Pentadentate Ligands. I. Nickel(II) Complexes of the Linear Schiff Base Ligands Derived from Substituted Salicylaldehydes and Diethylenetriamine and 2,2'-Bis(aminopropyl)amine

BY W. M. COLEMAN AND L. T. TAYLOR*

Golden yellow nickel(II) complexes of linear potentially pentadentate Schiff base ligands derived from variously substituted salicylaldehydes and diethylenetriamine or 2,2'-bis(aminopropyl)amine have been characterized by elemental analysis, mass spectra, infrared–visible–ultraviolet spectra, and magnetic susceptibility measurements in the solid state and in pyridine. The solid complexes appear to be pseudo square planar with magnetic moments of *ca.* 1.2 BM. The anomalous magnetism arises either from a singlet–triplet spin-state equilibrium due to the weak in-plane field of the ligand or from the coexistence of nonreadily interconvertible high- and low-spin complexes in the solid state. In pyridine the complexes are pseudooctahedral high-spin nickel(II) species. A monopyridine adduct isolated for one of the complexes exhibits properties similar to the complexes dissolved in pyridine.

Introduction

Pentadentate ligands are probably the least studied of the higher multidentate chelating agents.[1] The known structural types, Figure 1, include (1) linear, open
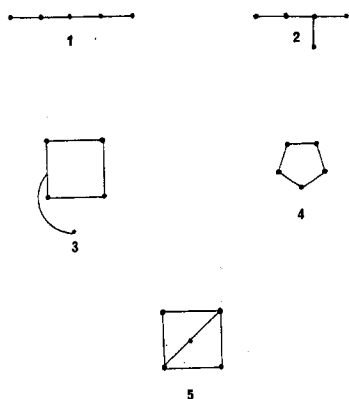
Figure 1.—Types of pentadentate ligands.

chain, (2) branched chain where the bifurcation occurs at the donor atom, (3) a tetradentate macrocyclic ligand to which is attached a side chain containing a fifth donor atom, (4) a macrocyclic[2,3] ligand in which all five potential donors are in the ring, and (5) a "basket-like" macrocyclic ligand.[4] The linear open-chain ligands have been investigated to the greatest extent although much of this work is found in the older chemical literature. Sacconi[5] has recently reinvestigated the metal complexes of the pentadentate ligand derived from salicylaldehyde and 3,3'-bis(aminopropyl)amine and has shown them to be high spin five-coordinate. We wish to report here our results concerning the nickel complexes of the pentadentate ligands derived from various substituted salicylaldehydes and diethylenetriamine, structure Ia, hereafter referred to as H₂-Xsaldien (X = 5-H, 5-Br, 5-CH₃, 3-CH₃O, 3-(CH₃)₂CH).
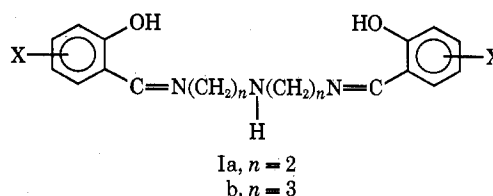
(1) H. A. Goodwin, "Chelating Agents and Metal Chelates," F. D. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, p 167.

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

(3) S. M. Nelson, P. Bryan, and D. H. Busch, *Chem. Commun.* 641 (1966).

(4) V. Katović, L. T. Taylor, and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 2122 (1969).

(5) L. Sacconi and I. Bertini, *ibid.*, **88**, 5180 (1966).

Ia, n = 2
b, n = 3

Experimental Section

Materials.—Diethylenetriamine (dien) and salicylaldehyde (sal) were obtained from the Aldrich Chemical Co., Milwaukee, Wis., and used without further purification. Technical grade 3-methoxysalicylaldehyde (*p*-vanillin), also from Aldrich Chemical Co., was recrystallized from 95% ethanol in the presence of decolorizing charcoal. All other chemicals and solvents were of reagent grade or equivalent.

