

tions.<sup>39</sup> In the radical ion mechanism, the bridging ligand is first reduced to a radical which subsequently reduces the oxidizing metal center to which it is coordinated. In the resonance transfer or exchange mechanism, the bridging ligand acts merely as a mediator, and no radical ion intermediate is formed. Nordmeyer and Taube<sup>40</sup> have argued that in the radical ion mechanism the reduction of the ligand is rate determining, and consequently the nature of the metal ion center in the oxidant should not affect appreciably the reaction rate. In contrast, for the resonance mechanism the identity of the oxidizing metal center is quite important in determining the reaction rate. On this basis, they suggested that a possible test to distinguish between the radical ion and exchange mechanisms involves a comparison of the rate of chromium(II) reduction of  $\text{Co}(\text{NH}_3)_5\text{L}^{n+}$  and the rate of chromium(II) ex-

(39) P. George and J. S. Griffith in "The Enzymes," Vol. 1, Academic Press, New York, N. Y., 1959, p 347.

(40) F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1162 (1968).

change with  $\text{Cr}(\text{OH}_2)_5\text{L}^{n+}$ . For  $\text{L}^- = \text{F}^-, \text{Cl}^-, \text{OH}^-$ , and  $\text{NCS}^-$ , the ratios of the rate constant for reduction to the rate constant for exchange are larger than  $3 \times 10^4$ , and it was suggested that the exchange mechanism obtains. For  $\text{L} =$  isonicotinamide, the ratio is  $\sim 10$ , and the radical ion mechanism was favored.<sup>40</sup> A similar comparison can be made by considering the rate of reduction of  $\text{cis-Co}(\text{en})_2(\text{HCO}_2)^{2+}$  via the singly bridged pathway (eq 9) with the rate of the chromium(II) catalyzed dissociation of  $\text{cis-Cr}(\text{OH})_2(\text{HCO}_2)_2^+$  (eq 11). A

$$\text{cis-Cr}(\text{OH})_2(\text{HCO}_2)_2^+ + \text{Cr}^{2+} + \text{H}_3\text{O}^+ \longrightarrow \text{Cr}(\text{OH})_5(\text{HCO}_2)^{2+} + \text{Cr}^{2+} + \text{HCO}_2\text{H} \quad (11)$$

preliminary measurement of the rate constant  $k_{11}$  for reaction 11 has been carried out in this laboratory. At  $25^\circ$  and  $[\text{HClO}_4] = 0.10 \text{ M}$ ,  $k_{11} \sim 5 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ . Since the rate constant  $k_9$  for reaction 9 is  $100 \text{ M}^{-1} \text{ sec}^{-1}$ , it is concluded that  $k_9/k_{11} \sim 5 \times 10^5$ . Using this ratio as a diagnostic of mechanism, it appears that the chromium(II) reductions of the formatoaminocobalt(III) complexes proceed by the resonance transfer mechanism.

## Donor Properties of Positively Charged Ligands. Pseudotetrahedral Transition Metal Complexes Containing a Monoquaternized Tertiary Diamine

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**Abstract:** The halide salts,  $(\text{L}^+)\text{X}$ , of the monoquaternized diamine,  $\text{L} = 1,4\text{-diazabicyclo}[2.2.2]\text{octane}$ , react under anhydrous conditions with the halides of the divalent transition metals,  $\text{Mn}(\text{II})$  to  $\text{Zn}(\text{II})$ , forming crystalline compounds of the stoichiometry  $\text{MX}_2 \cdot (\text{L}^+)\text{X}$ . On the basis of their electronic and vibrational spectra, magnetic susceptibilities, and X-ray powder diffraction patterns, these compounds are formulated as the high-spin, four-coordinate complexes  $[\text{M}(\text{L}^+)\text{X}_3]$ , having a pseudotetrahedral stereochemistry with  $\text{C}_{3v}$  symmetry. These crystalline complexes containing a positively charged ligand coordinated to a (positively charged) metal ion are remarkably stable, and the various factors contributing to their stability are discussed.

This work is part of a general study on the donor properties of positively charged ligands,<sup>1</sup> in particular monoquaternized diamines. The cation formed by monoquaternizing a diamine still has a donor nitrogen atom capable of coordination, and if this cation ligates to a metal ion, the resulting coordination compound will have the novel feature of containing two or more centers of positive charge, the central metal ion and the quaternized N atom of the ligand(s). In the presence of anions with poor donor properties, such as the perchlorate, complex cations of unusually high ionic charge can be formed; for example,  $[\text{Ni}(\text{L}^+)_6]^{8+}$  if  $\text{L}^+$  is a monoquaternized ethylenediamine.<sup>2</sup> With anions of moderate to good donor properties, such as the halides, both the cation ligand and the an-

ions can coordinate, and the unusual metal ion to anion ratio resulting from the presence of the positive charge on the ligands may favor the formation of uncharged (or low-charged) complex species of uncommon stoichiometry and geometry. Furthermore, the electronic configuration of the central metal ion may be indirectly affected by the presence of a positive charge on the amine ligand(s), since this positive charge has a marked effect on the basicity of the N-donor atom.

It is known that the basicity of a diamine generally decreases by less than 2  $\text{pK}_a$  units upon monoquaternization if the nitrogen atoms are separated by two or more  $-\text{CH}_2-$  groups; but if the nitrogen atoms are closer the effect is much more pronounced. For example, upon monoprotonation the  $\text{pK}_a$  of  $\text{NH}_2-(\text{CH}_2)_8\text{NH}_2$  decreases<sup>3</sup> from 10.9 to 10.1, that of  $\text{NH}_2-(\text{CH}_2)_2\text{NH}_2$  decreases<sup>3</sup> from 9.97 to 6.97, and that of hydrazine,  $\text{H}_2\text{N}-\text{NH}_2$ , decreases<sup>4</sup> by a factor of 9  $\text{pK}_a$

(1) J. V. Quagliano and L. M. Vallarino, "Proceedings of the 9th International Conference on Coordination Chemistry," St. Moritz, Switzerland, 1966, Verlag Helvetica Chimica Acta, Basel, Switzerland, 1966, pp 216-218.

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

(3) E. J. Shepherd and J. A. Kitchener, *J. Chem. Soc.*, 2448 (1956).

(4) G. Schwarzenbach, *Helv. Chim. Acta*, **19**, 178 (1936).

