TRANSITION METAL COMPLEXES OF PENTADENTATE LIGANDS

by

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To Linda

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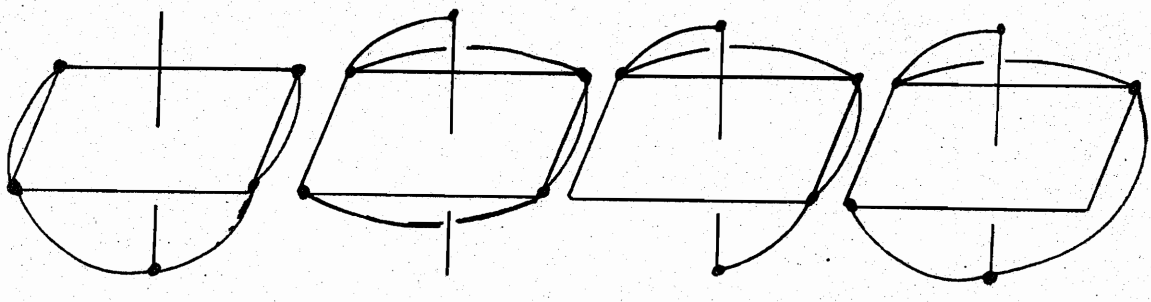
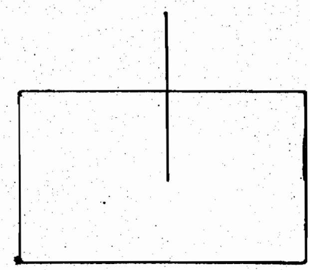
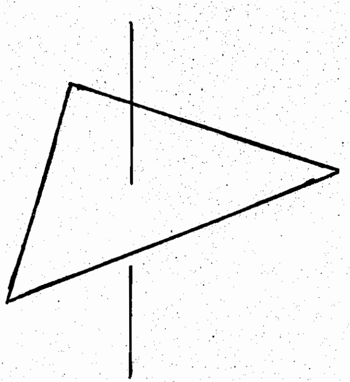
INTRODUCTION

Of the higher polydentate ligands, those containing five donor atoms are the least investigated. This is probably due to the fact that there are few ligands which posses five donor atoms in such a stereochemical arrangement that would lend themselves for coordination to a single metal atom. The attachment of a pentadentate ligand to an octahedral metal ion may occur in one or more of the following manners.[1]



Recently there has been an increasing interest in five-coordinate nickel(II) complexes. Five-coordination is unusual for nickel(II) complexes and when encountered, its existence depends on several factors other than the tendency on the part of the nickel ion to attain this structure. It is known from crystal field arguments that either octahedral or tetrahedral complexes of nickel(II) are more favored. The five-coordinate species known have been found to adopt either distorted square pyramidal or trigonal bipyramidal configurations.



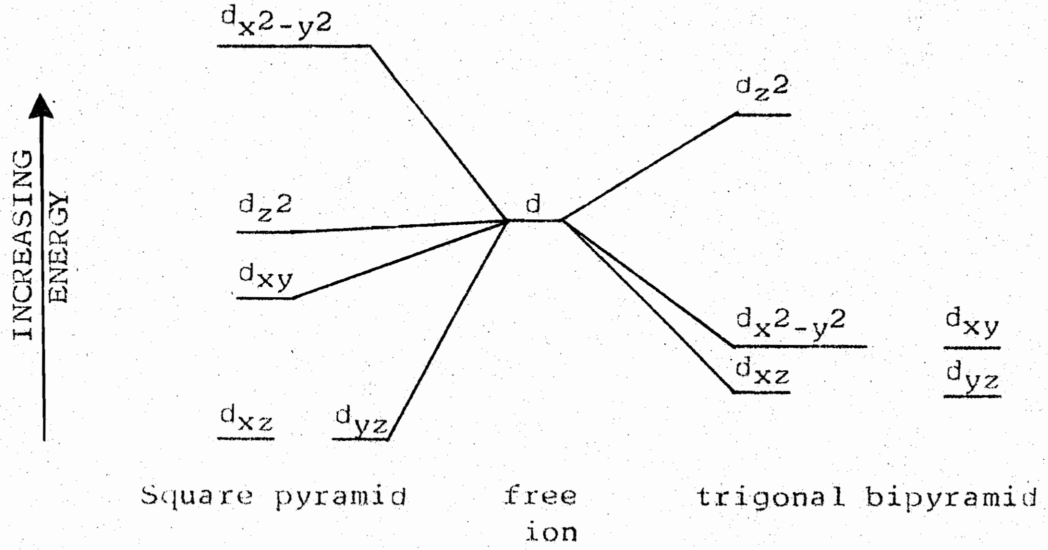


Ligands with a wide variety of donor atoms have been employed (i.e., nitrogen, oxygen, halogens, sulfur, phosphorus, and arsenic). The most suitable ligands to date have been bulky (i.e., $N(CH_2\text{-}CH_2\text{-}PPh_2)_3$, $N(CH_2\text{-}CH_2\text{-}AsPh_2)_3$, etc.) the idea being to fill all the space around a metal ion with a five-coordination environment, thereby sterically preventing six-coordination to occur. While the number of five-coordinate nickel(II) complexes continues to grow,[2] the utilization of the five donor sites of a pentadentate ligand to achieve the desired structure is totally lacking except for one recent example which will be dealt with later.[3]

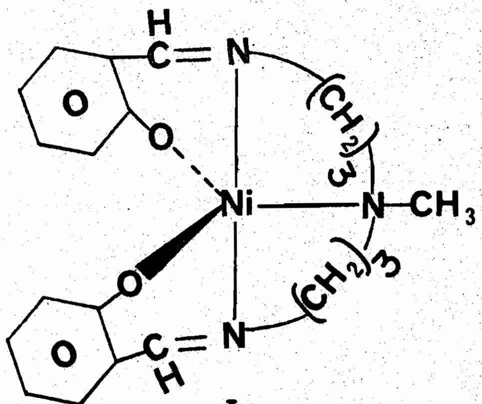
The assignment of a definite geometry to a five-coordinate complex is hazardous. It has been shown[4] that the trigonal bipyramid is most favored if one considers ligand-ligand repulsions. However, if a distorted square pyramid is considered with the metal at an angle of 10° above the inplane field, this structure is almost as stable as the trigonal bipyramid.[4]

Gillespie[5] has found that in the case described above, the trigonal bipyramid is only 8 per cent more stable than the square pyramid. He states that if the interaction of the ligand electron pairs with themselves is more important than their interaction with the non-bonding d-electron pairs, the trigonal bipyramidal configuration is favored. It is reasonable to suppose that when there is a strong interaction between ligand valence-shell electron pairs and a d^7, d^8, d^9 shell that the square pyramid configuration for the ligand five-electron pairs may become more stable than the trigonal bipyramid.

The energy difference between the two regular configurations calculated from d orbital splitting diagrams is not large. The difference has been estimated at 3.74 D_q for high-



spin complexes and 4.12 D_q for low-spin complexes.[6] In fact the complex (H-SALIMeDPT)Ni(II) (I) has been shown to be five-coordinate and the geometrical arrangement of the donor atoms is intermediate between that of trigonal bipyramid and square pyramid.[2]



I

Therefore, one can conclude that the conditions required for five-coordination to occur with nickel(II) are to a great extent stereochemical in nature, and that the shape of the complex is determined to a large extent by the shape attainable by and size of the ligand.

An intriguing feature of five-coordinate nickel(II) complexes is that they may be either diamagnetic or paramagnetic, which until recently was thought to depend on the particular donor atoms involved.[7] Ligands with low π-bond forming ability (i.e., oxygen, nitrogen, etc.) were thought to form only paramagnetic complexes whereas ligands with high π-bond forming ability (i.e., sulfur, phosphorus, etc.) gave rise to diamagnetic complexes. The high π-bond forming ligands are capable of accepting d-electrons from the metal, hence removing the paramagnetism.

Complexes of type (I) have been shown to be high-spin paramagnetic. As of the present, these are the only known five-coordinated complexes of 3d metals with a single pentadentate ligand.

The purpose of this thesis is dual in nature. The aim of a part of this thesis is to investigate the potentially five-coordinate complexes of Ni(II) derived from the Schiff bases formed by the condensation of substituted salicylaldehydes with (1) diethylenetriamine, hereafter referred to as (X-SALDIEN) and (2) with bis(2-aminoethyl)sulfide, hereafter referred to as (X-SALDAES).

The objective of the second part to this thesis is to investigate sigma bonded alkyl and aryl derivatives of a formally cobalt(III) complex as a possible model for Vitamin B_{12}. Other model systems have been studied also; however, to date such studies have been limited to low-spin four-coordinate square planar complexes such as Co(SALEN), Co(BAE) and Co(DMG)[a]. Schrauzer[9] in this country, and Costa[10] in Italy, have been especially active in this field.

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[a] SALEN is N,N'bis(salicylidene)-1,2-diaminoethane. BAE is bis(acetylacetone) ethylenediimine dianion. DMG is bis-dimethylglyoxime dianion.

These organocobalt compounds may be synthesized by several procedures. First, reduction of cobalt(II) to cobalt(I) with borohydride, sodium amalgam, etc. and subsequent reaction of the reduced species with an alkyl halide may yield the alkyl derivative.[11]

$$\mathrm{Co(II)} \xrightarrow{\mathrm{BH_4^-}} \mathrm{Co(I)} + \overset{\mathrm{R-X}}{} \longrightarrow \mathrm{Co{-}R} + \mathrm{X^-}$$

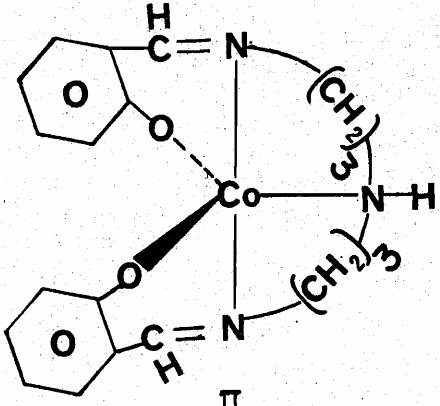
Secondly, these complexes have been prepared by the reaction of a Co(III) halide with a Grignard reagent.[12]

$$\mathrm{Co(III)} - \mathrm{X} + \mathrm{RMgX} \longrightarrow \mathrm{Co{-}R} + \mathrm{MgX_2}$$

The third general method which is applicable to the formation of transition metal to-carbon σ-bonds is the thermal odd electron (free radical) reaction that has been observed to occur between a d^4 or d^7 metal ion in its complex and an alkyl halide.[13]

When the alkyl derivative is subsequently formed, the best description of the system would be one that contained a d^6 low-spin Co(III) ion bonded to a carbanion. However, it is just as conceivable to think of the system as being either Co(II) and an alkyl radical or as Co(I) and an alkyl carbonium ion. Reasons for considering it as Co(III) will become apparent in the forthcoming discussion.

Organocobalt derivatives employing five-coordinate cobalt(II) complexes as precursors have not been investigated.[14] Also, no high-spin complexes have been studied. The second part of this thesis involves the preparation and characterization of alkyl derivatives starting with a previously reported high-spin five-coordinate complex, Co(SALDIPN), (II),

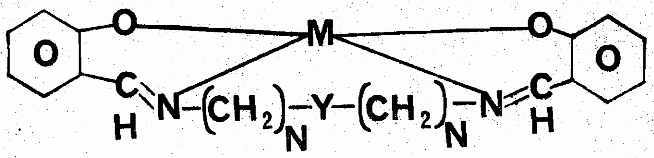


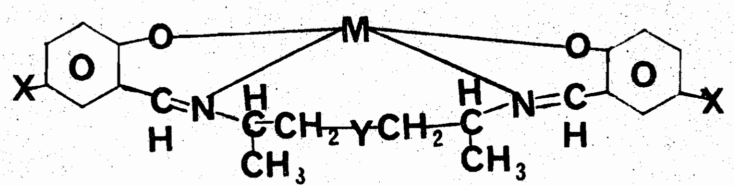
II

whose geometry has been suggested to be trigonal bipyramidal or distorted trigonal bipyramidal.[3]

TABLE I

ABBREVIATED REPRESENTATIONS OF THE COMPLEXES



COMPOUND	M	Y	N	X
Ni(X-SALDIEN)	Ni	N-H	2	5-Hydrogen
	Ni	N-H	2	5-Methyl
	Ni	N-H	2	5-Bromo
	Ni	N-H	2	3-Methoxy
	Ni	N-H	2	3-Isopropyl
Ni(X-SALDAES)	Ni	S	2	5-Hydrogen
	Ni	S	2	5-Methyl
	Ni	S	2	5-Bromo
	Ni	S	2	3-Methoxy
	Ni	S	2	3-Isopropyl
Co(X-SALDIPN)	Co	N-H	3	5-Hydrogen
Ni(X-SALPN) 	Ni	N-H	-	5-Hydrogen

EXPERIMENTAL

Materials

Diethylenetriamine (DIEN), bis(3-aminopropyl)amine (DIPN), bis(2-aminopropyl)amine (PN), and salicylaldehyde (SAL) were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin, and used without further purification. Bis(2-aminoethyl)sulfide (DAES) was donated by the Dow Chemical Company Midland, Michigan, and used without further purification. Technical grade 3-methoxysalicylaldehyde (o-vanillin), from Aldrich Chemical Company, was recrystallized from 95 per cent ethanol in the presence of decolorizing charcoal. Reagent grade inorganic chemicals were employed without further purification. All other chemicals and solvents were of reagent grade or equivalent.

