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The Donor Properties of Positively Charged Ligands. Five-Coordinate Transition Metal Complexes Containing a Monoquaternized Tertiary Diamine

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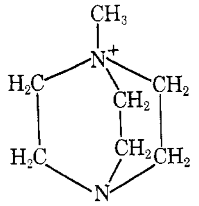
A novel series of five-coordinate transition metal complexes, of the general formula $M(L^+)(Y)X_3$, has been prepared with M = Mn(II), Fe(II), Cu(II), Ni(II), Co(II); L^+ = N-methyl-1,4-diazabicyclo[2.2.2]octonium cation; Y = H_2O, NH_3; and X = Cl, Br. These complexes are of the high-spin type and can be assigned a trigonal-bipyramidal stereochemistry with the three X ligands in the equatorial plane. Evidence for this formulation is obtained from electronic and vibrational spectra, magnetic properties, and X-ray powder diffraction patterns. These five-coordinate complexes are unusual in that they contain only σ-bonding monodentate ligands, one of which is positively charged, and thus represent an example of five-coordination induced and stabilized by electronic factors and lattice energy rather than by the steric requirements of a polydentate ligand.

Introduction

It has become evident in recent years that metal complexes of coordination number 5, although not as common as those of coordination numbers 4 and 6, can be obtained with a variety of ligands and metals.[1] Most five-coordinate complexes so far known for high-spin transition metal ions contain polydentate ligands whose stringent steric requirements allow only five donor atoms to surround the metal ion.[2-6] With only monodentate ligands, examples of high-spin five-coordinate transition metal complexes are still very scarce.[7-10]

This paper reports the preparation and structural investigation of a novel series of five-coordinate complexes of the divalent transition metal ions, Mn(II) to Cu(II), containing only monodentate ligands, one of which is a positively charged ligand. This study was prompted by our previous investigations on the donor properties of cation ligands, which had shown that a positive charge on a ligand does not prevent its coordination to (positively charged) metal ions but, in fact, increases the lattice energy of the resulting complexes thus stabilizing unusual stoichiometries and structures.[11] In particular, our previous work[12] demonstrated that the cation ligands formed by monoquaternization of the ditertiary amine 1,4-diazabicyclo-[2.2.2]octane (called dabco for brevity) have unusually favorable characteristics because of their rigid, compact, and nearly spherical cagelike structure. The positively charged ligand obtained by the monomethylation of dabco was therefore chosen for this investigation, and the work includes the divalent metal ions of the first transition series, with d^5 to d^9 electron configurations, which offer the opportunity to study crystal field effects on the basis of electronic spectra.



N-methyldabconium cation ligand

Results and Discussion

The reaction of the divalent metal ions Mn(II) to Cu(II) with the positively charged N-donor ligand N-methyldabconium, L^+, in the presence of halide ions and in anhydrous medium, yields a series of four-coordinated pseudotetrahedral complexes, $M(L^+)X_3$.[12] However, if a small quantity of water is present in the reaction mixture or if the $M(L^+)X_3$ complexes are exposed to moisture, a different series of complexes is formed, having the stoichiometry $M(L^+)X_3 \cdot H_2O$. The reaction $M(L^+)X_3 + H_2O \rightarrow M(L^+)X_3 \cdot H_2O$ occurs readily when X = Cl, but only with difficulty when X = Br; the iodo complexes $M(L^+)I_3$ do not add water. The ease of formation of the complexes of stoichiometry $M(L^+)Cl_3 \cdot H_2O$ follows approximately the order Mn < Fe $\sim$ Ni > Cu; the cobalt(II) and zinc(II) complexes could not be obtained under any of the conditions tried. A parallel order is observed for the stability of these complexes with respect to thermal loss of water; thus, the nickel(II) complex slowly loses the molecule of water at 100°, whereas the manganese(II) complex

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(1) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

(2) M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6**, 1261 (1967), and references therein.

(3) F. Lions, I. G. Dance, and J. Lewis, *J. Chem. Soc., A*, 565 (1967), and references therein; P. Pauling, G. B. Robertson, and G. A. Rodley, *Nature*, **207**, 73 (1965).

(4) S. M. Nelson and J. Rogers, *Inorg. Chem.*, **7**, 1390 (1967), and references therein.

(5) L. Sacconi, G. P. Speroni, and R. Morassi, *ibid.*, **7**, 1521 (1968); L. Sacconi, R. Morassi, and S. Midollini, *J. Chem. Soc., A*, 1510 (1968); L. Sacconi, *Transition Metal Chem.*, **4**, 232 (1968).

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(9) R. C. Slade, A. A. G. Tomlinson, B. J. Hathaway, and D. E. Billing, *J. Chem. Soc., A*, 61 (1968), and references therein.

(10) A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *Inorg. Chim. Acta*, **2**, 111 (1968), and references therein.

(11) J. V. Quagliano, J. T. Summers, S. Kida, and L. M. Vallarino, *Inorg. Chem.*, **3**, 1557 (1964).

(12) J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Am. Chem. Soc.*, in press.