Table I. Some Properties and Analytical Data for Metal-Dabconium Complexes

Complex	Color	Magnetic moment, $\mu_{\text{eff}}$ , BM <sup>a</sup>	Electronic d-d absorptions, <sup>b</sup> kK	Analyses					
				Metal, %		Halogen, %		Nitrogen, %	
				Found	Calcd	Found	Calcd	Found	Calcd
[Mn(L+CH <sub>3</sub> )Cl <sub>3</sub> ]	White	5.95		19.0	19.05	36.7	36.89	9.6	9.71
[Mn(L+CH <sub>3</sub> )Br <sub>3</sub> ]	White <sup>c</sup>	5.85		12.9	13.03	56.9	56.85	6.5	6.64
[Mn(L+CH <sub>3</sub> )I <sub>3</sub> ]	Peach	5.90		9.5	9.76	67.7	67.66	4.8	5.12
[Mn(L+H)Cl <sub>3</sub> ]	White	5.89		20.2	20.03	38.7	38.78	10.0	10.20
[Mn(L+H)Br <sub>3</sub> ]	White <sup>c</sup>	5.90		13.5	13.47	58.6	58.80	6.9	6.87
[Mn(L+H)I <sub>3</sub> ]	Peach	5.93		9.9	10.01	69.5	69.38	4.9	5.10
[Fe(L+CH <sub>3</sub> )Cl <sub>3</sub> ]	White	5.10	4.80	19.1	19.31	36.9	36.78	9.9	9.68
[Fe(L+CH <sub>3</sub> )Br <sub>3</sub> ]	Cream	5.01	4.75	13.0	13.22	56.9	56.73	6.6	6.63
[Fe(L+CH <sub>3</sub> )I <sub>3</sub> ]	Brown	4.93	4.60	10.1	9.91	68.0	67.55	4.5	4.97
[Fe(L+H)Cl <sub>3</sub> ]	White	5.24	4.7	20.4	20.29	38.4	38.65	10.0	10.17
[Fe(L+H)Br <sub>3</sub> ]	Cream	5.15	4.7	13.7	13.67	58.7	58.67	6.4	6.85
[Fe(L+H)I <sub>3</sub> ]	Brown	<i>d</i>	<i>d</i>	10.2	10.16	70.0	69.27	5.1	5.10
[Co(L+CH <sub>3</sub> )Cl <sub>3</sub> ]	Blue	4.55	<i>e</i>	19.9	20.14	36.7	36.39	9.9	9.57
[Co(L+CH <sub>3</sub> )Br <sub>3</sub> ]	Blue	4.52	<i>e</i>	13.7	13.84	56.5	56.32	6.7	6.58
[Co(L+CH <sub>3</sub> )I <sub>3</sub> ]	Green	4.63	<i>e</i>	10.2	10.40	67.2	67.19	5.0	5.40
[Co(L+H)Cl <sub>3</sub> ]	Blue	4.50	<i>e</i>	21.3	21.16	38.4	38.23	9.7	10.06
[Co(L+H)Br <sub>3</sub> ]	Blue	4.57	<i>e</i>	14.5	14.31	58.9	58.67	6.7	6.80
[Co(L+H)I <sub>3</sub> ]	Green	4.60	<i>e</i>	10.2	10.66	68.9	68.88	5.1	5.07
[Ni(L+CH <sub>3</sub> )Cl <sub>3</sub> ]	Blue	3.63	<i>e</i>	19.9	20.10	36.4	36.42	9.6	9.59
[Ni(L+CH <sub>3</sub> )Br <sub>3</sub> ]	Blue	3.66	<i>e</i>	13.7	13.80	56.2	56.34	6.5	6.58
[Ni(L+CH <sub>3</sub> )I <sub>3</sub> ]	Brown	3.30	<i>e</i>	10.3	10.36	66.9	67.21	4.9	4.94
[Ni(L+H)Cl <sub>3</sub> ]	Blue	3.63	<i>e</i>	21.0	21.11	37.9	38.25	10.1	10.07
[Ni(L+H)Br <sub>3</sub> ]	Blue	3.60	<i>e</i>	14.1	14.29	58.2	58.25	6.8	6.80
[Ni(L+H)I <sub>3</sub> ]	Brown	3.35	<i>e</i>	10.4	10.62	69.1	68.01	5.0	5.07
[Cu(L+CH <sub>3</sub> )Cl <sub>3</sub> ]	Yellow	1.90	7.3, 11.3	21.2	21.39	35.8	35.82	9.4	9.43
[Cu(L+CH <sub>3</sub> )Br <sub>3</sub> ]	Brown	1.89	6.6, 10.3	15.0	14.77	55.7	55.71	6.4	6.50
[Cu(L+H)Cl <sub>3</sub> ]	Yellow	1.92	7.3, 11.2	22.3	22.46	37.5	37.61	10.1	9.90
[Cu(L+H)Br <sub>3</sub> ]	Brown	1.89	6.6, 10.2	15.3	15.26	57.7	57.59	6.8	6.73
[Zn(L+CH <sub>3</sub> )Cl <sub>3</sub> ]	White	Diam. <sup>f</sup>		21.9	21.88	35.3	35.61	9.4	9.37
[Zn(L+CH <sub>3</sub> )Br <sub>3</sub> ]	White	Diam.		15.2	15.17	55.3	55.65	6.6	6.50
[Zn(L+CH <sub>3</sub> )I <sub>3</sub> ]	White	Diam.		11.5	11.40	66.4	66.43	4.9	4.88
[Zn(L+H)Cl <sub>3</sub> ]	White	Diam.		23.0	22.95	37.4	37.37	9.8	9.83
[Zn(L+H)Br <sub>3</sub> ]	White	Diam.		15.3	15.64	57.1	57.33	6.4	6.70
[Zn(L+H)I <sub>3</sub> ]	White	Diam.		11.8	11.69	67.9	68.09	4.9	5.01

<sup>a</sup> At room temperature. <sup>b</sup> Reflectance spectra at room temperature. <sup>c</sup> With a tinge of pink. <sup>d</sup> Decomposed because of air oxidation. <sup>e</sup> Values and assignments are listed in Table II. <sup>f</sup> Diam. = diamagnetic.

units from +7.93 to -2.95. Thus, diamines in which the nitrogen atoms are separated by two -CH<sub>2</sub>- groups appear to be well suited to investigate the influence of the positively charged "quaternized" nitrogen atom on the donor properties of the "free amine" nitrogen atom.

