$(NO_2)_2]^-$ and $(-)[Co(EDDA)(NO_2)_2]^-$ assigned Λ and Δ, respectively, based on above arguments, both form the less soluble diastereomer with $(-)_D[Co(en)_2ox]^+$.

The interpretation of CD spectra of Co(III) chelates is usually complicated by difficulty in identifying the CD peaks and in tracing these peaks through a series of related complexes with different crystal fields. Because of the large vicinal effect associated with s-cis EDDA complexes and the fixed chelate ring configurational and conformational contributions of EDDA, these complexes are well suited for the study of structural origins of optical activity in metal complexes.

Registry No. $(+)[Co(EDDA)(NH_3)_2]NO_3$, 37480-72-1; $(-)[Co(EDDA)(NH_3)_2]NO_3$, 37480-73-2; $(\pm)[Co(DMEDDA)(NH_3)_2]NO_3$, 37480-80-1; *s-cis*-$[Co(DEEDDA)(NH_3)_2]NO_3$, 37480-81-2; $(+)[Co(EDDA)tn]NO_3$, 37480-82-3; $(-)[Co(EDDA)tn]NO_3$, 37480-83-4; $[Co(C_{11}H_{24}N_4O_4)]NO_3$, 37480-84-5; $[Co(C_{13}H_{28}N_4O_4)]NO_3 \cdot 2H_2O$, 37475-79-9; $K[Co(C_6H_{10}N_4O_8)]$, 37480-85-6; $(+)K[Co(DEEDDA)(NO_2)_2]$, 37480-86-7; $K[Co(C_8H_{14}N_4O_8)]$, 37480-87-8.

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106,
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Four-, Five-, and Six-Coordinate Complexes of Nickel(II) with the Macrocyclic Ligand 2,4,4-Trimethyl-10,11-benzo-1,5-diaza-8,13-dithiacyclopentadeca-1,10-diene

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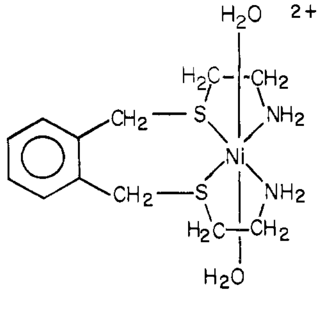
The reaction of the nickel(II) complex of 1,10-diamino-3,8-dithia-5,6-benzodecene with acetone in methanol solution results in the formation of the nickel(II) complex of the new macrocyclic ligand 2,4,4-trimethyl-10,11-benzo-1,5-diaza-8,13-dithiacyclopentadeca-1,10-diene. The perchlorate, thiocyanate, chloride, bromide, and iodide derivatives of this new complex ion have been prepared and characterized. In the solid state and in aqueous or methanol solutions the perchlorate derivative possesses a low-spin, square-planar structure as deduced from spectral and magnetic measurements. The solid thiocyanate derivative exhibits properties characteristic of a high-spin, six-coordinate nickel(II) complex. In the solid state and in methanol solution the halide derivatives are shown to be examples of high-spin, five-coordinate nickel(II) complexes by conductance, spectral, and magnetic measurements. In aqueous solutions, the halide derivatives dissociate to yield a low-spin, square-planar complex ion.

Introduction

A variety of synthetic routes have been developed leading to the preparation of metal complexes containing macrocyclic ligands.[1] A particularly novel reaction which results in macrocyclic ligand formation has been reported by Curtis.[2] In this reaction two molecules of acetone condense with two coordinated primary amine functions to yield a six-membered chelate ring. Curtis has applied this reaction to a variety of metal complexes containing aliphatic diamine and tetramine ligands to produce an extensive series of macrocyclic complexes.[3] In this laboratory similar amine condensation reactions have been found[4,5] and the properties of metal complexes arising from these reactions have been extensively studied.[6] In all cases so far reported, the macrocyclic complexes obtained by these condensation reactions have contained only nitrogen donor atoms.

