

basic reasonableness of this crude model is supported by the fact that both the ratio of the $p-1$ to $p-3$ intensities¹⁶ and the relative phase measurements suggest that H_2 elimination is faster in the case of methanol than in the case of propanol.¹⁷ Thus, fluorine substitution would be expected to enhance the production of H_2 in either reaction 2 or 3. On the other hand, as $(CF_3)_2CHOH$ is a poorer Bronsted base than is $(CH_3)_2CHOH$ and if BH_3 acts like a proton, fluorine substitution would reduce the formation of the adduct in reaction 1. Therefore, the fact that we see no reaction with $(CF_3)_2CHOH$ again suggests that the donor-acceptor adduct is prerequisite to H_2 elimination and that reactions 1 and 2 constitute the proper detailed mechanism.

These results are in accord with ideas based upon the chemistry of more complex reaction systems.^{3,18} Although this agreement is pleasing and shows that the previous ideas are more than formal rationalizations, these results have

(16) Here p represents the parent ion mass.

(17) In this argument the CH_3 group is taken to exhibit an electron-donor character with respect to H.¹³

added significance. They suggest that the initial rapid reactions of a species containing an unused valence orbital consist solely of forming donor-acceptor adducts. Once formed, such adducts react by a variety of paths and rates all of which depend upon the details of how the electronic structures of the two species are modified in the donor-acceptor interaction. Therefore, the key to an understanding of the reactivity of these species is the donor-acceptor interaction itself.

Registry No. BH_3 , 13283-31-3; $(CD_3)_2CDOD$, 22739-76-0; $(CH_3)_2CHOD$, 3979-51-9; $(CH_3)_2CHOH$, 67-63-0; CH_3OH , 67-56-1; $(CD_3)_2CO$, 666-52-4; $(CH_3)_2CO$, 67-64-1; $(CF_3)_2CHOH$, 920-66-1; $(CF_3)_2CO$, 684-16-2.

Acknowledgments. The support of the National Science Foundation under Grant No. GP 28320 is gratefully acknowledged.

(18) E. L. Muetterties in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, Chapter 1.

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Donor Properties of Positively Charged Ligands. Metal Complexes of the *N*-Chloromethyl-Dabconium Ligand

L. M. VALLARINO*, V. L. GOEDKEN, and J. V. QUAGLIANO

Received May 11, 1972

In a series of positively charged ligands obtained from the ditertiary amine Dabco, $N(CH_2CH_2)_3N$, by monoquaternization, the *N*-chloromethyl-Dabconium cation, $[N(CH_2CH_2)_3N^+CH_2Cl]$ (abbreviated L^+CH_2Cl), appears to be unique in its ability to form a variety of complexes with nickel(II) chloride. The complexes $[NiCl_3(L^+CH_2Cl)]$ (four-coordinate, pseudotetrahedral monomer), $[Ni_2Cl_4(L^+CH_2Cl)_2]$ (chloro-bridged, five-coordinate dimer), $[NiCl_3(L^+CH_2Cl)_2]X$ (with $X^- = Cl^-, ClO_4^-$) (five-coordinate, trigonal-bipyramidal cation), $[NiCl_3(L^+CH_2Cl)_2][NiCl_4]$ (five-coordinate, trigonal-bipyramidal cation, tetrahedral anion), and $[NiCl_3(H_2O)(L^+CH_2Cl)] \cdot (L^+CH_2Cl)Cl$ (five-coordinate, trigonal bipyramidal) were obtained in the crystalline state and were identified by analyses, magnetic properties, and spectra (d-d electronic, vibrational, and X-ray powder diffraction). In solution, the complexes of Ni(II) with the *N*-chloromethyl-Dabconium ligand give rise to unusual equilibria involving four-, five-, and six-coordinate species, with the five-coordinate species being the most stable in a well-defined temperature interval.