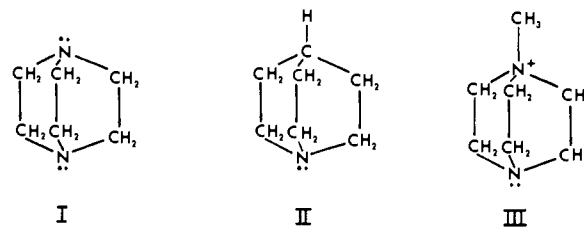
The positive-ion ligands chosen from this study are those formed by monoprotonation or monomethylation of 1,4-diazabicyclo[2.2.2]octane. This ditertiary amine, for brevity referred to as "dabco," has the symmetrical rigid cage-like structure I, with the two nitrogen atoms only 2.64 Å apart.<sup>5</sup> The relatively short distance of the two nitrogen atoms in dabco is very likely responsible for their strong interaction, as shown by the following data: (1) The first p*K*<sub>a</sub> of dabco,<sup>6</sup> 8.60, is appreciably smaller than the p*K*<sub>a</sub>, 10.65, of the similarly shaped monotertiary amine, quinuclidine,<sup>7</sup> II. (2) The basicity of the monoprotonated or monomethylated dabconium species (p*K*<sub>a</sub> = 2.90-2.75) is dramatically lower than that of dabco itself. (3) The esr spectrum of the positively charged radical formed by the removal of an electron from dabco indicates that the environment of the two nitrogen atoms is equivalent.<sup>8</sup>

(5) T. Wada, E. Kishida, Y. Tomiie, H. Suga, S. Seki, and I. Nitta, *Bull. Chem. Soc. Jap.*, **33**, 1317 (1960).

(6) G. Schwarzenbach, B. Maissen, and H. Ackermann, *Helv. Chim. Acta*, **35**, 2333 (1952).

(7) R. J. Bruchman and F. H. Verhoek, *J. Am. Chem. Soc.*, **70**, 1401 (1948).

(8) T. M. McKinney and D. H. Geske, *ibid.*, **87**, 3013 (1965).



The monoquaternized dabconium cations might be expected to behave as poor ligands because their donor atom is a tertiary nitrogen of very low basicity, and does not offer the possibility of  $\pi$  back-donation from the metal ions. However, the rigid and compact cage-like structure of the dabconium cations constitutes an unusually favorable characteristic, for it effectively relieves the steric hindrance to coordination, which in tertiary aliphatic amines arises from the flexibility of the nitrogen-bonded alkyl groups. Also, the rigid and nearly spherical shape of the dabconium cations prevents the structural complications associated with the conformational isomerism of the ligand, and should favor the formation of metal complexes having a regular and relatively compact crystal lattice.<sup>9</sup> Thus, the monoquaternized dabconium cations, III, appeared to be especially suitable to investigate the influence of the positive charge on the coordinating ability of a nitrogen

(9) F. Basolo, *Coord. Chem. Rev.*, **3**, 213 (1968).

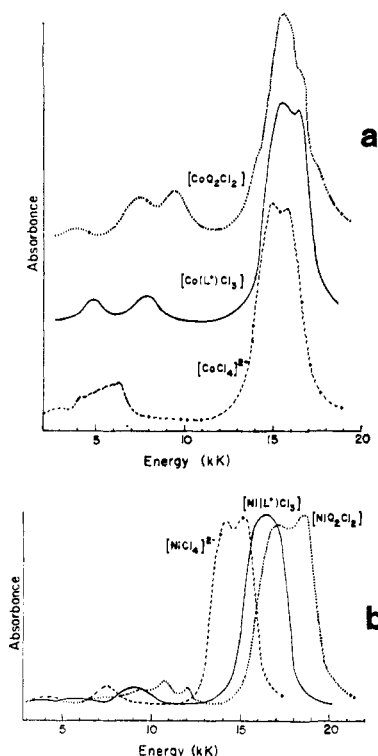


Figure 1. d-d electronic spectra (reflectance) of complexes with  $T_d$ ,  $C_{3v}$ , and  $C_{2v}$  symmetry: (a), Co(II); (b), Ni(II).

donor atom, as well as the effect on the coordination number, symmetry, and electronic configuration of the resulting metal complexes.

## Results

The chlorides, bromides, and iodides of the divalent first-row transition metals from Mn(II) to Zn(II) react with the corresponding halides of the monoprotonated and monomethylated dabconium cations,  $(L^+) = L+H$  and  $L+CH_3$ , to form compounds of the stoichiometry  $MX_2 \cdot (L^+)X$ . When the reaction is carried out under carefully controlled anhydrous conditions, as described in the Experimental Section, the compounds  $MX_2 \cdot (L^+)X$  are obtained in almost quantitative yields as crystalline powders. Well-formed large crystals can be obtained as described elsewhere.<sup>10</sup>

These compounds were investigated to determine the coordination number and stereochemistry of the central metal ion, to establish whether the dabconium cation is coordinated, and if so to study the effect of the positive charge on the donor properties of the cation ligand. Because the compounds of stoichiometry  $MX_2 \cdot (L^+)X$  are insoluble in most organic solvents (hydrocarbons and their chloro derivatives, alcohols, esters, ethers, and ketones), and dissolve with solvation in liquids of high dielectric constant (e.g., dimethyl sulfide, dimethylformamide, acetonitrile, nitromethane, and water), their investigation was essentially limited to solid state properties (see Tables I and II). The most significant experimental data can then be summarized as follows.

**X-Ray Powder Patterns.** The X-ray powder diffraction patterns show that for each ligand  $L^+$  (monoprotonated or monomethylated dabconium) and for

(10) B. B. Garrett, V. L. Goedken, and J. V. Quagliano, *J. Am. Chem. Soc.*, **92**, 489 (1970).

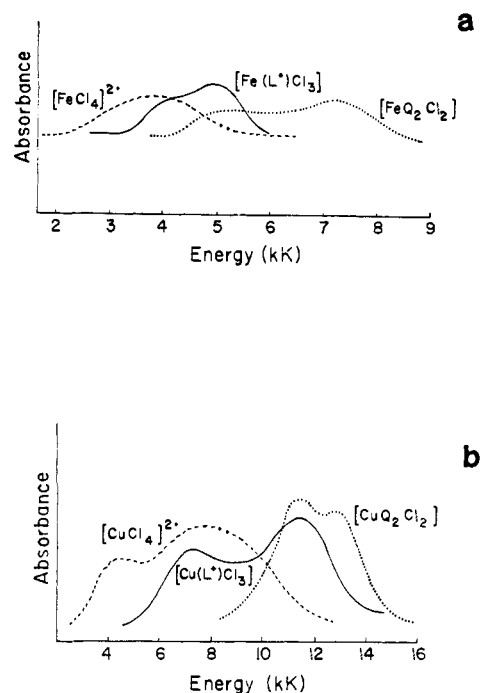


Figure 2. d-d electronic spectra (reflectance) of complexes with  $T_d$ ,  $C_{3v}$ , and  $C_{2v}$  symmetry: (a), Fe(II); (b), Cu(II).

each halide X (Cl, Br, or I), the compounds of stoichiometry  $MX_2 \cdot (L^+)X$  are isomorphous when M is Mn(II), Fe(II), Co(II), Ni(II), and Zn(II). Hence the structures of these compounds can be considered to be virtually identical.