5-Bromosalicylaldehyde was prepared by adding bromine to an equivalent amount of a cold solution of salicylaldehyde dissolved in glacial acetic acid. 5-Methylsalicylaldehyde was prepared by a modification of the Reimer–Tieman[6] reaction employing *p*-cresol and chloroform in a highly alkaline medium. 3-Isopropylsalicylaldehyde was prepared according to the general procedure of the Duff[7] reaction starting with *o*-isopropylphenol. The bis(salicylaldehydo)nickel(II) complexes were obtained as green hydrated solids following the method of Holm.[8]

Uncomplexed pentadentate ligands were prepared by adding one molecular equivalent of dien to two molecular equivalents of sal dissolved in absolute ethanol at room temperature. After stirring for 15 min, the volume of the solution was reduced until only an oil remained which was identified *via* nmr and infrared analysis as slightly impure H₂Xsaldien.

General Preparation of Ni(Xsaldien).—The appropriately substituted Ni(sal)₂·2H₂O (0.01 mol) was suspended in approximately 200 ml of ethanol. The suspension was brought to reflux with stirring, and dien (0.01 mol) dissolved in a small amount of ethanol was added all at once. The color of the solution immediately began turning dark red-brown as the green solid slowly disappeared. The reaction mixture was refluxed for 3–6 hr. Upon allowing the flask to come to room temperature, yellow to yellow-orange needles were precipitated which were filtered, washed with ether, and dried *in vacuo* at 100° for 12 hr. More material could be isolated from the filtrate by cooling overnight (5°).

Preparation of the Pyridine Adduct of Ni(5-Br(saldien)).—Ni(5-Br(saldien)) (1.0 g, 0.0019 mol) was suspended in 50 ml of Spectrograde pyridine and the resulting mixture was refluxed for 2 hr. The compound dissolved in pyridine on heating. The solution was then allowed to come to room temperature whereby a green powder was precipitated. The material was filtered and

(6) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York, N. Y., 1961, p 824.

(7) J. C. Duff, *J. Chem. Soc.*, 547 (1941).

(8) R. H. Holm, *J. Amer. Chem. Soc.*, **83**, 4683 (1961).

dried at room temperature and atmospheric pressure over KOH in a pyridine atmosphere. *Anal.* Calcd for Ni(5-Br(saldien))-(py): C, 45.43; H, 4.15; N, 9.22. Found: C, 45.62; H, 3.64; N, 9.26.

Preparation of Ni(saldipn).—This material was prepared following the method previously described for the preparation of Ni(Xsaldien) except that 2,2'-bis(aminopropyl)amine (dipn) was substituted for diethylenetriamine.

Alternative Method of Preparation of Ni(Xsaldien).—H$_2$X-saldien (1.55 g, 0.005 mol) was dissolved in 100 ml of absolute ethanol, and the solution was brought to reflux. To this hot solution was added Ni(C$_2$H$_3$O$_2$)$_2$·4H$_2$O (1.24 g, 0.005 mol) dissolved in 200 ml of absolute ethanol. The color of the solution changed from pale yellow to deep red-brown. Refluxing was continued for 1 hr. Upon cooling the solution, a yellow-brown solid precipitated which was filtered, washed with ethanol, and dried *in vacuo* for 12 hr at room temperature.

Physical Measurements.—Infrared spectra were obtained in the region 5000–400 cm^{-1} using a Perkin-Elmer Model 621 spectrophotometer. Solid-state spectra were recorded as KBr pellets and as 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 spectrometer. Spectra of solid samples were obtained by a diffuse transmittance technique.[9] Solution spectra were obtained utilizing Spectroquality organic solvents.

Magnetic susceptibility measurements on solid samples were obtained by the Faraday method. Solution magnetic measurements were determined by an nmr method[10] using a Varian A-60 spectrometer. Diamagnetic corrections were made employing Pascal's constants.[11] Special coaxial cells with precision spacing of the inner tube (Wilmad Glass Co.) were used. Measurements were performed at 10 and 20° using a Varian Model V-6040 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 as low a value as possible to prevent decomposition of the samples. The source temperature was maintained at approximately the temperature of the solid probe. Analyzer tube and ion source pressures of less than 10^{-6} Torr were employed. Where necessary mass to charge ratios were calibrated with perfluorokerosene.

Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and in this laboratory using a Perkin-Elmer Model 240 C, H, and N analyzer.

Results and Discussion

Complexes of the composition Ni(Xsaldien) have been isolated except for the 5-methyl derivative which contains a water molecule of hydration. Analytical data for carbon, hydrogen, and nitrogen have been obtained and support the proposed composition of these materials. Two preparative procedures have been successfully employed for preparing these materials which include (1) a metal template reaction of the appropriately substituted bis(salicylaldehydo)nickel-(II) complex with dien and (2) treating the previously isolated pentadentate ligand with nickel(II) acetate tetrahydrate.