Five-bromosalicylaldehyde was prepared by dissolving salicylaldehyde (30 g, .245 mole) in 60 ml of cold glacial acetic acid. To the stirring solution, Br_2 (39.3 g, .245 mole) dissolved in a small amount of glacial acetic acid was added dropwise. After addition was complete, a yellow-orange solid formed. It was filtered and washed with H_2O, thereby removing the unreacted Br_2 leaving white crystals behind.

The product was recrystallized from ethanol-water (60:40) and dried *in vacuo* at room temperature.

Five-methylsalicylaldehyde was prepared by a modification of the Reimer-Tieman Reaction as follows. Sodium hydroxide (192 g of a 50 per cent aqueous solution) was placed in a 2 liter-3 neck flask. Then para-cresol (43.2 g, 0.4 mole) was added. An immediate white solid formed, (i.e., the sodium salt of p-cresol). The mixture was brought to 70°C with stirring whereupon $CHCl_3$ (94.4 g) was added dropwise. Refluxing was continued for three hours after which the solution was acidified with concentrated HCl and then steam distilled yielding white crystals which were isolated and dried *in vacuo* at room temperature.

Three-isopropylsalicylaldehyde was prepared according to the general procedure of the Duff Reaction[15] starting with o-isopropylphenol.

The bis(salicylaldehyde)nickel(II) complexes were obtained as green hydrated solids by treating aqueous ethanol solutions of two molecular equivalents of salicylaldehyde with a saturated aqueous solution of one molecular equivalent of nickel acetate. In some cases cooling of the reaction mixture was necessary in order to permit the formation of a microcrystalline product. The crude complexes were filtered, washed with water, cold ethanol and ether, in that order. After drying for twelve hours at room temperature under reduced pressure, the complexes were used directly in the reactions described below and were not characterized further.

Co(SALDIPN) was prepared according to the method of Calvin[16], with one exception. No O_2 was allowed to come into contact with the compound until the mother liquor had been washed away with ether and allowed to dry to yield a yellow-brown crystalline product. This material was then "recrystallized" in an inert atmosphere with a warm ethanol-H_2O mixture yielding green needles.

The ligands derived from substituted salicylaldehydes and bis(2-aminoethyl)sulfide, hereafter referred to as X-SALDAES, were prepared by the following procedures. Since these are new materials, their preparation is described in detail. Their composition and structure have been determined by elemental analysis, infrared spectra and n.m.r. spectra.

Preparation of H-SALDAES

To a stirring solution of salicylaldehyde (12.21 g, 0.1 mole) dissolved in 200 ml of 95 per cent ethanol was added dropwise DAES (6.00 g, 0.05 mole) dissolved in 50 ml of 95 per cent ethanol. Soon after addition was begun, bright yellow crystals formed in the solution. Stirring was continued for one hour after addition was complete. The material was filtered and dried *in vacuo* at room temperature.

Preparation of 5-MeSALDAES

Five-methylsalicylaldehyde (5.44 g, .04 mole) was dissolved in 150 ml of 95 per cent ethanol. To this stirring solution was added dropwise DAES (2.56 g, .02 mole) dissolved in 25 ml of 95 per cent ethanol. Immediately upon addition a yellow crystalline material was formed. After stirring for one hour, the yellow solid was filtered and dried *in vacuo* at room temperature.

Preparation of 5-BrSALDAES

Five-bromosalicylaldehyde (7.55 g, .0373 mole) was dissolved in 300 ml of 95 per cent ethanol. To this stirring solution, DAES (2.24 g, .0187 mole) dissolved in 50 ml of 95 per cent ethanol was added dropwise over a period of about one hour. After thirty minutes, a yellow crystalline material formed in the flask. The reaction mixture was stirred for an additional hour, after which the yellow product was filtered and dried *in vacuo* at room temperature.

Preparation of 3-MeoSALDAES

Recrystallized ortho-vanillin (7.6 g, .05 mole) was dissolved in 250 ml of absolute ethanol. To this stirring solution was added dropwise DAES (3.0 g, .025 mole) dissolved in 50 ml of absolute ethanol, the addition requiring about one hour. The solution, after stirring for an additional hour, was reduced by one-half in volume and placed in a cold room overnight, whereby yellow crystals were precipated, filtered and dried in vacuo at room temperature.

PREPARATION OF THE COMPLEXES

Preparation of Ni(H-SALDIEN)

$Ni(SAL)_2 \cdot 2H_2O$[17] (3.37 g, .01 mole) was suspended in 200 ml of absolute ethanol. The suspension was brought to reflux with stirring, and DIEN (1.03 g, .01 mole) dissolved in a small amount of absolute ethanol was added. The color of the solution turned dark red-brown as the green solid quickly disappeared. The reaction mixture was refluxed for three hours. Upon allowing the flask to come to room temperature, yellow-brown needles were precipitated. This material was filtered, washed with ether and dried in vacuo at 100°C for twelve hours. More material could be isolated from the filtrate after it remained in the cold room (5°C) for one day.

Preparation of Ni(5-BrSALDIEN)

$Ni(5\text{-}BrSAL)_2 \cdot 2H_2O$[17] (4.95 g, .01 mole) was suspended in absolute ethanol and brought to reflux with stirring. DIEN (1.03 g, .01 mole) in a small amount of absolute ethanol was added in one addition. An orange-red solution formed almost immediately. After refluxing for one hour, an orange precipitate formed. The solution was filtered, washed with diethyl ether and dried at 100°C in vacuo for twelve hours.

Preparation of Ni(5-MeSALDIEN)$\cdot H_2O$

Ni(5-MeSAL)$_2\cdot 2H_2O$[17](2.76 g, .0075 mole) was suspended in 125 ml of absolute ethanol and brought to reflux with stirring. To this suspension DIEN (.77 g, .0075 mole) in a small amount of absolute ethanol was added in one addition. No immediate color change was noticed. Upon refluxing for three hours, the color gradually changed from light green to orange with dissolution of the green solid. Refluxing was continued for six more hours after which the reaction was allowed to come to room temperature. Orange crystals formed which were collected by filtration and dried *in vacuo* at 100°C for twelve hours.

Preparation of Ni(3-MeoSALDIEN)

Ni(3-MeoSAL)$_2\cdot 2H_2O$[17](3.99 g, .008 mole) was suspended in 125 ml of absolute ethanol and brought to reflux with stirring. DIEN (.82 g, .008 mole) in a small amount of ethanol was added to the suspension in one addition. The green solid quickly disappeared and a dark red-brown solution developed. The solution was refluxed for three and one-half hours then cooled overnight (5°C). A yellow solid precipitated which was collected by filtration and dried *in vacuo* at 100°C for twelve hours. It was recrystallized from hot methanol.

Preparation of the Pyridine Adduct of Ni(5-BrSALDIEN)

One gram of Ni(5-BrSALDIEN) was suspended in 50 ml of spectro-grade pyridine and the resulting mixture was refluxed for two hours. The compound dissolved in pyridine upon heating. The solution was then allowed to come to room temperature whereby a green powder was precipitated. The material was filtered and dried at room temperature and atmospheric pressure over KOH in a pyridine atmosphere.

Preparation of Ni(SALPN)

$Ni(SAL)_2 \cdot 2H_2O$[17] (10.11 g, .03 mole) was suspended in 100 ml of absolute ethanol and brought to reflux with stirring. To this suspension PN (3.93 g, .03 mole) in a little absolute ethanol was added in one addition. The solution became orange in color almost immediately followed by the precipitation of a yellow-orange material. Refluxing was continued for one and one-half hours. The reaction mixture was allowed to come to room temperature after which the material was collected and dried *in vacuo* at 100°C for twelve hours, and will be referred to as Ni(SALPN).

Preparation of Ni(H-SALDAES)

H-SALDAES (3.26 g, .01 mole) was dissolved in 200 ml of absolute ethanol and brought to reflux. Nickel acetate, $Ni(OAc)_2 \cdot 4H_2O$, (2.49 g, .01 mole) dissolved in 125 ml of absolute ethanol was added dropwise. A green solid formed approximately after one-half of the nickel solution had been added. After addition was complete, refluxing was continued for two hours, and then the flask was allowed to come to room temperature. A green powder was isolated and dried *in vacuo* at 100°C for twelve hours.

Preparation of Ni(H-SALDAES)(H_2O)

To H-SALDAES (1.64 g, .005 mole) dissolved in methanol was added a solution of Ni(OAc)$_2$·4H_2O (1.44 g, .005 mole) dissolved in methanol. The mixture was refluxed for four hours. No immediate precipitate formed upon mixing. After two hours a bright green precipitate formed. It was filtered, washed with diethyl ether, and dried *in vacuo* at room temperature for twelve hours. This material could be recrystallized from hot chloroform.

Preparation of Ni(5-BrSALDAES)

To a solution of 5-BrSALDAES (4.86 g, .01 mole) dissolved in 150 ml of hot N,N-dimethylformamide with stirring, was added dropwise a solution of Ni(OAc)$_2$·4H_2O (2.49 g, .01 mole) dissolved in 125 ml of methanol. A green solid formed halfway through the nickel addition. The reaction mixture was refluxed for one hour, then allowed to come to room temperature and filtered and dried as described above.

Preparation of Ni(5-MeSALDAES)

5-MeSALDAES (3.56 g, .01 mole) was dissolved in 75 ml of N,N-dimethylformamide and brought to reflux with stirring. A solution of $Ni(OAc)_2 \cdot 4H_2O$ (2.49 g, .01 mole) dissolved in 125 ml of absolute ethanol was then added dropwise. About halfway through addition, a green solid formed, but refluxing was continued an additional hour after addition was complete. Green crystals were filtered and dried in vacuo at 100°C for twelve hours.

Preparation of Ni(3-MeoSALDAES)

3-MeoSALDAES (19.5 g, .05 mole) was dissolved in 400 ml of absolute ethanol and brought to reflux with stirring. A solution of $Ni(OAc)_2 \cdot 4H_2O$ (12.44 g, .05 mole) dissolved in 250 ml of absolute ethanol was added dropwise. Again a green solid appeared after about half the nickel solution had been added. Refluxing was continued for one hour after the addition was complete. The green solid was collected by filtration and dried in vacuo at 100°C for twelve hours.

Preparation of Ni(3-IsopropylSALDAES)

To a solution prepared by dissolving 3-Isopropylsalicylaldehyde (4.36 g, .03 mole) in 50 ml of 95 per cent ethanol, which also contained triethylorthoformate (4.44g, .03 mole) and triethylamine (3.03 g, .03 mole), was added dropwise

DAES (1.80 g, .015 mole) with stirring. The resulting mixture was yellow in color. A solution prepared by dissolving $Ni(OAc)_2 \cdot 4H_2O$ (3.74 g, .015 mole) in 200 ml of absolute ethanol was then added dropwise to the yellow solution. Refluxing was continued for three hours after nickel addition was complete. The reaction mixture was allowed to come to room temperature, whereupon green crystals formed which were filtered and dried *in vacuo* for twelve hours at 100°C.

Preparation of the Pyridine Adduct of Ni(H-SALDAES)

Approximately 1.0 g of Ni(H-SALDAES) was dissolved in about 10 ml of pyridine. The solution was heated for about one-half hour then allowed to come to room temperature, followed by addition of H_2O whereupon a green solid precipitate formed. The material was filtered and dried *in vacuo* at 100°C.

Preparation of the Pyridine Adduct of Ni(3-MeoSALDAES)

Approximately 1.0 g of Ni(3-MeoSALDAES) was dissolved in pyridine and stirred for one-half hour. Then H_2O was added causing a green material to precipitate. The material was isolated and dried *in vacuo* at 100°C.

Preparation of Me-Co(SALDIPN)

Co(SALDIPN) (1.0g, .0025 mole) was dissolved in 75 ml of methanol and the solution flushed with N_2. Methyl iodide (1.07 g, .0075 mole) dissolved in 10 ml of MeOH was added, followed by two drops of a 10 per cent $PdCl_2$ solution in methanol along with 0.1 g of $NaBH_4$. Immediately there was a rapid evolution of H_2. After stirring for a short while 4 ml of a 50 per cent NaOH solution was added dropwise. Soon afterwards, a red solid appeared. Stirring was continued for one hour. The material was filtered and dried *in vacuo* at 100°C for twelve hours.

Preparation of Et-Co(SALDIPN)

Co(SALDIPN) (1.0 g, .0025 mole) was dissolved in 75 ml of MeOH and the solution flushed with N_2. Two drops of a 10 per cent $PdCl_2$ solution in MeOH was added. Then ethyl iodide (1.17 g, .0075 mole) dissolved in 10 ml of MeOH was added, followed by 0.1 g of $NaBH_4$. There was an immediate evolution of H_2. The solution was stirred for a few minutes then 3 ml of a 50 per cent aqueous NaOH solution was added. After a short while a red solid formed. It was isolated and dried *in vacuo* at 100°C for twelve hours.

The remaining alkyl derivatives were prepared in the above manner, using the appropriate alkyl halide.

Physical Measurements

Infrared absorption spectra were obtained in the region 5000-400cm^{-1} using Perkin-Elmer Model 621 Grating spectrophotometer and a Beckman IR-5A recording spectrophotometer. Solid state spectra were recorded as KBr pellets and Nujol or hexachlorobutadiene mulls. Solution spectra were taken in spectroquality solvents using matched solution cells. Ultraviolet-visible-near infrared spectra were obtained with a Cary 14 recording spectrophotometer. Spectra of solid samples were obtained by diffuse transmittance employing Nujol mulls impregnated on Whatman No. 1 filter paper.[18] Solution spectra were obtained utilizing spectroquality organic solvents.

