] Solutions were examined in glass cells with a pathlength of 10.0 cm. All spectra were taken at room temperature.

TABLE I

ABBREVIATED REPRESENTATIONS OF THE COMPLEXES



COMPOUND	X
Ni (X-SALDAPE)	5-Hydrogen
M = Ni, Y = O	5-Bromo
	3-Isopropyl
Ni (X-SALDAPS)	5-Hydrogen
M = Ni, Y = S	5-Bromo
	3-Isopropyl
	3-Methoxy
Co (X-SALDAPE)	5-Hydrogen
M = Co, Y = O	
Co (X-SALDAPS)	5-Hydrogen
M = Co, Y = S	3-Isopropyl

RESULTS AND DISCUSSION OF THE NICKEL(II) COMPLEXES

The nickel(II) coordination complexes of composition Ni(X-SALDAPE) and Ni(X-SALDAPS) have been prepared and isolated. The following procedures were used successfully in preparing the nickel compounds: (1) the dropwise addition of nickel acetate tetrahydrate to a solution of the previously isolated pentadentate ligand, (2) reaction of the appropriately substituted bis(salicylaldehydo)nickel(II) complex with DAPS and (3) the dropwise addition of nickel(II) acetate tetrahydrate to a solution prepared by combining DAPE or DAPS with the proper salicylaldehyde.

The resulting products are neutral and olive green in color. All complexes are readily soluble in pyridine and partially soluble in N,N-dimethylformamide with the exception of the 3-isopropylsalicylaldehyde derivatives which are soluble in DMF. The complexes are very sparingly soluble in methanol, hot dimethylsulfoxide, hot chloroform, and hot benzene. They are insoluble in water, 1,2-dimethoxyethane, nitromethane, and acetonitrile.

Analytical data supporting the proposed compositions of the nickel(II) materials are given in Table II.

Most of the complexes are thermally stable melting somewhere above 200°C. Ni(3-$(CH_3)_2$CH-SALDAPE) and Ni(3-$(CH_3)_2$CH-SALDAPS), however, undergo decomposition at 104-106°C with a change in color from olive green to dark brown.

TABLE II

ANALYTICAL DATA FOR THE NICKEL(II) COMPLEXES[a]

Compound		Analyses C	H	N
Ni(H-SALDAPE)	Calcd.	60.49	5.58	7.05
	Found	60.68	5.36	6.96
Ni(5-BrSALDAPE)	Calcd.	43.24	3.60	5.05
	Found	43.53	3.51	4.80
Ni(3-$(CH_3)_2$CH-SALDAPE)	Calcd.	64.89	7.07	5.82
	Found	63.79	7.06	5.51
Ni(H-SALDAPS)	Calcd.	58.11	5.33	6.78
	Found	58.03	5.11	6.56
Ni(5-BrSALDAPS)	Calcd.	42.03	3.50	4.90
	Found	42.03	3.80	4.90
Ni(3-$(CH_3)_2$CH-SALDAPS)	Calcd.	62.79	6.89	5.63
	Found	62.46	6.65	5.40
Ni(3-CH_3O-SALDAPS)	Calcd.	55.84	5.54	5.92
	Found	56.29	5.14	5.54

[a]All complexes were dried at 100°C *in vacuo* before C, H, and N analyses were obtained with the exception of the isopropylsalicylaldehyde derivatives. As a result, the observed values for these compounds deviate slightly from calculated percentages.

Positive ion mass spectra were obtained on the nickel complexes according to previously described conditions. The complexes gave intense parent ion isotopic clusters as shown in Table III. The most intense peak in each spectrum was in agreement with the calculated M/e value of greatest relative abundance. A spectrum of Ni(3-$(CH_3)_2$CH-SALDAPS) was unobtainable due to decomposition of the compound on the mass spectrometer probe. The sample could not be vaporized at a temperature lower than that of its decomposition point. Mass spectra of all complexes were scanned above the parent ion mass to charge ratios for evidence of dimer formation on the gas phase. No such peaks were found and the compounds are considered to be monomeric.

Infrared spectra were obtained as Nujol mulls or as solid melts in the case of the free ligand. Spectral data with band assignments are shown in Table IV for Ni(X-SALDAPE), Ni(X-SALDAPS) and the corresponding free ligands. The C=N stretching frequency is of special importance in determining the structures of the nickel compounds. The aromatic Schiff base C=N stretching frequency is reported by one source[49] to occur at 1630 cm^{-1} and near 1640 cm^{-1} in another.[50] Similar band positions are found for the C=N stretch of the free ligands; 1630 cm^{-1} for the unsubstituted and 1635 cm^{-1} for the bromo derived ligand. An observable shift in the C=N stretch occurs when the ligands are complexed with nickel(II). For Ni(X-SALDAPS) there is a shift of 15-20 cm^{-1} to lower energy indicating that the imine nitrogens are coordinated to the metal.

TABLE III
MASS SPECTRAL DATA ON THE NICKEL(II) COMPLEXES

Compound	Probe Temp. °C	Parent Isotopic Cluster
Ni(H-SALDAPE) $C_{20}H_{22}O_3N_2Ni$	≈ 180	393,394,395,396*,397
Ni(5-BrSALDAPE) $C_{20}H_{20}O_3N_2Br_2Ni$	130	550,552,553,554*,555,556,557,558
Ni(3-$(CH_3)_2$CH-SALDAPE) $C_{26}H_{34}O_3N_2Ni$	≈ 120	478,480*,481,482
Ni(H-SALDAPS) $C_{20}H_{22}N_2O_2SNi$	≈180	412*,413,414,415,416
Ni(5-BrSALDAPS) $C_{20}H_{20}N_2O_2Br_2SNi$	180	566,567,568,569,570*,571,572,573,574
Ni(3-CH_3O-SALDAPS) $C_{22}H_{26}O_4N_2SNi$	200	470,472*,473,474,475,476

*M/e for the most intense peak
(Relative abundances calculated from raw spectra did not agree with calculated abundances due to hydrogen loss from parent ion.

TABLE IV

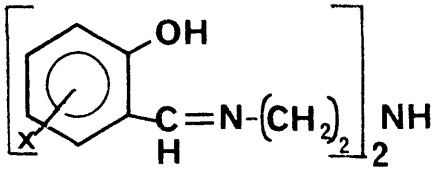
INFRARED SPECTRA (cm^{-1})[a] OF THE NICKEL(II) COMPLEXES[b] AND LIGANDS

Complex	Assignments	
	C=N str.	C-O-C str.
Ni(H-SALDAPE)	1609 ssh	1100 b
Ni(5-BrSALDAPE)	1611 ssh	1111 b
Ni(3-$(CH_3)_2$CH-SALDAPE)	1617 ssh	1110 b
Ni(H-SALDAPS)	1615 ssh	-
Ni(5-BrSALDAPS)	1615 ssh	-
Ni(3-$(CH_3)_2$CH-SALDAPS)	1615 ssh	-
Ni(3-CH_3O-SALDAPS)	1615 ssh	-
Free Ligands		
H-SALDAPE	1630 ssh	1110 b
5-BrSALDAPE	1635 ssh	1123 b
H-SALDAPS	1630 ssh	-
5-BrSALDAPS	1635 ssh	-

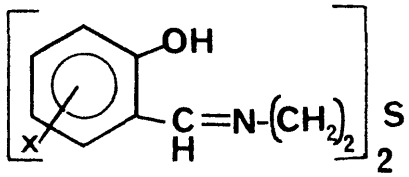
[a] Abbreviations used: s, strong; sh, sharp; b, broad

[b] Complex ion spectra show no band above 3000 cm^{-1}.