In each case the resulting neutral complexes are golden yellow in appearance, being partially soluble in methanol, ethanol, water, and dimethyl sulfoxide and insoluble in methylene chloride, *N,N*-dimethylformamide, acetonitrile, and 1,2-dimethoxyethane. Over a period of 1 day at room temperature they dissolve in pyridine; whereas, they immediately dissolve in hot pyridine. Melting with decomposition around 200° indicates the products are relatively thermally stable.

A complex of analogous composition, Ni(saldipn), and properties was also prepared by substituting 2,2'-bis(aminopropyl)amine for diethylenetriamine in its reaction with bis(salicylaldehydo)nickel(II) complexes, II. The color, solubility, thermal properties, and general features of this compound were similar to those of Ni(Xsaldien).

H$_2$saldipn

II
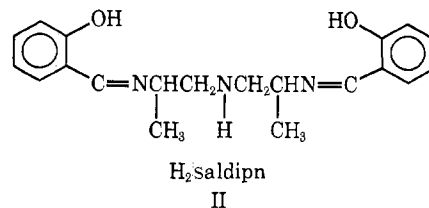
Positive ion mass spectra were determined under the least severe conditions that would allow an interpretable spectrum (*i.e.*, minimum temperature and electron energy). Only Ni(5-Hsaldien), [Ni(5-CH$_3$saldien)]·H$_2$O, and Ni(saldipn) gave relatively intense isotopic clusters corresponding to the parent ion (*i.e.*, *m/e* 367, 369 for Ni(5-Hsaldien), 395, 397 for [Ni(5-CH$_3$-saldien)]·H$_2$O, and 395, 397 for Ni(saldipn) omitting the observed isotope patterns for ^{13}C). The other derivatives probably have a very low vapor pressure and hence could not be transformed into the gas phase except with considerable decomposition. The mass spectra of most derivatives show a peak corresponding to the parent ion minus the nickel atom. Fragmentation patterns that would be expected from the basic ligand structure are observed in all the mass spectra. The mass spectra were measured above the basic molecular ion to the *m/e* value expected for the dimer but no such peak was observed which suggests the complexes are essentially monomeric in the gas phase rather than dimeric as has been postulated for some Schiff base complexes.[12] Sufficient solubility in a suitable solvent precluded a molecular weight determination in solution.

Infrared spectra were obtained both as Nujol and as hexachlorobutadiene mulls and as KBr pellets on the complexes and free ligands. A considerable shift to lower energy (1630–1595 cm^{-1}) is observed in the strong, sharp C=N stretching frequency upon complexation with nickel which suggests the imine nitrogen atoms are coordinated. Only the 5-methyl derivative complex exhibits relatively intense absorption in the 3700–3100-cm^{-1} region. This has been attributed to the O–H symmetric and asymmetric stretching modes of water. The broadness of this absorption indicates the water is not coordinated.

A band assignable to a secondary nitrogen–hydrogen stretching vibrational mode could not be conclusively found in the infrared spectra of most of the complexes. However, a weak, broad band centered at 3150 cm^{-1} was observed in the Nujol spectrum of Ni(5-Br-(saldien)). The free ligand, 5-Br(saldien), exhibits a weak, sharp band at 3305 cm^{-1} assignable to the secondary nitrogen–hydrogen stretch. Several of the derivatives in various solvents including pyridine showed no meaningful absorption in the region of interest, (*i.e.*, 3400–3000 cm^{-1}). The spectrum of Ni(Hsaldien) in pyridine was investigated quite closely in an unsuccessful effort to find an N–H stretching

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

(10) D. R. Evans, *J. Chem. Soc.*, 2003 (1959).

(11) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. J. Wilkins, Ed., Interscience, New York, N. Y., 1960.

(12) E. P. Dudek, E. Chaffee, and G. Dudek, *Inorg. Chem.*, **3**, 1278 (1964).

mode. Langenbeck and coworkers[13] had earlier reported a band around 3450 cm^{-1} in the spectrum of a pyridine solution of Ni(Hsaldien) and had assigned the absorption to an N–H stretching mode. We have repeated this experiment a number of times and believe this band is characteristic of Spectrograde pyridine. In fact, the infrared spectrum of pyridine shows an identically positioned band. This assumption is supported by the observation[14] that secondary aliphatic amines usually absorb weakly in the range 3350–3310 cm^{-1}. Deuteration in slightly basic D$_2$O again revealed no bands in the anticipated N–D stretching region.