TABLE I

ANALYTICAL DATA AND SOME PROPERTIES OF THE $M(L^+)(Y)X_3$ COMPLEXES

Formula	Color	μ_{eff}, BM	% metal		% halogen		% nitrogen	
			Calcd	Found	Calcd	Found	Calcd	Found
$Mn(L^+)(H_2O)Cl_3$	White	5.95	17.93	17.5	34.77	35.0	9.15	8.9
$Mn(L^+)(H_2O)Br_3$	Peach tinge	5.93	12.49	12.3	54.52	54.7	6.37	6.5
$Mn(L^+)(NH_3)Cl_3$	White	6.00	18.01	18.3	34.87	34.7	13.87	13.7
$Mn(L^+)(NH_3)Br_3$	White	5.97	12.52	12.4	54.64	54.3	9.57	9.4
$Fe(L^+)(H_2O)Cl_3$	White	5.12	18.27	18.1	34.62	34.9	9.11	8.9
$Fe(L^+)(H_2O)Br_3$	Light tan	4.98	12.67	12.5	54.41	54.4	6.35	6.2
$Fe(L^+)(NH_3)Br_3$	Light tan	5.00	12.70	12.5	54.54	54.3	9.55	9.6
$Co(L^+)(NH_3)Cl_3$	Violet	4.61	19.5	18.9	34.39	34.2	14.22	13.9
$Co(L^+)(NH_3)Br_3$	Violet	4.73	13.31	13.5	54.16	54.3	9.94	9.8
$NI(L^+)(H_2O)Cl_3$	Red	3.69	18.88	18.8	34.30	34.4	9.03	9.3
$Ni(L^+)(H_2O)Br_3$	Red	3.69	13.24	13.0	54.05	54.2	6.31	6.2
$Ni(L^+)(NH_3)Cl_3$	Golden brown	3.85	18.99	18.6	34.42	34.2	13.6	13.2
$Ni(L^+)(NH_3)Br_3$	Golden brown	3.76	13.27	13.3	54.18	54.1	9.94	10.0
$Cu(L^+)(H_2O)Cl_3$	Pale yellow	1.89	20.17	20.3	33.78	33.5	8.89	8.9
$Cu(L^+)(H_2O)Br_3$	Mustard	1.87	14.76	14.6	53.6	53.0	6.26	6.1
$Cu(L^+)(NH_3)Cl_3$	Mustard	1.91	20.24	20.0	33.88	33.8	13.4	13.4
$Cu(L^+)(NH_3)Br_3$	Green	1.85	14.20	14.4	53.60	53.5	9.39	9.4

begins to lose water only at a temperature of 150°. The bromo complexes, which are more difficult to form than the corresponding chloro complexes, are all very sensitive to mild heating (40–60°) and also to dehydrating agents; for example, the nickel(II) complex of stoichiometry $Ni(L^+)Br_3 \cdot H_2O$ loses water on warming to 40° or on standing overnight at room temperature over phosphoric anhydride.

A similar series of complexes, with stoichiometry $M(L^+)X_3 \cdot NH_3$, is formed when the $M(L^+)X_3$ compounds are treated with ammonia in a 1:1 mole ratio; these ammine complexes are fairly stable and generally do not lose ammonia until heated to 140° or higher.

The aquo and ammine complexes reported in this paper are crystalline substances, insoluble in organic solvents of poor donor properties and soluble with extensive solvation in good donor solvents such as water, dimethyl sulfoxide, and acetonitrile. The colors, magnetic moments, and analytical data for the complexes of stoichiometries $M(L^+)X_3 \cdot H_2O$ and $M(L^+)X_3 \cdot NH_3$ are listed in Table I. The results of their structural investigation, necessarily limited to solid-state properties, can be summarized as follows.

Magnetic Susceptibilities.—The room-temperature magnetic moments of the complexes, listed in Table I, are all within the ranges expected for high-spin electron configurations of these metal ions. The values of μ_{eff} of the Co(II) and Ni(II) complexes, for which the orbital contribution to the magnetic moment is particularly sensitive to stereochemistry and symmetry, apparently discount the possibility of octahedral coordination. In fact the magnetic moments of the $Co(L^+)X_3 \cdot NH_3$ complexes are too low, and those of the $Ni(L^+)X_3 \cdot H_2O$ and $Ni(L^+)X_3 \cdot NH_3$ complexes are too high, compared with the magnetic moments commonly observed for octahedral, high-spin d^7 and d^8 systems (μ_{eff}: 4.9–5.3 BM for octahedral Co(II); 3.0–3.4 BM for octahedral Ni(II)).

X-Ray Powder Diffraction Spectra.—The X-ray powder patterns of the complexes $M(L^+)X_3 \cdot H_2O$ (M = Mn(II), Fe(II), and Ni(II)) indicate that they are isomorphous. The complexes $M(L^+)X_3 \cdot NH_3$ [M = Mn(II), Fe(II), Co(II), and Ni(II)] are also isomorphous with one another, but not with the corresponding aquo complexes. In both the aquo and ammine series, the Cu(II) complexes are not strictly isomorphous with the complexes of the other metal ions. Thus, if a structure can be assigned to the Ni(II) or Co(II) complexes or both, on the basis of their spectral properties, the corresponding complexes of the other metal ions, except Cu(II), can also be considered to have the same structure.

d–d Electronic Spectra.—The spectra of the Co(II) and Ni(II) complexes, which are most helpful in establishing the stereochemistry, will be discussed first.