A shift of 21-24 cm^{-1} for Ni(X-SALDAPE) indicates similar behavior. These results are comparable to the C=N shift reported by Coleman and Taylor[23] for X-SALDIEN (Structure IX) where the ligand stretch at 1630 cm^{-1} is reduced to 1595 cm^{-1} on complexation with the metal. A similar shift of 25 cm^{-1} is observed for X-SALDAES derivatives (Structure X).[25]

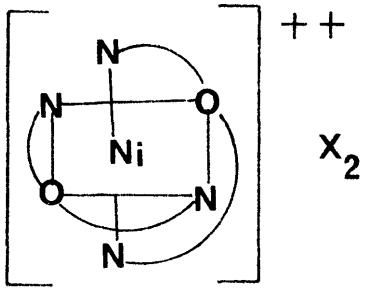


STRUCTURE IX



STRUCTURE X

Infrared spectra of the X-SALDAPE compounds exhibit bands in the 1110 cm^{-1} region assigned to the C-O-C asymmetric stretching mode. Generally, aliphatic ethers ($-CH_2-O-CH_2-$) display a band at 1125 cm^{-1}.[49] Table IV shows a band at 1110 cm^{-1} for H-SALDAPE and 1123 cm^{-1} for 5-BrSALDAPE. These free ligand C-O-C stretching bands are slightly shifted by approximately 10 cm^{-1} to lower energy in the nickel complex. The shift is too small to prove coordination of the ether group to the nickel ion. King and Taylor[51] have reported a more pronounced shift in the C-O-C stretch of the DAPE ligand on coordination with nickel(II). Complexes of the type $Ni(dape)_2X_2$ (Structure XI) where X = Br^-, I^-, NO_3^-, and ClO_4^- show a C-O-C asymmetric stretching band at 1033-40 cm^{-1} as opposed to 1105 cm^{-1} in the free ligand. This shift of 65 cm^{-1} is indicative



STRUCTURE XI

of an interaction between the ether oxygen and the nickel(II) ion. A different phenomenon, however, is observed for $Ni(dape)_2(SCN)_2$ and $Ni(dape)_2(SeCN)_2$. A strong band is present at 1020 cm^{-1} and a new intense band appears at 1095 cm^{-1}, both attributed to a C-O-C asymmetric stretch. The former band is believed to be due to coordinated ether oxygen and the latter to non-coordinated or weakly coordinated ether. The latter band at 1095 cm^{-1} represents a shift of only 10 cm^{-1} from the free ligand at 1105 cm^{-1} and is very similar to the shift between X-SALDAPE and Ni(X-SALDAPE) bands. It can therefore be postulated that the ether oxygen in Ni(X-SALDAPE) is at best very weakly interacting with the metal ion. It is difficult to predict the relationship of the sulfur atom in Ni(X-SALDAPS) with nickel(II). The C-S-C stretching region is obscured by other ligand absorption and no specific band can be distinguished as the C-S-C asymmetric stretch.

Magnetic susceptibility measurements for the nickel compounds are presented in Table V. The resulting magnetic moments are higher than predicted for a low-spin d^8 nickel complex. The calculated magnetic moment for the low-spin nickel(II) ion is zero. When possible contributions to the magnetic moment from temperature independent paramagnetism or spin-orbit coupling are considered, the observed moments are still too high to render the compounds completely diamagnetic. However, the moments are lower than would be expected for high-spin d^8 nickel(II) complexes. The theoretical spin-only magnetic moment for nickel(II) having two unpaired electrons is 2.83 B.M. (Bohr magnetons).[52] Any possible contribution from spin-orbit coupling would be much too slight to lower a high-spin nickel(II) moment to the observed range. From the available susceptibility data, the nickel(II) complexes of X-SALDAPE and X-SALDAPS are found to exhibit anomalous magnetic behavior. This unusual phenomenon is shared by other analogous Schiff base complexes of nickel(II).[53]

Anomalous magnetic behavior can be explained by several mechanisms. 1) A low-spin diamagnetic complex of either square planar or five-coordinate structure could be contaminated with a small amount of high-spin paramagnetic tetrahedral, five-coordinate, or octahedral material. 2) Molecular association can be the cause of anomalous paramagnetism.[53] The diamagnetic complex bis(N-methylsalicylaldiminato) nickel(II) is transformed into a paramagnetic, polymeric isomer above 180° due to association of

TABLE V

ROOM TEMPERATURE MAGNETIC PROPERTIES OF THE NICKEL(II) COMPLEXES

Compound	Temp. °C	$X_M^a(10^6)$	μ_{eff}^b, B.M.[c]
Ni(H-SALDAPE)	24	296	1.06,1.05
Ni(5-BrSALDAPE)	24	988	1.54
Ni(3-$(CH_3)_2$CH-SALDAPE)	26	1,388	1.83
Ni(H-SALDAPS)	27.3	482	1.08,1.04
Ni(5-BrSALDAPS)	26	150	0.60
Ni(3-$(CH_3)_2$CH-SALDAPS)	26	487	1.08

[a]Molar susceptibilities have been corrected for diamagnetic ligands.

[b]Values for μ_{eff} were taken at a field strength of 8,000 gauss.

[c]μ_{eff} was found to decrease only slightly with increasing field strength.

molecules.[54, 55] The same species is also found to be associated in frozen benzene.[56] Association is thus said to be the cause of anomalous behavior in this particular example. 3) A diamagnetic low-spin complex in equilibrium with a high-spin complex can give rise to an anomalous moment. Tetrahedral and square complexes are reported to occur together in the same crystalline state.[57] In solution, complexes of the type $Ni(X\text{-}Sal\text{-}N\text{-}R)_2$ where R is a secondary alkyl group form an equilibrium between planar and tetrahedral species.[58] An even more complicated situation is known for Schiff base complexes of Ni(II) where a three-way equilibrium occurs in solution between octahedral, planar, and tetrahedral species.[59] 4) Antiferromagnetism arising from Ni-Ni spin-spin coupling could produce anomalous magnetic behavior. If antiferromagnetic, a substance should follow the Curie-Weiss law above the characteristic Neel temperature. Below T_N the susceptibility should drop with decreasing temperatures. Magnetic properties of Ni(X-SALDAPE) and Ni(X-SALDAPS) in the solid state will be studied at both low and high temperatures in the near future. 5) The phenomenon of singlet-triplet spin state isomerism offers an important explanation for anomalous magnetism. If two energy levels of different multiplicity occur with kT of each other, it is possible that both levels may become populated. The existence of a thermal equilibrium between singlet and triplet states is thus feasible. For a complex near the "magnetic crossover point" population of singlet and triplet states would be governed according to a Maxwell-Boltzmann distri-

bution.[60] Although the theory accompanying spin state isomerism was presented by Maki[61] in 1958, only recently has it proved to be convincing. There are numerous examples[60] of the singlet-triplet equilibrium in crystalline Ni(II) complexes of the same symmetry. It is highly probable that the anomalous magnetic moments of Ni(X-SALDAPE) and Ni(X-SALDAPS) are due to the effects of spin state isomerism.