Introduction

Previous investigations of the donor properties of the monoquaternized ditertiary amine 1,4-diazabicyclo[2.2.2]octane (Dabco) showed that monoquaternization reduced the basicity of the remaining lone pair by a factor of 10^6 , but the resulting cationic amine L^+ (Figure 1a) could still function as a ligand.¹⁻⁴ In the presence of an excess of metal halides, the four-coordinate pseudotetrahedral complexes of the type $[MX_3(L^+)]$ were generally formed,¹ but these had a tendency to take on a fifth ligand (water, ammonia, or an additional *N*-alkyl-Dabconium cation) to form unusual five-coordinate complexes. It was also found that minor variations in the quaternizing group of the Dabconium cation markedly affected the type of complex

formed. For example, nickel(II) chloride reacted in anhydrous ethanol solution with an excess of protonated Dabconium chloride to yield the deep pink, five-coordinate⁴ cation $[NiCl_3(L^+H)_2]^+$. Under similar experimental conditions, the *N*-methyl-Dabconium chloride formed the four-coordinate complex $[NiCl_3(L^+CH_3)]$, having a pseudotetrahedral stereochemistry with C_{3v} symmetry.² However, if an excess of perchlorate ions (as $LiClO_4$) was added and the reaction mixture was diluted with nitromethane to prevent precipitation of the *N*-methyl-Dabconium perchlorate (insoluble in either pure ethanol or pure nitromethane, but moderately soluble in 1:1 ethanol-nitromethane mixture), then the deep pink, five-coordinate complex $[NiCl_3(L^+CH_3)_2]ClO_4$ separated readily from solution. It thus appeared appropriate to explore systematically the metal complexes of Dabconium cation ligands containing different quaternizing groups, chosen to provide a variety of electronic and steric effects.

Results and Discussion

Monoquaternization of Dabco can be accomplished

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

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

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

(4) L. M. Vallarino, V. L. Goedken, and J. V. Quagliano, *Inorg. Chem.*, **11**, 1466 (1972).

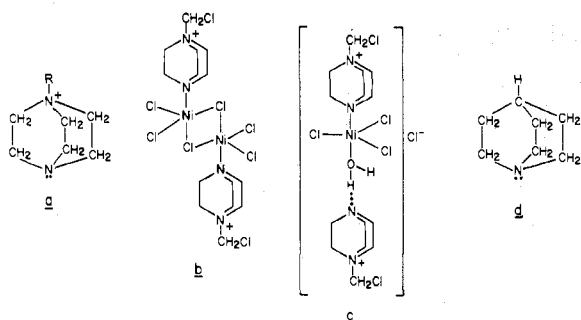


Figure 1. (a) 1-Alkyl-1,4-diazabicyclo[2.2.2]octonium, *N*-alkyl-Dabconium; (b) schematic formula of the purple $[\text{NiCl}_2(\text{L}^+\text{CH}_2\text{Cl})_2]\text{Cl}$; (c) schematic formula of $[\text{NiCl}_3(\text{H}_2\text{O})(\text{L}^+\text{CH}_2\text{Cl})](\text{L}^+\text{CH}_2\text{Cl})\text{Cl}$; (d) 1,4-azabicyclo[2.2.2]nonane, quinuclidine.

Table I. Formulas and Stereochemistries of Ni(II) Complexes^a Formed by Reaction of NiCl_2 with Various Monoquaternized Dabconium Ligands

| Quaternizing group, R, of (L^+R) ligands ^b | Complex isolated ^c | |
|---|---|---|
| | In ethanol, with only Cl^- present | In ethanol-nitromethane (1:1), with both Cl^- and ClO_4^- present |
| H | A, B | C ^d |
| CH_3 | A | C |
| C_2H_5 | A | C |
| <i>n</i> - C_3H_7 | A | C |
| $\text{CH}_2\text{C}_6\text{H}_5$ | A | C ^d |
| CH_2Cl | A, B, D, E | C |
| CHClCH_2Cl | A, B | e |
| CH_2CN | A, B | e |
| CBr_3 | f | f |
| $\text{C}(\text{C}_6\text{H}_5)_3$ | A, B | C |

^a A = $[\text{NiCl}_3(\text{L}^+\text{R})]$, pseudotetrahedral with C_{3v} symmetry; B = $[\text{NiCl}_3(\text{L}^+\text{R})_2]^+\text{Cl}^-$, five-coordinate, trigonal-bipyramidal complex cation; C = $[\text{NiCl}_3(\text{L}^+\text{R})_2]^+\text{ClO}_4^-$, same complex cation as in B; D = $[\text{NiCl}_3(\text{L}^+\text{R})_2]_2[\text{NiCl}_4]$, same complex cation as in B and C, tetrahedral complex anion; E = $[\text{Ni}_2\text{Cl}_6(\text{L}^+)_2]$, five-coordinate, chloro-bridged dimer. ^b L = 1,4-diazabicyclo[2.2.2]octane, Dabco.