In order to extend this series of macrocyclic complexes to ligands containing donor atoms other than nitrogen, we have employed the Curtis reaction with a previously known nickel(II) complex (1) of a linear tetradentate ligand containing as donor atoms two thioether groups and two terminal primary amine functions.[7] Macrocyclic complexes, 2, containing both imine and thioether donors have been prepared previously[7] *via* reaction of two coordinated mercaptide groups with a difunctional alkylating agent.



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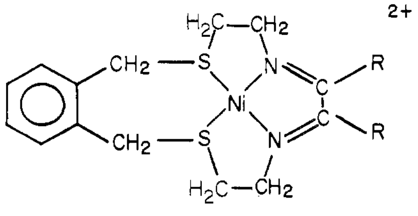

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[1] L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, 6, 1 (1971).

[2] N. F. Curtis and D. A. House, *Chem. Ind.* (*London*), 1708 (1961).

[3] N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

[4] T. E. MacDermott and D. H. Busch, *J. Amer. Chem. Soc.*, 89, 5780 (1967).

[5] T. E. MacDermott, B. E. Sewall, and D. H. Busch, *J. Amer. Chem. Soc.*, 89, 5784 (1967).

[6] L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, 89, 703 (1967); 90, 6938 (1968).

[7] M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.*, 86, 3651 (1964).

Recently, macrocyclic ligands containing four[8] or eight[9] thioether donors have been reported which coordinate one or two transition metal ions, respectively. Studies of these macrocyclic complexes[8-10] and simpler complexes containing thioether donors[11-15] have been carried out to determine the donor ability of these sulfur ligands. Macrocyclic complexes, in general, have provided useful models for studying the factors which influence the electronic structures of nickel(II) complexes. Examples of tetragonal and five-coordinate structures[16,17] as well as spin-state isomerism[18] have arisen from the study of these complexes.

Experimental Section

$Ni(EX)Cl_2 \cdot H_2O$. The preparation of 1,10-diamino-3,8-dithia-5,6-benzodecene (EX) and the nickel(II) complex of this ligand, $Ni(EX)Cl_2 \cdot H_2O$, was carried out in a manner similar to that reported by Thompson and Busch.[7]

$Ni(AEX)Cl_2 \cdot H_2O$. The macrocyclic complex dichloro(2,4,4-trimethyl-10,11-benzo-1,5-diaza-8,13-dithiacyclopentadeca-1,10-diene)nickel(II) monohydrate ($Ni(AEX)Cl_2 \cdot H_2O$) was prepared in the following manner. To 300 ml of a methanol solution containing 1.0 g (0.0025 mol) of $Ni(EX)Cl_2 \cdot H_2O$ was added 15 ml of reagent grade acetone. The solution was allowed to stand at room temperature for 3 days, after which the volume of the solution was reduced to ~50 ml and the solution was cooled. The resulting feathery blue crystals were filtered off, recrystallized twice from absolute methanol, and dried *in vacuo* at room temperature for 12 hr. *Anal.* Calcd for $C_{18}H_{28}N_2S_2NiCl_2 \cdot H_2O$: C, 44.65; H, 6.25; N, 5.79; S, 13.24; Cl, 14.65. Found: C, 45.05; H, 6.31; N, 5.66; S, 13.08; Cl, 14.76.

The bromide, iodide, thiocyanate, and perchlorate derivatives were prepared from the chloride *via* metathesis with a methanol solution of an appropriate salt.

$Ni(AEX)Br_2$ was obtained as light blue crystals and dried *in vacuo* at 80° for 12 hr. *Anal.* Calcd for $C_{18}H_{28}N_2S_2NiBr_2$: C, 38.95; H, 5.08; N, 5.05; S, 11.55; Br, 28.79. Found: C, 38.88; H, 5.51; N, 5.03; S, 10.72; Br, 26.00.