The d–d electronic spectra of the violet complexes $Co(L^+)X_3 \cdot NH_3$, measured as reflectance and mull spectra at room temperature, show two intense absorptions and several weaker ones. The pattern and energies of these absorptions cannot be reconciled with either a tetrahedral or an octahedral stereochemistry, but rather resemble those of Co(II) complexes known from X-ray studies to have coordination number 5. Thus it is logical to formulate the complexes of stoichiometry $Co(L^+)X_3 \cdot NH_3$ as the five-coordinate, nonionic species $Co(L^+)(NH_3)X_3$. A comparison of the spectra of the $Co(L^+)(NH_3)X_3$ complexes with those of the five-coordinate, trigonal-bipyramidal $[CoBr(Me_6tren)]Br$ ($Me_6tren = \{(CH_3)_2NCH_2CH_2\}_3N)$[13] and of the square-pyramidal $[Co(ClO_4)\{OAs(CH_3)(C_6H_5)_2\}_4]ClO_4$[3] reveals that the over-all pattern of the absorptions is very much the same for the three complexes. Several other five-coordinate Co(II) complexes,[5,8,10,14] which have been considered to approach either a square-pyramidal or a trigonal-bipyramidal stereochemistry, also have very similar spectra, once allow-

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

(14) M. Di Vaira and P. L. Orioli, *Chem. Commun.*, 590 (1965); M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, **5**, 45 (1966); M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, **1**, 222 (1966); M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); **6**, 445 (1967); M. Di Vaira and P. L. Orioli, *ibid.*, **6**, 955 (1967); L. Sacconi, I. Bertini, and R. Morassi, *ibid.*, **6**, 1548 (1967); L. Sacconi and G. P. Speroni, *ibid.*, **7**, 295 (1968).

TABLE II

ELECTRONIC SPECTRA OF FIVE-COORDINATE Co(II) AND Ni(II) COMPLEXES

	Absorption maxima, kK[b]					
	Assigned to the transitions from the ground state, $^4A_2'(F)$, to the excited states					
Complex[a]		$^4E''$ F)	$^4E'(F)$	$^4A_2'(P)$	$^4E''(P)$	
$Co(L^+)(NH_3)Cl_3$			10.5	14.8	17.4–18.3 (18.7)	
$Co(L^+)(H_2O)Br_3$		6.5	10.2	14.3	17.0–17.7 (17.8)	
	Assigned to the transitions from the ground state $^3E'(F)$ to the excited states					
	$^3E''(F)$	$^3A_1''(F)$, $^3A_2''(F)$	$^3A_2'(F)$	$^1A_1'(D)$, $^1E'(D)$, $^1E''(D)$	$^3E''(P)$	$^3A_2'(P)$
$Ni(L^+)(H_2O)Cl_3$	5.0	(8.0)	10.8	(16.0)	(18.0)	20.7
$Ni(L^+)(H_2O)Cl_3$[c]	5.4	8.7	10.5	(16.0) 17.2[d]	(18.5)	21.0
$Ni(L^+)(H_2O)Br_3$	5.5		10.5	(16.4)		20.0
$Ni(L^+)(NH_3)Cl_3$	5.8		11.7	(17.2) (17.8)	(19.7)	22.0
$Ni(L^+)(NH_3)Br_3$	5.8		11.8	16.2[d]	(18.6)	21.6

[a] L = N-methyl-1,4-diazabicyclo[2.2.2]octonium = N-methyldabconium cation. [b] Absorption maxima are from reflectance spectra unless otherwise indicated; shoulders are given in parentheses. [c] Absorption maxima from mull spectrum at liquid nitrogen temperature. [d] Sharp, weak band.

ance is made for the ligand absorptions and for the low resolution and intensity enhancements of room-temperature reflectance spectra. However, the energy separation between the two main absorption bands is generally greater for square-pyramidal than for trigonal-bipyramidal complexes, and this experimental observation is well explained by the energy level diagrams recently published by Ciampolini and Bertini.[15]

These diagrams show that, although the pattern of the energy levels is somewhat similar for both square-pyramidal and trigonal-bipyramidal high-spin Co(II), for the former the energy levels diverge more steeply with increasing field strength. In addition, the square-pyramidal configuration has one more low-energy excited level than the trigonal bipyramidal. This, however, is not expected to result in an easily observable spectral difference, since for both configurations the lower energy spin-allowed transitions should appear below 6000 cm^{-1}—a region difficult to observe with the commonly available reflectance spectrophotometers and complicated by the presence of the vibrational modes of the organic ligands.

In light of these close similarities between the spectra of square-pyramidal and trigonal-bipyramidal Co(II) complexes, a quantitative comparison of the observed and calculated absorption energies for the $Co(L^+)(NH_3)X_3$ complexes becomes necessary. Assuming the average "*Dq*" to be essentially the same[15] for six-coordinate and five-coordinate Co(II), the average *Dq* of the CoN_2X_3 chromophore is calculated to be about 0.8 kK. (The experimental *Dq* for the tetrahedral anions CoX_4^{2-} is 2.9 kK for X = Cl or Br;[12] the *Dq* for octahedral CoX_6, and hence approximately also for CoX_5, is then $Dq_{O_h} = {}^9/_4 Dq_{T_d} \simeq 0.65$ kK for X = Cl or Br. The values of *Dq* for CoO_6 and CoN_6 are taken to be 0.9 and 1.1 kK, respectively, from the spectra of $Co(H_2O)_6^{2+}$ and $Co(NH_3)_6^{2+}$.[16]) For this average *Dq* value, the energies of the observed d–d transitions of the $Co(L^+)(NH_3)X_3$ complexes are in fair agreement (Figure 1) with those calculated from the energy level diagram for trigonal-bipyramidal Co(II). Only the lowest energy absorption in the spectrum of $Co(L^+)(NH_3)X_3$—a weak broad band centered at 6.5 kK—disagrees widely with the value calculated for the transition $^4A_2'(F) \rightarrow {}^4E''(F)$. It should be noted, however, that even for the complex $[CoBr(Me_6tren)]Br$, discussed as a model by Ciampolini and Bertini, the lowest energy band (5.7 kK) does not agree with the calculated values unless corrections for geometrical and field strength distortions are included. No reasonable agreement, on the other hand, can be obtained by fitting the spectra of $Co(L^+)(NH_3)X_3$ with the energy diagrams of square-pyramidal Co(II). Thus it appears that a fairly reliable structural assignment for the $Co(L^+)(NH_3)X_3$ complexes can be made on the basis of