Free ligands were prepared for most of the derivatives although only the bromo derivative showed a band in the region of interest assignable to an N–H stretching mode. Nevertheless, all free ligands gave essentially identical nmr spectra except for those regions which can be attributed to the presence of various functional groups located at either the 3 or 5 position on the benzene ring. In every case the nmr spectra are consistent with structure Ia.

These observations concerning the free ligands and the neutral complexes are consistent with the secondary amine participating in hydrogen bonding. Infrared measurements on various concentrations of free ligand and complex suggest intramolecular type hydrogen bonding. The absence of a sharp N–H stretching band in the complex indicates that the secondary nitrogen is not coordinated to the nickel ion.[15] Efforts to obtain a time-averaged nmr spectrum of the complexes in order to look for a contact-shifted amine proton were precluded by insolubility in an appropriate solvent.

Magnetic susceptibilities for Ni(Xsaldien) and Ni(saldipn) were determined by the Faraday method, Table I. The magnetic moments are *higher* than would

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TABLE I
ROOM-TEMPERATURE MAGNETIC DATA ON THE NICKEL
COMPLEXES IN THE SOLID STATE[a,b]

Compound	$10^6 \chi_m$, cgsu	μ_{eff}, BM
Ni(5-Hsaldien)[c]	270.5–234.3	0.80–0.75
Ni(5-Br(saldien))[c]	797.1–480.1	1.40–1.08
Ni(3-CH$_3$Osaldien)[c]	449.9–330.6	1.05–0.90
[Ni(5-CH$_3$saldien)]·H$_2$O[c]	633.7–384.5	1.24–0.97
Ni(3-i-C$_3$H$_7$saldien)	844.3–797.8	1.42–1.39
Ni(saldipn)[c]	1044.2–527.7	1.59–1.13
Ni(5-Br(saldien))(py)	4659.2–4410.8	3.34–3.25

</div>

[a] Magnetic susceptibilities are corrected for diamagnetic ligands. [b] Magnetic susceptibilities show a slight inverse dependence on field strength. The numbers reported correspond to the maximum and minimum values measured at four different field strengths ranging from 6800 to 11,800 G. [c] Duplicate measurements on independently prepared samples.

be predicted for a low-spin d^8 nickel complex.[16] Even if one allows for the contribution made by temperature-independent paramagnetism and the inherent error in trying to correct for diamagnetic susceptibilities, the moments are too high to consider the compounds completely diamagnetic. On the other hand the moments are *lower* than would be expected for high-spin nickel-

(II). Several mechanisms may give rise to these anomalous moments. First, the complexes may be essentially diamagnetic low-spin ones that are contaminated with (or in equilibrium with) a small percentage of some high-spin species (*i.e.*, a low-spin square-planar or five-coordinate material with a small fraction of a high-spin octahedral, square-planar, tetrahedral, or five-coordinate complex). Precedence[17] for such behavior is known. Second, a spin-state isomerism[18] between singlet and triplet states for a pseudo-square-planar complex may be envisioned. In other words two energy levels of different multiplicity are positioned within kT of each other (*i.e.*, the complex is near the "magnetic crossover point") whereby population of both states becomes probable. The latter rationalization is quite tenable in light of the fact that it has been shown[19] that increasing the carbon chain that joins Schiff base imine nitrogen atoms simultaneously weakens the in-plane ligand field. The magnetic properties of the complexes as a function of temperature are presently being studied in detail in order to test this hypothesis.