The cause of such magnetic behavior in Ni(X-SALDAPE) and Ni(X-SALDAPS) is not due to any steric changes in the complexes. Ni(SalDPT),[20] has the same ligand structure as those mentioned above except for a secondary amine group in place of an oxygen or sulfur atom as a fifth donor. Sacconi's Ni(SalDPT) is reported to be high-spin with a normal magnetic moment of 3.4 B.M. Such evidence tends to indicate that the ether oxygen in Ni(X-SALDAPE) and the sulfur atom in Ni(X-SALDAPS) are not coordinated to the metal strongly enough to unpair electrons.

Solution magnetic susceptibilities were determined on the complexes in pyridine by a nuclear magnetic resonance method aforementioned. Results in Table VI show the nickel complexes to be paramagnetic. Evidently a change in spin state has occured. Dissolution of the solid low-spin compounds in pyridine shifts the following equilibrium to the far right due to coordination of the solvent in one or both axial positions. Although the spin-only value for two unpaired electrons is 2.83 B.M., observed moments can range from 2.8 to 4.0 B.M. due to contributions from orbital

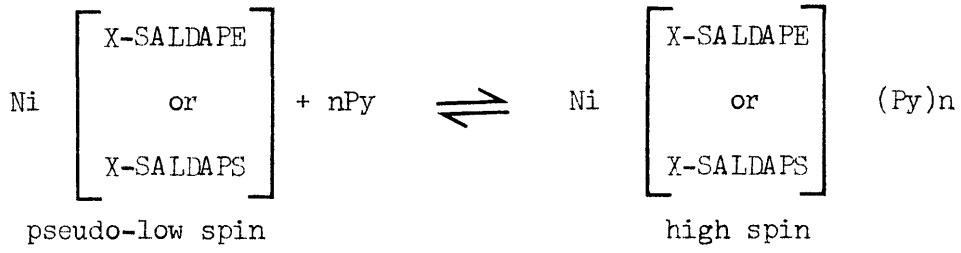
TABLE VI

MAGNETIC DATA[a] ON THE NICKEL COMPLEXES IN PYRIDINE

Compound	Temp (°C)	conc. (g/ml)	X_m (10^6)[b]	μ_{eff} B.M.
Ni(H-SALDAPE)	25.5	.0123	3916.4	3.07
	12	.0123	4045.0	3.05
	-11	.0123	4507.1	3.09
	19.5	.0373	3152.0	2.73
Ni(5-BrSALDAPE)	19.5	.0099	4064.4	3.10
	19.5	.0395	3222.5	2.76
Ni(3-$(CH_3)_2$CH-SALDAPE)	19.5	.0058	3907.6	3.04
	19.5	.0207	4267.5	3.18
Ni(H-SALDAPS)	22	.0101	3418.6	2.93
Ni(5-BrSALDAPS)	19.5	.0110	4023.3	3.08
Ni(3-$(CH_3)_2$CH-SALDAPS)	17.5	.0047	4898.1	3.39

[a]Magnetic moments are calculated on the basis of the percent nickel present.

[b]Molar susceptibilities are corrected for diamagnetism of the metal.



angular momentum.[52] The solution moments in Table VI are approximately 3.0 B.M. These results are similar to magnetic moments reported for nickel complexes of X-SALDIEN and X-SALDAES in pyridine (Structures IX and X). Values range from 2.84 - 3.07 for Ni(X-SALDIEN)[23] and 2.64 to 3.07 for Ni(X-SALDAES).[25] Susceptibility measurements for the SALDAPE and SALDAPS complexes were performed at varying temperatures and concentrations. The magnetic moments in pyridine are temperature independent and only slightly dependent on concentration within experimental error. Magnetic moments are calculated on the basis of the percent nickel present in solution. Calculations assuming coordination of a single pyridine molecule are slightly higher than the observed moments in Table VI. As calculations for the addition of two pyridine molecules would yield even higher values, it is assumed that only one molecule is attached to the metal. The monopyridine adducts of Ni(5-BrSALDIEN),[23] Ni(3-MeOSALDAES) and Ni(H-SALDAES)[25] have been isolated as green solids with magnetic moments of 3.25, 2.69, and 2.71 respectively. Pyridine adducts of Ni(H-SALDAPE) and Ni(5-BrSALDAPE) were attempted but infrared spectra indicated that pyridine was not a part of the

isolated solid. The coordination of pyridine in a vacant position on the complexes will be further verified by their visible spectra.

Electronic absorption spectra for the complexes Ni(X-SALDAPE) and Ni(X-SALDAPS) were obtained on solid samples and solutions of the complexes in both non-coordinating and coordinating solvents. Solid state spectra were performed according to the Nujol mull diffuse transmittance method. Solution spectra were obtained using N,N-dimethylformamide as the non-coordinating solvent where solubilities permitted. Pyridine was employed as the coordinating solvent. The resulting data are shown in Tables VII and VIII.

The solid state spectra of the nickel complexes (Table VII) exhibit two bands at 16,000 cm^{-1} and approximately 23,000 cm^{-1} with a broad shoulder around 19,200 cm^{-1}. The band at 16,000 cm^{-1} seems to fall in the region distinctive of a square planar d-d transition. Ni(Salen)[5] has its d-d transition band around 19,000 cm^{-1}. If Ni(X-SALDAPE) and Ni(X-SALDAPS) are indeed characteristic of a square planar structure, their spectra should show a bathochromic shift of the d-d transition band from 19,000 cm^{-1}. Lengthening the methylene carbon chain joining the imine nitrogen atoms of such compounds is known to weaken the inplane field thereby decreasing the d-d transition energy. Holm has reported a red shift of 1720 cm^{-1} between dimethylene and trimethylene bridges and a 720 cm^{-1} shift between the trimethylene and tetramethylene bridges. Visible spectral data[5] for the bis(salicylaldehyde)diimine nickel(II)

TABLE VII

ELECTRONIC SPECTRAL DATA ON THE NICKEL(II) COMPLEXES[a] IN NUJOL AND DMF MEDIUMS

Compound	Medium	Band Maxima (cm^{-1})			
Ni(H-SALDAPE)	Nujol	15,890	19,200 (sh)	23,500	
Ni(5-BrSALDAPE)	Nujol	16,390	19,200 (sh)	22,990	
	DMF	16,130 (20)	--	26,200 (8300)	
Ni(3-$(CH_3)_2$CH-SALDAPE)	Nujol	16,230	19,200 (sh)	24,390	
	DMF	16,170 (45)	--	27,050 (8600)	29,450 (6200)
Ni(H-SALDAPS)	Nujol	16,190	19,200 (sh)	23,260	
	DMF	16,340 (12)	--	26,920 (9,000)	
Ni(5-BrSALDAPS)	Nujol	16,330	19,200 (sh)	22,100	
Ni(3-$(CH_3)_2$CH-SALDAPS)	Nujol	15,940	18,500 (sh)	23,950	
	DMF	16,380 (84)	--	26,370 (8400)	30,200 (5600)
Ni(3-CH_3O-SALDAPS)	Nujol	15,940	--	21,930	

[a] Numbers in parentheses are molar extinction coefficients.