Magnetic measurements on solid specimens were obtained by either the Gouy or Faraday methods. Both systems were calibrated with $Hg(Co(SCN)_4)$. Diamagnetic corrections were made employing Pascal's constants.[19] Susceptibilities for paramagnetic species in solution were determined by the n.m.r. method given by Evans[20] using a Varian A60 spectrometer. In the equation:

$$\chi_g = \frac{3\Delta f}{2\pi f m} + \chi_0 + \frac{\chi_0(d_0 - d_s)}{m}$$

where

Δf = frequency shift between sample and reference

f = frequency of measurement

m = grams of sample per ml of solution

X_o = bulk diamagnetic susceptibility of solvent

d_o = density of solvent

d_s = density of solution

Δf was determined from the shift of an inert reference material (TMS) placed in both reference solvent and sample solution. Special n.m.r. coaxial cells with precision spacing of the inner tube (Wilmad Glass Company) were used. The last two terms in the susceptibility equation were neglected when determining the values by this method. Measurements were performed at 10°C and 20°C and the temperatures were controlled using a Varian Model V6040 NMR variable temperature controller.

Mass spectra were obtained on a Hitachi-Perkin-Elmer RMU-7 double focusing mass spectrometer using a solid inlet probe. The solid probe temperature was maintained at a value to prevent decomposition of the sample. The same temperature was maintained at approximately the temperature of the solid probe. Analyzer tube pressures of less than 1×10^{-6} torr and ion source pressures of less than 1×10^{-6} torr were employed. Where necessary, the mass to charge ratios were calibrated using perfluorokerosene as a standard.

Elemental analyses were performed by Galbraith Microanalytical Laboratory, Knoxville, Tennessee, and in this laboratory using a Perkin-Elmer Model 240 carbon, hydrogen, nitrogen analyzer.

Nuclear magnetic resonance spectra were determined in deuterated chloroform, dimethylsulfoxide and water employing a Varian A60 NMR spectrometer with TMS as an internal standard.

X-Ray powder pattern data were obtained using a General Electric-XRD-5 powder diffractometer.

RESULTS AND DISCUSSION OF NI(X-SALDIEN) COMPLEXES

The microcrystalline complexes were prepared by a metal template reaction of the appropriately substituted bis(salicylaldehyde)-nickel(II) complex with DIEN. Complexes of the following composition were isolated Ni(X-SALDIEN), except for the 5-methyl derivative which contained a molecule of water of hydration.

The resulting neutral complexes are golden yellow in appearance and are partially soluble in methanol, ethanol, water, and dimethylsulfoxide. They are very soluble in pyridine if allowed to shake for a day and very soluble immediately in hot pyridine. These observations are probably due to a reaction with pyridine that is discussed later. The complexes are insoluble in methylene chloride, DMF, acetonitrile, and glyme.[a] They are relatively thermally stable, melting around 200°C with decomposition. Complexes of analogous composition and properties were also prepared by substituting bis(2-aminopropyl)amine for diethylenetriamine in its reaction with bis(salicylaldehyde)nickel(II) complexes.

Analytical data supporting the elemental composition of the complexes is shown in Table II.

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[a] glyme is 1,2-dimethoxyethane.

TABLE II

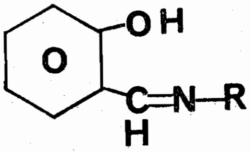
Analytical Data[A] For The Nickel(II) Complexes Of N,N'bis(salicylidene)-1,5-diamino-3-azapentane

COMPOUND		C	H	N
Ni(H-SALDIEN)	Calc	58.89	4.95	11.45
	Found	58.72	5.26	11.19
Ni(5-BrSALDIEN)	Calc	41.11	3.26	7.99
	Found	40.98	3.17	7.72
Ni(5-MeSALDIEN)(H_2O)	Calc	57.97	6.04	10.14
	Found	57.71	6.04	9.66
Ni(3-MeoSALDIEN)	Calc	56.10	5.43	9.82
	Found	55.81	5.50	9.90
Ni(3-IsoSALDIEN)	Calc	63.73	6.92	9.29
	Found	63.23	6.26	9.31
Ni(5-BrSALDIEN)(PY)	Calc	45.43	4.15	9.22
	Found	45.62	3.64	9.26
Ni(SALPN)	Calc	60.63	5.86	10.61
	Found	60.51	5.72	10.41

[A] Analyses are accurate to approximately ± 0.3 per cent.

Positive ion mass spectra were determined under conditions described earlier. All of the derivatives gave relatively intense parent isotope clusters with the exception of the Ni(5-BrSALDIEN) and Ni(3-MeoSALDIEN) derivatives, see Table III. These particular derivatives may have a very low vapor pressure and hence cannot be transformed into the gas phase except with considerable decomposition. The mass spectra of Ni(H-SALDIEN), Ni(5-MeSALDIEN) and Ni(SALPN) also show a peak corresponding to the parent minus the Ni atom (i.e., the ligand). The mass spectra were scanned above the basic molecular ion to the mass to charge ratio expected for the dimer. No such peak was observed. This evidence supports the hypothesis that these complexes are monomers and not dimers in the gas phase.[21] Insufficient solubility in a suitable solvent prevented molecular weight determination in solution.

Infrared spectra were obtained as Nujol and hexachlorobutadiene mulls and KBr pellets. Of particular interest are the C=N and N-H stretching frequencies and aromatic C-H bending frequencies. It has been found that compounds of the type shown here



show a C=N stretching frequency in the region 1656-1629cm^{-1}.[22] With this fact in mind along with other references,[23],[24] the following assignments are shown in Table IV for a representative

TABLE III

MASS SPECTRAL DATA ON THE COMPLEXES[A]

COMPOUND	MOLECULAR FORMULA	PROBE TEMP. °C	ISOTOPIC CLUSTER
Ni(H-SALDIEN)	$C_{18}H_{19}N_3O_2Ni$	-	367,369
Ni(H-SALPN)	$C_{20}H_{23}N_3O_2Ni$	-	395,397
Ni(5-MeSALDIEN)	$C_{20}H_{23}N_3O_2Ni$	200°	395,397
Ni(3-MeoSALDAES)	$C_{20}H_{22}N_2SO_4Ni$	-	444,446
Ni(3-IsoSALDAES)	$C_{24}H_{30}N_2SO_2Ni$	-	468,470
Ni(5-MeSALDAES)	$C_{20}H_{22}N_2SO_2Ni$	-	412,414
Me-CoSALDIPN	$C_{21}H_{26}N_3O_2Co$	-	411,412
Et-CoSALDIPN	$C_{22}H_{28}N_3O_2Co$	110	425,426
Pr-CoSALDIPN	$C_{23}H_{30}N_3O_2Co$	145	439,440
Bu-CoSALDIPN	$C_{24}H_{32}N_3O_2Co$	135	453,454
Pent-CoSALDIPN	$C_{25}H_{34}N_3O_2Co$	125	467,468

[A] Isotope patterns for C^{13} were observed for the Ni complexes but are not included here.

TABLE IV

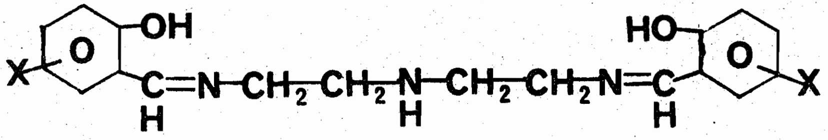
INFRARED DATA ON 5-BrSALDIEN AND ITS Ni COMPLEX

FUNCTIONAL GROUP	FREE LIGAND	COMPLEX
N-H	3305,very weak,sharp	Absent
C=N	1630,strong,sharp	1595,strong,sharp
C-H BEND Aromatic Nucleus	825,strong,sharp	795,strong,sharp

complex and its corresponding ligand. Spectra of the remaining ligands and their complexes exhibit similar band positions. It can be seen that there is a considerable shift to lower energy in the stretching frequency of the C=N upon complexation with the metal, see Appendix Figure II. This means that the energy required to stretch the bond has been reduced. This can be interpreted to mean that the imine nitrogen is coordinated.[25]

The infrared spectra of Ni(SALPN) and all Ni(X-SALDIEN) complexes revealed no bands in the 3700-3100cm^{-1} region which could be assigned to an N-H stretching vibrational mode. Only in the 5-methyl derivative is an absorption found, and this has been attributed to O-H symmetric and asymmetric stretching modes.[24] The broadness of this absorption probably results from the presence of non-coordinated water. Infrared spectra of several of the derivatives in various solvents also indicated no meaningful absorption in the 3700-3100cm^{-1} region. The spectrum of Ni(H-SALDIEN) in pyridine was investigated in an attempt to find the N-H stretching vibrational mode. Earlier, Langenbeck[26] and co-workers had reported a band around 3450cm^{-7} in the infrared spectrum of a pyridine solution of Ni(H-SALDIEN) and had assigned the band to an N-H stretching mode. The observation of a band at this high energy was suggested by these workers to be due to a non-coordinated secondary nitrogen. We have repeated this experiment and conclude this band is characteristic of spectrograde pyridine. In fact, the infrared spectrum of pyridine shows such a band in the region of interest. This assumption is supported by the observation that secondary aliphatic amines usually absorb weakly in the range 3350-3310cm^{-1}.[23] Deuteration of the secondary amine in slightly basic D_2O was also attempted and its infrared spectrum determined, but again no bands in the anticipated N-D stretching region were noted.

Free ligands, X-SALDIEN, were prepared for most of the derivatives in the **hopes** of being able to observe the N-H stretching mode but only the bromo derivative exhibited the band of interest (See Table IV). All free ligands give essentially identical n.m.r. spectra except for those regions which can be attributed to the presence of various functional groups located at either the three or five position on the benzene nucleus. The n.m.r. spectra are consistent with the following structural formulation:



These observations concerning the free ligands and the neutral complexes are consistent with the secondary amine being involved in hydrogen bonding which may be inter- or intra-molecular.

Infrared measurements on various concentrations of free ligand and complex suggest the hydrogen-bonding is intramolecular in both since the spectra are independent of concentration. It has been well established that hydrogen-bonding in amines tends to broaden, weaken, and shift to lower energy the N-H stretching band.[23] The absence of a sharp N-H stretching band in the complex also suggests that the secondary nitrogen is not coordinated to the nickel ion. A medium sharp singlet would be expected for a coordinated secondary amine.

The magnetic susceptibilities of Ni(SALPN) and the Ni(X-SALDIEN) complexes were determined by the Faraday method[19] and the results are presented in Table V. The magnetic moments are <u>higher</u> than would be predicted from the spin-only formula which yields a magnetic moment of zero for low-spin d^8 nickel complexes. Even if one allows for the contribution made by temperature independent paramagnetism and the inherent error in trying to correct the susceptibilities for diamagnetism, the moments are too high to consider the compounds completely diamagnetic. The moments are also <u>lower</u> than the spin-only formula predicts for high-spin nickel(II) of 2.83B.M. (i.e., 2 unpaired electrons). The anomalous moments can rise from several mechanisms. First, the complexes may be essentially diamagnetic low-spin ones that are

TABLE V

Magnetic Data On The Ni^{+2} N,N'bis(salicylidene)-1,5-diamino-3-azapentane $^{-2}$ And Ni^{+2} N,N'bis(salicylidene)-1,5-diamino-3-thiopentane $^{-2}$ Complexes In The Solid State^{A}

COMPOUND	TEMP, °C	$X_g \times 10^6$	$X_m^B \times 10^6$g	μ_{eff} B.M.
Ni(SALDIEN)	-	-	91.1	-
Ni(5-BrSALDIEN)	27	1.09-.49	576.3-259.2	1.40-1.08
Ni(3-MeoSALDIEN)	23	.685-.404	290.4-171.1	1.05-.896
Ni(5-MeSALDIEN)(H_2O)	27	1.12-.490	443.5-194.3	1.24-.965
Ni(SALPN)	27	2.36-.960	871.8-355.3	1.59-1.13
Ni(5-BrSALDIEN)(PY)				
Ni(SALDAES)(H_2O)	23	8.48	3623.4	2.94
Ni(SALDAES)			482.8	1.11
Ni(5-BrSALDAES)	23.5	41.39	436.13	1.02
Ni(5-MeSALDAES)	25	.464-.231	191.1	0.95
Ni(3-MeoSALDAES)	23	.866	385.37	1.15
Ni(3-IsoSALDAES)	26	2.16-1.28	1015.4-602.1	1.75-1.43

TABLE V

COMPOUND	TEMP, °C	$X_g \times 10^6$	$X_m{}^B \times 10^{6}g$	μ_{eff} B.M.
Ni(SALDAES)(PY)	27	6.31-5.92	2929.2-2745.5	2.38-2.26
Ni(3-MeoSALDAES)(PY)	26	3.91-3.46	2048.0-1815.5	2.38-2.26

[A] Molar susceptibilities show a dependence on field strength.