Magnetic susceptibilities on Ni(5-Br(saldien)) and Ni(3-CH$_3$Osaldien) in pyridine show the complexes to be fully paramagnetic high-spin nickel(II) compounds, Table II. The change in spin state probably arises from

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TABLE II
MAGNETIC DATA ON THE NICKEL COMPLEXES IN PYRIDINE

——Ni(5-Br(saldien))——			——Ni(3-CH$_3$Osaldien)——		
Temp, °C	Concn, g/ml	μ_{eff}, BM	Temp, °C	Concn, g/ml	μ_{eff}, BM
26	0.0378	2.86	20	0.0162	2.84
20	0.1029	2.98	10	0.0162	2.90
10	0.0129	3.07	20	0.0131	2.98
26	0.0110	2.84	10	0.0131	2.90

</div>

pyridine coordinating to the complex in one or both axial positions. The magnetic susceptibilities are slightly dependent on both concentration and temperature within experimental error. The solubility of Ni(saldipn) in pyridine was not sufficient for a magnetic susceptibility measurement.

A change in coordination number when the complexes are placed in pyridine is further corroborated by the appearance of a new broad band in the 10,500-cm^{-1} region for Ni(Xsaldien) and at 12,000 cm^{-1} for Ni(saldipn). The visible spectra of the complexes in pyridine and Ni(5-Br(saldien))(py) in the solid state coincide quite well except for slight shifts in the band maxima (*vida infra*).

A pale green pydidine adduct has been isolated which retains pyridine up to 100° at reduced pressure. Elemental analyses are in agreement with the composition Ni(5-Br(saldien))(py). The monopyridinate has a magnetic moment typical of pseudooctahedral nickel-(II). Visible spectra in Nujol and chloroform support this contention. The bands at 11,630 and 18,520 cm^{-1} may be assigned in O_h symmetry to the transitions $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$, respectively. Surprisingly the infrared spectrum of the pyridine adduct

(13) W. Langenbeck, M. Augustin, and H. J. Kerrinnes, *J. Prakt. Chem.*, **26**, 130 (1963).

(14) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966.

(15) K. Nakamato, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(16) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1968.

(17) B. T. Kilbourn, H. M. Powell, and F. A. C. Darbyshire, *Proc. Chem. Soc., London*, 207 (1963); R. H. Holm and K. Sawaminathan, *Inorg. Chem.*, **2**, 181 (1963); L. Sacconi, *Transition Metal Chem.*, **4**, 227 (1968).

(18) S. M. Nelson and W. S. F. Kelley, *Chem. Commun.*, 436 (1968); E. K. Barefield, S. M. Nelson, and D. H. Busch, *Quart. Rev., Chem. Soc.*, **22**, 457 (1968).

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

shows an N–H stretching mode. The position of this band is shifted approximately 35 cm^{-1} to lower energy relative to the free ligand. It is tempting to suggest the pseudooctahedral structure in the solid state is achieved by coordination of the secondary nitrogen and one pyridine moiety at the axial sites rather than both sites being filled by pyridine molecules.

In the solid-state spectra of Ni(saldipn) and Ni(Xsaldien) two bands are observed: 23,000 and 30,500 cm^{-1}, Table III. Both bands are tentatively assigned as spin-

TABLE III
ELECTRONIC ABSORPTION SPECTRA (CM^{-1})
OF THE NICKEL COMPLEXES

| Compound	Medium	Band maxima[a],[b]
Ni(5-Hsaldien)	Nujol	23,260, 30,770
	Methanol	26,320 (7120), 30,300
	Pyridine	10,870 (17.9), 25,970 (7100), 31,500 (5200)
[Ni(5-CH$_3$saldien)]·H$_2$O	Nujol	23,260, 24,940, 30,130
	Methanol	25,320 (5630), 30,130 (13,300)
	Pyridine	10,360 (24.7), 25,000 (4950), 30,300 (3900)
Ni(5-Br(saldien))	Nujol	23,030, 30,680
	Methanol	25,640 (8270), 30,537 (8770)
	Pyridine	10,204 (69.7), 18,200 (18.8), 25,000 (7170), 30,540 (5580)
Ni(3-CH$_3$Osaldien)	Nujol	22,730, 30,000
	Methanol	25,640 (2700), 30,300 (12,130)
	Pyridine	10,846 (9.9), 12,580 (5.2), 17,620 (9.2), 21,570 (3240)
Ni(3-i-C$_3$H$_7$saldien)	Nujol	25,130, 30,300
Ni(saldipn)	Nujol	23,670, 24,840, 30,540
	Methanol	25,970 (4100), 30,540 (9700)
	Pyridine	12,200 (404), 14,290 (70.8), 19,230 (606), 25,640 (3640)
Ni(5-Br(saldien))(py)	Nujol	11,630 vb, 18,500, 24,390
	Chloroform	11,630 vb (70), 18,520 (100), 25,970 (7300)
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.
[b] Abbreviations: v, very; b, broad.