Table II. d-d Electronic Spectra of  $[M(L^+)X_3]$  Complexes

Complex	Absorption maxima <sup>a</sup> (kK) and assignments <sup>b</sup>			
	$^4A_2(F) \rightarrow$			
	$^4E(T_2,F)$	$^4A_2(T_1,F)$	$^4E(T_1,F)$	$\begin{cases} ^4E(T_1,P) \\ ^4A_2(T_1,P) \end{cases}$
$[Co(L+CH_3)Cl_3]$	3.2	4.7	7.7	15.4 (256)
$[Co(L+H)Cl_3]$		4.9	7.8	15.7
$[Co(L+CH_3)Br_3]$	3.2	4.3	7.4	15.2 (371)
$[Co(L+H)Br_3]$			7.4	15.1
$[Co(L+CH_3)I_3]$		4.2	6.9	13.8 (645)
$[Co(L+H)I_3]$		4.4	6.7	13.8
	$^3E(T_1,F) \rightarrow$			
	$^3E(T_2,F)$	$^3A_1(T_2,F)$	$^3A_2(F)$	$\begin{cases} ^3E(T_1,P) \\ ^3A_2(T_1,P) \end{cases}$
$[Ni(L+CH_3)Cl_3]$	5.1	6.5	8.9	16.3 (175)
$[Ni(L+H)Cl_3]$	5.1	6.5	9.0	16.4
$[Ni(L+CH_3)Br_3]$	4.9	6.3	8.7	15.5 (198)
$[Ni(L+H)Br_3]$	4.9	6.1	8.9	15.4
$[Ni(L+CH_3)I_3]$	4.5	6.1	8.5	13.8 (443)
$[Ni(L+H)I_3]$	4.5	5.7	8.2	13.5

<sup>a</sup> The reported values refer to transmission spectra of mulls in Nujol and hexachlorobutadiene; they agreed within experimental error with reflectance spectra and transmission spectra of nitromethane solutions. The numbers in parentheses are molar extinction coefficients in nitromethane solution.

**d-d Electronic Absorption Spectra.** The d-d electronic spectra of the  $MX_2 \cdot (L^+)X$  compounds (Figures 1 and 2) represent the most significant individual piece of information in regard to the stereochemistry of the metal ions, especially for cobalt(II) and nickel(II). The qualitative features of the d-d spectra of the compounds

$\text{CoX}_2 \cdot (\text{L}^+)\text{X}$  (Figure 1(a)) and  $\text{NiX}_2 \cdot (\text{L}^+)\text{X}$  (Figure 1(b)) resemble those of known four-coordinate, high-spin, tetrahedral complexes such as the tetrahalometalates,  $[\text{CoX}_4]^{2-}$  and  $[\text{NiX}_4]^{2-}$ ;<sup>11,12</sup> there are, however, some important differences. For example, the low-energy region of the d-d spectrum of  $\text{NiCl}_2 \cdot (\text{L}^+)\text{Cl}$  shows two broad bands, centered at 5100 and 6550  $\text{cm}^{-1}$ , so the total number of the d-d absorptions observed for this compound is four, instead of three, as theoretically expected for  $T_d$  symmetry. Moreover, the energy values of any three of the four observed bands cannot be satisfactorily fitted with the Liehr-Ballhausen diagram for Ni(II) in a crystal field of  $T_d$  symmetry,<sup>13</sup> assuming an average ligand field environment. To account for the number as well as for the energies and relative polarizations of all observed d-d transitions of the  $\text{CoX}_2 \cdot (\text{L}^+)\text{X}$  and  $\text{NiX}_2 \cdot (\text{L}^+)\text{X}$  compounds, it is necessary to consider a pseudotetrahedral crystal field of  $C_{3v}$  rather than  $T_d$  symmetry. On the basis of this model, which is discussed in detail in the following paper,<sup>10</sup> the absorptions observed for these compounds are assigned as shown in Table II.

A structurally important implication of these spectral assignments is that the dabconium cation,  $\text{L}^+$ , as well as the three halide ions, X, must be coordinated to the central Co(II) and Ni(II) in the compounds of stoichiometry  $\text{MX}_2 \cdot (\text{L}^+)\text{X}$ . These compounds, therefore, can be considered to consist of nonionic, mononuclear entities,  $[\text{M}(\text{L}^+)\text{X}_3]$ . A similar structure can logically be attributed to the isomorphous complexes of Mn(II), Fe(II), and Zn(II), and the d-d electronic spectra of the Fe(II) complexes also support this formulation. In fact, the spectrum of  $[\text{Fe}(\text{L}^+\text{CH}_3)\text{Cl}_3]$ , which shows a single broad absorption in the near-infrared, closely resembles that of the  $[\text{FeCl}_4]^{2-}$  ion ( $T_d$  symmetry). Furthermore, in the series of tetrahedral complexes  $[\text{FeCl}_4]^{2-}$ ,  $[\text{Fe}(\text{L}^+\text{CH}_3)\text{Cl}_3]$ , and  $[\text{FeQ}_2\text{Cl}_2]$  (where Q is the tertiary amine quinuclidine, II), there is a regular shift of the observed d-d transition toward higher frequencies (Figure 2(a)) as expected for successive substitutions of a chloro ligand by a nitrogen-donor ligand.

For the  $\text{CuX}_2 \cdot (\text{L}^+)\text{X}$  compounds, which are not isomorphous with the corresponding Co(II) and Ni(II) species but have nearly identical vibrational spectra, the d-d electronic spectra are again indicative of a pseudotetrahedral stereochemistry. Only one d-d transition would be expected for Cu(II) in a ligand environment of  $T_d$  symmetry. However, the spectra of the tetrahalocuprate(II) anions,  $[\text{CuX}_4]^{2-}$ , which in ionic crystals are generally distorted to  $D_{2d}$  symmetry,<sup>14</sup> consist of two very broad overlapping bands, centered at about 8.0 and 4.5 kK.<sup>15</sup> Similarly, the spectra of the compounds of stoichiometry  $\text{CuX}_2 \cdot (\text{L}^+)\text{X}$  consist of two broad bands, centered approximately at 11.3 and 7.3 kK.

(11) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961); D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *ibid.*, **83**, 4161 (1961); C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectrosc.*, **2**, 342 (1958); A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

(12) H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1961); J. Ferguson, *ibid.*, **39**, 116 (1963).