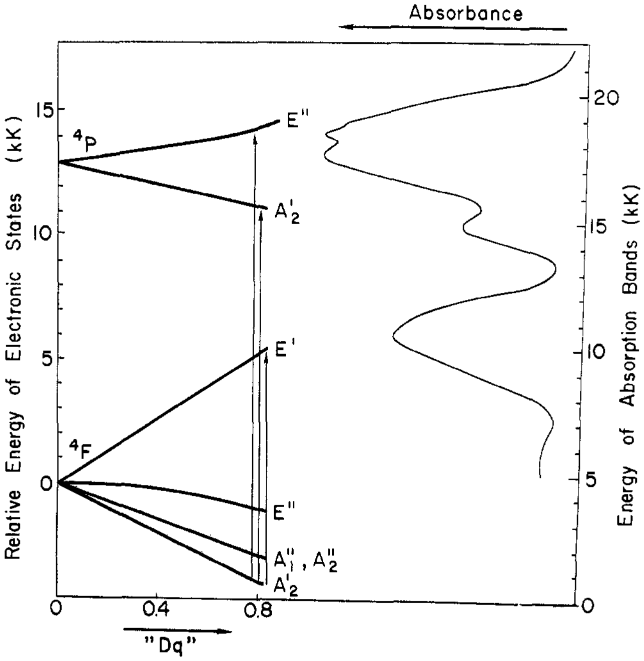

Figure 1.—Electronic spectrum of $Co(L^+)(NH_3)Cl_3$ at room temperature, compared with the energy level diagram for high-spin Co(II) in a trigonal-bipyramidal configuration of five equivalent dipoles (after Ciampolini and Bertini[15]).

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(15) M. Ciampolini and I. Bertini, *J. Chem. Soc., A*, 2241 (1968).

(16) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966, p 242.

Ciampolini and Bertini's diagrams, on the assumption that no major geometrical or ligand field distortions occur other than those considered by them. This assumption can logically be made for these complexes, where an essentially trigonal-bipyramidal stereochemistry with the three X ligands in the trigonal plane would result in the most symmetrical, minimum-repulsion structure. Accordingly, the $Co(L^+)(NH_3)X_3$ complexes are considered to have an essentially trigonal-bipyramidal structure, and their d–d absorptions are tentatively assigned as shown in Table II. These assignments follow those of Ciampolini for $[Co(Me_6\text{-}tren)Cl]Cl$; Wood[17] has assigned the transitions for the same complex somewhat differently.

Let us now consider the Ni(II) complexes of stoichiometries $Ni(L^+)X_3 \cdot H_2O$ and $Ni(L^+)X_3 \cdot NH_3$, which have intense red colors, unusual for high-spin nickel(II) in an environment of nitrogen, oxygen, and chloro or bromo ligands. The spectra of these complexes consist of three main absorptions, whose patterns again exclude either a tetrahedral or an octahedral coordination and closely resemble those of Ni(II) complexes known to be five-coordinate. Thus, our complexes can be formulated as the five-coordinate, nonionic species $Ni(L^+)(H_2O)X_3$ and $Ni(L^+)(NH_3)X_3$. The available literature shows that the electronic spectra of high-spin Ni(II) complexes with either a square-pyramidal or a trigonal-bipyramidal stereochemistry resemble one another closely in general appearence.[18] This experimental observation can be rationalized on the basis of the energy diagrams of the two configurations,[19] which are very similar especially for low values of μ. Only an accurate fitting of the observed absorption energies with those calculated from the diagrams may then provide an indication of the most likely stereochemistry. Also, it would be prudent to consider as tentative any structural assignment based solely on such spectral data, since both geometrical distortions and different strengths of the axial and equatorial ligands may markedly influence the pattern of the energy levels. It should be noted that single-crystal polarized spectra do not allow one to differentiate unambiguously between the two configurations on the basis of different relative polarizations of the observable absorption bands, because the selection rules are very similar for D_{3h} and C_{4v} symmetries. For the $Ni(L^+)(H_2O)X_3$ complexes, assuming μ to be 3.2–3.4 D, the agreement of the observed absorptions (Figure 2) with Ciampolini's diagrams is more satisfactory for an undistorted trigonal-bipyramidal configuration than for the square-pyramidal configurations with an $L_{\text{axial}}\text{–}L_{\text{basal}}$ angle of 90 or 100°. However, if μ is assumed to be about 3.9–4.1 D, the agreement is almost equally satisfactory for the distorted square-pyramidal structure having an $L_{\text{axial}}\text{–}L_{\text{basal}}$ angle of 110°. Thus, owing to the uncertainty in the estimate of μ for compounds with unknown metal-to-ligand bond lengths, the spectra of the $Ni(L^+)(H_2O)X_3$ complexes, while they are diagnostic of five-coordination, do not give an unambiguous indication of the stereochemistry.