allowed charge-transfer transitions. The band at 23,000 cm^{-1} is in the region where d–d transitions peculiar to square-planar nickel(II) are found but other observations rule against this assignment. First, square-planar Ni(salen)[20] has its d–d transition located around 19,000 cm^{-1}. If Ni(Xsaldien) is in fact square planar, its d–d transition should be of comparable or lower energy since lengthening the chain joining the imine nitrogen atoms is known to reduce the d–d transition energy. Second, the solid-state spectrum of 5-Br-(saldien) shows a band around 23,000 cm^{-1}. Third, the extinction coefficients in methanol for these bands are much too large to have arisen from a d–d transition. We, therefore, conclude that the band of interest is characteristic of the ligand and is not a d–d transition. The complexes however are very likely square planar where the d–d transition is masked because of a relatively low-energy parity-allowed band.

A comparison of the behavior in pyridine of Ni(salen) and Ni(salophen) with Ni(Xsaldien), III–V, reveals the

(20) salen is *N,N*-bis(salicylidene)-1,2-diaminoethane.
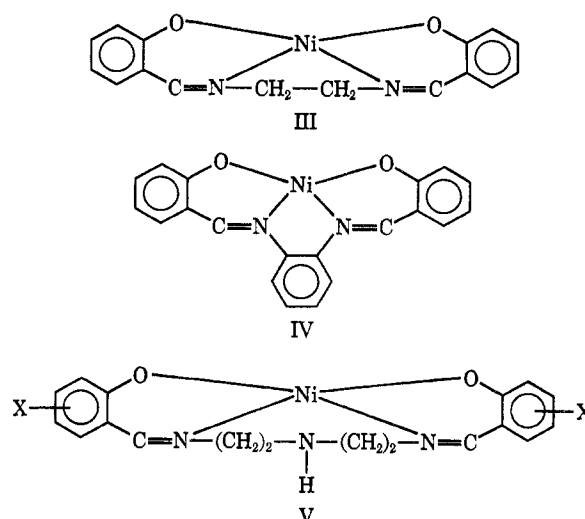
following points. The former two complexes have been shown to be nearly planar and diamagnetic in the solid state.[19] When dissolved in pyridine Ni(salen) remains diamagnetic whereas Ni(salophen) becomes partially paramagnetic (2.5 BM) at room temperature.[21] Temperature-dependent magnetic studies have shown that the moments decrease as the temperature increases. An equilibrium involving coordinated and noncoordinated pyridine has been postulated similar to our results with Ni(saldien) in pyridine. The major difference appears to be that the latter is fully paramagnetic in pyridine. The reason for this probably lies in the fact that the in-plane field strength of Xsaldien is expected to be diminished relative to that of salen or salophen. This may come about by two sources: (1) the chain length between imine nitrogen atoms has increased and (2) the secondary nitrogen atom may offer some degree of axial perturbation thereby effectively lowering the in-plane field strength. Both effects may be interpreted in terms of the relative d-orbital energies for a nickel(II) ion (Figure 2). The energy difference between the two
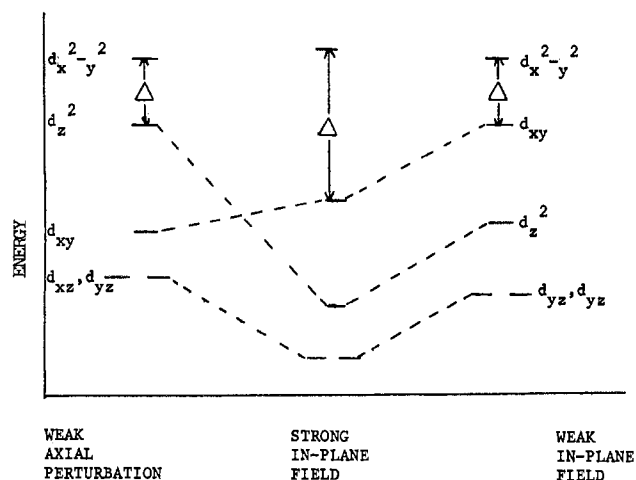

Figure 2.—Relative d-orbital energies for a nickel(II) ion in an essentially square-planar environment.