(13) A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N. Y.)*, **6**, 134 (1959).

(14) L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **84**, 1176 (1962); B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **13**, 807 (1960); M. Bonamico, G. Dessy, and A. Vacicigo, *Theor. Chim. Acta*, **7**, 367 (1967).

(15) C. Furlani and G. Morpurgo, *ibid.*, **1**, 102 (1963); W. E. Hatfield, and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964).

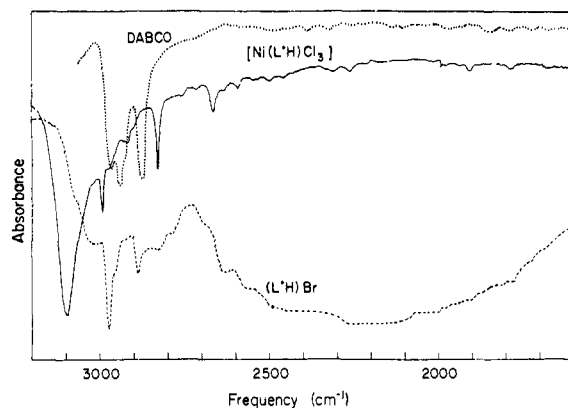


Figure 3. Vibrational spectrum of the monoprotonated dabconium cation in its bromide salt and in the  $[\text{Ni}(\text{L}^+\text{H})\text{Cl}_3]$  complex (C-H and N-H stretching region). The spectrum of "free" dabco is shown for comparison.

The higher energies of these bands, as compared with those of the  $[\text{CuX}_4]^{2-}$  species, may be considered to indicate a stronger average ligand field, resulting from the substitution of a halo ligand by a nitrogen-donor ligand (Figure 2(b)). Thus, the  $\text{CuX}_2 \cdot (\text{L}^+)\text{X}$  compounds may also be formulated as nonionic, pseudotetrahedral  $[\text{Cu}(\text{L}^+)\text{X}_3]$  complexes. It should be kept in mind that for these Cu(II) complexes, as for the Fe(II) complexes previously discussed, the decrease in the symmetry of the field potential also undoubtedly accounts, to some extent, for the observed spectral shifts.

**Magnetic Properties.** The values of the room temperature magnetic moments,  $\mu_{\text{eff}}$ , listed in Table I indicate that the  $[\text{M}(\text{L}^+)\text{X}_3]$  complexes all have high-spin electron configurations (except of course those of zinc(II), a  $d^{10}$  system). The magnetic moments of the Ni(II) and Co(II) complexes are within the ranges generally observed for tetrahedral coordination, although the moments of the  $[\text{Ni}(\text{L}^+)\text{X}_3]$  complexes are somewhat lower than those of the corresponding  $[\text{NiX}_4]^{2-}$  anions.

**Vibrational Spectra.** The vibrational spectrum of dabco has a large number of absorptions, some of which are still unassigned even though this molecule has been studied by normal coordinate analysis and polarized spectra.<sup>16</sup> As may be expected, the N-methyl-dabconium cation has a spectrum very similar to that of dabco, except for a few additional absorptions arising mainly from the vibrations of the  $\text{N}^+\text{-CH}_3$  group.<sup>17</sup> Also, coordination to metal ions does not cause any major changes in the vibrational spectra of the N-methyl-dabconium cation, since its symmetry is not appreciably altered by the formation of the  $\text{M} \leftarrow \text{N}$  bond. The small observed changes are probably due to minor distortions arising from crystal lattice effects.

The spectrum of the monoprotonated dabconium cation (in its halide and perchlorate salts) differs appreciably from that of neutral dabco. Its most significant new feature is a very intense absorption between 1800 and 2800  $\text{cm}^{-1}$ , which is assigned to the stretching vibration of the  $\text{N}^+\text{-H}$  group. The extreme broadness and

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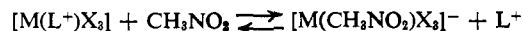
(17) R. D. Hill and G. D. Meakins, *J. Chem. Soc.*, 760 (1958); J. T. Braunholtz, E. A. V. Ebsworth, F. G. Mann, and N. Sheppard, *ibid.*, 2780 (1958).

multiple structure of this band—features often observed for substituted ammonium salts<sup>18</sup>—indicates that the N<sup>+</sup>-H groups of the dabconium cations are strongly hydrogen bonded and also are present in different environments in the crystal lattice. When the monoprotonated dabconium cation is coordinated to a metal ion in the  $[M(L^+H)X_3]$  complexes, the broad multiple absorption band in the 1800–2800-cm<sup>-1</sup> region is replaced by a sharp intense band at much higher frequency, 3100 cm<sup>-1</sup> (Figure 2). The unusual sharpness of the N<sup>+</sup>-H stretching vibration of the coordinated dabconium cation in the  $[M(L^+H)X_3]$  complexes, as compared with that of the “free” dabconium cation in its simple salts, indicates that the environment of the N<sup>+</sup>-H groups is very much the same for all the  $[M(L^+H)X_3]$  complex entities, thus implying a relatively simple and highly ordered crystal lattice. It is also interesting to notice that the 3100-cm<sup>-1</sup> band, which is virtually identical in all crystalline  $[M(L^+H)X_3]$  complexes, closely resembles in frequency and contour the N-H stretching vibration of associated secondary amines.<sup>19</sup>

In addition to the characteristic ligand absorptions, the infrared spectra of the  $[M(L^+)X_3]$  complexes are expected to show absorptions arising from the M-N and M-X vibrational modes. No bands assignable to the M-N stretching vibrations could be observed, probably because they occur below the frequency range (4000–250 cm<sup>-1</sup>) examined in this work, as is usually the case for tertiary N atoms.<sup>20</sup> The metal-chlorine stretching modes, on the other hand, can be readily observed (the M-Br and M-I vibrational modes again absorb below the range examined), and appear<sup>21</sup> as a strong band between 310 and 300 cm<sup>-1</sup> and a medium band between 280 and 260 cm<sup>-1</sup>. The presence of two M-Cl absorptions in this region is consistent with the C<sub>3v</sub> symmetry assigned to the  $[M(L^+)Cl_3]$  complexes, which allows both the antisymmetric and the symmetric stretching vibrations to be infrared active.