TABLE VIII

ELECTRONIC SPECTRAL DATA ON SOLUTIONS OF THE NICKEL(II) COMPLEXES[a] IN PYRIDINE

Compound	Medium	Band Maxima (cm^{-1})			
Ni(H-SALDAPE)	Pyridine	10,160 (25)	17,240 (16)	26,600 (3200)	
Ni(5-BrSALDAPE)	Pyridine	10,000 (6)	17,380 (6)	25,650 (2900)	30,300 (2700)
Ni(3-$(CH_3)_2$CH-SALDAPE)	Pyridine	10,160 (16)	17,240 (15)	26,400 (6800)	
Ni(H-SALDAPS)	Pyridine	10,200 (16)	17,100 (12)	26,500 (2000)	
Ni(5-BrSALDAPS)	Pyridine	10,200 (16)	17,240 (17)	26,190 (4700)	
Ni(3-$(CH_3)_2$CH-SALDAPS)	Pyridine	10,260 (12)	17,100 (9)	26,190 (5400)	
Ni(3-CH_3O-SALDAPS)	Pyridine	10,160 (24)	17,100 (12)		

[a]Numbers in parentheses are molar extinction coefficients.

complexes are reproduced below. The band near 23,000 cm^{-1} in Table VII is assigned to a spin-allowed charge-transfer transition[23]

Bridging Group	λ max (cm^{-1})
$(CH_2)_2$	18,520
$(CH_2)_3$	16,800
$(CH_2)_4$	16,080

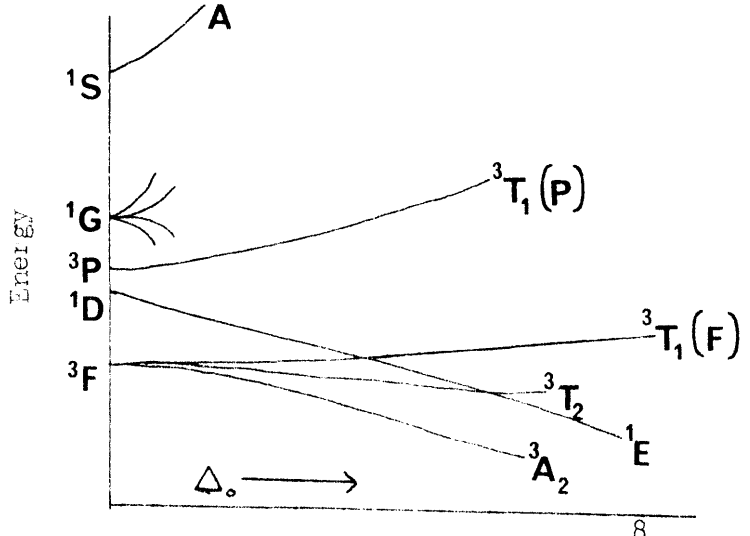
characteristic of the ligand. Low-spin trigonal bipyramidal complexes[62] are known to give bands at 17,500 cm^{-1} and 26,000 cm^{-1} corresponding to the transitions $^1A_1' \longrightarrow {}^1E'$ and $^1A_1' \longrightarrow {}^1E''$ in weak-field notation. Although these bands are close in nature to the 16,000 cm^{-1} and 26,000 cm^{-1} bands of Ni(X-SALDAPE) and Ni(X-SALDAPS) in DMF, the extinction coefficient of the former band is much lower than that in the five-coordinate complex. However, five-coordinate complexes with intermediate type structures[63] give bands at 17,000, 20,000, and 25,000 cm^{-1}. These band positions compare more favorably with the compounds in question and help explain the occurrence of the shoulder at 19,200 cm^{-1}.* The nickel SALDAPE and SALDAPS complexes can be visualized in the solid state as pseudo-square planar type structures approaching five-coordination due to axial perturbation from the ether oxygen and sulfur atoms.

In a non-coordinating solvent such as DMF, the shoulder at 19,200 cm^{-1} disappears and two bands remain at 16,000 cm^{-1} and

*The electronic spectrum of Ni(3-CH_3O-SALDAPS) does not show a shoulder at 19,200 cm^{-1} probably due to overlap with the intense charge transfer band at 22,000 cm^{-1}.

approximately 26,000 cm^{-1}. The band at 16,000 cm^{-1} represents the square planar d-d transition and is confirmed by a low extinction coefficient. Extinction coefficients for bands in this region belonging to five-coordinate complexes range from values of 1,000 to 5,000.[64] The higher energy band in the ultraviolet region is due either to a ligand-to-metal charge transfer, metal-to-ligand charge transfer, or an intraligand transition.[65] The complexes achieve a more pronounced square-planar configuration in DMF than in the solid state. Any interaction the ether oxygen or sulfur atom might have with the metal ion is minimized in DMF due to solvation by solvent molecules.

Coordinating solvent spectra of the complexes presented in Table VIII, show bands at 10,000 cm^{-1}, 17,000 cm^{-1}, and 26,000 cm^{-1} indicating an octahedral structure. According to the energy level diagram (Figure 7) for a d^8 ion, three spin-allowed transitions are



Energy level diagram for a d^8 ion

Figure 7

expected for an octahedral complex.[66] Band assignments of spectra for two very characteristic octahedral nickel(II) complexes are shown in Table IX. Molar absorbtivities of all three bands are relatively low, generally between 1 and 10.[66] The specified band positions of the Ni(II) complexes dissolved in pyridine (Table VIII) agree with those of the octahedral compounds presented in Table IX. The extinction coefficient of the 26,000 cm^{-1} band, however, is unusually high due to an overlap with a ligand absorption band. Several of the spectra show an additional band in the ultraviolet region around 30,000 assigned also to ligand absorption. The nickel complexes have been converted from a pseudo-square planar structure in a non-coordinating solvent to an octahedral one in a coordinating solvent. Pyridine molecules are bound to the nickel ion at one or both axial positions causing the complex to adopt a pseudo-octahedral configuration.