highest energy orbitals, Δ, decreases in going from (1) a strong to a weaker in-plane field and/or (2) a very weak

(21) R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966); S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi, and K. Iwasaki, *Coord. Chem. Rev.*, **3**, 247 (1968).

axial perturbation to a stronger axial perturbation. Energywise less and less CFSE is gained by electron pairing; therefore, the high-spin state becomes more favored. It should be easier for pyridine to unpair electrons for a weak in-plane field than for a strong in-plane field because Δ is smaller. Consequently, one might argue that (1) Ni(salen) is diamagnetic in pyridine because of the strong ligand field presented by salen, (2) Ni(salophen) is partially paramagnetic because salophen presents a weaker field arising from the lower coordinating ability of the imine nitrogen atoms which are in conjunction with the aromatic ring systems, and (3) Ni(Xsaldien) is fully paramagnetic and pseudooctahedral in pyridine since Xsaldien should present the weakest in-plane ligand field in that five atoms join the imine nitrogens. Alternatively the secondary nitrogen atom may present some small degree of axial perturbation, the degree being limited by the steric requirements of the ligands and the metal–ligand distance. For metal–donor atom distances of 2.3–2.5 Å, saldien has been shown to function as a planar pentadentate ligand with a stable noneclipsed conformation

of its aliphatic chain.[22] This conformation is not anticipated for first-row transition ions since the metal to donor atom distance is approximately 2.0 Å. The extent of this perturbation is difficult to measure but it would seem that it becomes more pronounced if a donor occupies the other axial position. That the pyridine adduct of Ni(5-Br(saldien)) shows a sharp N–H stretch in the infrared spectrum supports the postulate.

The suggested weaker in-plane field for Ni(Xsaldien) lends credence to our contention that the anomalous magnetic moments in the solid state may arise from a thermal population of singlet and triplet states.

(22) M. N. Akhtar, E. D. McKenzie, R. E. Paine, and A. J. Smith, *Inorg. Nucl. Chem. Lett.*, **5**, 673 (1969).

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An Investigation of the Diamagnetic–Paramagnetic Equilibrium of Two Nickel(II)–Schiff Base Complexes in Several Coordinating Solvents

BY L. RUSNAK AND R. B. JORDAN*

The temperature dependence of the diamagnetic–paramagnetic equilibrium of the Schiff base complex of nickel(II) with the quadridentate ligand 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene has been studied in water, methanol, *N,N*-dimethylformamide, dimethyl sulfoxide, and acetonitrile. Observations disclose that the diamagnetic form of the complex is thermodynamically favored at higher temperatures. The equilibrium was quantitatively characterized by studies of the magnetic susceptibility and chemical shift of the ligand azomethine methyl resonance. Equilibrium parameters are consistent with a square-planar–octahedral structural change accompanying the spin-state change. Similar measurements in water and *N,N*-dimethylformamide were performed on the analogous complex in which a methyl group replaces the secondary amine hydrogen in the macrocyclic ligand.

Introduction

This paper reports the results of a study of the diamagnetic–paramagnetic equilibrium for the solvated nickel(II) complex of 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (Ia), henceforth referred to as $NiCR^{2+}$, and its methylated analog, Ib, $NiCRCH_3^{2+}$.

Ia, X = H
b, X = CH₃
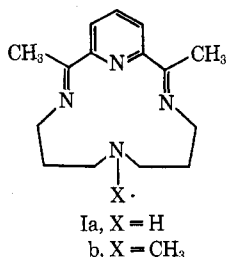
The study of this equilibrium was necessary in order to interpret the solvent nmr line broadening properties of

these nickel(II) complexes.[1] The diamagnetic–paramagnetic equilibrium has been studied as a function of temperature in water, methanol, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetonitrile. The changes in magnetic susceptibility and in ligand proton contact shift have been measured.

The presence of a diamagnetic–paramagnetic equilibrium in the $NiCR^{2+}$ system is not surprising in view of the observations of Busch and Karn[2–4] on these systems in the solid state. Similar results on complexes less closely related to those studied here have been reviewed recently by Barefield, Busch, and Nelson.[4]

Several types of reactions have been associated with the diamagnetic–paramagnetic change in nickel(II) complexes. In the solid state, where ligand movement is restricted, a simple equilibrium between electronic

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