**Solubility and Solution Behavior.** The  $[M(L^+)X_3]$  complexes are virtually insoluble in most organic solvents and are decomposed by water and other strong donor solvents. Nitromethane appears to be the only solvent in which the  $[M(L^+)X_3]$  complexes dissolve slightly, retaining at least in part their identity. In general, the monoprotonated dabconium complexes are much less soluble than the corresponding N-methyl-dabconium complexes, and for each ligand, the solubility increases in the order chloro complexes < bromo complexes < iodo complexes. (Solubility, moles/l. at 25°:  $[Co(L^+CH_3)Cl_3]$ ,  $3.0 \times 10^{-4}$ ;  $[Co(L^+CH_3)Br_3]$ ,  $4.3 \times 10^{-4}$ ;  $[Co(L^+CH_3)I_3]$ ,  $5.6 \times 10^{-4}$ ;  $[Ni(L^+CH_3)Cl_3]$ ,  $0.8 \times 10^{-5}$ ;  $[Ni(L^+CH_3)Br_3]$ ,  $3.6 \times 10^{-4}$ ; and  $[Ni(L^+CH_3)I_3]$ ,  $1.4 \times 10^{-3}$ .)

The electronic d-d spectra of nitromethane solutions of the  $[Co(L^+)X_3]$  and  $[Ni(L^+)X_3]$  complexes show the existence of a solvation equilibrium involving the replacement of the dabconium ligand by a nitromethane molecule



The solvated species has a tetrahedral coordination with C<sub>3v</sub> symmetry, similar to the original  $[M(L^+)X_3]$  complex, and its spectrum is almost identical with that of the species formed by nitromethane solvation of the tetrahalocobaltate(II) and tetrahalonickelate(II) anions.<sup>22</sup> The above solvation equilibrium also explains the slight electrical conductivity of solutions of  $[Co(L^+)X_3]$  and  $[Ni(L^+)X_3]$ ; the solvation is effectively repressed by the presence of an excess of the dabconium halide. Thus, a saturated solution of  $[Co(L^+)Br_3]$  containing a tenfold excess of L<sup>+</sup>Br<sup>-</sup> has an electronic spectrum almost identical with that of the crystalline complex; a small quantity (less than 5%) of the  $[MBr_4]^{2-}$  species is also observed. It is significant that the  $[Co(L^+)X_3]$  and  $[Ni(L^+)X_3]$  species are formed in preference to the  $[CoX_4]^{2-}$  and  $[NiX_4]^{2-}$  species, even though both the dabconium cation, L<sup>+</sup>, and the halide anion, X<sup>-</sup>, are present in equal excess in the solution. The crystal field stabilization of the electronic ground state of Co(II) and Ni(II) in complexes of C<sub>3v</sub> symmetry, which is about 1500–1800 cm<sup>-1</sup> greater than that of similar complexes of T<sub>d</sub> symmetry, undoubtedly plays an important role in shifting the solution equilibrium toward the formation of the  $[M(L^+)X_3]$  species.

### Discussion and Conclusions

All the  $[M(L^+R)X_3]$  complexes reported in this paper contain a divalent metal ion, M(II), tetrahedrally surrounded by one dabconium cation ligand, L<sup>+</sup>, and three halide ions, X<sup>-</sup>, so that the molecular symmetry is C<sub>3v</sub>. This formulation is based on the following evidence: (1) The magnetic moments of the complexes of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) indicate a high-spin electron configuration of these metal ions, and for the Co(II) and Ni(II) complexes are in the range usually observed for tetrahedral four-coordination. (2) The d-d electronic spectra of the nickel(II) and cobalt(II) complexes have the characteristic features of a tetrahedral ligand environment, but crystal field calculations and single crystal polarized spectra indicate that the symmetry is C<sub>3v</sub> rather than T<sub>d</sub>. The d-d spectra of the copper(II) and iron(II) complexes are also compatible with a pseudotetrahedral stereochemistry. In the  $[M(L^+)X_3]$  complexes (M = Cu(II), Fe(II), Co(II), and Ni(II)) the energies of the d-d absorptions fall midway between those of the corresponding  $[MX_4]^{2-}$  and  $[M(N-donor)_2X_2]$  complex species. (3) The infrared spectra of all of these complexes have metal-chloride stretching frequencies compatible with pseudotetrahedrally coordinated divalent metal ions and indicate a symmetry lower than T<sub>d</sub>. (4) The  $[M(L^+R)X_3]$  complexes from Mn(II) through Zn(II) with the exception of Cu(II) are isomorphous. Thus the Mn(II) and Zn(II) complexes, for which the magnetic susceptibilities and d-d electronic spectra are not structurally definitive, can also be assigned a pseudotetrahedral geometry of C<sub>3v</sub> symmetry.

The  $[M(L^+)X_3]$  complexes may be considered to have a zwitterion structure in which the formal center of positive charge—the quaternized nitrogen atom of the dabconium ligands, N<sup>+</sup>-R (where R = H or CH<sub>3</sub>)—is appreciably separated from the formal center of negative charge, the MX<sub>3</sub><sup>-</sup> trigonal group. Hence, the complete lack of solubility of the  $[M(L^+)X_3]$  complexes

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in halocarbon solvents, as compared with the ready solubility of the  $[ML_2X_3]$  complexes ( $L =$  uncharged 2-methylpyridine, quinuclidine, or quinoline) may be attributed to a high lattice energy arising from intermolecular attractions among  $(N^+-R)$  and  $(MX_3^-)$  moieties of adjacent  $[M(L^+)X_3]$  units in the crystal lattice. For the monoprotonated dabconium cation ligand, intermolecular hydrogen bonding undoubtedly contributes to the stabilization of the crystalline  $[M(L^+)X_3]$  complexes. It is significant, in this respect, that (neutral) dabco itself reacts with an ethanol solution of  $NiCl_2$  to form the mononuclear complex of the monoprotonated dabconium cation,  $[Ni(L^+H)Cl_3]$ , rather than a polynuclear complex containing bridging dabco ligands, similar for example to the polynuclear  $[Ni(\text{pyrazine})Br_2]_n$ .<sup>23</sup> The remarkable stability of the crystalline  $[M(L^+)X_3]$  complexes is also shown by the thermal behavior of the solid tetrachloronickelate(II) of protonated N-methyl-dabconium,  $[CH_3N^+(CH_2CH_2)_3N^+H][NiCl_4]$ . When this complex salt is heated to about 150°, gaseous HCl is eliminated and the nonionic  $[Ni(L^+CH_3)Cl_3]$  complex results, instead of an ionic complex containing "free" N-methyl-dabconium cations and the well-known<sup>24</sup> polynuclear trichloronickelate(II) anions,  $(NiCl_3)_n^-$ . In fact, under no conditions were the monoquaternized dabconium cations found to behave as "free" cations in the presence of transition metal ions or other suitable acceptors. Thus it appears that the positive charge, while it lowers the basicity of the dabconium cations by a factor of about  $10^6$  with respect to dabco, does not prevent their coordination to positively charged metal ions. Actually, the presence of the positive charge on the ligand facilitates the isolation of the metal-dabconium complexes by giving rise to a highly favorable lattice energy even for nonionic species such as  $[M(L^+)X_3]$ . Also, because the metal-dabconium complexes are relatively easy to prepare in a pure form, the low basicity of the dabconium cation effectively eliminates one of the chief difficulties usually encountered in preparing complexes of highly basic tertiary amines, namely the formation of hydroxo complexes in the presence of even minute quantities of water.