Electronic spectral data on the nickel complexes have further confirmed the theory that these complexes occupy a considerably weakened tetragonal field. Holm has stated that the strength of the average ligand field of tetragonal symmetry must lie very near the magnetic cross-over point between singlet and triplet spin states. Introduction of a z-component to a weak tetragonal field is enough to cause a decrease in singlet-triplet separation.[5] In the particular case of Ni(X-SALDAPE) and Ni(X-SALDAPS), a fifth ligand has been introduced as a z-component in the form of an oxygen ether or thioether atom. Axial perturbation is evident

TABLE IX

OCTAHEDRAL ELECTRONIC SPECTRA (cm^{-1})

Transition	$(Ni(H_2O)_6)^{2+}$	$(Ni(en)_3)^{2+}$
$^3A_{2g} \rightarrow {}^3T_{2g}$	9,000	11,000
$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)	14,000	18,500
$^3A_{2g} \rightarrow {}^3T_{1g}$ (P)	25,000	30,000

not only in the visible spectra of these complexes but by their anomalous magnetic behavior. Ni(Salen) is diamagnetic both as a solid and dissolved in pyridine due to a strong ligand field. The nickel complexes of SALDAPE and SALDAPS, however, are fully paramagnetic in pyridine. It is expected that a coordinating molecule such as pyridine should find it less difficult to unpair electrons for a weak in-plane field since the energy difference between the two highest d orbitals is smaller than for a strong in-plane field.

The degree to which the ether oxygen and sulfur atoms of Ni(X-SALDAPE) and Ni(X-SALDAPS) are actually perturbing the metal ion can only be speculated. A single crystal x-ray diffraction study would be necessary to prove five-coordination. A comparison of visible spectra of the nickel complexes with similar compounds might be helpful in acquiring structural information. Four-coordinate Ni(SALDIEN)[23] has no low energy band in the visible region as does Ni(SALDAES)[25] which is thought to be five-coordinate. The solid spectra of the SALDAPE and SALDAPS complexes are similar to those of Ni(X-SALDAES) with the additional shoulder at higher energy. All four types of complexes give octahedral electronic spectra in pyridine. Of special interest is the low energy band in pyridine which measures the average ligand field about the nickel(II) ion. As shown below, there is a considerable bathochromic shift from 10,900 cm^{-1} for Ni(X-SALDIEN) to the 10,100 region characteristic of the latter compounds.

Compound	ν_{max} (cm^{-1})	
Ni(X-SALDIEN)	10,900	17,000
Ni(X-SALDAES)	10,100	17,400
Ni(X-SALDAPE)	10,100	17,300
Ni(X-SALDAPS)	10,200	17,100

If the latter complexes were strictly cis-planar NiN_2O_2 structures as postulated for Ni(X-SALDIEN), all spectra in pyridine should be identical with that of Ni(X-SALDIEN)$(Py)_2$, NiN_4O_2. The low energy shift may be rationalized as follows. An environment such as NiN_3O_2S or NiN_3O_3 should produce a smaller Dq value thus enabling the formation of only a mono-adduct rather than a dipyridine adduct.

The actual structure of the nickel(II) complexes is probably one of the following:

1) square planar

2) pseudo-square planar wherein the nickel ion is raised above the N_2O_2 plane or one in which the two in-plane chelate rings are twisted at a slight angle relative to each other

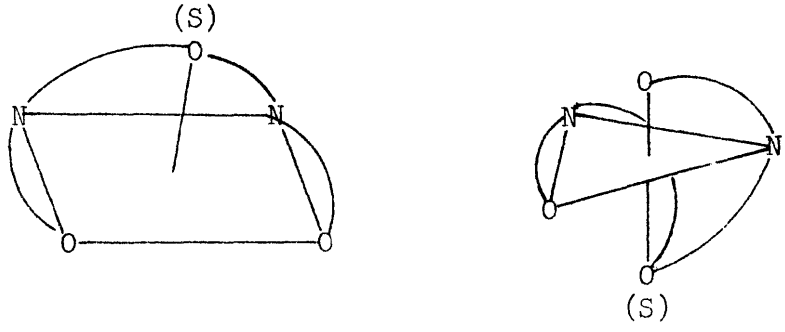
3) trigonal bipyramid

4) square pyramid

5) intermediate between 3 and 4

The complexes are believed to be psuedo-square planar in DMF where solvent molecules are possibly surrounding the ether or sulfur atoms thereby reducing coordinating ability. If Ni(X-SALDAPE) and Ni(X-SALDAPS) are fully five-coordinate they would be expected to have trigonal bipyramidal or square pyramidal configurations as

pictured below. Sacconi's Ni(X-SalDPT)[20] is reported to have a



structure in between the two configurations. It is possible that the SALDAPE and SALDAPS nickel complexes are approaching such an intermediate structure. Ni(X-SALDAES)[25] is thought to be five-coordinate in which axial perturbation is severely restricted sterically by the short ethylene bridge. The five atom bridge of Ni(SALDAES) is increased to seven atoms in Ni(SALDAPE) and Ni(SALDAPS). Subsequently, steric strain near the fifth coordination site must be greatly minimized and possibilities for bond formation more favorable. Nevertheless, the relatively poor donor properties of an ether oxygen or thioether group with respect to nickel(II) rules against a strongly five-coordinate structure in the solid state or in a non-coordinating solvent.

RESULTS AND DISCUSSION OF THE COBALT(II) COMPLEXES

The cobalt(II) complexes in Table I were prepared by one of the following procedures: (1) the addition of a methanol solution of the cobalt(II) ion to an ethanol solution of the previously formed pentadentate ligand or (2) the addition of a methanol solution of the metal ion to an ethanol solution of the appropriate salicylaldehyde with one-half molar equivalent of DAPS or DAPE. The addition of small amounts of DMF to the reaction mixtures was necessary on occasion in order to prevent tarring. The menace of tarring in these reactions might be eliminated altogether by experimenting with new solvent systems. All of the cobalt compounds were prepared and collected under a nitrogen atmosphere to avoid oxidation of cobalt(II) to cobalt(III). Analytical data on the complexes are given in Table X.

The dry cobalt complexes appear to be powdery and relatively stable. When wet, the complexes immediately turn black upon exposure to the air indicating that oxidation has occurred. They range in color from dark gold to brown. The Co(SALDAPS) compounds are thermally stable melting over 200°C. Co(SALDAPE) decomposes at 85°C.

TABLE X

Analytical Data For The Cobalt(II) Complexes

Compound		Analyses C	H	N
Co(H-SALDAPE)	Calcd.	60.46	5.58	7.05
	Found	60.22	5.30	7.18
Co(H-SALDAPS)	Calcd.	58.11	5.37	6.78
	Found	57.86	5.36	6.48
Co(3-$(CH_3)_2$CH-SALDAPS)	Calcd.	64.86	7.12	5.82
	Found	64.79	7.40	6.10

Mass spectral data obtained on the complexes are given in Table XI. Mass to charge ratios correspond to expected isotopic patterns. It was not possible to obtain a spectrum of Co(SALDAPE) because of its low temperature of decomposition. No peaks were observed higher than those of the parent ion. The possibility of the formation of dimeric species was thus excluded.