$Ni(AEX)I_2 \cdot H_2O$, deep green crystals from methanol, was dried at room temperature *in vacuo* for 12 hr. *Anal.* Calcd for $C_{18}H_{28}N_2S_2NiI_2 \cdot H_2O$: C, 32.41; H, 4.53; N, 4.20; S, 9.60; I, 38.0. Found: C, 32.21; H, 4.43; N, 4.06; S, 9.65; I, 38.05.

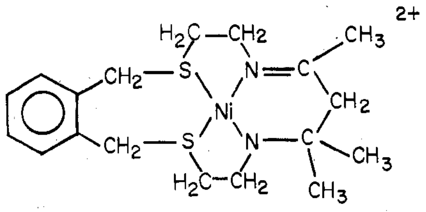
$Ni(AEX)(NCS)_2$ was obtained as a violet powder and dried *in vacuo* at 80° for 12 hr. *Anal.* Calcd for $C_{20}H_{28}N_4S_4Ni$: C, 46.97; H, 5.52; N, 10.96; S, 25.07. Found: C, 47.10; H, 5.53; N, 10.85; S, 25.16.

$Ni(AEX)(ClO_4)_2 \cdot H_2O$, obtained as deep red crystals from methanol, was dried *in vacuo* at 80° for 12 hr. *Anal.* Calcd for $C_{18}H_{28}N_2S_2NiCl_2O_8 \cdot H_2O$: C, 35.28; H, 4.94; N, 4.58; S, 10.47; Cl, 11.45. Found: C, 35.45; H, 4.90; N, 4.63; S, 10.59; Cl, 11.40.

Physical Measurements. Infrared spectra were obtained using pressed KBr pellets or Nujol mulls between sodium chloride plates with a Perkin-Elmer Model 337 spectrophotometer. Electronic spectra were measured in solution and in the solid state (diffuse transmittance of Nujol mulls supported on filter paper)[19] with a Cary Model 14 recording spectrophotometer. Magnetic moments were measured by the Gouy and Faraday methods using $Hg[Co(NCS)_4]$ as a calibrant. Diamagnetic corrections for the ligands were calculated from tables of Pascal's constants.[20] The conductivity measurements were made with an Industrial Instruments Model RC 16B2 conductivity bridge and a conductivity cell having a cell constant of 1.434 ± 0.007 cm^{-1}. Analyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

The composition of the product resulting from the reaction of $Ni(EX)Cl_2 \cdot H_2O$ with acetone indicates that two acetone residues have been incorporated into the complex. Since acetone can undergo simple simple Schiff base formation with primary amines, it is necessary to demonstrate that cyclization of the isopropylidene groups has occurred. Evidence that a macrocyclic ligand has been produced is obtained from the infrared spectrum of the product. The primary amine N-H stretching and deformation bands assigned at 3300 and 1600 cm^{-1}, respectively,[21,22] present in the spectrum of $Ni(EX)Cl_2 \cdot H_2O$, are absent in the spectrum of the product. Instead, new infrared absorption bands appearing in the spectrum of the product at 3125, 1667, and 1375 cm^{-1} are attributed to the secondary N-H stretching frequency, the C=N stretching frequency, and the deformation mode of the *gem*-dimethyl groups, respectively. These data agree with the values reported by Curtis[23,24] for the infrared absorptions of similar macrocyclic complexes. In addition, hydrolysis of the complex leads to the formation of mesityl oxide as indicated by a gas chromatographic analysis of the hydrolysis products. On this basis it is concluded that cyclization has occurred and the formulation of the macrocyclic product is given by **3**. The disposition of the molecule of water is not known; however the position of the OH stretching band (3600 cm^{-1}) suggests that the water is not coordinated to the nickel ion.



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The conditions utilized for the preparation of this macrocyclic complex are significantly milder than those reported by Curtis[25] for the analogous reactions of tetramine complexes with acetone. This no doubt reflects the increased ease with which the reactive amine groups in the more flexible tetradentate ligand, EX, can occupy cis positions in the present complex.