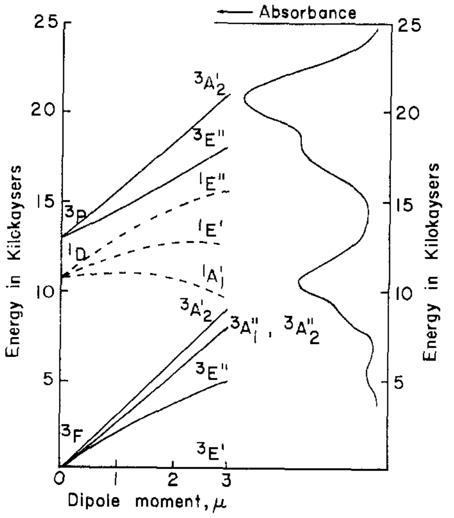

Figure 2.—Electronic absorption spectrum of $Ni(L^+)(H_2O)Cl_3$ at room temperature, compared with the energy level diagram for high-spin Ni(II) in a trigonal-bipyramidal configuration of five equivalent dipoles (after Ciampolini[19]).

A trigonal-bipyramidal stereochemistry, only slightly distorted from C_{3v} symmetry, has been established for the complex $Ni(L^+)(H_2O)Cl_3$ by Stucky and Ross[20] by three-dimensional X-ray analysis. Accordingly, the absorptions of this complex are assigned as shown in Table II. This table also reports, for comparison, the spectrum of $Ni(L^+)(H_2O)Cl_3$ at liquid nitrogen temperature. At this temperature all absorptions sharpen and become better resolved, revealing a broad weak band at about 8.7 kK, which is assigned to the transition to the $^3A''_1(F)$ and $^3A''_1(F)$ degenerate levels. (At room temperature, this absorption is not resolved from the strong 10.8-kK band.) Also, the absorptions on the low-energy side of the intense 20.7-kK band, which at room temperature are ill-defined, at liquid nitrogen temperature appear as two distinct shoulders at 16.0 and 18.5 kK and a weak sharp band at 17.2 kK. The shoulder at 18.5 kK is assigned to the transition to the $^3A_2'(F)$ level, while the others most likely correspond to spin-forbidden transitions to the three components of the ^1D level. Thus, when the spectrum is measured at a sufficiently low temperature, the absorptions expected for a trigonal-bipyramidal, high-spin d^8 system are indeed observed in the spectrum of $Ni(L^+)(H_2O)Cl_3$.

The spectra of the nickel(II)–ammine complexes $Ni(L^+)(NH_3)X_3$ are similar to those of the corresponding aquo complexes, with the absorption maxima occurring at higher energies, as expected for the stronger ligand field of ammonia. By analogy with the nickel(II)–aquo complexes and with the isomorphous cobalt(II)–ammine complexes, the $Ni(L^+)(NH_3)X_3$

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(17) J. W. Wood, *Inorg Chem.*, **7**, 852 (1968).

(18) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965); L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).

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

(20) G. D. Stucky and F. Ross, *ibid.*, in press.

TABLE III

INFRARED ABSORPTION FREQUENCIES[a] OF AMMONIA IN FIVE-COORDINATE METAL COMPLEXES

Complex	NH str				NH_3 degen def	NH_3 sym def	$M-NH_3$ rock
$Mn(L^+)(NH_3)Cl_3$	3330 s	2353 m	3209 w	3177 w	1612 s	1199 s	561 w
$Mn(L^+)(NH_3)Br_3$	3334 s	3250 m	3198 w	3171 w	1604 s	1202 s	560 w
$Fe(L^+)(NH_3)Cl_3$	3340 s	3254 m	3205 w	3175 w	1611 s	1195 s	578 w
$Co(L^+)(NH_3)Cl_3$	3337 s	3255 m	3210 w	3178 w	1612 s	1198 s	604 m
$Co(L^+)(NH_3)Br_3$	3332 s	3248 m	3200 w	3175 w	1605 s	1205 s	610 w
$Ni(L^+)(NH_3)Cl_3$	3340 s	3256 m	3210 w	3169 w	1611 s	1200 s	640 m
$Ni(L^+)(NH_3)Br_3$	3332 s	3248 m	3200 w	3172 w	1605 s	1217 s	647 w
$Cu(L^+)(NH_3)Cl_3$	3330 s	3234 m	3208 w	3173 w	1608 s		
$Cu(L^+)(NH_3)Br_3$	3337 s	3250 s	3183 w	3158 w	1594 s	1220 s	645 w

[a] Spectra were taken in Nujol and hexachlorobutadiene mulls. Frequencies are in cm^{-1}. Abbreviations: s, strong; m, medium; w, weak.

complexes are considered to have a trigonal-bipyramidal stereochemistry. The observed d–d absorptions are accordingly assigned as shown in Table II.

