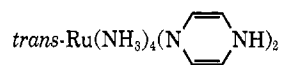


sweep is allowed to traverse the range of potentials occupied by the second peak. It seems likely that the sharp anodic peak corresponds to oxidation of the uncharged complex



which is apparently adsorbed (or precipitated) at the electrode surface.

Acknowledgment.—We are grateful to Professor Peter Ford and Dr. Carol Creutz for helpful hints about the syntheses of several of the complexes studied. We are indebted to Dr. S. V. Srinivasan for performing the infrared absorption intensity measurements. This work was supported by the National Science Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA 32306

Donor Properties of Positively Charged Ligands. Five-Coordinate, Trigonal-Bipyramidal Complexes of Manganese(II), Iron(II), Nickel(II), and Copper(II) with a Monoprotonated Ditertiary Amine

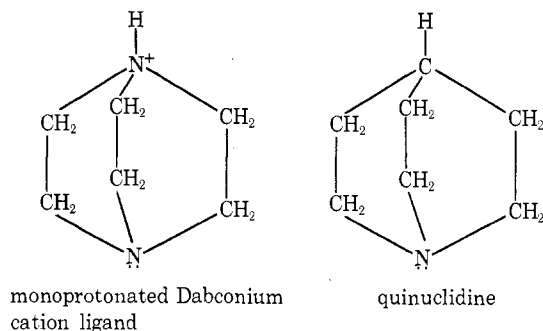
By L. M. VALLARINO,* V. L. GOEDKEN, AND J. V. QUAGLIANO

Received September 17, 1971

A series of complexes of formula $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$ was obtained, where M is Mn(II), Fe(II), Ni(II), and Cu(II); X is Cl and Br; and L^+H is the monoprotonated ditertiary amine 1,4-diazabicyclo[2.2.2]octane (Dabco). The five-coordinate complex cations $[\text{MX}_3(\text{L}^+\text{H})_2]^+$ have a trigonal-bipyramidal configuration with D_{3h} symmetry and represent an unusual example of this stereochemistry for high-spin transition metal ions coordinated solely by monodentate ligands.

Introduction

In preceding papers of this series¹⁻³ we pointed out that the positively charged ligands obtained by monoquaternization of the cage-like ditertiary amine 1,4-diazabicyclo[2.2.2]octane (Dabco) have unusual coordination properties which can logically be related to several cooperating factors. First, the presence of a positive charge on the ligand itself may be expected to give rise to strong electrostatic interactions even in complexes which do not carry net ionic charges, thus increasing their overall lattice energy and hence their solid-state stability. Also, the rigid cage-like structure of Dabco might be expected to minimize the steric requirements which ordinarily hinder coordination of tertiary aliphatic amines to metal ions. Finally, in the monoprotonated Dabconium ligand the availability of the lone pair on the N donor atom may be drastically reduced by direct electronic interaction with the positively charged, quaternized N atom, as reflected by the dramatic decrease in basicity compared to similar uncharged tertiary amines—for example, the $\text{p}K_a$ of quinuclidine⁴ is 10.65 vs. 2.97 for the monoprotonated Dabconium cation.⁵ This change in the electronic requirements of the N donor atom of the Dabconium ligands may then result in the stabilization of metal complexes of unusual coordination numbers and geometries.



Results and Discussion

The reaction between the chlorides and bromides of manganese(II), iron(II), nickel(II), and copper(II)—but not cobalt(II) and zinc(II)—and an excess of the corresponding halide of the monoprotonated Dabconium cation ligand (L^+H) yields, as described in the Experimental Section, a series of compounds having the simple formula $\text{MX}_2 \cdot 2(\text{L}^+\text{H})\text{X}$ ($\text{M} = \text{Mn(II), Fe(II), Ni(II), Cu(II)}$; $\text{X} = \text{Cl, Br}$). These compounds are crystalline solids, which dissolve with complete solvation in water and in other solvents of good donor properties (e.g., dimethyl sulfoxide) and are insoluble in nonpolar solvents or polar organic solvents such as alcohols and ketones. The structural elucidation of these compounds is based on the following experimental evidence.