The electronic spectra and magnetic moments (Table I) for the derivatives of this macrocyclic complex vary widely as a function of the associated anions. Information regarding the arrangement of the macrocyclic ligand about the metal ion and the tendency for the complex ion to coordinate solvent molecules in solution is obtained from the physical properties of the perchlorate derivative. In the solid state, the perchlorate salt of the complex ion is diamagnetic and exhibits a single, broad absorption band at 20,500 cm^{-1}.

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(8) W. Rosen and D. H. Busch, *Chem. Commun.*, 148 (1969); *J. Amer. Chem. Soc.*, 91, 4694 (1969); *Inorg. Chem.*, 9, 262 (1970).

(9) K. Travis and D. H. Busch, *Chem. Commun.*, 1041 (1970).

(10) G. R. Brubaker and D. H. Busch, *Inorg. Chem.*, 5, 2114 (1966).

(11) R. Backhouse, M. E. Foss, and R. S. Nyholm, *J. Chem. Soc.*, 1714 (1957).

(12) R. L. Carlin and E. Weissberger, *Inorg. Chem.*, 3, 611 (1964).

(13) D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *J. Amer. Chem. Soc.*, 86, 3642 (1964).

(14) F. A. Cotton and D. L. Weaver, *J. Amer. Chem. Soc.*, 87, 4189 (1965).

(15) C. D. Flint and M. Goodgame, *J. Chem. Soc. A*, 2178 (1968).

(16) J. L. Karn and D. H. Busch, *Nature (London)*, 211, 160 (1966).

(17) E. B. Fleischer and S. W. Hawkinson, *Inorg. Chem.*, 7, 2312 (1968).

(18) G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.*, 86, 4830 (1964).

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

(20) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, p 403.

(21) M. L. Morris and D. H. Busch, *J. Amer. Chem. Soc.*, 82, 1521 (1960).

(22) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955); 2712 (1956).

(23) M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 2016 (1962).

(24) D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 86, 1331 (1964).

(25) D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 84, 3248 (1962).

Table I. Spectral and Magnetic Properties of the $Ni(AEX)^{2+}$ Derivatives

Complex	Electronic spectra, $\bar{\nu}_{max}$, cm^{-1} (ϵ_{max}) Solid state[a]	Electronic spectra, $\bar{\nu}_{max}$, cm^{-1} (ϵ_{max}) Methanol soln	Spectral assignment	μ'_{eff}, BM
$[Ni(AEX)Cl]Cl \cdot H_2O$	8,500	8,500 (5.8)	$^3B_1 \to {}^3E(1)^b$	2.80
	10,900	11,200 (2.7)	$^3B_1 \to {}^1A_1$	
	13,000	13,200 (7.1)	$^3B_1 \to {}^3A_2$ or $^3B_2$	
	16,900	17,100 (15.0)	$^3B_1 \to {}^3E(2)$	
$[Ni(AEX)Br]Br$	8,340		$^3B_1 \to {}^3E(1)^b$	3.20
	10,370		$^3B_1 \to {}^1A_1$	
	13,450		$^3B_1 \to {}^3A_2$ or $^3B_2$	
	16,900		$^3B_1 \to {}^3E(2)$	
$[Ni(AEX)I]I \cdot H_2O$	7,200		$^3B_1 \to {}^3E(1)^b$	3.01
	9,500		$^3B_1 \to {}^1A_1$	
	13,500		$^3B_1 \to {}^3A_2$ or $^3B_2$	
	17,500		$^3B_1 \to {}^3E(2)$	
$[Ni(AEX)(NCS)_2]$	10,580		$^3B_{1g} \to {}^3E_g{}^a$ or $^3B_{2g}{}^c$	
	11,540		$^3B_{1g} \to {}^3E_g{}^a$ or $^3B_{2g}$	3.10
	17,900		$^3B_{1g} \to {}^3E_g{}^b$ and $^3A_{2g}$	
$[Ni(AEX)](ClO_4)_2 \cdot H_2O$	20,500	20,500 (29.9)	$^1A_{1g} \to {}^1B_{1g}{}^d$	0.6

[a] Measured by diffuse transmittance of Nujol mulls. [b] Transition assignment based on C_{4v} symmetry; *cf.* ref 25. [c] Transition assignment based on D_{4h} symmetry (triplet ground state). [d] Transition assignment based on D_{4h} symmetry (singlet ground state).