The d–d electronic absorption spectra of the Mn(II) and Fe(II) complexes are less informative than those of the Ni(II) and Co(II) complexes. The manganese(II) complexes show only sharp, very weak spin-forbidden absorptions, as expected for a high-spin d^5 system. $Fe(L^+)(H_2O)Cl_3$, $Fe(L^+)(NH_3)Cl_3$, and $Fe(L^+)(NH_3)Br_3$ show only weak, symmetrical absorptions centered at about 8.0, 9.5, and 8.0 kK, respectively. This spectral pattern differs markedly from that characteristic of Fe(II) in tetrahedral or octahedral environments and resembles that reported for some five-coordinate Fe(II) species.[10,21] (Compare, for example, the value of 9.8 kK for the main absorption of the five-coordinate, trigonal-bipyramidal $FeBr(Me_6\text{-}tren)]Br$.)[21]

Finally, the d–d electronic spectra of the Cu(II) complexes of stoichiometries $Cu(L^+)X_3 \cdot H_2O$ and $Cu(L^+)X_3 \cdot NH_3$, which are not isomorphous with the corresponding compounds of Co(II) and Ni(II), again suggest a five-coordinate structure, very likely with a somewhat distorted trigonal-bipyramidal configuration. The spectra consist of an almost symmetrical, broad and intense band centered at about 9 kK for the aquo complexes $Cu(L^+)(H_2O)X_3$ and at about 10 kK for the ammine complexes $Cu(L^+)(NH_3)X_3$. These spectra are, therefore, quite different from those of distorted tetrahedral complexes such as the tetrahalocuprate(II) anions CuX_4^{2-} (X = Cl, Br), which consist[7] of a very broad, doubly humped band with maxima at about 4.3–4.5 and 7.9–9.00 kK. Also, the absorption maxima observed in the spectra of the $Cu(L^+)(H_2O)X_3$ and $Cu(L^+)(NH_3)X_3$ complexes are at lower energies than expected for copper(II)–halo complexes with either a square-planar or a distorted octahedral stereochemistry. (Compare the values of 14.3–13.1 kK for the square-planar $CuCl_4^{2-}$ species in $[Pt(NH_3)_4][CuCl_4]$ and 12.2 kK for the six-coordinate Cu(II) in the tetragonal "$CuCl_2$."[7]) On the other hand, the spectra of the $Cu(L^+)(H_2O)X_3$ and $Cu(L^+)(NH_3)X_3$ complexes closely resemble that of $Cu(NCS)_2(NH_3)_3$, which from X-ray studies is known to have a regular trigonal-bipyramidal stereochemistry[10] (this compound has an intense absorption at 12.8 kK, with a shoulder at 14.5 kK).

Vibrational Spectra.—The (infrared) vibrational spectra of the five-coordinate complexes $M(L^+)(H_2O)X_3$ and $M(L^+)(NH_3)X_3$, measured in the 4000–250-cm^{-1} region, all showed the absorptions characteristic of the N-methyldabconium cation, similar to those observed in the four-coordinate pseudotetrahedral complexes $M(L^+)X_3$.[12] Also, the spectra of the chloro complexes $M(L^+)(H_2O)Cl_3$ and $M(L^+)(NH_3)Cl_3$ have a strong absorption centered near 250 cm^{-1}, which is absent in the corresponding bromo complexes and is assigned to the M–Cl antisymmetric stretching mode. For each metal ion the frequency of the band is lower than that for the Ni–Cl stretching vibration of four-coordinate (tetrahedral) chloro complexes but higher than that of six-coordinate (octahedral) chloro complexes.[22]

In addition to these absorptions, the spectra of the ammine complexes $M(L^+)(NH_3)X_3$ show a number of bands which are assigned to the vibrational modes of the coordinated NH_3 molecule (Table III). The symmetric and antisymmetric N–H stretching vibrations appear as two sharp, intense absorptions in the 3340–3250-cm^{-1} region, accompanied by two sharp but weaker absorptions near 3200 and 3175 cm^{-1}. The degenerate NH_3 deformation vibrations appear as a very sharp, strong band between 1612 and 1590 cm^{-1}, and the symmetric deformation and rocking modes occur at about 1200 cm^{-1} and about 640 cm^{-1}, respectively. The frequencies, contours, and intensities of these absorptions agree with those commonly observed for the ammine complexes of these metal ions.[23] It is interesting to note that for both the chloro and bromo five-coordinate complexes $M(L^+)(NH_3)X_3$ the $M-NH_3$ rocking mode, which is very sensitive to the strength of the M–N bond as well as to the crystalline environment of the coordinated NH_3 molecule,[24] increases regularly in the order: $Mn < Fe < Co < Ni \sim Cu$.

The spectra of the aquo complexes $M(L^+)(H_2O)Cl_3$

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show a number of intense absorptions which are assigned to the vibrations of coordinated water. The O–H stretching modes appear as an intense doublet in the 3400–3320-cm^{-1} region, and the H–O–H deformation mode appears as a very sharp band at about 1590 cm^{-1}. A medium-to-weak band also appears in the 550–510-cm^{-1} range. All of these bands are relatively sharp compared with the broad, unresolved absorptions usually observed in compounds containing lattice water,[25] and indicate that in the $M(L^+)(H_2O)X_3$ complexes the H_2O molecule is coordinated and also that the crystal lattice environment is very much the same for each coordinated H_2O molecule. As may be expected, the O–H stretching vibrations appear at lower frequencies for those $M(L^+)(H_2O)X_3$ complexes which are more stable toward loss of water. Thus, within each halogen series the O–H stretching frequencies follow the order Mn(II) < Fe(II) $\sim$ Ni(II) > Cu(II), and for each metal ion these frequencies are lower for the chloro than for the bromo complex. A reverse frequency trend is observed for the medium–weak absorption in the 550–510-cm^{-1} region.