The d-d electronic spectra of the Ni(II) compounds—the deep pink $\text{NiCl}_2 \cdot 2(\text{L}^+\text{H})\text{Cl}$ and the pink-violet $\text{NiBr}_2 \cdot 2(\text{L}^+\text{H})\text{Br}$ (Table II and Figure 1)—cannot be assigned to either a tetrahedral or an octahedral stereochemistry but rather strongly support a trigonal-bipyramidal coordination. In fact, the spectrum of

(1) J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Amer. Chem. Soc.*, **92**, 482 (1970).

(2) V. L. Goedken, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, **8**, 2331 (1969).

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

(4) R. J. Bruehlman and F. H. Verhoek, *ibid.*, **70**, 1401 (1948).

(5) P. Paoletti, J. H. Stern, and A. Vacca, *J. Phys. Chem.*, **69**, 3759 (1965).

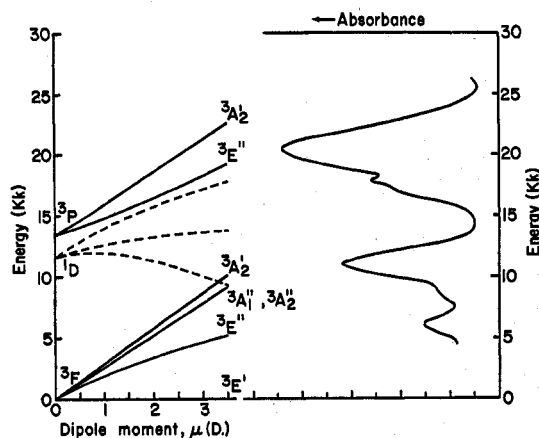


Figure 1.—The d-d electronic absorption spectrum of $[\text{NiCl}_3(\text{L}^+\text{H})_2]\text{Cl}$ (mull at liquid nitrogen temperature), compared with the energy level diagram for high-spin Ni(II) in a trigonal-bipyramidal environment of five equivalent dipoles of $\mu = 3.5 \text{ D}$ (after Ciampolini⁷).

$\text{NiCl}_2 \cdot 2(\text{L}^+\text{H})\text{Cl}$ is almost identical with that of the red complex $[\text{NiCl}_3(\text{H}_2\text{O})(\text{L}^+\text{CH}_3)]$, where L^+CH_3 is the *N*-methyl-Dabconium ligand,² for which a single-crystal X-ray study⁶ has shown Ni(II) to have an almost undistorted trigonal-bipyramidal environment with the three Cl atoms in the equatorial plane. Furthermore, the number and energies of the observed d-d absorption bands are in very good agreement with those expected for Ni(II) in a ligand field of D_{3h} symmetry. For example, the room-temperature reflectance spectrum of $\text{NiCl}_2 \cdot 2(\text{L}^+\text{H})\text{Cl}$ shows four absorption maxima at 5.5, 10.7, 17.7, and 20.4 kK, respectively. In addition, a tail appears on the low-energy side of the band at 10.7 kK, which becomes better resolved when the spectrum is examined in hexachlorobutadiene mull at liquid nitrogen temperature and gives rise to a new absorption at about 8.5 kK. The observed energies of these five bands agree satisfactorily with the energy level diagram of Ciampolini⁷ for an average value of the ligand dipoles $\mu = 3.5 \text{ D}$; the relative assignments are shown in Figure 1. Thus for the compounds of simple formula $\text{NiX}_2 \cdot 2(\text{L}^+\text{H})\text{X}$ two likely structural formulas can logically be proposed, $[\text{NiX}_3(\text{L}^+\text{H})_2]\text{X}$ and $(\text{L}^+\text{H})[\text{NiX}_4(\text{L}^+\text{H})]$, each involving a trigonal-bipyramidal coordination of Ni(II). The first formula, favored on simple symmetry considerations, is also the more likely on the basis of the d-d electronic spectrum, since the average field strength arising from three Cl (or Br) ligands and two N atoms of Dabconium ligands is expected to be close to that of $[\text{NiCl}_3(\text{H}_2\text{O})(\text{L}^+\text{CH}_3)]$. In the second proposed structural formula the environment of four Cl (or Br) ligands and one N atom of a Dabconium ligand would result in an appreciably weaker average ligand field.