[B] Molar susceptibilities are corrected for diamagnetic ligands.

contaminated with a small percentage of some paramagnetic high-spin species (i.e., a low-spin square planar or five-coordinate material contaminated with a high-spin octahedral, five-coordinate or tetrahedral complex). Second,several structures may co-exist in equilibrium with each other (i.e., one that is high-spin and one that is low-spin such as a tetrahedral $\rightleftharpoons$ square planar). There is a case in which both tetrahedral and square complexes are found together in the same crystalline state.[27] Also there is evidence for such an equilibrium in solution.[28] Thirdly, spin-spin interaction or anti-ferromagnetism arising from Ni-Ni interaction could produce an abnormal moment. One would expect a magnetic moment for tetrahedral geometry to lie between 3.0-3.4B.M., but if the phenomonon were operating, a small interaction of this type could cause an anomalously low moment.

Finally, and probably the most pertinent rationalization is the phenomonon of spin state isomerism.[29] This may be pictured as a thermal equilibrium between singlet and triplet states. In other words, there exist two energy levels that are within kT of each other, and hence, population of both states becomes probable. It has been suggested that in situations such as this, the complex is at the "magnetic cross-over point" where the ground state changes from singlet to triplet (I) or vice versa (II).

$$\begin{array}{ccc} \underline{\text{TRIPLET}} & & \underline{\text{SINGLET}} \\ & \rightleftharpoons & \\ \underline{\text{SINGLET}} & & \underline{\text{TRIPLET}} \\ \text{I} & & \text{II} \end{array}$$

Magnetic susceptibilities in solution were determined by an n.m.r. method. Pyridine was employed as the solvent. It was found that a change in the spin state occurred evidently arising from pyridine coordinating to the complex. The magnetic moments in pyridine are listed in Table VI. It can be seen that the two complexes listed here are both paramagnetic in the coordinating solvent pyridine. Precedence for this type behavior has been observed before.[30] Other information indicating that the pyridine is coordinated is dealt with later. Although the values are above the spin-only value of 2.83B.M. for two unpaired electrons, the difference is probably due to a significant orbital contribution to the moment. Variation of both concentration and temperature was employed. From the results obtained, it may be concluded that the magnetic susceptibilities are independent of both concentration and temperature, within experimental error, and that the equilibrium

$$\underset{\mu = 1.0\text{B.M.}}{\text{Ni(X-SALDIEN)} + n\text{PY}} \rightleftharpoons \underset{\mu = 3.2\text{B.M.}}{\text{Ni(X-SALDIEN)(PY)}_n}$$

TABLE VI

Magnetic Data[A] On Ni N,N'bis(salicylidene)-1,5-diamino-3-azapentane And Ni N,N'bis(salicylidene)-1,5-diamino-3-thiopentane Complexes in Pyridine

COMPOUND	TEMP, °C	CONC g/ml	$X_g \times 10^6$	$X_m^B \times 10^6$	μ_{eff} B.M.
Ni(SALDAES)	26	.0439	7.52	3699.9	2.99
	26	.0128	8.00	3923.6	3.08
	20	.0128	8.68	4237.2	3.16
Ni(3-MeoSALDAES)	20	.0109	7.52	4241.2	3.16
	10	.0109	8.02	4501.6	3.21
	20	.0229	6.58	3747.5	2.98
	10	.0229	7.36	4156.4	3.08
Ni(3-IsoSALDAES)	10	.0152	7.02	4127.7	3.07
	20	.0152	8.75	5074.4	3.46
	10	.007	8.96	5109.7	3.44
	20	.007	8.73	5066.5	3.46
Ni(5-BrSALDIEN)	26	.0378	6.04	4441.42	3.26
	26	.0110	6.97	5075.54	3.49
	10	.0129	7.84	5670.22	3.58
	20	.0129	6.38	4671.98	3.32
Ni(3-MeoSALDIEN)	20	.0162	7.97	5002.10	3.44
	10	.0162	8.70	5429.88	3.52
	10	.0131	9.10	5664.38	3.58
	20	.0131	8.37	5236.50	3.52

[A] Magnetic moments are calculated assuming a dipyridine adduct.

[B] Molar susceptibilities are corrected for diamagnetic ligands.

is shifted completely to the right. Insufficient solubility of Ni(H-SALPN) in pyridine precluded our determining its magnetic moment in this solvent.

Visible spectra were obtained under three conditions: solid, non-coordinating solvent, and coordinating solvent, in an effort to obtain information concerning the geometry around the Ni atom. The data are presented in Table VII.

In the solid state spectra of Ni(SALPN) and Ni(X-SALDIEN) (Nujol mull diffuse transmittance spectra) two bands are observed: one located at 23,000cm^{-1}; the other located at 30,500cm^{-1}. Both bands are tentatively assigned as spin-allowed charge transfer transitions. The band at 23,000cm^{-1} is in the region where d-d transitions peculiar to square planar nickel(II) are found,[31] but other data rule against this assignment. First, square planar Ni(SALEN) has its d-d transition located around 19,000cm^{-1}.[32] It is expected that if Ni(X-SALDIEN) is in fact square planar, its d-d transition should be of comparable or lower energy. Holm has found that lengthening the chain joining the two Schiff base linkages reduces the d-d transition energy.[32] Second, the solid state spectrum of 5-BrSALDIEN shows a band around 23,000cm^{-1}. We, therefore, conclude that the band of interest is peculiar to the ligand and is not a d-d transition. This assumption is supported by the fact that the extinction coefficients in

TABLE VII

Electronic Spectra^A (cm^{-1}) Of The Ni N,N'bis(salicylidene)-1,5-diamino-3-azapentane Complexes

COMPOUND	MEDIUM	BAND MAXIMA			
Ni(H-SALDIEN)	Nujol	23,260	30,770		
	Methanol	26,320 (7.17×10^3)	30,300 (1.01×10^4)		
	Pyridine	10,870 (17.9)	25,970 (7.1×10^3)	31,500 (5.2×10^3)	
Ni(5-MeSALDIEN)	Nujol	23,260	24,940	30,130	
	Methanol	25,320 (5.63×10^3)	30,130 (13.3×10^3)		
	Pyridine	10,360 (24.74)	25,000 (4.95×10^3)	30,300 (3.90×10^3)	
Ni(5-BrSALDIEN)	Nujol	23,030	30,680		
	Methanol	25,640 (8.27×10^3)	30,537 (8.27×10^3)		
	Pyridine	10,204 (69.72)	18,200 (18.75)	25,000 (7.17×10^3)	30,540 (5.58×10^3)
Ni(3-MeoSALDIEN)	Nujol	22,730			
	Methanol	25,640 (2.70×10^3)	30,300 (12.13×10^3)		
	Pyridine	10,846 (9.9)	12,580 (5.2)	17,620 (9.2)	21,570 (3.24×10^3)

TABLE VII

COMPOUND	MEDIUM	BAND MAXIMA			
Ni(H-SALPN)	Nujol	23,670	24,840	30,540	
	Methanol	25,970 ($4.1x10^3$)	30,540 ($9.7x10^3$)		
	Pyridine	12,200 (404)	14,290 (70.78)	19,230 (606)	25,640 ($3.64x10^3$)
Ni(5-BrSALDIEN)(PY)	Nujol	$11,630^{VB}$	18,520	24,390	
	Chloroform	11,630VB (70)	18,520 (100)	25,970 ($7.3x10^3$)	
	Pyridine	-	-	-	-
Ni(SALEN)	Nujol	19,610	23,530	30,300	
Ni(SALOPHEN)	Nujol	18,020	19,610	26,320	

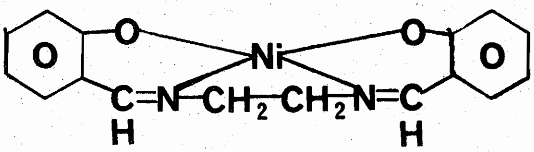
[A] Numbers in parentheses are molar extinction coefficients.

methanol for these bands are much too large to have arisen from a d-d transition. The charge transfer bands may be either a ligand-ligand transition, a charge transfer from metal to ligand, or a charge transfer from ligand to metal. It can be seen from the data that the species in the solid state is the same as it is in methanol as evidenced by similar band positions. However, in pyridine there is a new broad band in the 10,500cm^{-1} region for Ni(X-SALDIEN) complexes and at 12,000cm^{-1} for Ni(SALPN). This band is characteristic of octahedral nickel(II),[31] that probably arises from coordination of pyridine in either one or both of the axial positions. To test this hypothesis, the pyridine adduct of Ni(5-BrSALDIEN) was made and isolated. The magnetic, spectral, and analytical data are presented in the appropriate table.

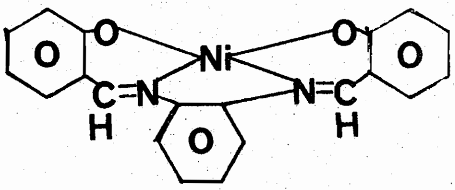
The pyridine adduct is pale green, not golden yellow. The infrared spectra of the pyridine adduct, unlike the Ni(X-SALDIEN) complexes, shows an N-H stretch which is shifted 30-35cm^{-1} to lower energy relative to the free ligand, see Appendix, Figure II. The visible spectra of the pyridine adduct and Ni(5-BrSALDIEN) in pyridine are similar except for slight shifts in the band maxima. It can be concluded that in both species we are dealing with an octahedral nickel(II) ion. Analytical, magnetic, and spectral data support this postulate. See Tables II, V, and VII. Since the adduct is a mono-pyridinate and the N-H stretching vibrational mode is shifted considerably to lower energy, it is tempting to suggest the pseudo-octahedral structure in the solid state is achieved by interaction of the secondary nitrogen and one pyridine moiety at the axial sites rather than both sites being filled by pyridine molecules.

It is interesting to speculate concerning the energy difference between the first transition of the pyridine solution of Ni(H-SALPN) and that of the Ni(X-SALDIEN) complexes. Dreiding and Fisher-Hershfelder-Taylor stereomodels allow some insight into rationalizing this observation. One should recognize to begin with that PN is a potentially optically active amine with two asymmetric carbon atoms. Being a symmetrical molecule, the possible enantiomers are dd, ll, and meso. When the secondary nitrogen is placed in its closest approach to the Ni ion, one can see from a study of models that the methyl groups on the PN backbone occupy the same region in space in one particular conformation of the meso form, and one methyl interferes with the methylene hydrogens in both the dd and ll forms regardless of the conformation. Only in one configuration of the meso form is the secondary nitrogen near the Ni ion without any interaction of the methyl groups with other atoms. This means that the likelihood of the secondary nitrogen being in a perturbing position is lessened due to these steric factors since racemic triamine was employed. This possibly suggests that pyridine occupies both axial positions to the exclusion of the secondary nitrogen in the SALPN complex as opposed to the X-SALDIEN complexes. This postulate is supported by the fact that pyridine produces a larger field strength than does a secondary nitrogen. This larger field strength would cause an increase in energy for the first transition which is observed.

In comparison Ni(X-SALEN) and Ni(X-SALOPHEN) shown below,



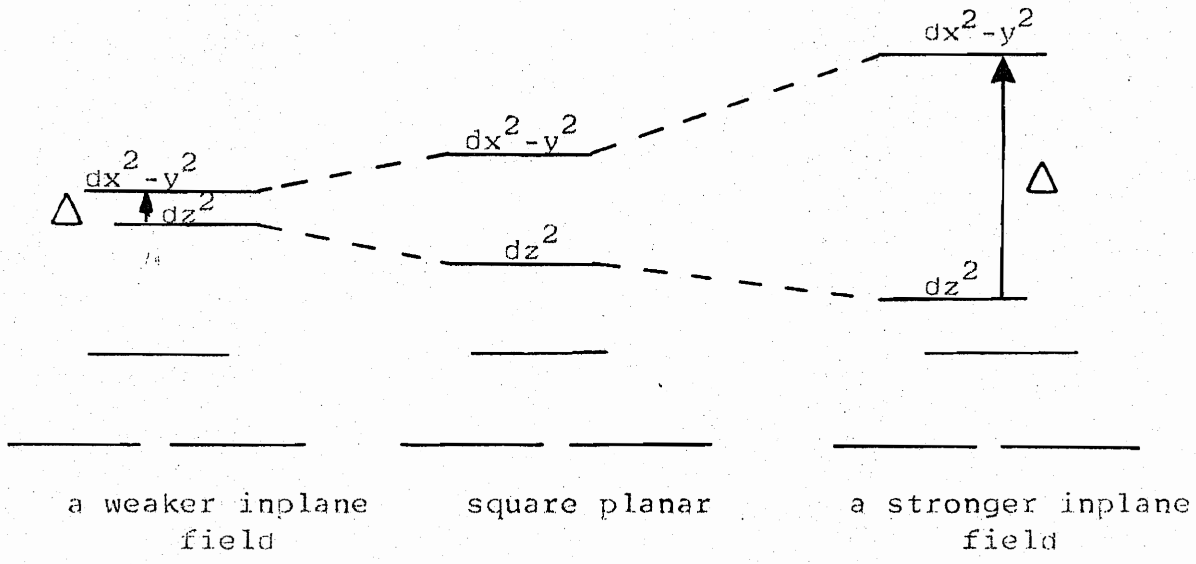
Ni(X-SALEN)



Ni(X-SALOPHEN)

have been shown to be planar or nearly so in the solid state.[32] Under anhydrous conditions, these complexes have been shown to be diamagnetic. When dissolved in pyridine Ni(X-SALEN) remains diamagnetic but Ni(X-SALOPHEN) becomes partially paramagnetic with a moment of 2.5 B.M. at room temperature. Temperature dependent magnetic studies show that the moments decreased with temperature.[33] The results lead to the postulation of an equilibrium between coordinated pyridine and non-coordinated complex as we have postulated for Ni(X-SALDIEN) in pyridine (the major difference being that Ni(X-SALDIEN) is fully paramagnetic in pyridine). This could be explained by the existence of a degree of perturbation of one of the axial positions by the secondary nitrogen, the degree being limited by the steric requirements of the ligand. That this type behavior is not observed in Ni(X-SALEN)[33] may be due to the fact that none of the axial positions is constantly under the influence of a donor atom. It has been shown that for a metal to donor atom distance between 2.3 and 2.5Å, H-SALDIEN can function as a planar pentadentate ligand, with a stable (non-eclipsed) conformation of its aliphatic chain.[34] The extent of this influence is difficult to measure, but it would seem that it becomes more pronounced if a donor ligand occupies the other axial position. That the pyridine adduct of Ni(5-BrSALDIEN) shows as N-H stretch in the infrared spectrum is evidence for this. An N-H stretch would be expected to be observed if the secondary nitrogen were coordinated.