This behavior is characteristic of a square-planar nickel(II) complex with a singlet ground state.[26] Thus in the absence of coordinating anions the macrocyclic ligand occupies the essentially planar orientation about the nickel(II) ion shown in **3**. It is unlikely that the presence of unidentate anions would induce folding of the macrocyclic ligand, and it is concluded that if the complex ion expands its coordination number, the entering ligands would occupy axial positions.

The perchlorate derivative dissolved in methanol or water exhibits essentially the same electronic spectrum as in the solid state. Aqueous solutions of $Ni(AEX)(ClO_4)_2$, however, exhibit weak absorptions in the spectral region corresponding to high-spin nickel(II) transitions and this may reflect an equilibrium of the type $[Ni(AEX)]^{2+} + H_2O \rightleftharpoons [Ni(AEX)(H_2O)]^{2+}$. The situation is complicated by the fact that the macrocyclic complex is hydrolytically unstable and decomposes within a few hours to yield a solution of $[Ni(EX)(H_2O)_2]^{2+}$ which also exhibits a typical high-spin spectrum.[7] Complexes of macrocyclic ligands are usually quite resistant to hydrolysis.[3,27] Curtis has noted, however, that the macrocyclic complex derived from trimethylenediamine and acetone is much less stable toward hydrolysis and reagents such as dimethylglyoxime than is the corresponding complex derived from ethylenediamine.[28] He attributes this to the effect of larger ring size. In the macrocyclic complex $[Ni(AEX)]^{2+}$, the combination of the weak donor ability of the thioether groups together with the large chelate ring size between the sulfur donors may account for the decreased hydrolytic stability.

Conductance measurements of the perchlorate derivative in both methanol and water reveal that it behaves as a 2:1 electrolyte in these solvents, confirming that the anions are not associated with the complex ion. In the absence of coordinating anions, therefore, the complex $[Ni(AEX)]^{2+}$ has little apparent tendency to coordinate solvent molecules in methanol or water. The inability of water to enter the coordination sphere of macrocyclic complexes has been noted before.[29] The hydrophobic character of the macrocyclic ligand may structure the surrounding water to an extent where it is difficult for an individual solvent molecule to leave the structured bulk solvent and coordinate to the complex ion.[29] It is unlikely that steric hindrance provides the explanation for this observation, for (*vide infra*) even bulky anions can enter the coordination sphere of the complex.

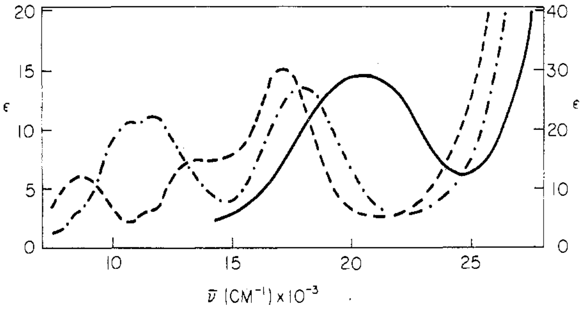

Figure 1. Electronic spectra of $Ni(AEX)^{2+}$ derivatives: ——, $Ni(AEX)Cl_2 \cdot H_2O$, 0.05 *M* in H_2O solution (right coordinate axis); — · — · —, $Ni(AEX)(NCS)_2$, solid-state diffuse-transmittance spectrum, absorbance axis is arbitrary; - - - -, $Ni(AEX)Cl_2 \cdot H_2O$, 0.010 *M* in methanol solution (left coordinate axis).