If the compounds $\text{NiX}_2 \cdot 2(\text{L}^+\text{H})\text{X}$ actually have the structural formula $[\text{NiX}_3(\text{L}^+\text{H})_2]\text{X}$, containing a "free" halide (Cl^- or Br^-) ion, then it should be possible to substitute this halide ion with a suitable univalent anion of poor donor properties, such as the perchlorate, ClO_4^- . The preparation of complexes of the type $[\text{NiX}_3(\text{L}^+)_2]\text{ClO}_4$ was therefore attempted, and a complex of simple formula $\text{NiCl}_2 \cdot (\text{L}^+\text{CH}_3)\text{Cl} \cdot (\text{L}^+\text{CH}_3)-$

ClO_4 was obtained in a pure state with the *N*-methyl-Dabconium ligand. This deep pink crystalline substance contains "free" ClO_4^- ions, as shown by its vibrational spectrum, and has a d-d electronic spectrum identical with that of $\text{NiCl}_2 \cdot 2(\text{L}^+\text{H})\text{Cl}$. This complex of the *N*-methyl-Dabconium ligand can, therefore, be confidently formulated as the ionic species $[\text{NiCl}_3(\text{L}^+\text{CH}_3)_2]\text{ClO}_4$. By analogy, the halide complexes $\text{NiX}_2 \cdot 2(\text{L}^+\text{H})\text{X}$ are assigned the ionic formula $[\text{NiX}_3(\text{L}^+\text{H})_2]\text{X}$. The perchlorate complex $[\text{NiCl}_3(\text{L}^+\text{H})_2]\text{ClO}_4$ was also isolated, although it included a little of the relatively insoluble "free" monoprotonated Dabconium perchlorate. Finally, a five-coordinate complex chloride salt containing the *N*-methyl-Dabconium ligand was obtained but only as the "double salt" $[\text{NiCl}_3(\text{L}^+\text{CH}_3)_2]\text{Cl} \cdot (\text{L}^+\text{CH}_3)\text{Cl}$, which crystallized in well-formed, large, deep red crystals.

The Mn(II) and Fe(II) complexes are isomorphous with the corresponding Ni(II) complex as indicated by their identical X-ray powder patterns. Hence, they can be similarly assigned an ionic formula, $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$, with the complex cation $[\text{MX}_3(\text{L}^+\text{H})_2]^+$ having a trigonal-bipyramidal stereochemistry. As may be expected for a series of isostructural compounds, the vibrational spectra of the Mn(II), Fe(II), and Ni(II) complexes are almost superposable. The infrared spectra of these complexes consist primarily of the characteristic absorptions of the Dabco molecule. In addition, there are a number of intense absorptions between 3000 and 2250 cm^{-1} , which all shift to lower frequencies upon deuteration and are assigned to the $\text{N}^+\text{-H}$ stretching mode of the coordinated and hydrogen-bonded protonated Dabconium ligands.¹ Several new bands also appear in the 1600–700- cm^{-1} region and may be tentatively considered to arise from the $\text{N}^+\text{-H}$ deformation vibration coupled with CH_2 deformation, CH_2 rocking, and skeletal modes. It is interesting to note that the entire vibrational spectra of the protonated Dabconium ligand in the $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$ complexes, and in particular the patterns of the N^+H stretching region, are identical for all these complexes regardless of the metal ion M or of the halide X. However, this pattern differs appreciably from that of the previously reported pseudotetrahedral complexes of formula $[\text{MX}_3(\text{L}^+\text{H})]$, showing that the vibrational spectrum of the protonated Dabconium ligand is influenced to a marked extent by the general formula of the complex and probably also by the stereochemical environment of the metal ion.

The Cu(II) complexes $\text{CuX}_2 \cdot 2(\text{L}^+\text{H})\text{X}$ are not isomorphous with the corresponding complexes of Mn(II), Fe(II), and Ni(II) but probably have a closely related structure. The single, intense, and symmetrical absorption band which appears in their d-d electronic spectra—at 8.8 kK for the chloro complex and 8.5 kK for the bromo complex—differs in energy, intensity, and contour from the absorptions generally observed for Cu(II) in tetrahedral, square-planar, or octahedral compounds but it closely resembles that of five-coordinate, trigonal-bipyramidal Cu(II) in such complexes as the CuCl_5^- and $\text{Cu}_2\text{Cl}_8^{4-}$ anions.^{8–10} Furthermore,

(6) F. K. Ross and G. D. Stucky, *Inorg. Chem.*, **8**, 2734 (1969).

(7) M. Ciampolini, *ibid.*, **5**, 35 (1966).