Infrared spectra of the cobalt complexes were obtained as Nujol mulls. Band assignments for the complexes and corresponding free ligands are shown in Table XII. Of special interest is the C=N stretch at 1605 cm^{-1} for Co(SALDAPE) and 1600 cm^{-1} for Co(SALDAPS). In both spectra there is a shift of 25-30 cm^{-1} to lower frequency from the free ligand positioned at 1630 cm^{-1}. This is sufficient evidence to show coordination of the imine nitrogens to the metal ion. Upon coordination, the C=N bond strength is reduced and the stretching frequency lowered. The C=N shift for the cobalt complexes is greater than that observed for the nickel(II) complexes suggesting that the imine nitrogens of the cobalt compounds are more strongly attached to the metal. This evidence is in agreement with the fact that coordination or perturbation of a donor atom in an axial position weakens the strength of the in-plane field. Such axial interaction was indeed observed earlier with the nickel complexes.

The C-O-C stretching frequency of Co(SALDAPE) at 1110 cm^{-1} occurs at exactly the same position for H-SALDAPE. There is no change between the complex and ligand bands which indicates that

TABLE XI

Mass Spectral Data on the Cobalt(II) Complexes*

Compound	Probe Temp. °C	Observed Parent Ion Peaks
Co(H-SALDAPS)	180	410, 411, 412, 413, 414, 415
Co(3-$(CH_3)_2$CH-SALDAPS)	170	477, 478, 479, 480, 481, 482

*Spectra are complicated by presence of P-1 and P-2 peaks.

TABLE XII

Infrared Data on the Cobalt(II) Complexes (cm^{-1})

Complex	Assignments	
	C=N Str.	C-O-C Str.
Co(H-SALDAPE)	1605	1110
Co(H-SALDAPS)	1600	--
Free Ligand		
H-SALDAPE	1630	1110
H-SALDAPS	1630	--

the ether oxygen is not coordinated or even perturbing the metal ion. On the contrary, the nickel(II) complexes offered a slight shift between complex and ligand C-O-C frequencies. The shift, though small, was proof of some interaction between the ether and nickel atoms.

The magnetic properties of cobalt(II) complexes can prove useful in determining the actual coordination geometry around the metal ion. Table XIII summarizes the magnetic moment data of Co(II) with predicted geometries. Low-spin divalent cobalt complexes with one unpaired electron give moments ranging from a spin-only value of 1.73 to 2.9 B.M. depending upon the degree of orbital contribution. The observed moments of Co(SALDAPE) and Co(SALDAPS), however, are reported in Table XIV to be 4.3-4.5 B.M. indicating a spin-free complex. High-spin cobalt(II) compounds possess three unpaired electrons and deviate from the spin-only value of 3.89 B.M. according to their stereochemistries. The deviation for tetrahedral complexes is somewhat lower than for octahedral or tetragonal cases because the ground state, $e^4t_2^3$, makes no orbital contribution to the magnetic moment. Observed tetrahedral moment values[67] (4.2 - 4.8 B.M.) are high due to a mixing in of higher levels such as $e^3t_2^3\ (4p)^1$. Although there is little data on high-spin five-coordinate complexes, moments generally fall in the range of 4.2 - 4.6 B.M. Sacconi has reported moments for (H-SalDPT)Co at 4.28 B.M. and (5-Cl-SalMeDPT)Co at 4.41 B.M.[20] High-spin octahedral complexes are more easily

TABLE XIII

Magnetic Moments of Cobalt(II)[60]

	6-coord.	5-coord.	Tetrahedral 4-coord.	Planar 4-coord.	Anomalous
High-Spin	4.7-5.2	4.2-4.6	4.2-4.8	-	2.9-4.2
Low-Spin	1.9-2	1.7-2.1	-	2.1-2.9	-

TABLE XIV

Magnetic Properties of the Cobalt(II) Complex in the Solid State

Compound	Temp. °C	$X_m^a \times 10^6$	$\mu_{eff.}$ (B.M.)[b,c]
Co(H-SALDAPE)	21	7900	4.33
Co(H-SALDAPS)	21	7780	4.30
Co(3-$(CH_3)_2$CH-SALDAPS)	19	8550	4.49

[a]Molar susceptibilities have been corrected for diamagnetic ligands.

[b]Magnetic moments are reported at a field strength of 8,000 gauss.

[c]μ_{eff} was found to decrease only slightly with increasing field strength.

distinguished by moment values unusually high due to the orbital contributions from both ground state and the first excited state.

The observed moments for the cobalt complexes shown in Table XIV would eliminate any low-spin square planar, etc., or high-spin octahedral stereochemistry for Co(SALDAPE) and Co(SALDAPS). The moments of these compounds are very similar to those of the tetradentate Schiff base complexes represented by Structure VIII. When the methylene bridge is raised to n = 4 or higher, the complexes become tetrahedral with the magnetic moments shown below.

Imine bridge	eff. B.M.
$(CH_2)_4$	4.36
$(CH_2)_5$	4.41
$(CH_2)_6$	4.33

Although the moments for Co(SALDAPE) and Co(SALDAPS) agree with those above, the possibility that the complexes may be five-coordinate must not be overlooked. Electronic spectral data should be reviewed before any conclusions are drawn.

The electronic spectra of the cobalt(II) complexes are presented in Table XV. Spectra were obtained only on solid samples using the Nujol mull technique previously described. In order to establish the exact structural features of the cobalt complexes, it is necessary to compare their spectra with those of other known compounds containing similar ligands.

TABLE XV

Electronic Spectra of the Cobalt(II) Complexes

Compound	Band Maxima (cm^{-1})[a]					
Co(H-SALDAPE)	7,800 vb[b]	11,400 vb	17,100	21,500	26,000	
Co(H-SALDAPS)	8,300 vb	11,100 vb	17,200	19,400	21,500	26,000
Co(3-$(CH_3)_2$CH-SALDAPS)	7,800 vb	11,360 vb	17,700	21,500	26,660	

[a] All spectra were obtained using Nujol as a Medium.

[b] vb = very broad.

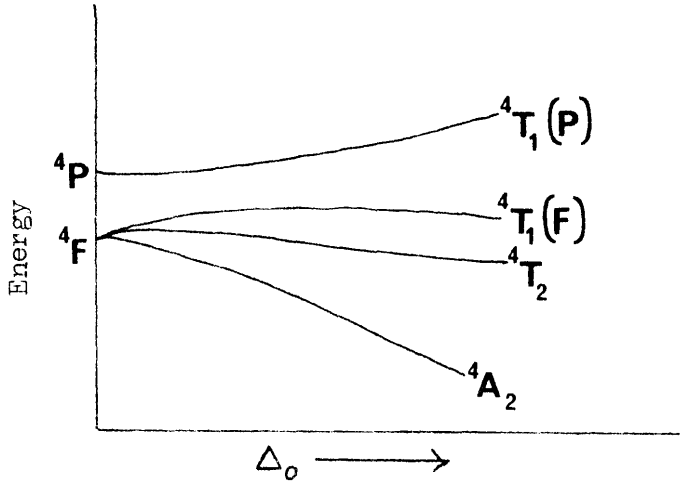
Bis(N-phenylsalicylaldiminato)cobalt(II) is known through crystallographic studies[68] to be a pseudo-tetrahedral complex. The compound's electronic spectrum[59] shows bands at 7600, 10,700, 16,700(sh), and 19,230 cm^{-1}. The N,N'-bis(salicylidene)polymethylenediaminocobalt(II) complexes (Structure VIII) reported by Urbach[32] exhibit very similar spectra and hold pseudo-tetrahedral configurations for those complexes containing four to six bridging methylene groups. Co(Salen),[32] containing only two methylene bridging groups, has an absorption band at 8100 cm^{-1} which is characteristic of a square-planar complex. The trimethylene derivative is somewhat intermediate between square-planar and tetrahedral configurations. As the bridging groups are increased, the ligand becomes more flexible and can better accommodate a tetrahedral geometry. The near-infrared band maxima for the 3-isopropylsalicylaldehyde derived complexes in a non-donor solvent are presented below along with extinction coefficients. These