^c The complexes were characterized by elemental analyses (Ni, ionic Cl) and by their d-d electronic and infrared vibrational spectra.

^d The complex was obtained as a double salt with "free" ligand perchlorate. ^e No crystalline complex was isolated. ^f Upon addition of the NiCl_2 solution the quaternizing group is split off, and polymeric complexes of the bridging, neutral Dabco ligand are formed.

readily with a wide variety of alkyl halides, and the dramatic lowering in pK_a of the remaining tertiary nitrogen atom prevents diquaternization except under drastic conditions. The reaction of a number of monoquaternized Dabconium cations with nickel(II) chloride yielded a series of related complexes of varied formulas and geometries. The quaternizing groups of the Dabconium ligands and the types of complexes obtained with Ni(II) under different conditions are listed in Table I. The reaction conditions—solvent, ratio of metal to ligand, presence of noncoordinating anions, and to a lesser extent also temperature—play an important role in determining the type of complex formed. Thus, in ethanol-nitromethane solution and in the presence of an excess of LiClO_4 the complex formed is nearly always the five-coordinate salt $[\text{NiCl}_3(\text{L}^+\text{R})_2]\text{ClO}_4$, whereas in pure ethanol solution and with a large excess of metal halide the complex obtained is usually the four-coordinate pseudotetrahedral zwitterion $[\text{NiCl}_3(\text{L}^+\text{R})]$. However, under appropriate conditions—for example, in ethanol solution with only Cl^- present and a rather large excess of ligand over metal—the nature of the quaternizing group R apparently determines whether the four-coordinate species $[\text{NiCl}_3(\text{L}^+\text{R})]$, or the five-coordinate species $[\text{NiCl}_3$ -

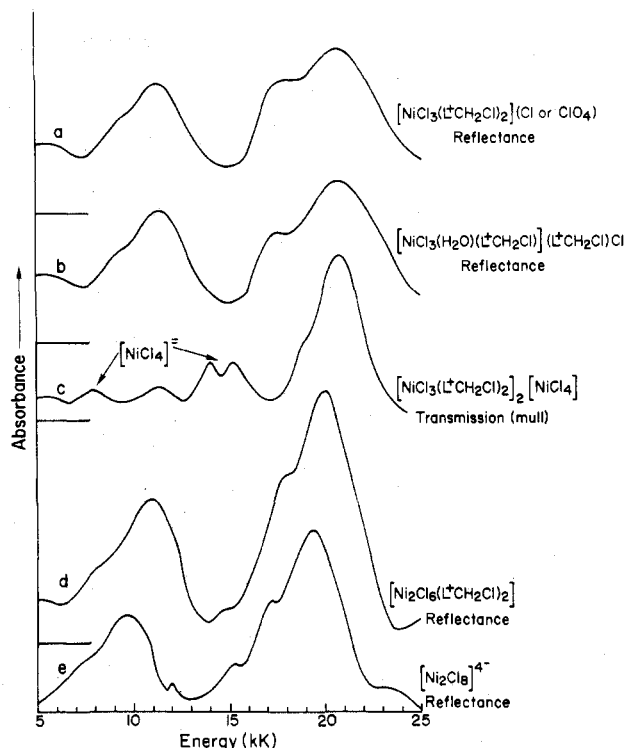


Figure 2. d-d electronic spectra of the complexes.

$(\text{L}^+\text{R})_2]\text{Cl}$, or still another type of complex is actually formed. The results obtained with the ligands listed in Table I appear to indicate that, at least in the crystalline state, neither the electron-donating properties of the quaternizing group R nor its size has a well-defined effect on the stoichiometry and/or stereochemistry of the Ni(II) complexes. The observed structural variations may then arise from a balance of various factors, among which a favorable lattice energy certainly plays an important role.