(8) W. E. Hatfield and T. S. Piper, *ibid.*, **3**, 841 (1964).

(9) K. N. Raymond, D. W. Meek, and J. A. Ibers, *ibid.*, **7**, 1111 (1968).

(10) D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *ibid.*, **10**, 1081 (1971).

the infrared vibrational spectra of the Cu(II) complexes are again almost identical with those of the five-coordinate compounds of Ni(II), Fe(II), and Mn(II). In view of these close similarities, the Cu(II) complexes are also assigned a five-coordinate structure, $[\text{CuX}_3(\text{L}^+\text{H})_2]\text{X}$, very likely with a nearly trigonal-bipyramidal geometry.

A characteristic feature of these $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$ complexes is a remarkable thermal stability. The complexes remain unaltered up to about 200°, and at this temperature the slow decomposition which sets in apparently involves the N⁺-H group of the Dabconium ligand. The crystalline $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$ complexes all decompose in the presence of atmospheric moisture, the bromo complexes being generally far more sensitive than the chloro complexes. As mentioned previously, the complexes $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$ are generally insoluble. When warmed in the presence of solvents—ethanol, for example—which can dissolve the protonated Dabconium halide, the solid five-coordinate $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$ complexes dissociate to yield the solid four-coordinate, pseudotetrahedral complexes $[\text{MX}_3(\text{L}^+\text{H})]$ and a solution of $(\text{L}^+\text{H})\text{X}$. This dissociative process, which occurs more readily for the bromo than for the chloro complexes, appears to be accelerated by the presence of atmospheric moisture and can be reversed by the addition of a large excess of ligand halide to the solution.

It should be mentioned that the reaction of protonated Dabconium halides with the halides of Co(II) and Zn(II), under conditions similar to those described for the preparation of the five-coordinate complexes of Mn(II), Fe(II), Ni(II), and Cu(II), yielded only the four-coordinate, pseudotetrahedral zwitterion complexes $[\text{MX}_3(\text{L}^+\text{H})]$.¹ This preference for tetrahedral coordination is most likely related for Co(II) to its relatively high crystal field stabilization energy in a tetrahedral environment and for Zn(II) to the high ΔH of formation of its tetrahedral complexes.¹¹

Conclusions

The series of isostructural complexes $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$ represents a rather uncommon example of five-coordination for high-spin divalent transition metal ions coordinated solely by monodentate ligands. Another unusual structural feature of these complexes is the 1:1 association of a very large complex cation, $[\text{MX}_3(\text{L}^+\text{H})_2]^+$, and a relatively small nonatomic anion X^- , with no tendency toward inclusion of solvent or other small molecules in their crystal lattice. Apparently, the network of hydrogen bonds formed through the N⁺-H of the protonated Dabconium ligands greatly contributes to the stabilization of the crystalline $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$ complexes. For the *N*-methyl-Dabconium ligand, which cannot form hydrogen bonds, five-coordinate ionic complexes of this kind fail to form unless a larger counteranion, such as the perchlorate, is also present. Alternatively, the "free" ligand halide is included in the lattice giving rise to the "double salts" of the type $[\text{MX}_3(\text{L}^+\text{CH}_3)_2]\text{X} \cdot (\text{L}^+\text{CH}_3)\text{X}$.

Much of the stability of the $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$ complexes can be attributed to the unusual structure of the trigonal-bipyramidal coordination entity. Although

this structure is not known in detail at present, it is logical to assume that the C_3 axis of each protonated Dabconium ligand will be aligned with the C_3 axis of the coordination sphere. The coordination entity may then be visualized as having a highly symmetrical structure, with an uncommon charge distribution consisting of two opposite regions of positive charge—the quaternized N⁺-H moieties of the two Dabconium ligands—separated by a symmetrically placed "doughnutlike" region of negative charge—the MX_3 moiety of the complex. The coordination entity has a net ionic charge of 1+ but is in effect a double zwitterion (+, -, +) without a resulting dipole. The high symmetry of the coordination entity and the compact cage-like structure of Dabco thus cooperate to give a favorable overall charge distribution.