Alternatively, let us consider the following hypothesis. It has been shown by Holm[32] that increasing the chain length between the imine nitrogens weakens the inplane field strength. On this basis, one would expect the inplane field strength of X-SALDIEN to be weaker than the inplane field strength of X-SALEN because the DIEN has five atoms whereas the ethylenediamine has two atoms. When we say the inplane field is weakened, this means that the energies of the d orbitals are changed in energy. Consider the following allignment of the d orbitals and concentrate on the movement of the x^2-y^2 and z^2 orbitals in particular.



One can see that the energy level difference, Δ , has decreased in going from a strong inplane field to a weaker inplane field. This means that there is less energy required to unpair the electrons on the Ni atom if the inplane field is weaker. Let us assume that pyridine has an ability to unpair electrons. It is obvious that it would be easier for pyridine to unpair the electrons in a weak inplane field than in a strong inplane field because the energy difference is smaller. This can account for the fact that the Ni(X-SALDIEN) complexes are fully paramagnetic in pyridine whereas the Ni(X-SALEN) complexes remain diamagnetic in pyridine, X-SALEN being a stronger inplane field. One might argue, however, that Ni(X-SALOPHEN) goes partially paramagnetic in pyridine. This could be due to the fact that the basicity of the imine nitrogens are reduced by conjugation with the three aromatic ring systems, thereby lowering the coordinating ability which lowers the inplane field strength.

The weaker inplane field would also lend explanation to the anomolous moments observed for the Ni(X-SALDIEN) complexes in the solid state whereas Ni(X-SALEN) is diamagnetic. Therefore, we would conclude that there could exist a thermal population of both dx^2-y^2 and dz^2 at room temperature in the Ni(X-SALDIEN) complexes.

RESULTS AND DISCUSSION OF Ni(X-SALDAES) COMPLEXES

The complexes were prepared by adding dropwise a solution of $Ni(OAc)_2 \cdot 4H_2O$ to a solution of the pre-formed Schiff base. Complexes of the following composition were isolated Ni(X-SALDAES). See Table VIII for analytical data.

The complexes are dark green in appearance and are insoluble in most organic solvents with the exception of pyridine. Ni(3-IsoSALDAES) and Ni(H-SALDAES) are partially soluble in CH_2Cl_2 and $CHCl_3$. They are all relatively very stable, melting above 250°C.

Mass spectra were determined on these complexes under the least severe conditions. The majority of the complexes gave a series of M/e corresponding to the isotope pattern of complex with no higher mass fragments that might result from dimers, see Table III. As seen in the X-SALDIEN complexes, the bromo derivative here gave no parent ion peak.

Infrared spectra on these complexes were obtained as either Nujol mulls or KBr pellets. The infrared of X-SALDAES and X-SALDIEN complexes are essentially the same. Of specific interest is the C=N stretching frequency. There was observed a shift of $25 cm^{-1}$ to lower energy in the band attributed to the C=N stretching mode when the complex and free ligand were compared. This would indicate that the imine nitrogen is

TABLE VIII

Analytical Data[A] For The Ni N,N'bis(salicylidene)-1,5-diamino-3-thiopentane Complexes

COMPOUND		C	H	N
Ni(H-SALDAES)	Calc	56.13	4.72	7.28
	Found	55.95	4.77	7.29
Ni(5-MeSALDAES)	Calc	58.13	5.38	6.78
	Found	58.41	5.32	6.53
Ni(H-SALDAES)(H_2O)	Calc	53.62	5.01	6.95
	Found	53.69	4.91	6.53
Ni(5-BrSALDAES)	Calc	39.82	2.98	5.16
	Found	39.90	2.87	5.17
Ni(3-MeoSALDAES)	Calc	53.95	4.99	6.29
	Found	54.19	5.02	6.31
Ni(3-IsoSALDAES)	Calc	61.42	6.46	5.97
	Found	61.51	6.46	6.16
Ni(H-SALDAES)(PY)	Calc	59.50	5.00	9.05
	Found	59.46	4.87	8.91
Ni(3-MeoSALDAES)(PY)	Calc	57.27	5.20	8.02
	Found	57.09	5.43	7.79

[A] Analyses are accurate to ± 0.3 per cent.

coordinated. Rationalizations such as these can be found in several cases already investigated.[25] Infrared spectra of Ni(H-SALDAES)(PY) and Ni(3-MeoSALDAES) were run in an attempt to find the bands associated with pyridine. Comparison of these spectra with the Sadtler Catalogue[35] spectra confirmed the presence of pyridine (i.e., bands at 1220, 1120, 1060 could be assigned to pyridine). Present in the analytical table is anhydrated compound, Ni(H-SALDAES)(H_2O), which was also prepared whose formulation was arrived at partially by the presence of H_2O in the infrared at 3250cm^{-1}.

Magnetic susceptibilities of the Ni(X-SALDAES) complexes were determined by the Gouy and Faraday methods and results are presented in Table VI. These moments are, in most instances, very similar to the results obtained with Ni(X-SALDIEN). The reasons for this behavior are similar to those put forward in the discussion of the magnetic data for Ni(X-SALDIEN).

The magnetic susceptibilities were determined by an n.m.r. method also. No dependence on temperature or concentration was observed. However, in pyridine these complexes became spin free. The rationale here again is that the pyridine coordinates in the sixth position resulting in a pseudo-octahedral structure, thereby causing the electrons to become unpaired. The spectral evidence which indicates that pyridine is coordinated is dealt with later.

Visible spectra were obtained as Nujol mulls, and dissolved in pyridine and CH_2Cl_2 where solubility permitted. Bands appeared at 16,000cm^{-1} and 23,000cm^{-1} in all cases. This may be characteristic of low spin five-coordinate nickel(II) complexes or may arise from a square planar configuration in which the inplane field is rather weak.

In pyridine, the spectra is characteristic of an octahedral species. The characteristic Laporte forbidden transitions v_1, v_2, v_3 can be obtained directly from the spectra. The transitions being $^3A_2 \longrightarrow {}^3T_2$, v_1; $^3A_2 \longrightarrow {}^3T_1(F)$, v_2; $^3A_2 \longrightarrow {}^3T_1(P)$, v_3. Also observed is a charge transfer band. The data and assignments are presented in Table IX. In some of the spectra, a splitting of the lowest energy band is observed which probably arises as a result of tetragonal distortion from octahedral symmetry.

Two additional species, Ni(H-SALDAES)(PY) and Ni(3-Meo-SALDAES)(PY) were prepared (analyses, etc. in appropriate tables). It can be seen that these species in the solid state and in solution exhibit similar spectra as Ni(H-SALDAES) and Ni(3-MeoSALDAES) do in pyridine. Therefore, it can be concluded that in solution one is dealing with the same type species in both cases, that being a pseudo-octahedral one. An equilibrium such as the following may be envisioned to account for this observation.

TABLE IX

Electronic Spectra[A] (cm^{-1}) Of The Ni N,N'bis(salicylidene)-1,5-diamino-3-thiopentane Complexes

COMPOUND		BAND MAXIMA				
Ni(SALDAES)(H_2O)	Nujol	8403	15,620	24,390	30,770	
	$CHCl_3$	8700 (23.3)	16,000 (30.1)	26,320 (4.95×10^2)	30,300 (3.5×10^2)	
	Pyridine	10,420 (9.71)	17,390 (12.62)	25,970 (6.7×10^3)	31,250 (3.97×10^3)	31,750 (3.98×10^2)
Ni(H-SALDAES)	Nujol	16,060	23,120	30,080		
	Pyridine	10,420 (9.32)	17,390 (12.42)	25,970 (5.59×10^3)	31,750 (5.28×10^3)	
Ni(5-BrSALDAES)	Nujol	16,393	22,220	25,000	30,300	
	Pyridine	10,360 (40.65)	17,780 (40.65)	25,320 (7.72×10^3)	30,080 (5.28×10^3)	
Ni(5-MeSALDAES)	Nujol	15,390	22,730	31,250		
	Pyridine	10,310 (37.52)	17,390 (46.90)	25,160 (8.63×10^3)	30,300 (6.75×10^3)	
Ni(3-IsoSALDAES)	Nujol	15,560	20,830	24,540	30,300	
	CH_2Cl_2	16,130 (1.36×10^3)	25,320 (3.71×10^3)	30,300 (6.4×10^3)	40,400 (2.77×10^4)	
	Pyridine	11,330 (195)	17,360 (260)	25,710 (1×10^4)	28,990 (1.11×10^4)	30,300 (1.15×10^4)

TABLE IX

COMPOUND		BAND MAXIMA				
Ni(3-MeoSALDAES)	Nujol	16,000	22,990	23,530	25,320	29,850
	Pyridine	10,100	12,660	17,390		
		(9.0)	(1.9)	(9.0)		
Ni(3-MeoSALDAES)(PY)	Nujol	11,630	15,870	24,390	25,620	29,410
	$CHCl_3$	12,500	16,130	24,390	25,640	30,300
		(60)	(210)	(3.5×10^3)	(4.1×10^3)	(6.5×10^3)
Ni(H-SALDAES)(PY)	Nujol	11,360	16,950	25,640		
	$CHCl_3$	8,770	10,640	16,130		
		(20.12)	(20.12)	(80.48)		

[A] Numbers in parentheses are molar extinction coefficients.

$$\text{Ni(X-SALDAES)} + 1\text{PY} \rightleftharpoons \text{Ni(X-SALDAES)(PY)}$$

Low spin four- or five-coordinate | High spin six-coordinate

Our findings with the nickel complexes of X-SALDIEN and X-SALDAES cannot be easily interpreted. Whether the secondary nitrogen and/or the sulfur atom is in fact coordinated to the nickel(II) ion can only be confirmed by a single crystal X-ray diffraction study. The major differences between both series of complexes is found in their visible spectra and X-ray powder patterns, see Table X. As evidenced by powder pattern data, the structures of Ni(X-SALDIEN) and Ni(X-SALDAES) are not the same. Visible spectra (Nujol mulls) also differ in that Ni(X-SALDAES) has a significant low energy band around 16,000cm^{-1} which is missing from the visible spectra of Ni(X-SALDIEN). All complexes become highly paramagnetic in pyridine giving rise to pseudo-octahedral species,but judging from the band positions (specifically v_1 which is an indication of the average ligand field strength), the octahedral species are not identical.

The true structure may be one or some compromise of the following structures:

a) square planar

b) distorted square planar (metal ion raised above the plane defined by the four donor atoms or distorted tetrahedral structure)

TABLE X

X-Ray Data On The Ni Complexes Of N,N'bis(3-methoxysalicylidene)-1,5-diamino-3-azapentane),3-MeoSALDIEN, And N,N'bis(3-methoxysalicylidene)-1,5-diamino-3-thiopentane), 3-MeoSALDAES

Ni(3-MeoSALDIEN)		Ni(3-MeoSALDAES)	
d Value	Intensity	d Value	Intensity
14.730	28	10.782	45
12.627	18	8.845	58
11.191	40	8.192	25
10.281	25	6.026	25
7.254	8	5.438	22
6.326	17	4.575	19
5.906	40	4.270	15
5.391	14	4.114	22
5.277	23	3.934	60
5.096	19	3.850	43
4.796	12	3.633	48
4.529	15	3.363	38
3.619	25	3.220	12
3.520	40	2.921	20
3.401	30		

c) trigonal bipyramid or square pyramid.

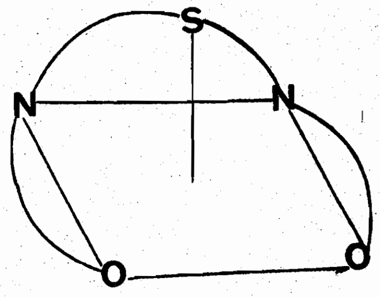
Four-coordination is characteristic of (a) and (b) while five-coordination is exemplified by (c).

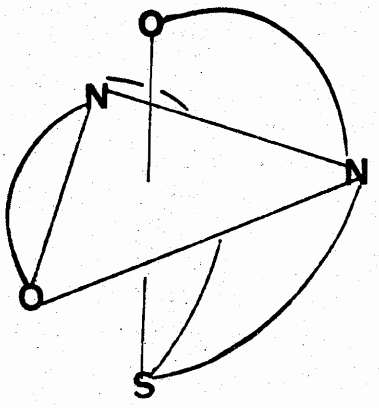
In conclusion, we believe our results concerning Ni(X-SALDIEN) are in best agreement with (a) or (b). Only in the solid pyridine adduct do we find any evidence which indicates coordination of the secondary amine. Structure (b) is strongly suggested in light of the anomolous magnetic results.