The $M(L^+)(H_2O)X_3$ species represent a unique series of isostructural aquo complexes containing a single H_2O molecule, and a detailed investigation of their far-infrared spectra is in progress to establish the trend of the metal–oxygen bond strengths for these five-coordinate transition metal ions, as well as the effect of hydrogen bonding.

Conclusions

On the basis of the described experimental results, it can be concluded that in the complexes $M(L^+)(H_2O)X_3$ and $M(L^+)(NH_3)X_3$ the divalent transition metal ions, M(II), are five-coordinate and have high-spin electron configurations. For the Co(II) complexes, a trigonal-bipyramidal stereochemistry is clearly indicated by the d–d electronic absorption spectra, which agree with those expected for a d^7 high-spin system in a field of five ligands arranged to give a D_{3h} symmetry. For the Ni(II) complexes, the d–d electronic spectra are again diagnostic of five-coordination, even though they are not unambiguously indicative of a trigonal-bipyramidal stereochemistry. For all of the $M(L^+)(H_2O)X_3$ and $M(L^+)(NH_3)X_3$ complexes the vibrational spectra support a five-coordinate structure, as they indicate the H_2O and NH_3 ligands to be coordinated, and show metal–chlorine stretching vibrations intermediate between those characteristic of four-coordinate (tetrahedral) and six-coordinate (octahedral) metal complexes.

A single-crystal X-ray analysis, by Stucky and Ross,[20] has established that the complex $Ni(L^+)(H_2O)Cl_3$ indeed is five-coordinate and has an essentially trigonal-bipyramidal configuration, only slightly distorted from C_{3v} symmetry. An analogous stereochemistry is assigned to the complexes of Mn(II), Fe(II), and Co(II), primarily on the basis of their isomophism with the corresponding $Ni(L^+)(H_2O)Cl_3$ complex; the magnetic and spectral data also support the assigned structure. As may be expected, the Cu(II) complexes are not strictly isomorphous with the other members of the series. Their infrared spectra, however, are extremely similar to those of the complexes of the other metal ions, thus suggesting a similar even if somewhat distorted structure. Also, the electronic spectra of the $Cu(L^+)(H_2O)X_3$ and $Cu(L^+)(NH_3)X_3$ complexes closely resemble that of the complex $Cu(NCS)_2(NH_3)_3$, known to have a regular trigonal-bipyramidal stereochemistry.

The $M(L^+)(H_2O)X_3$ and $M(L^+)(NH_3)X_3$ complexes are unusual in that they contain only unidentate σ-bonding ligands—one of which is a cation of very low basicity ($pK_A = 2.75$)—and represent a unique case of five-coordination induced chiefly by electronic factors. The high lattice energy arising from the intermolecular attractions between the N^+–CH_3 groups of the cation ligands and the neighboring chloro or bromo ligands undoubtedly contributes to the stabilization of the crystalline $M(L^+)(H_2O)X_3$ and $M(L^+)(NH_3)X_3$ complexes.

Experimental Section

Starting Materials.—The $M(L^+)X_3$ complexes were prepared as described elsewhere.[12] Analytical reagent and spectrograde solvents were dried over 4A molecular sieves before use.

Preparation of the Complexes. (1) **Complexes of the General Formula $M(L^+)(H_2O)X_3$.**—The Ni(II) complexes were prepared as follows. One-half gram of the N-methyldabconium chloride, $(L^+)Cl^-$, dissolved in 50 ml of anhydrous ethanol, was added to 25 ml of an ethanol solution of $NiCl_2 \cdot 6H_2O$ at 50°. A red precipitate of $Ni(L^+)(H_2O)Cl_3$ formed immediately, but the suspension was stirred for 0.5 hr to promote larger particle growth. If any of the deep blue intermediate complex $Ni(L^+)Cl_3$ was observed in the precipitate, several drops of water were added and the suspension was further stirred for an additional 0.5 hr. The precipitate was then filtered, washed several times with ethanol, and dried *in vacuo* for 2 hr. The analogous Mn(II), Fe(II), and Cu(II) complexes were obtained in a similar manner. However, the preparation of the Fe(II) complex was carried out under a nitrogen atmosphere to prevent oxidation to Fe(III). In the preparation of the Cu(II) complex, it was usually necessary to add several drops of water to the reaction mixture to convert the initially formed yellow $Cu(L^+)Cl_3$ completely to the very pale yellow $Cu(L^+)(H_2O)Cl_3$.

(2) **Complexes of the General Formula $M(L^+)(H_2O)Br_3$.**—The Mn(II), Fe(II), and Cu(II) complexes were prepared as follows. A 0.3 *M* solution of the hydrated metal salt in ethanol (10 ml) was added to 0.25 g of dabconium bromide dissolved in 25 ml of ethanol at 40°. A precipitate formed immediately which consisted chiefly of the desired $M(L^+)(H_2O)Br_3$ complex but contained small amounts of $M(L^+)Br_3$. The addition of several drops of water, followed by refrigeration overnight, converted any $M(L^+)Br_3$ to $M(L^+)(H_2O)Br_3$. The precipitate was then filtered, washed with 95% ethanol, dried *in vacuo* for 0.5 hr, and stored in sealed vials. The iron(II) complex was prepared in a nitrogen atmosphere to prevent oxidation to iron(III). The $Ni(L^+)(H_2O)Br_3$ complex, which could not be obtained from an ethanol solution, was prepared by exposing the blue crystalline $Ni(L^+)Br_3$ to a humidity of about 50% at 30° for several days. Under these conditions the original blue complex slowly coordinated one molecule of water, turning red-purple.