Bridging group			
$(CH_2)_4$	6250 (27)	11,240 (55)	17,240 sh (45)
$(CH_2)_5$	7690 (53)	11,110 (38)	17,090 (42)
$(CH_2)_6$	7580 (57)	11,110 (34)	17,990 (47)

spectra are similar to those for the cobalt complexes with seven to ten methylene bridging groups.[31] Lengthening the diimine bridge enables the complexes to achieve a regular tetrahedral configuration.

The near-infrared and visible spectra of Co(SALDAPE) and Co(SALDAPS) shown in Table XV correspond very favorably with spectra of known pseudo-tetrahedral species. These spectra are entirely different from those representing a five-coordinate complex. Co(H-SalDPT),[20] a known five-coordinate complex, absorbs at approximately 6,000 and 15,000 cm^{-1}. Therefore, the possibility of a pentacoordinated species for the Co(II) complexes can be eliminated.

Band assignments can be made according to the Orgel diagram in Figure 8 for a tetrahedral d^7 ion. Bands in the 17,000-19,000



Partial energy level diagram for a d^7 ion in a tetrahedral field

Figure 8

cm^{-1} region are assigned to the $^4A_2 \longrightarrow {}^4T_1(P)$ transition.[32] The other transitions which lie outside the visible region are attributed to $^4A_2 \longrightarrow {}^4T_2$ and $^4A_2 \longrightarrow {}^4T_1(F)$. The former lies around 3,000 to 5,000 cm^{-1} but is seldom seen; it is extremely weak due to orbital

selection ruling.[70] The latter transition, however, is observed more frequently. The 8,000 and 11,000 cm^{-1} transitions[4] represent low-symmetry components of the transition from the $^4A_2$ ground state to the $^4T_1(F)$ state. Absorption bands at 20,000 cm^{-1} or greater have been previously assigned to charge-transfer and ligand-ligand transitions due to their positions and intensities.[33]

An interesting trend[33] has been revealed in the spectra of the previously discussed salicylaldehyde derived polymethylene-diaminocobalt(II) complexes. The separation between the two low-symmetry components of the $^4A_2 \longrightarrow {}^4T_1(F)$ transition decreases as the number of methylene groups in the diimine bridge increases. The decrease in splitting is thought to indicate a diminishing of the distortion from tetrahedral symmetry. The trimethylene derivative is very strongly distorted, whereas higher homologs approach more pronounced tetrahedral structures. The actual separation of the two $^4A_2 \longrightarrow {}^4T_1(F)$ transition bands decreased from 6000 to 1500 cm^{-1} upon expanding the central ring from three to six methylene groups. The separations for Co(SALDAPE), Co(SALDAPS) and Co(3-$(CH_3)_2$CH-SALDAPS) bands range from 2800 to 3600 cm^{-1} possibly indicating the degree of distortion from a regular tetrahedral structure in comparison to Urbach's methylene bridged compounds.

Studies on the complexes formed by coordination of potential pentadentate ligands, SALDAPE and SALDAPS, with cobalt(II) have proved the compounds to be only four-coordinate. Magnetic and

spectral data allow further characterization of the compounds as pseudo-tetrahedral in structure. Urbach has shown that an increase in the methylene bridge of N,N'-bis(salicylidene)polymethylene-diamine ligands produces pseudo-tetrahedral complexes with cobalt(II). Co(SALDAPE) and Co(SALDAPS) fall accordingly into the range for a five atom bridge or greater. The cobalt(II) derivatives of SALDAPE and SALDAPS display a much greater tendency toward tetrahedral formation than do the nickel(II) series of complexes.

APPENDIX

BIBLIOGRAPHY

1. L. Sacconi, "Transition Metal Chemistry," Vol. 4, (ed. by Richard L. Carlen) Marcel Dekker, Inc., New York, N.Y., 1968, p. 200.

2. R.H. Abeles, "Bioinorganic Chemistry," (ed. by R. Dessy, J. Dillard, L. Taylor) American Chemical Society, Washington, D.C., 1971, p. 346.

3. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2d. ed., Interscience Publishers, New York, N.Y., 1966, p. 878.

4. P. Pfeiffer, E. Breith, E. Lubbe and T. Tsumaki, Ann., 503, 84 (1932) and later papers.

5. R.H. Holm, J. Amer. Chem. Soc., 82, 5632 (1960).

6. H. Irving and J.B. Gill, Proc. Chem. Soc., 168 (1958). H. Irving, J.B. Gill, and W.R. Cross, J. Chem. Soc., 2087 (1960).