The presence of the positive charge on the monoquaternized dabconium ligands, and the reduced basicity of their "free" nitrogen atom, are the chief factors which favor the ready isolation from solution of the crystalline complexes  $[M(L^+)X_3]$ . Once these crystalline complexes are formed, however, a somewhat different argument must be invoked to explain the good donor properties of the N-donor atom of the dabconium ligands. The strong electronic interaction of the two nitrogen atoms of dabco, which is considered responsible for the dramatic decrease in basicity upon monoprotonation, might logically be expected to result in a similar decrease of the donor properties toward transition metal ions. The criterion that the basicity of a ligand, as measured by its  $pK_a$  in aqueous solution, will somewhat parallel its donor properties toward a transition metal ion in a crystalline complex, as measured by the d-d electronic splitting of the metal ion, is obviously debatable. However, for complexes of essentially  $\sigma$ -bonding ligands such an assumption is commonly ac-

cepted, and indeed agrees fairly well with the observed spectral trends. This is not the case for the dabconium complexes,  $[M(L^+)X_3]$ . The d-d electronic spectra of the  $[Co(L^+)X_3]$  and  $[Ni(L^+)X_3]$  complexes are, in fact, practically superposable with those of the corresponding  $[MLX_3]^-$  complexes of much stronger N-donor bases, for example, pyridine ( $pK_a = 5.17$ ) and quinuclidine ( $pK_a = 10.65$ ). Since for these metal-dabconium complexes it is difficult to envision appreciable  $\pi$ -bonding and hyperconjugation effects, some other explanation must be suggested for the fact that the dabconium cation ligands have a relatively high field strength despite their very low basicity. One logical explanation is based on the assumption that the  $[M(L^+)X_3]$  complexes, similar to the closely related five-coordinate<sup>25</sup> complex  $[Ni(L^+)(H_2O)Cl_3]$ , whose structure has been established by X-ray analysis,<sup>26</sup> have a highly ordered crystal lattice with the zwitterion entities arranged head-to-tail. In a structure of this kind, which would give rise to a most favorable interaction among adjacent zwitterions, the positive charge of the quaternized N<sup>+</sup>-R groups might be effectively neutralized by electron delocalization from the neighboring  $MX_3^-$  groups. The donor properties of the nitrogen atom coordinated to the metal ion may then approach those of the more basic amines, pyridine and quinuclidine. Significant support for this suggested explanation is offered by the preliminary results of a study of the magnetic and dielectric properties of the  $[M(L^+)X_3]$  complexes at low temperatures,<sup>27</sup> which indicate that these complexes behave as semiconductors, thus implying the possibility of extensive electron delocalization within the crystal lattice.

### Experimental Section

**Starting Materials.** dabco of 99.5% purity (Houdry Processing Company) and "Analytical Reagent" grade metal salts were used without purification. Zinc(II) iodide, manganese(II) bromide and iodide, nickel(II) iodide, and iron(II) bromide and iodide, which were unavailable commercially as pure products, were prepared by standard procedures.

**Preparations of the Ligands.** Analytical data for the ligands are listed in Table III. **N-Methyl-dabconium Iodide**,  $[N(CH_2CH_2)_3N^+CH_3]I^-$ . An excess of methyl iodide (10 g) in 100 ml of acetone was added dropwise to a solution of 20 g of dabco dissolved in 200 ml of acetone at room temperature. A white crystalline precipitate began to form immediately; after the reaction mixture had been allowed to stand for 4 hr, the precipitate was filtered, washed several times with acetone, recrystallized from an ethanol-acetone solution, and dried *in vacuo*. The compound is soluble in water, ethanol, methanol, nitromethane, and acetonitrile and is sparingly soluble or insoluble in nonpolar solvents.

Table III. Analytical Data for Dabconium Ligands

Ligand	—% nitrogen—		—% halogen—	
	Found	Calcd	Found	Calcd
$(L^+H)Cl = C_6H_{13}ClN_2$	18.7	18.86	23.9	23.88
$(L^+H)Br = C_6H_{13}BrN_2$	14.3	14.50	41.1	41.38
$(L^+H)I = C_6H_{13}IN_2$	11.7	11.71	53.1	53.08
$(L^+CH_3)I = C_7H_{15}IN_2$	10.9	11.02	49.9	49.94
$(L^+CH_3)Br = C_7H_{15}BrN_2$	13.5	13.52	38.4	38.58
$(L^+CH_3)Cl = C_7H_{15}ClN_2$	17.0	17.21	21.8	21.80

N-Methyl-dabconium chloride,  $[N(CH_2CH_2)_3N^+CH_3]Cl^-$ , and N-methyl-dabconium bromide,  $[N(CH_2CH_2)_3N^+CH_3]Br^-$ , were

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prepared from the iodide by ion exchange, using Dowex 1-X-8 anionic resin (100-200 mesh). The crude products were dissolved in ethanol containing a small amount of 2,2-dimethoxypropane as dehydrating agent, and reprecipitated as pure crystals by addition of diethyl ether. The N-methyldabconium chloride and bromide are more soluble in polar solvents than the corresponding iodide, and are extremely deliquescent; they do not crystallize except under strictly anhydrous conditions.

**Monoprotonated Dabconium Chloride, Bromide, and Iodide,  $[N(CH_2CH_2)_3N^+HX]$  ( $X = Cl, Br, I$ ).** A solution of dabco in warm acetone (10 g in 100 ml) was added with stirring to a warm (50°) solution prepared from 10 ml of the concentrated halogen acid and 15 ml of dimethoxypropane as a dehydrating agent. The monoprotonated dabconium halide precipitated immediately as a white crystalline solid. The precipitate was allowed to stand in contact with the solution at 40° for 1 hr; the precipitate was then filtered, washed several times with acetone, recrystallized from ethanol, and dried *in vacuo*. The monoprotonated dabconium halides are less soluble than the corresponding N-methyldabconium salts.

**Preparation of the Metal Complexes.** Most complexes were obtained by the general preparation described below; those which required special procedures are discussed individually. The analytical data of the complexes are listed in Table I.