The ease of formation and the general stability of the five-coordinate complexes $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$ markedly decrease from the chloride to the bromo derivatives, and with iodo ligands only the four-coordinate, pseudotetrahedral $[\text{MI}_3(\text{L}^+\text{H})]$ complexes are formed.¹ Thus the tendency to attain five-coordination varies in the opposite order to the polarizability of the halide ions and may be logically related to the availability of the electron pair on the N donor atom of the Dabconium ligand. With the more polarizable halide, the iodide, an environment of three iodo ligands and one nitrogen ligand of low basicity such as protonated Dabconium ($pK_a = 2.97$) apparently provides sufficient electron density to satisfy the requirements of the central metal ion. With the less polarizable chloride ion and to some extent also with the bromide ion, however, coordination of an additional Dabconium ligand may help to provide the most favorable electronic environment, and the five-coordinate species $[\text{MCl}_3(\text{L}^+\text{H})_2]\text{Cl}$ and $[\text{MBr}_3(\text{L}^+\text{H})_2]\text{Br}$ are formed. The fact that the tertiary amine quinuclidine—identical with protonated Dabconium in all structural features but far more basic ($pK_a = 10.65$)—forms exclusively four-coordinate pseudotetrahedral complexes¹² with these metal ions strongly supports the above considerations. It should not be ignored, however, that the size of the halide ions varies in the same order as their polarizability. So if steric requirements were to oppose the formation of a five-coordinate species with two bulky tertiary-nitrogen ligands, their importance would again vary in the order $\text{Cl} < \text{Br} < \text{I}$. These considerations still leave somewhat unanswered the question whether in these complexes five-coordination is induced chiefly by the special electronic properties of the Dabconium ligands, with ionic lattice energy and hydrogen bonding playing an auxiliary role, or is determined by the steric requirements of the bulky Dabconium ligands. It is hoped that a systematic investigation of the donor properties of other structurally related positively charged ligands, in which steric and electronic factors, as well as the ability to hydrogen bond, are gradually varied, will bring some new insight into these interesting problems.

Experimental Section

Monoprotonated Dabconium chloride and bromide and *N*-methyl-Dabconium chloride were prepared as described previously.¹

(11) S. F. Ashcroft and C. T. Mortimer, "Thermochemistry of Transition Metal Complexes," Academic Press, London and New York, N. Y., 1970, p 297.

(12) V. L. Goedken, J. V. Quagliano, and L. M. Vallarino, to be submitted for publication.

TABLE I
ANALYTICAL DATA AND SOME PROPERTIES OF FIVE-COORDINATE COMPLEXES
CONTAINING THE PROTONATED DABCONIUM LIGAND

Complex ^a	Color	μ_{eff} , BM	% metal		% halogen		% nitrogen	
			Calcd	Found	Calcd	Found	Calcd	Found
[MnCl ₃ (L ⁺ H) ₂]Cl	White	5.89	12.99	13.0	33.54	33.7	13.25	13.5
[MnBr ₃ (L ⁺ H) ₂]Br	White with pink tinge	5.83	10.55	10.7	46.04	45.7	10.75	10.8
[FeCl ₃ (L ⁺ H) ₂]Cl	White	5.21	13.18	13.2	33.47	33.7	13.22	12.8
[FeBr ₃ (L ⁺ H) ₂]Br	Pale tan	5.13	10.70	10.3	45.95	45.7	10.73	10.4
[NiCl ₃ (L ⁺ H) ₂]Cl	Deep pink	3.73	13.76	13.5	33.25	33.4	13.13	13.1
[NiBr ₃ (L ⁺ H) ₂]Br	Pink-violet	3.65	11.19	11.0	45.70	45.4	10.67	10.6
[CuCl ₃ (L ⁺ H) ₂]Cl	Pale yellow	1.95	15.19	15.1	32.74	32.8	12.93	12.6
[CuBr ₃ (L ⁺ H) ₂]Br	Mustard	1.87	11.23	10.9	45.07	45.1	10.55	10.7

^a L = Dabco = 1,4-diazabicyclo[2.2.2]octane.

Preparation of the Complexes. [MCl₃(L⁺H)₂]Cl (M = Mn(II), Fe(II), Ni(II), Cu(II)).—A solution of the anhydrous metal chloride (2 mmol) in anhydrous ethanol was added slowly to a warm solution of protonated Dabconium chloride (about 10 mmol) in the same solvent. The mixture was stirred vigorously for 0.5 hr and the precipitate which formed was filtered, washed several times with anhydrous ethanol, and dried *in vacuo*. Analytical data are listed in Table I; d-d absorptions, in Table II.