We believe Ni(X-SALDAES) to be five-coordinate in which perturbation at the fifth position is severely restricted by the steric requirements of the short ethylene bridges. Sulfur is better able to coordinate as a result of its larger size relative to a secondary nitrogen atom as evidenced by their respective van der Waal's radii.

Further evidence supporting the interaction of the sulfur with the nickel ion was found concerning observations that were made upon studying the visible spectra of both complexes in pyridine. Band maxima at 10,900 and 17,000cm^{-1} for Ni(X-SALDIEN) and at 10,100 and 17,400cm^{-1} for Ni(X-SALDAES) coupled with the fact that both complexes are paramagnetic as indicated by magnetic susceptibility measurements in solution by n.m.r. technique strongly suggest that both complexes now posses six-coordinate metal ions in pyridine. If Ni(X-SALDAES) and Ni(X-SALDIEN) were both solely cis-planar NiN_2O_2 structures, it is anticipated that their spectra in pyridine would give identically positioned band maxima. This was not observed. The lower energy band is shifted 800cm^{-1} to lower energy for Ni(X-SALDAES) relative to Ni(X-SALDIEN). It is felt that this difference can probably be attributed to an NiN_3O_2S environment for Ni(SALDAES) in pyridine vs. an NiN_4O_2 environment for Ni(X-SALDIEN) in pyridine. The shift to lower energy can be explained by the fact that a thio ether linkage produces a smaller Dq than a pyridine molecule.[36]

These results may be rationalized in several ways. The sulfur atom because of its orbital extension in space may be perturbing excited states of the nickel ion without forming a direct ground-state metal-sulfur bond, or production of a five-coordinate species has occurred with formation of a metal-sulfur bond. The postulated five-coordinate Ni(X-SALDAES) may be ideally envisioned to have a square pyramidal or trigonal-bipyramidal structure as discussed before.





Dreiding and Fisher-Hershfelder-Taylor stereo models do not rule out structure I although II is reported to be preferred by a somewhat analogous pentadentate ligand.[3] Regardless of the structure, the ligand must undergo severe steric strain in order for the sulfur atom to be situated near a coordination site. A somewhat analogous situation has been recently reported concerning a nickel(II) complex with a macrocyclic tetradentate ligand.[37] The diamagnetic complex was postulated to be five-coordinated with the four N donor atoms of the macrocyclic coordinated to the metal in the plane with a Br^- ion coordinated to the metal in one of the axial positions. It was postulated that the diamagnetism arises as a result of a water of solvation being strongly hydrogen-bonded to the coordinated Br^- ion, thereby reducing its coordinating ability. The results with the X-SALDAES is analogous in that the axial perturbation is considerably weakened by steric requirements of the ligand.

Finally, it has been previously stated that complexes of the type X-SALDAES give rise to "complexes of indefinite composition".[38] However, it has been found that this statement is not correct; and stable, pure complexes of X-SALDAES have been isolated and characterized.

RESULTS AND DISCUSSION OF ALKYL DERIVATIVES OF Co(SALDIPN)

The cobalt(II) complex Co(SALDIPN) containing the pentadentate ligand derived from salicylaldehyde and bis(3-aminopropyl)amine reacts with alkyl halides to form sigma-bonded organocobalt derivatives. The reaction is carried out by alkylating the reduced cobalt species (i.e., cobalt(I) under strongly alkaline conditions with $PdCl_2$ as a catalyst.) This method is similar to one which Schrauzer[39] has recently described.

Sacconi has reported Co(SALDIPN) to be a high-spin five-coordinate complex.[3] Since to date all vitamin B_{12} model systems have been prepared starting with low-spin four-coordinate square planar cobalt(II) complexes, we have repeated many of Sacconi's measurements in order to prove that our Co(SALDIPN) is the same as that reported by Sacconi. In agreement with Sacconi, we find (1) that the yellow-brown crude Co(SALDIPN) is hydrated, (2) the water may be removed by drying at 100°C for twelve hours under reduced pressure, (3) both crude and dried Co(SALDIPN) are high spin with a magnetic moment equal to 4.15 B.M., and (4) the visible spectra are similar except for the absence of a band around $6000 cm^{-1}$ in our Co(SALDIPN). In contrast, we find that recrystallization from warm ethanol-water under nitrogen yields nicely formed green needles. The "recrystallized" and crude material differ in many respects as follows: (1) visible spectra in solution and in the solid state are dissimilar, (2) the green product is essentially diamagnetic (μ_{eff} = 1.0 B.M.), (3) X-ray powder patterns of both show them to be different structures and (4) CHN analyses do not agree. On the other hand, the infrared spectra, mass spectra and reactivity with alkyl halide of recrystallized and crude material are identical. The structure of this green material is at the present unknown and unfortunately time did not permit a detailed investigation of it. The infrared spectrum of our crude Co(SALDIPN) differs significantly in the N-H stretching region. A single band at $3180cm^{-1}$ is assigned to this vibrational mode, see Appendix, Figure I. Sacconi,[3] in comparison, reports a band at $3250cm^{-1}$. The location of the N-H stretching mode at this frequency is inconsistent with the secondary nitrogen being coordinated. This finding is substantiated by the fact that the N-H stretching mode in SALDIPN, which we have prepared, occurs at $3255cm^{-1}$. Finally, mass spectra on both crude and dried Co(SALDIPN) were measured under the conditions previously discussed. The highest mass peak in both materials corresponds to a monomeric formulation for Co(SALDIPN).

The complexes R-Co(SALDIPN) (R = methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-decyl) are red in color, crystalline, and very stable in air and H_2O. They are stable thermally melting above 150°C, and are soluble in $CHCl_3$ and DMSO. Analytical data supporting the composition R-Co(SALDIPN) are presented in Table XI.

Infrared spectra of the ligand, parent complex, and alkyl derivatives were obtained as KBr pellets and Nujol mulls. Of particular interest is the position of the N-H stretch and the C=N stretch, see Appendix, Figure I. All of the alkyl derivatives behave as the R = methyl, so it will be discussed with the understanding that the discussion could well apply to all derivatives. A sample of the data is presented below.

Compound	Frequency	Assignment
SALDIPN	3255	N-Hst
Co(SALDIPN)	3180	N-Hst
MeCo(SALDIPN)	3255	N-Hst
SALDIPN	1640	C=Nst
Co(SALDIPN)	1620	C=Nst
MeCo(SALDIPN)	1620	C=Nst

The drop of 20cm^{-1} in the position of the C=N stretch between the ligand and two complexes occurs due to the fact that the imine nitrogen is coordinated which reduces the bond strength of the C=N and lowers the stretching frequency.

TABLE XI

Data On Co N,N'bis(salicylidene)-1,7-diamino-4-azaheptane And Their Alkyl Derivatives

COMPOUND		ANALYSES^{A}			δ_{CH_3}^{B}	γ_{CH_3}^{C}	$X_m \times 10^6$ ^{D}
		C	H	N			
Co(SALDIPN)(H_2O)	Calc	57.96	6.09	10.14	-	-	
	Found	58.50	6.23	9.67	-	-	
Co(SALDIPN) (crude)	Calc	60.60	5.86	10.60	-	-	7017.3
	Found	60.44	6.11	9.95	-	-	
Co(SALDIPN) Rep (EtOH,H_2O)	Calc	60.60	5.86	10.60	-	-	335.9
	Found	51.67	5.62	9.30	-	-	-166.1
MeCo(SALDIPN)	Calc	61.30	6.38	10.22	1385	2965	789.29
	Found	61.34	6.13	10.06		2890	
Et-Co(SALDIPN)	Calc	62.10	6.65	9.88	1380	2970	813.5
	Found	62.35	6.44	9.73		2870	-460.8
Pr-Co(SALDIPN)	Calc	62.85	6.89	9.56	1380	2950	401.7
	Found	62.75	6.96	9.56		2860	-239.4
Bu-Co(SALDIPN)	Calc	63.56	7.13	9.27	1385	2955	2189.0
	Found	63.37	7.18	9.22		2860	-1786.5
Pent-Co(SALDIPN)	Calc	64.22	7.35	8.99	1388	2955sh	
	Found	63.95	7.28	8.88		2890	

TABLE XI

COMPOUND		ANALYSES[A]			δ_{CH_3}[B]	γ_{CH_3}[C]	$X_m \times 10^6$[D]
		C	H	N			
Hex-Co(SALDIPN)	Calc	64.84	7.55	8.73	1388	2960sh	
	Found	64.59	7.49	8.68		2890sh	
HEPT-Co(SALDIPN)	Calc	65.43	7.74	8.48		2960	
	Found	65.19	7.60	8.36	1385	2890	
OCT-Co(SALDIPN)	Calc	65.98	7.93	8.25		2960	
	Found	65.75	7.79	8.11	1388	2890	
DEC-Co(SALDIPN)	Calc	67.01	8.27	7.82		2960	
	Found	66.92	8.06	7.72	1385	2890	

[A] Analyses are accurate to ± 0.3 per cent.

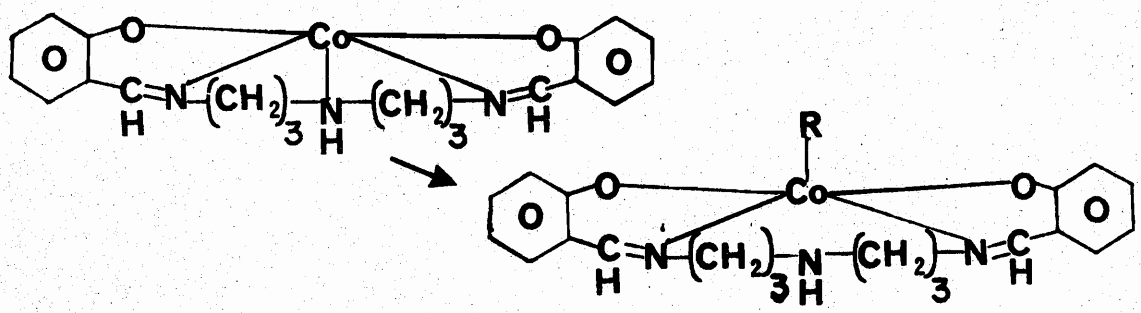
[B] Carbon-hydrogen bending modes

[C] Carbon-hydrogen symmetric and asymmetric stretching modes

[D] Molar susceptibilities show dependence on field strength.

One will notice that this shift of 20cm^{-1} is not as great as the shift of 35cm^{-1} observed with the Ni(X-SALDIEN), see Appendix, Figures II and III, and Ni(X-SALDAES) complexes. It has been shown that coordination of a donor atom in an axial position weakens the inplane ligand field strength.[40] In other words, the inplane donor atoms are not coordinated as strongly as before. This supports the fact that the secondary N-H in the Co(SALDIPN) is coordinated.

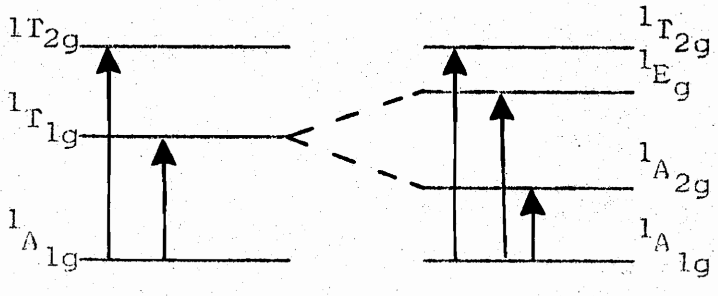
Of particular interest is the fluctuating position of the N-H stretch. When Co(SALDIPN) is converted to R-Co-(SALDIPN), one sees that the N-H stretch returns to the position in the free ligand. This suggests that R-Co(SALDIPN) may be a five-coordinate species or a six-coordinate structure in which the secondary nitrogen is very weakly bound to the cobalt. In other words, both Co(SALDIPN) and R-Co(SALDIPN) are possibly five-coordinate; however, the difference is in the groups coordinated to the cobalt as shown below.



The infrared of the methyl derivative shows peaks at 2965 and approximately 2890cm^{-1} which can be assigned to the C-H stretching modes for a methyl group. Also a band at 1385cm^{-1} can be assigned as a methyl bending mode. The conclusive bit of evidence is that these bands are not present in the parent complex. These bands along with the presence of the strong N-H stretch support the formulation R-Co(SALDIPN), see Table XI.

It has been reported that the ability of Co(SALDIPN) to be an oxygen carrier is an apparent contridiction in properties due to the fact that Co(II) prefers five-coordination to six-coordination.[3] Our observations present a very interesting observation and might tend to explain why the Co(SALDIPN) is an oxygen carrier, i.e., the secondary N-H not being coordinated in the O_2 complex, and the complex maintaining its five-coordinate geometry.

Visible spectra of the alkyl derivatives are consistent with a pseudo-octahedral environment around a Co(III) ion, of low spin in the solid state, see Table XII. For a regular octahedral Co(III) complex, for example, $Co(en)_3{}^{3+}$, en = NH_2-$(CH_2)_2$-NH_2, the energy level diagram will be as follows, and two absorption bands will be found in the visible



regular octa. distorted octa.