In contrast to the square-planar $[Ni(AEX)](ClO_4)_2 \cdot H_2O$, the thiocyanate derivative is assigned a high-spin, six-coordinate nickel(II) formulation from its magnetic moment and ligand field spectrum (Table I and Figure 1). The two low-energy absorption bands centering at 11.0 and 17.9 kK may be assigned as being derived from the $^3A_{2g} \to {}^3T_{2g}$ and $^3A_{2g} \to {}^3T_{1g}(F)$ transitions of octahedral nickel(II),[30] respectively. The additional transition $^3A_{2g} \to {}^3T_{1g}(P)$ is obscured by the onset of an intense charge-transfer band. There is a pronounced splitting of the low-energy band, and the positions of maxima for the two, almost equal, components are 10.6 and 11.5 kK. These two components may represent a tetragonal component[31] in this trans thiocyanate complex. Insolubility of the thiocyanate derivative precluded solution spectral or conductance data.

In the solid state, the three halide derivatives do not display electronic spectral characteristic of either six-coordinate or square-planar nickel(II) (Table I). In methanol solution the halide derivatives exhibit electronic spectra identical with those obtained in the solid state (Figure 1). Aqueous solutions of the Cl and Br derivatives, on the other

(26) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 264.

(27) N. F. Curtis, *J. Chem. Soc.*, 4409 (1960).

(28) D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 86, 223 (1964).

(29) D. H. Busch, *Advan. Chem. Ser.*, No. 62, "Werner Centennial," 616 (1967).

(30) Reference 26, p 261.

(31) A. B. P. Lever, *Coord. Chem. Rev.*, 3, 119 (1968).

hand, were found to exhibit a spectrum identical with the spin-paired perchlorate salt.

Conductance measurements were employed to determine the nature of the chloride derivative in methanol and water. In water, the chloride derivative is a 2:1 electrolyte and thus exhibits the same tendency not to increase the coordination number of the nickel(II) ion in aqueous solution demonstrated by the perchlorate salt. The equivalent conductance, Λ_e, of $Ni(AEX)Cl_2 \cdot H_2O$ in methanol varies systematically from 72.7 to 58.3 $cm^2\ ohm^{-1}\ equiv^{-1}$ between 2.00 and 10.00 m*M*. A plot of Λ_e *vs.* $\sqrt{C}$ yields a straight line over this concentration range in agreement with the Onsager limiting law, $\Lambda_e = \Lambda_0 - A\sqrt{C_e} = \Lambda_0 - (B_1\Lambda_0 + B_2)\sqrt{C_e}$. The experimentally determined value of $A = 260$ may be compared with a calculated value of A. Using literature[32] values of B_1 and B_2 and evaluating $\Lambda_0 = 84.8\ cm^2\ ohm^{-1}\ mol^{-1}$, we calculate $A = 233$ in reasonable agreement with the experimental value. From these data, $Ni(AEX)Cl_2 \cdot H_2O$ is formulated as a 1:1 electrolyte over the range 2-10 m*M*.

The lower dielectric constant of methanol favors ion-pair association and a comparison of the spectral properties of the perchlorate and the halide derivatives in methanol solution reveals that the associated halide ion must be coordinated to the nickel ion. This observation, coupled with the failure of the $[Ni(AEX)]^{2+}$ complex ion to coordinate solvent molecules in methanol, leads to the formulation of the halide species in methanol as high-spin, five-coordinate nickel(II) complexes. Since the solid halide derivatives exhibit electronic spectra identical with those obtained in methanol, it is concluded that the five-coordinate geometry is present in the solid complexes also. The room-temperature magnetic moments for the solid-state bromide and iodide derivations are in the range for previously reported[33] high-spin five-coordinate nickel(II) complexes. The value of μ'_{eff} for the chloride derivative is anomalously low, lying even below the spin-only value for a d^8 configuration. No explanation is available at present for this low magnetic moment.