**General Method of Preparation for  $[Co(L^+CH_3)Cl_3]$ ,  $[Co(L^+CH_3)Br_3]$ ,  $[Co(L^+CH_3)I_3]$ ;  $[Ni(L^+CH_3)Cl_3]$ ,  $[Ni(L^+CH_3)Br_3]$ ,  $[Ni(L^+CH_3)I_3]$ ;  $[Cu(L^+CH_3)Br_3]$ ;  $[Zn(L^+CH_3)Cl_3]$ ;  $[Zn(L^+CH_3)Br_3]$ , and  $[Zn(L^+CH_3)I_3]$ .** A hot solution of N-methyldabconium halide in anhydrous ethanol was added slowly and with stirring to a hot ethanol solution of the anhydrous metal halide. Only one complex was formed in each case, regardless of the ratio metal halide:N-methyldabconium halide. The complex precipitated immediately, but heating and stirring were continued for about 20 min to promote a more crystalline form. The precipitate was filtered, washed several times with 10-ml portions of anhydrous ethanol, and dried *in vacuo*.

**Preparation of  $[Mn(L^+CH_3)Cl_3]$ ,  $[Mn(L^+CH_3)Br_3]$ ,  $[Fe(L^+CH_3)Cl_3]$ ,  $[Fe(L^+CH_3)Br_3]$ , and  $[Fe(L^+CH_3)I_3]$ .** These complexes are prepared by the general method described above, except that all operations were carried out in a drybox. Also, both the metal halide and ligand halide solutions were dehydrated before use by refluxing for 1 hr with about 10% of dimethoxypropane. The iron(II) complexes, which are sensitive to both moisture and air, were prepared in a dry nitrogen atmosphere.

**Preparation of  $[Cu(L^+CH_3)Cl_3]$ .** The reaction of anhydrous  $CuCl_2$  with  $(L^+CH_3)Cl^-$  in ethanol initially yields a gold-colored precipitate, which, on standing in the presence of its mother liquor, transforms into pure, deep yellow, crystalline  $[Cu(L^+CH_3)Cl_3]$ .

**Preparation of  $[Mn(L^+CH_3)I_3]$ .** This compound was difficult to prepare in a pure form because it tends to coprecipitate with the ligand iodide. A concentrated solution of anhydrous  $MnI_2$  in ethanol was added dropwise to a saturated solution of the ligand iodide in anhydrous ethanol at its boiling point. On prolonged heating and partial evaporation of the solvent, a peach-colored precipitate formed which was filtered from the hot solution, washed with several-milliliter portions of hot ethanol, and dried *in vacuo*.

**Preparation of the  $[M(L^+H)X_3]$  Complexes.** The complexes of the monoprotonated dabconium ligand were prepared similarly to the corresponding  $[M(L^+CH_3)X_3]$  complexes, but with one important difference. In the preparation of the chloro and bromo complexes an excess of  $(L^+H)X^-$  must be avoided to prevent the formation of the five-coordinate species  $[M(L^+H)_2X_3]X$ .<sup>21</sup>

**Solubility and Some Chemical Reactions of the  $[M(L^+)X_3]$  Complexes.** The  $[M(L^+)X_3]$  complexes have remarkable thermal stability, and generally do not decompose until heated above 250°. The Fe(II) complexes, however, are sensitive to air oxidation and could be kept and handled only in an oxygen-free atmosphere.

The  $[M(L^+)X_3]$  complexes are generally sensitive to moisture. The  $[M(L^+CH_3)Cl_3]$  and  $[M(L^+CH_3)Br_3]$  complexes ( $M = Mn(II), Fe(II), Cu(II)$ ), when exposed to moist air, tend to coordinate one molecule of water forming five-coordinate complexes  $[M(L^+CH_3)(H_2O)X_3]$ .<sup>25</sup> Under the same conditions, the  $[M(L^+H)X_3]$  complexes also slowly absorb moisture, but the resulting aquo complexes are generally ill-defined. When exposed to the atmosphere, the iodo complexes,  $[M(L^+)I_3]$ , slowly decompose with oxidation of the iodo ligands.

The  $[M(L^+CH_3)X_3]$  complexes [ $M = Mn(II), Fe(II), Co(II), Ni(II),$  and  $Cu(II)$ ;  $X = Cl, Br$ ] when suspended in anhydrous alcohol and treated with anhydrous ammonia in a 1:1  $NH_3$ :metal ratio, react immediately to form the five-coordinate complexes  $[M(L^+CH_3)(NH_3)X_3]$ .<sup>25</sup> With a larger  $NH_3$ :metal ratio, mixtures of octahedral complexes containing more than one molecule of ammonia are formed. If anhydrous ammonia is bubbled through a suspension of the  $[M(L^+H)X_3]$  complexes in ethanol, the protonated dabconium species are neutralized, and polymeric complexes containing bridging dabco molecules are formed.

**Physical Characterization of the Complexes.** Vibrational spectra were recorded in the 4000-250- $cm^{-1}$  range, using a Perkin-Elmer Model 521 spectrophotometer equipped with a dry air purge. Samples were examined both in Nujol and in hexachlorobutadiene mulls, using CsBr plates. d-d electronic spectra were recorded with a Cary Model 14 spectrophotometer (30,000-4000- $cm^{-1}$  range) and a Perkin-Elmer 521 spectrophotometer (5000-2000- $cm^{-1}$  range). The spectra of solid samples were obtained as diffuse reflectance spectra from 30,000 to 5000  $cm^{-1}$ , and as transmission spectra of hexachlorobutadiene mulls (between NaCl plates) from 30,000 to 2000  $cm^{-1}$ , with a hexachlorobutadiene film in the reference beam. Transmission spectra of solutions were taken using nitromethane, chlorobenzene, and dichloromethane as solvents.

X-Ray powder diffractographs were taken using nickel-filtered  $Cu K\alpha$  radiation. Magnetic susceptibilities were measured by the Gouy method for powdered samples at room temperature. Diamagnetic corrections from Pascal's tables were used in the calculation of  $\mu_{eff}$ . Conductivity measurements were made at 25° using spectrograde nitromethane as the solvent. The values of  $\Lambda_M$  for  $10^{-3} M$  solutions ranged from 20 to 65  $ohm^{-1} mol^{-1} cm^2$  (common range for 1:1 electrolytes, 70-100  $ohm^{-1} mol^{-1} cm^2$ ).

**Acknowledgment.** This investigation was supported in part by the U. S. Atomic Energy Commission and by the Public Health Service, Department of Health, Education, and Welfare, National Institutes of Health.