TABLE XII

Electronic Spectra^A (cm^{-1}) Of The Alkyl Complexes Derived From Co N,N'bis(salicylidene)-1,7-diamino-4-azaheptane

COMPOUND	MEDIUM	ν_1	ν_2	ν_3	ν_4
CH_3-Co(SALDIPN)	Nujol	18,020sh	22,990sh	25,640sh	
	Chloroform NL^B	15,630sh (165)	18,690sh (392)	26,140 (6,19x10^2)	35,710 (1.9x10^4)
	Chloroform L^C	15,680sh (166)	18,600sh (221)	26,670 (6,41x10^3)	
CH_3-CH_2-Co(SALDIPN)	Nujol	18,350sh	22,990sh	25,970sh	
	Chloroform NL	15,630sh (165)	18,520 (63.76)	25,970 (6.6x10^3)	35,710 (1.91x10^4)
	Chloroform L	15,810 (128)	18,600 (531)	25,970 (4.89x10^3)	39,600 (7.57x10^4)
$CH_3(CH_2)_2$-Co(SALDIPN)	Nujol	18,520sh	23,530sh	26,320sh	
	Chloroform NL	15,560 (164)	18,080 (240)	25,970 (5.4x10^3)	35,710 (1.86x10^4)
	Chloroform L	15,750 (12)	18,600 (513)	25,970 (5.02x10^3)	39,600 (4.41x10^4)
$CH_3(CH_2)_3$-Co(SALDIPN)	Nujol	18,520sh	23,810sh	25,970sh	
	Chloroform NL	15,680 (157)	18,350 (282)	25,030 (6.57x10^3)	35,710 (1.81x10^3)
	Chloroform L	15,630 (104)	18,600 (4.8)	25,970 (4,91x10^3)	39,600 (6.58x10^4)

TABLE XII

COMPOUND	MEDIUM	ν_1	ν_2	ν_3	ν_4
$CH_3(CH_2)_4$-Co(SALDIPN)	Nujol	18,180sh	22,470sh	24,690	
$CH_3(CH_2)_5$-Co(SALDIPN)	Nujol	18,180sh	22,470sh	25,320	
$CH_3(CH_2)_6$-Co(SALDIPN)	Nujol	18,180sh	21,740sh	22,730sh	25,320
$CH_3(CH_2)_7$-Co(SALDIPN)	Nujol	18,520sh	21,980sh	23,320	
$CH_3(CH_2)_9$-Co(SALDIPN)	Nujol	18,180sh	22,470sh	25,320	

[A] Numbers in parentheses are molar extinction coefficients.

[B] Solution exposed to no light

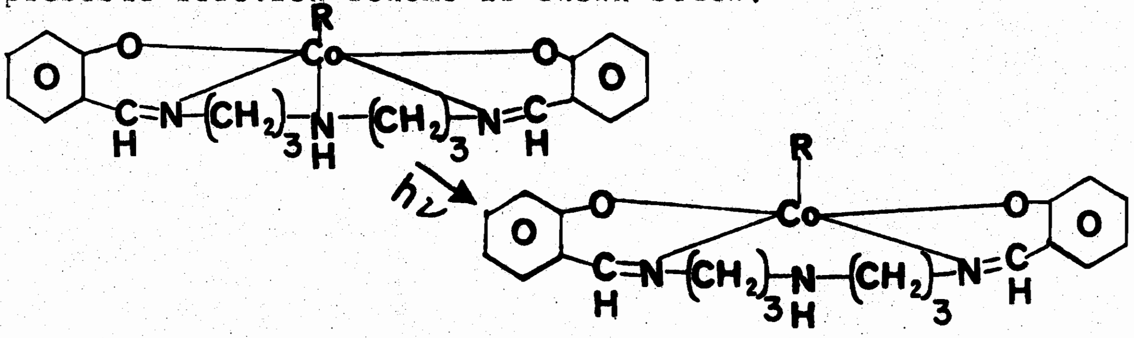
[C] Solution exposed to light

region at $20,000\text{cm}^{-1}$ and $28,000\text{cm}^{-1}$. In our case, however, we have non-equivalent donor atoms which result in a structure of lower symmetry, thereby causing a splitting of the $^1T_{1g}$ level. The $^1T_{2g}$ is not split enough to be observable as shown by theoretical results.[41]

We observe three transitions in the visible region assignable to the transitions from the $^1A_{1g}$ to the three excited states in the solid. This would indicate a pseudo-octahedral environment. The apparent contradiction with the infrared data could be explained by assuming that the secondary nitrogen does not form a ground state bond with the metal atom but does offer some perturbation.

It is noticed that when the alkyl derivatives are placed in $CHCl_3$ with a minimum exposure to any light, the visible spectrum exhibits three previously discussed band maxima and a new band at $15,500\text{cm}^{-1}$. Bands in the region $15,500\text{cm}^{-1}$ have been assigned to transitions resulting from five-coordinate geometry.[42] It is concluded that in $CHCl_3$ solution, two species are present, one being five-coordinate, the other being six-coordinate.

If these same solutions are exposed to normal daylight, we see an increase in intensity of the band at $15,500\text{cm}^{-1}$ along with a decrease in intensity of the $18,500\text{cm}^{-1}$ band, which possibly indicates that the species is going toward the five-coordinate geometry in $CHCl_3$ when exposed to light. A probable reaction scheme is shown below.



It could also be postulated that five-coordination could arise from dealkylation of the molecule. Gas chromatography was employed to test this possibility. A sample of MeCo-(SALDIPN) was dissolved in $CHCl_3$ and placed in the light for two days. A rubber septum was placed in the top of the flask to serve as a way to get samples of the vapor above the solution. Samples of the laboratory gas line were taken as standards and compared with the vapor above the solution. No peaks assignable to the presence of an alkane were observed in the gas chromatograms.

Mass spectra were determined on the alkyl derivatives employing conditions described earlier. For derivatives with R = Me, Et, But, Pent, the parent $^{M}/e$, see Table III, corresponding to the loss of the R, and $^{M}/e$ corresponding to the free ligand were observed. Mass spectra were scanned above the appropriate $^{M}/e$ to check for dimers but no such peaks were observed. This bit of evidence lends strong supports to the composition of R-Co(SALDIPN) in the gas phase.

In the cases for R = C_6, C_7, C_8 and C_{10}, no molecular ion was detected but $^M/e$ = 396 was observed which corresponded to the complex Co(SALDIPN). However, in every case there were patterns associated with fragmentation of the appropriate alkane. For instance, in the C_{10} derivative, we observed an $^M/e$ = 142 which corresponds to $C_{10}H_{22}$. The fragmentation expected from this alkane was observed.

Nuclear magnetic resonance spectra were obtained on the R = CH_3, C_2H_5, and C_3H_7 derivatives, see Appendix, Figure IV. The following set of data obtained from these spectra is presented below.

Compound	Range or Position (δ)	Assignment
CH_3-Co(SALDIPN)	7.54-6.40	vinyl and aromatic protons
	4.24	proton on secondary nitrogen
	3.36-2.04	the CH_3 bonded to the metal and the methylene protons on the backbone chain.
C_2H_5-Co(SALDIPN)	7.64-6.2	vinyl and aromatic protons
	4.24	proton on the secondary nitrogen
	3.32-2.00	-methylene protons on the ethyl group plus the methylene protons on the backbone chain
	.4 (triplet)	-methyl group on the ethyl group bound to the metal

Compound	Range or Position (δ)	Assignment
C_3H_7-Co(SALDIPN)	7.12-6.20	vinyl and aromatic protons
	4.20	proton on secondary nitrogen
	3.34-2.00	and methylene protons on the propyl group plus the methylene protons on the backbone chain
	1.0 (doubled)	methyl protons on the propyl group attached to the cobalt

The assignment of the alkyl methylene protons lying closest to the metal were not possible because they fell in the range found for the methylene protons on the backbone chain. Investigation of the free ligand offered no assistance in elucidating the position of the protons under consideration. However, the appearance at high field of a triplet in the case of the ethyl derivative and a poorly resolved doublet in spectrum of the propyl derivative confirms the alkyl group is attached to the cobalt atom.

All of the Co - σ alkyl bonds result from the reaction of a primary alkyl halide and not secondary or tertiary ones. It can be shown from molecular models that a secondary alkyl halide results in a group which is too bulky to occupy the sixth position. Secondary and tertiary groups place methyl groups in a position which is very close to the region of the aromatic cloud of electrons. The benzene rings must be in these positions (i.e., bent up) in order for the secondary nitrogen to coordinate, hence preventing the formation of a σ-alkyl bond with a secondary ion, a tertiary ion and the discussion could also extend to phenyl and benzyl groups since they have proved unsuccessful.

There is a distinct dependence on the halide anion insofar as the rate is concerned. Chloro derivatives seem to give no reaction at all. Bromo derivatives react very slowly. However, iodo derivatives react rapidly; in fact, the product forms almost immediately.

Magnetic data were obtained by the Faraday method and the results are presented in Table XI. The magnetic moments are too high to be the result of low-spin cobalt(III) entirely. Further work is planned in order to determine the explanation for these anomolous results.