The electronic spectra of five-coordinate nickel(II) complexes in idealized trigonal-bipyramidal and square-pyramidal geometries have been treated theoretically by Ciampolini,[34] and examples of experimental spectra of nickel(II) complexes, known to be five-coordinate from crystal studies, have been published.[33]

The simple addition of a halide ion to the coordination sphere of the planar macrocyclic complex ion **3** would produce an essentially square-pyramidal structure. Since the difference between square-pyramidal and trigonal-bipyramidal geometries is small, a slight distortion may produce a trigonal-bipyramidal complex.

Although the electronic spectra of the present series of complexes differ somewhat from previously reported spectra of complexes known to be square-pyramidal by crystallographic studies, a reasonable transition assignment may be made based on the theoretical square-pyramidal model.[34] These assignments are summarized in Table I. An assignment taken from Ciampolini,[34] Figure 5, with $\mu_{base} = 4.0$ D and $\mu_{ax}/\mu_{base} = 1.15$ yields the following data: ${}^3B_1 \rightarrow {}^3E$, 8000 cm^{-1}; ${}^3B_1 \rightarrow {}^1A_1$, 10,000 cm^{-1}; ${}^3B_1 \rightarrow {}^3A_2$ and ${}^3B_2$, 11,000–12,000 cm^{-1}; ${}^3B_1 \rightarrow {}^3E$, 17,000 cm^{-1}. Thus there is reasonable agreement with the spectral results for $[Ni(AEX)Cl]^+$ considering that the present complexes possess a much lower symmetry than C_{4v} and the ratio μ_{ax}/μ_{base} cannot be known with certainty. No such agreement could be obtained with the energy level diagrams available for a trigonal bipyramidal geometry.

The trend in the energy of the ${}^3B_1 \rightarrow {}^3E(1)$ transition within the series Cl^-, Br^-, I^- is also consistent with the square-pyramidal model; increasing the crystal field strength in going from I^- to Cl^- moves the ${}^3B_1 \rightarrow {}^3E(1)$ transition to higher energies as expected. The assignment of the second band to a spin-forbidden transition is supported by its weak intensity. The variation of this band position with varying axial perturbation is also consistent with the theoretical model. The third band (actually a broad shoulder) is thought to encompass the ${}^3B_1 \rightarrow {}^3A_2$ and ${}^3B_1 \rightarrow {}^3B_2$ transitions in view of the fact that these levels lie very close together in the region of the diagram where the energies of the transitions correspond to those obtained for the $[Ni(AEX)X]^+$ species. The band assigned as ${}^3B_1 \rightarrow {}^3E(2)$ shows a slight reverse trend from that anticipated for the halide series. The observation of further $d \rightarrow d$ bands is obscured by an intense transition, presumably a charge-transfer transition ($d \rightarrow \pi^*$) involving the azomethine group. It is therefore concluded that the halide derivatives, $[Ni(AEX)X]^+$, possess a five-coordinate, essentially square-pyramidal structure in the solid state and this geometry is retained in methanol solution.

Registry No. Acetone, 67-64-1; $Ni(EX)Cl_2 \cdot H_2O$, 37549-15-8; $Ni(AEX)Cl_2 \cdot H_2O$, 37549-14-7; $Ni(AEX)Br_2$, 37549-16-9; $Ni(AEX)I_2 \cdot H_2O$, 37549-17-0; $Ni(AEX)(NCS)_2$, 37523-53-8; $Ni(AEX)(ClO_4)_2 \cdot H_2O$, 37549-18-1.

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(32) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London, 1959, p 163.

(33) M. Ciampolini, *Struct. Bonding (Berlin)*, 6, 52 (1968).

(34) M. Ciampolini, *Inorg. Chem.*, 5, 35 (1966).