In general, the bromo complexes $M(L^+)(H_2O)Br_3$ are much more difficult to prepare than the corresponding chloro complexes; also, the bromo complexes are unstable toward loss of

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water and cannot be stored over desiccants. If exposed to the atmosphere for prolonged periods of time, these five-coordinate bromo complexes take on additional water to form mixtures of six-coordinate octahedral complexes, which were not further investigated at this time.

(3) **Complexes of the General Formula $M(L^+)(NH_3)X_3$.**—The preparation of these complexes requires rigorously anhydrous solvents to prevent the formation of hydroxo species. Ethanol solutions of the ligand halides and metal halides were dried over 4A molecular sieves for several days and then used to prepare the $M(L^+)X_3$ complexes as previously described.[12] A solution of NH_3 in anhydrous ethanol was added dropwise to the freshly prepared $M(L^+)X_3$ complexes suspended in their mother liquor, with vigorous stirring at 50°. The reactants were mixed in a 1:1 NH_3-to-metal ratio. The reaction was generally complete within 5 min provided the initial particle size of the $M(L^+)X_3$ complexes was sufficiently small. As the reaction progressed, the color of the suspended solid changed from blue to lavender for Co(II), from deep blue to golden brown for Ni(II), and from deep yellow to golden for Cu(II). The $M(L^+)(NH_3)X_3$ complexes were filtered, washed with anhydrous ethanol, and dried *in vacuo*. It was necessary to control the addition of the ammonia solution, because a considerable excess over a 1:1 NH_3-to-metal ratio leads to the formation of a mixture of ammine complexes which were not further investigated.

Characterization of the Complexes.—The complexes prepared were characterized by analyses, visible and infrared spectra (30,000–250 cm^{-1}), magnetic susceptibility, and X-ray powder diffraction measurements. For details, see ref 12.

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O,O′-Diethyl Diselenophosphate as a Ligand. Compounds of Nontransition Elements[1]

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O,O′-Diethyl diselenophosphate ($dsep^-$) complexes of Tl(I), Pb(II), Sn(II), As(III), Sb(III), Bi(III), and In(III) have been prepared and their spectral properties have been investigated. The infrared spectra give some evidence of the nature of bonding between the $>P(Se)Se$ group and the central ion. Some electronic transitions of these complexes have been tentatively assigned. Powder X-ray patterns have also been obtained.

Introduction

The investigation of organic selenium compounds as ligands in coordination chemistry is of relatively recent interest.[2–11] Recently Jørgensen[12] studied the electronic spectra of some transition metal diethyl diselenophosphates. Kudchadker, *et al.*,[13] prepared various dialkyl diselenophosphates and their potassium and chromium salts and studied their spectral properties.

Experimental Section

The organic solvents used in this study were of reagent grade and they were dried and distilled before use. The chemicals were of analytical reagent grade and they were used without further purification.

The infrared spectra of the compounds were measured as KBr pellets on a Beckman model IR-12 spectrometer. The electronic spectra were recorded on the Cary model 14-R spectrometer. The X-ray powder diffraction patterns were measured on a General Electric XRD-5 X-ray diffraction unit using Cu Kα radiation (λ 1.54050 Å).

Phosphorus pentaselenide and the potassium salt of O,O′-diethyldiselenophosphoric acid were prepared in the manner described by Kudchadker, *et al.*[13] The melting point of the potassium salt was found to be 134–136°; lit.[13] 132–136°.

(O,O′-Diethyl diselenophosphato)thallium(I).—An aqueous solution of potassium diethyl diselenophosphate (0.32 g in 20 ml) was added dropwise to an aqueous solution of thallium(I) chloride (0.20 g in 100 ml). A white precipitate was formed immediately upon addition of the potassium salt. It was filtered, washed with water, and dried *in vacuo* over P_4O_{10}. The thallium(I) compound was recrystallized from chloroform in the form of white flakes.

Bis(O,O′-diethyl diselenophosphato)lead(II).—An ethanolic solution of potassium diethyl diselenophosphate (0.64 g in 20 ml) was added dropwise to a solution of lead acetate (0.33 g in 40 ml) in ethanol. A creamy yellow compound separated which was crystallized from absolute ethanol and dried over P_4O_{10} *in vacuo*.

Bis(O,O′-diethyl diselenophosphato)tin(II).—This compound was prepared from $SnCl_2 \cdot 2H_2O$ in the manner just described. The compound was crystallized from ligroin.

Tris(O,O′-diethyl diselenophosphato)arsenic(III).—A solution of potassium diethyl diselenophosphate (1.02 g in 30 ml) in absolute ethanol was added dropwise in a solution containing 0.20 g of arsenic trichloride in 25 ml of the same solvent. During the course of the addition, the color of the arsenic(III) solution changed from pale yellow and the separation of elemental col-

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