TABLE II

d-d ELECTRONIC SPECTRA OF FIVE-COORDINATE COMPLEXES
CONTAINING THE PROTONATED DABCONIUM LIGAND

Complex ^a	Absorption maxima, kK ^b
[FeCl ₃ (L ⁺ H) ₂]Cl	8.3
[FeBr ₃ (L ⁺ H) ₂]Br	8.3
[NiCl ₃ (L ⁺ H) ₂]Cl	5.5, 10.7, 17.7, 20.4
[NiBr ₃ (L ⁺ H) ₂]Br	5.5, 10.1, 16.9, 19.4
[CuCl ₃ (L ⁺ H) ₂]Cl	8.8
[CuBr ₃ (L ⁺ H) ₂]Br	8.5

^a L = Dabco = 1,4-diazabicyclo[2.2.2]octane. ^b Values reported are midpoints of absorption bands from diffuse reflectance spectra at room temperature.

[MBr₃(L⁺H)₂]Br (M = Mn(II), Fe(II), Ni(II), Cu(II)).—A solution of the anhydrous metal bromide in anhydrous ethanol, cooled to about -30°, was added to a supersaturated solution of the ligand bromide in a 1:1 ethanol-nitromethane mixture at -30° (metal:ligand ratio ~1:10). The complexes which precipitated were filtered, washed with chilled (-30°) anhydrous ethanol, and dried *in vacuo*. The [NiBr₃(L⁺H)₂]Br complex, which is extremely sensitive to moisture, was prepared and handled in a drybox. The Mn(II) complex, which is more stable than the other bromo complexes, was prepared at room temperature in a similar manner. Analytical data are listed in Table I; d-d absorptions, in Table II.

[NiCl₃(L⁺CH₃)₂]ClO₄.—A solution of anhydrous nickel(II) chloride in anhydrous ethanol was added to a 1:1 ethanol-

nitromethane solution containing equimolar quantities of LiClO₄ and *N*-methyl-Dabconium chloride (approximate Ni:ClO₄:L⁺-CH₃ ratio 1:1:2). The red crystalline precipitate, which separated after repeated scratching of the vessel, was filtered, washed with a 1:1 ethanol-nitromethane mixture, and dried *in vacuo*. *Anal.* Calcd for NiC₁₄H₃₀N₄Cl₃(ClO₄): Ni, 11.31; Cl (ionic), 20.49; ClO₄⁻, 19.16. Found: Ni, 11.5; Cl, 20.6; ClO₄⁻, 18.8 (determined as Cl⁻ after ion exchange on a chloride resin). The d-d spectrum of this compound is superimposable on that of [NiCl₃(L⁺H)₂]Cl. The infrared spectrum shows the absorptions characteristic of ionic ClO₄⁻.

Attempts to prepare a similar complex with the monoprotonated Dabconium ligand yielded a red substance, which under the microscope appeared to be a mixture of red and white crystals. The d-d spectrum of this mixture was identical with that of the [NiCl₃(L⁺H)₂]Cl complex, and the infrared spectrum showed the presence of ionic ClO₄⁻ and of both coordinated and "free" L⁺H ligand.

[NiCl₃(L⁺CH₃)₂]Cl·(L⁺CH₃)Cl.—A hot solution of anhydrous NiCl₂ in a 1:1 mixture of methanol-nitromethane was added dropwise to a hot solution of the ligand chloride in the same solvent mixture (Ni:ligand mole ratio 1:10). Both the NiCl₂ solution and the ligand solution were dried over 4A molecular sieves for 2 days before use. The well-formed deep red crystals which separated slowly were filtered, washed with triethylorthoformate, and dried *in vacuo*. *Anal.* Calcd for NiC₂₁H₄₅N₈Cl₅: Ni, 9.50; Cl, 28.7. Found: Ni, 9.3; Cl, 29.0. The d-d spectrum of this compound is superimposable on that of [NiCl₃(L⁺H)₂]Cl.

Characterization of the Complexes.—The complexes were characterized by analyses, vibrational infrared spectra (4000–250 cm⁻¹), d-d electronic spectra (25–4 kK), room-temperature magnetic susceptibilities, and X-ray powder diffraction spectra. Details of the procedures were described elsewhere.¹

Acknowledgment.—This research was supported by the Atomic Energy Commission and the National Science Foundation.