APPENDIX

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FIGURE I

Top) Infrared Spectra of Co-SALDIPN MONOHYDRATE
Phase: Potassium Bromide Pellet

Bottom) Infrared Spectra of Et-Co-SALDIPN
Phase: Potassium Bromide Pellet

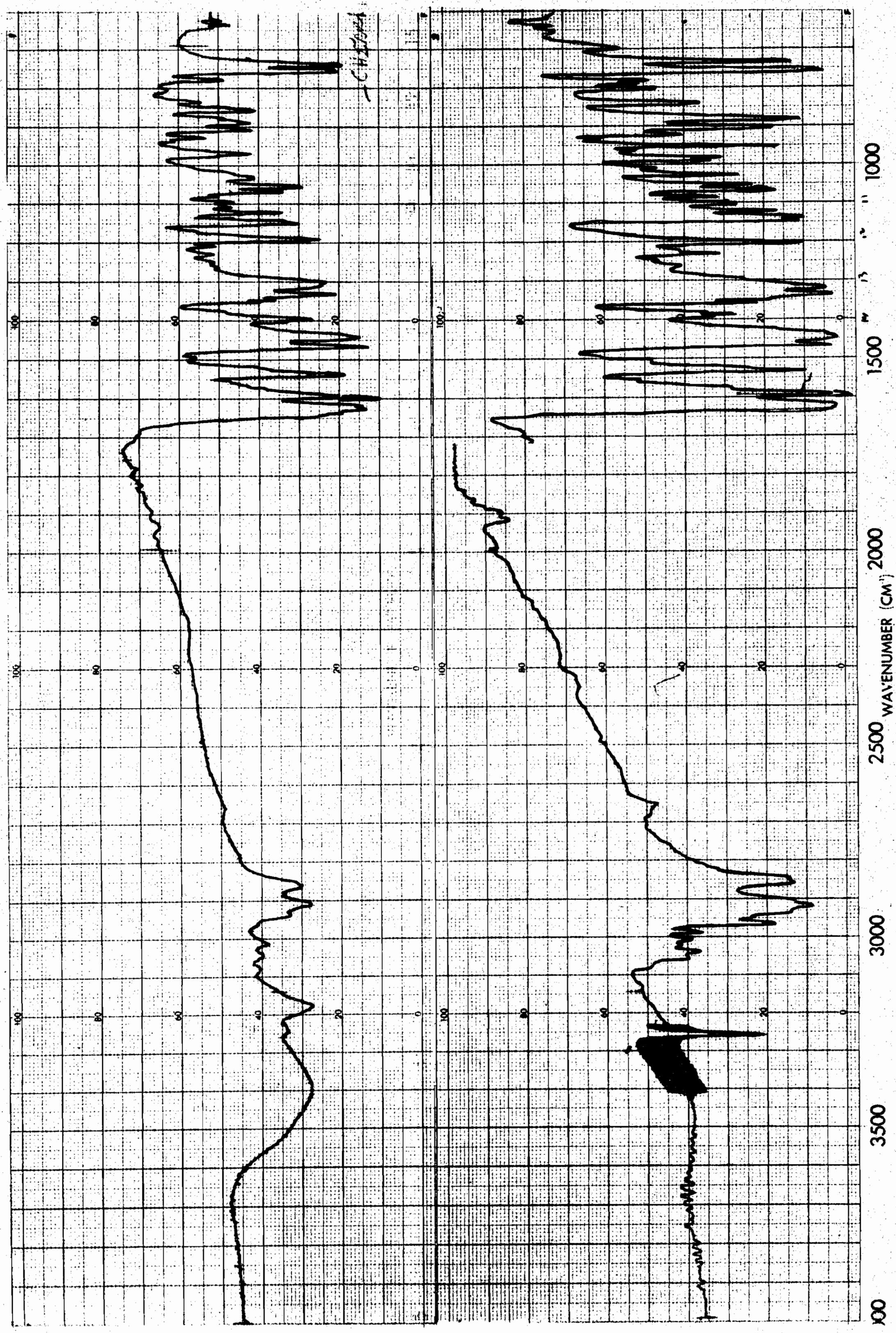

100
80
60
40
20
0
1000
1500
2000
2500 WAVENUMBER (CM⁻¹)
3000
3500
00

FIGURE 1

FIGURE II

Top) Infrared Spectra of 5-BrSALDIEN
Phase: Nujol

Bottom) Infrared Spectra of Ni(5-BrSALDIEN)MONOPYRIDINATE
Phase: Nujol

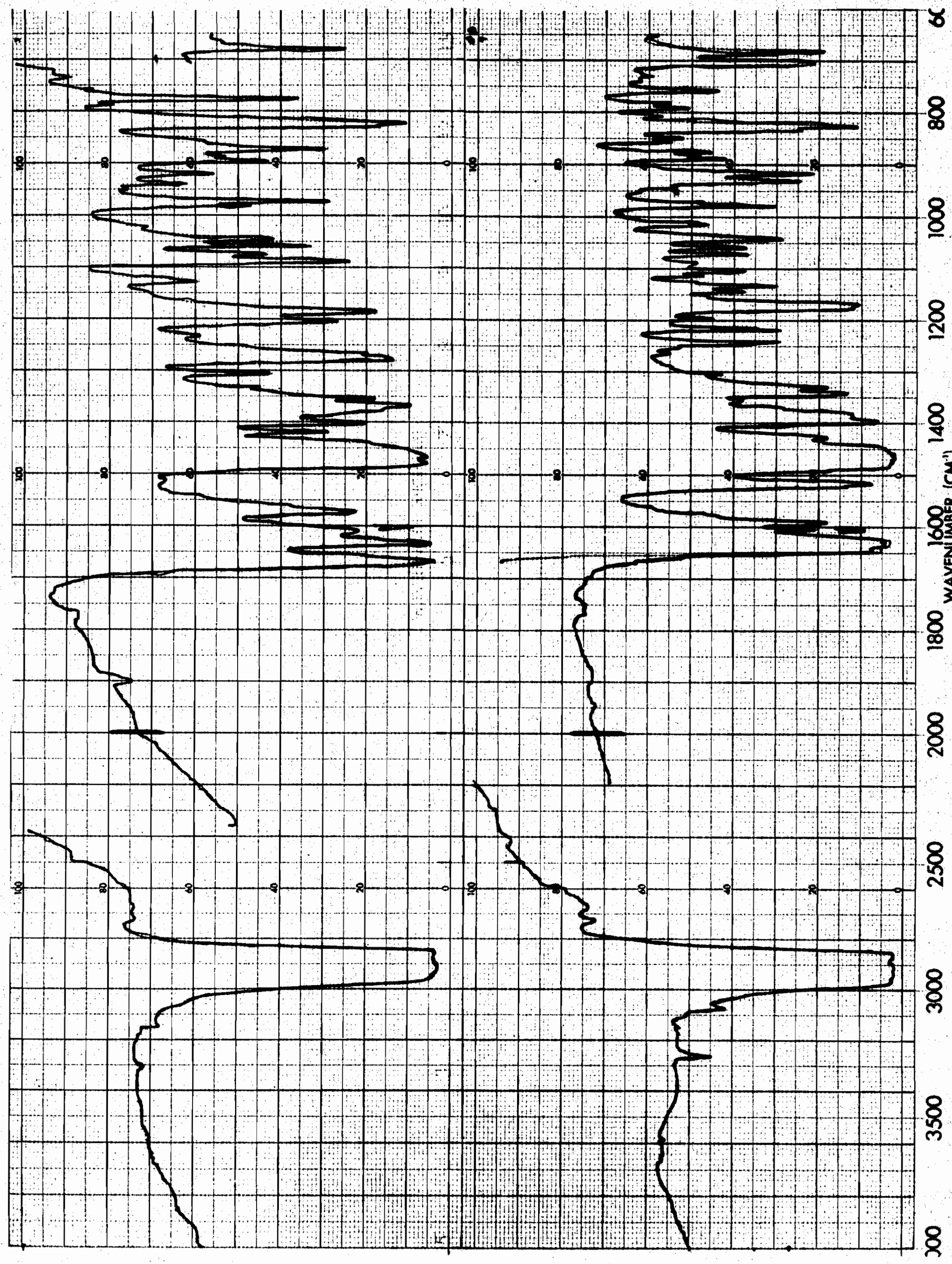

000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
60
WAVENUMBER (CM⁻¹)
100
80
60
40
20
0

FIGURE 11

FIGURE III

Infrared Spectra of Ni(5-BrSALDIEN)
Phase: Nujol

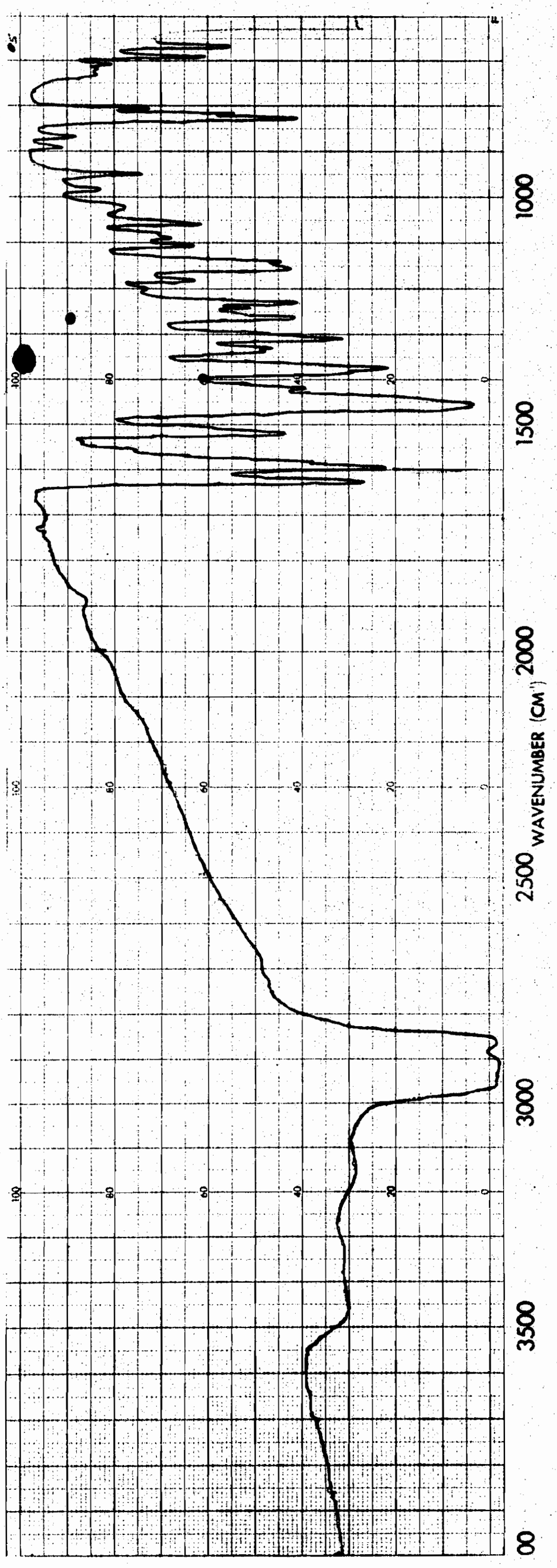

00
3500
3000
2500
WAVENUMBER (CM^{-1})
2000
1500
1000
100
80
60
40
20
0

FIGURE III

FIGURE IV

Top) NMR Spectrum of Et-Co(SALDIPN)
Solvent: $DMSO_{d6}$, Internal TMS

Bottom) NMR of 5-BrSALDIPN
Solvent: $CDCl_3$, Internal TMS

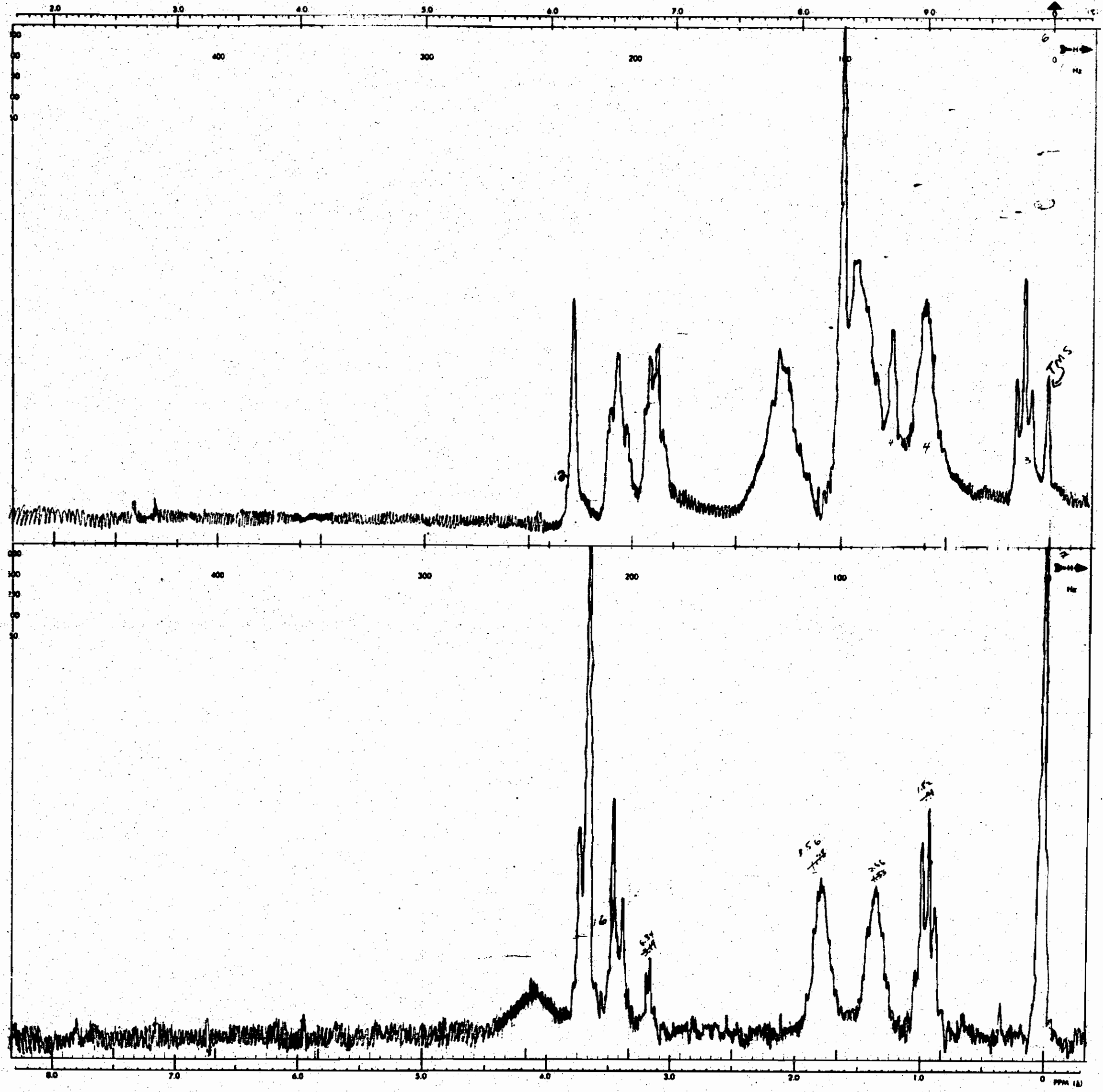


FIGURE IV

VITA

William Monroe Coleman, III was born on April 15, 1947, in Dillon, South Carolina. He was graduated from Latta High School of Latta, South Carolina, in 1965, and from the University of South Carolina in Columbia, South Carolina, with a Bachelor of Science Degree in Chemistry in 1969.

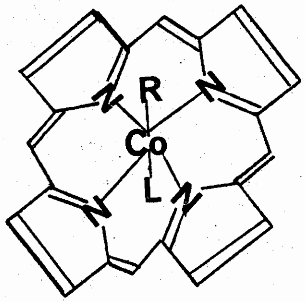
William Monroe Coleman, III

TRANSITION METAL COMPLEXES OF PENTADENTATE LIGANDS

William M. Coleman, III

ABSTRACT

The investigation of N,N'bis(salicylidene)-1,7-diamino-4-azaheptane, SALDIPN, N,N'bis(salicylidene)-1,5-diamino-3-azapentane, SALDIEN, and N,N'bis(salicylidene)-1,5-diamino-3-thiopentane, SALDAES, as pentadentate ligands is logical in that they offer an analogy to the environment around the cobalt atom in Vitamin B_{12}, I, represented below. These complexes might be expected to give some insight as to the behavior and role of the metal ion as it interacts with the five-donor atoms and hence an insight into the role of the metal ion in Vitamin B_{12}.



I

Compounds formed by the reaction of $Ni(XSAL)_2 \cdot 2H_2O$ with 1,5-diamino-3-azapentane, DIEN, and $Ni(OAc)_2 \cdot 4H_2O$ with X-SALDAES were isolated and characterized. In addition to

these, alkyl σ-bonded derivatives formed by the reaction of reduced Co(SALDIPN) with R-X were also isolated and characterized.

Mass spectra, magnetic moments, X-ray powder patterns, infrared, visible, and near infrared spectra were obtained on the majority of the compounds. Nuclear magnetic resonance spectra were obtained on the majority of the σ-bonded alkyl complexes.

It was concluded that the Ni(X-SALDIEN) complexes are square planar whereas the Ni(X-SALDAES) complexes are distorted square planar or possibly a five-coordinate species. Spin state changes were observed for both complexes when they were dissolved in pyridine which is in contrast to Ni(X-SALEN).

The alkyl derivatives were all primary in nature and very stable to light, air, and H_2O which is in contrast to the alkyl derivatives of Co(X-SALEN) which happen to be photolabile. The geometry around the cobalt atom in R-Co-(SALDIPN) was concluded to be pseudo-octahedral.

Reasons for certain anomolies (i.e., magnetic moments, etc.) were discussed in detail.