7. S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi, and K. Iwasaki, Coord. Chem. Rev., 3, 247 (1968).

8. R.H. Holm, G.W. Everett, and A. Chakravorty, Prog. Inorg. Chem., 7, 83 (1966).

9. L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, Inorg. Chem., 4, 943 (1965).

10. L. Sacconi, M. Ciampolini, and G.P. Speroni, J. Amer. Chem. Soc., 87, 3102 (1965).

11. G.S. Benner, W.E. Hatfield, and D.W. Meek, Inorg. Chem., 3, 1544 (1964).

12. M. Ciampolini and N. Nardi, Inorg. Chem., 5, 41 (1966).

13. M. Ciampolini and G.P. Speroni, Inorg. Chem., 5, 45 (1966).

14. Z. Dori and H.B. Gray, J. Amer. Chem. Soc., 88, 1394 (1966).

15. L. Sacconi and R. Morassi, J. Chem. Soc. (A), 2997 (1968).

16. A.J. Bruno, S. Chaberek, and A.E. Martell, J. Amer. Chem. Soc., 78, 2723 (1956).

17. J.D. Curry and D.H. Busch, J. Amer. Chem. Soc., 86, 592 (1964).

18. S.M. Nelson, P. Bryan, and D.H. Busch, Chem. Comm., 641 (1966).

19. V. Katovic, L.T. Taylor, and D.H. Busch, J. Amer. Chem. Soc., 91, 2122 (1969).

20. L. Sacconi and I. Bertini, J. Amer. Chem. Soc., 88, 5180 (1966).

21. F. Zemann, Z. Allgem. Chem., 324, 241 (1963).

22. F. Basolo and R.G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N.Y., 1958.

23. W.M. Coleman and L.T. Taylor, Inorg. Chem., 10, 2195 (1971).

24. S.M. Nelson and W.S.F. Kelley, Chem. Commun., 436 (1968).

25. W.M. Coleman and L.T. Taylor, J. Amer. Chem. Soc., 92, 1449 (1970); J. Inorg. Nucl. Chem., 33, 3049 (1971).

26. C.T. Spencer and L.T. Taylor, Inorg. Chem., 10, 2407 (1971).

27. R.L. Carlen, "Transition Metal Chemistry," Vol. 1, Marcel Dekker, Inc., New York, N.Y., 1965, p. 2.

28. S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, Acta Cryst., B25 (1969) 1671.

29. P.L. Orioli, Coord. Chem. Rev., 6, (1971) 306.

30. M. Calvin and C.H. Barkelew, J. Amer. Chem. Soc., 68, 2267 (1946).

31. H. Weigold and B.O. West, J. Chem. Soc., (A), 1310 (1967).

32. M. Hariharan and F.L. Urbach, Inorg. Chem., 8, 556 (1969).

33. M. Hariharan and F.L. Urbach, Inorg. Chem., 10, 2667 (1971).

34. A. Earnshaw, P.C. Hewlett, and L.F. Larkworthy, Nature 199, 483 (1963).

35. R.G. Wilkins, "Bioinorganic Chemistry," (ed. by R. Dessy , J. Dillard and L. Taylor), Amer. Chem. Soc. Publications, Washington, D.C., 1971, p. 111.

36. D.H. Busch, K. Farmery, V. Goedken, V. Katovic, A.C. Melnyk, C.R. Sperati, and N. Tokel, ibid., p. 73.

37. W.M. Coleman and L.T. Taylor, J. Amer. Chem. Soc., 3, 5446 (1971).

38. C.T. Spencer and L.T. Taylor, to be published.

39. M. Israel, J.S. Rosenfield and E.J. Modest, J. Med. Chem., 7, 710 (1964).

40. P.F. Wiley, J. Amer. Chem. Soc., 68, 1867 (1946).

41. O.F. Wiedeman and W.H. Montgomery, J. Amer. Chem. Soc., 67, 1994 (1945).

42. S. Gabriel and W.E. Lauer, Berichte 23a, p. 88 (1890).

43. J.C. Duff, J. Chem. Soc., 547 (1941).

44. R.H. Holm, J. Amer. Chem. Soc., 83, 4684 (1961).

45. B.N. Figgis and F. Lewis, "Modern Coordination Chemistry," J. Lewis and R.J. Wilkins, Eds., Interscience Publishers, Inc., New York, N.Y., 1960.

46. D.F. Evans, J. Chem. Soc., 2003 (1959).

47. Model A-60 Analytical NMR Spectrometer System Manual, Varian Associates, Palo Alto, California, 1962, p. 28.

48. R.H. Lee, E. Griswold, and J.K. Kleinberg, Inorg. Chem., 3, 1278 (1964).

49. N.B. Colthup, L.D. Daly and S.E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Third Ed., Academic Press, New York, N.Y., 1968, p. 282.

50. R.T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, 1966, p. 135.

51. A.G. King and L.T. Taylor, J. Inorg. Nucl. Chem., Vol. 33, (1971) 3057.

52. F.A. Cotton and G. Wilkinson, ibid., p. 637.

53. L. Sacconi, "Transition Metal Chemistry," ibid., p. 268.

54. L. Sacconi, P. Paoletti, and R. Cini, J. Inorg. Nucl. Chem., 8, 429 (1958); J. Amer. Chem. Soc., 80, 3583 (1958).

55. C.H. Harris, S.L. Lenzer and R.L. Martin, Australian J. Chem., 11, 331 (1958).

56. J. Ferguson, J. Phys. Chem., 63, 343 (1959).

57. B.T. Kilbourn, H.M. Powell, and F.A.C. Darbyshire, Proc. Chem. Soc., London, 207 (1963).

58. L. Sacconi, M. Ciampolini, and N. Nardi, J. Amer. Chem. Soc., 86, 819 (1964).

59. A. Chakravorty, J.P. Fennessey, and R.H. Holm, Inorg. Chem., 4, 26 (1965).

60. E.K. Barefield, D.H. Busch, and S.M. Nelson, Quart. Rev., Chem. Soc., 22, 457 (1968).

61. G. Maki, J. Chem. Phys., 28, 651 (1958); ibid., 29, 162 and 1129 (1958).

62. L. Sacconi, "Transition Metal Chemistry," ibid., p. 227.

63. L. Sacconi, "Transition Metal Chemistry," ibid., p. 230.

64. A.B.P. Lever, "Inorganic Electronic Spectroscopy," Elsvier Publishing Company, New York, N.Y., 1968, p. 347.

65. M.C. Day, Jr. and J. Selbin, "Theoretical Inorganic Chemistry," Reinhold Book Corporation, New York, N.Y., 1969, p. 497.

66. F.A. Cotton and G. Wilkinson, ibid., p. 881.

67. M.C. Day, Jr. and J. Selbin, ibid., p. 495.

68. E. Frasson and C. Panattoni, Z. Krist., 116, 154 (1961).

69. L. Sacconi, M. Ciampolini, F. Maggio, and F.P. Cavasino, J. Amer. Chem. Soc., 84, 3246 (1962).

70. F.A. Cotton and G. Wilkinson, ibid., p. 872.

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AN INVESTIGATION OF THE NICKEL(II) AND COBALT(II) COMPLEXES EMPLOYING PENTADENTATE LIGANDS DERIVED FROM SALICYLALDEHYDE AND BIS(3,3'-AMINOPROPYL)ETHER OR SULFIDE

Anne King St. Clair

ABSTRACT

Complexes of the general formula M(X-SALDAPE) and M(X-SALDAPS) formed by the reaction of substituted salicylaldehydes and bis(3,3'-aminopropyl)ether or bis(3,3'-aminopropyl)sulfide with nickel(II) and cobalt(II) have been isolated.

The complexes have been characterized by elemental analysis, mass spectra, infrared spectra, magnetic susceptibility measurements, and ultraviolet-visible-near infrared spectra.

In the solid state the nickel(II) complexes, Ni(X-SALDAPE) and Ni(X-SALDAPS), where X = H, 5-Br, 3-$(CH_3)_2CH$, or 3-CH_3O, are speculated as pseudo-square planar or weak low-spin five-coordinate structures. The complexes exhibit anomalous magnetic behavior explained in terms of a spin state isomerism between singlet and triplet spin states. In a non-coordinating solvent, the nickel complexes are pseudo-square planar losing all five-coordinate structural features due to solvation. When dissolved in a coordinating solvent, the complexes are high-spin pseudo-octahedral.

The cobalt(II) complexes, Co(H-SALDAPE) and Co(X-SALDAPS) where X = H, or 3-$(CH_3)_2CH$, were found to be high-spin pseudo-tetrahedral in the solid state with magnetic moments of approximately 3.4 B.M.

The olive green nickel complexes are stable to air and moisture. The brownish cobalt complexes are stable as dry solids, but very easily oxidized when wet.