Complexes of the *N*-Chloromethyl-Dabconium Ligand. One of the ligands investigated, the *N*-chloromethyl-Dabconium cation, $\text{L}^+\text{CH}_2\text{Cl}$, is unique as it forms at least six different complexes with nickel(II) chloride, depending on the reaction conditions: a bright blue complex of simple formula $\text{NiCl}_2 \cdot (\text{L}^+\text{CH}_2\text{Cl})\text{Cl}$, a deep pink complex $\text{NiCl}_2 \cdot (\text{L}^+\text{CH}_2\text{Cl})\text{Cl} \cdot (\text{L}^+\text{CH}_2\text{Cl})(\text{Cl} \text{ or } \text{ClO}_4)$, a blue-gray complex $3\text{NiCl}_2 \cdot 2(\text{L}^+\text{CH}_2\text{Cl})\text{Cl}$, a red complex $\text{NiCl}_2 \cdot 2(\text{L}^+\text{CH}_2\text{Cl})\text{Cl} \cdot \text{H}_2\text{O}$, and finally a purple complex also of simple formula $\text{NiCl}_2 \cdot (\text{L}^+\text{CH}_2\text{Cl})\text{Cl}$. The first three of these compounds were identified, on the basis of their d-d electronic and vibrational infrared spectra, as the nonionic, four-coordinate, pseudotetrahedral $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})]$, and the ionic, five-coordinate, trigonal-bipyramidal $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})_2]\text{Cl}$ and $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})_2] \cdot \text{ClO}_4$. These complexes are of the same type obtained with the other Dabconium ligands listed in Table I and generally resemble the corresponding complexes of the *N*-methyl-Dabconium and protonated Dabconium ligands previously reported.^{1,4} The blue $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})]$, however, differs from the other Dabconium complexes of this formula (Table I) since it tends to convert into its purple isomer, discussed later. The d-d absorption spectra of the five-coordinate complexes $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})_2]\text{Cl}$ and $[\text{NiCl}_3(\text{L}^+\text{CH}_2)_2]\text{ClO}_4$, shown in Figure 2a, are very similar to that of $[\text{NiCl}_3(\text{H}_2\text{O})(\text{L}^+\text{CH}_3)]$, for which a trigonal-bipyramidal geometry was established by a three-dimensional X-ray structural investigation reported

Table II. Some Properties of Ni(II) Complexes Containing the *N*-Chloromethyl-Dabconium Ligand

| Complex ^a | Color | d-d absorptions ^b (kK) and assignments | | Assigned structure | |
|---|-----------|---|--|--|--|
| [NiCl ₃ (L ⁺ CH ₂ Cl)] ^c | Blue | 6.0 | ³ A ₁ (T ₂ , F) ← ³ E(T, F) ^d | Four-coordinate pseudotetra- hedral zwitterion complex | |
| [NiCl ₃ (H ₂ O)(L ⁺ CH ₂ Cl)] · (L ⁺ CH ₂ Cl)Cl | Red | 8.9 | ³ A ₂ (F) | Five-coordinate, trigonal- bipyramidal, zwitterion complex with "free" ligand chloride in the lattice | |
| | | 16.4 ^e | ³ E', ³ A ₂ (T ₂ , F) | | |
| | | 5.0 | ³ E''(F) ← ³ E'(F) ^f | | |
| | | 10.8 | ³ A ₂ (F) | | |
| [NiCl ₃ (L ⁺ CH ₂ Cl) ₂]Cl (or ClO ₄) | Pink | 18.0 sh | ³ E''(P) | Ionic compound with five- coordinate, trigonal- bipyramidal complex cation | |
| | | 20.7 | ³ A ₂ '(P) | | |
| | | 5.7 | ³ E''(F) ← ³ E'(F) ^f | | |
| | | 10.9 | ³ A ₂ '(F) | | |
| | | 17.8 sh | ³ E''(P) | | |
| [NiCl ₃ (L ⁺ CH ₂ Cl) ₂] ₂ [NiCl ₄] | Blue-gray | Cation | 20.5 | ³ A ₂ '(P) | Ionic compound with five- coordinate, trigonal- bipyramidal complex cation and tetrahedral complex anion |
| | | | 5.7 | ³ E''(F) ← ³ E'(F) ^f | |
| | | | 11.1 | ³ A ₂ '(F) | |
| | Anion | 20.8 | ³ A ₂ '(P) | | |
| | | 7.6 | ³ T ₂ (F) ← ³ T ₁ (F) ^h | | |
| | | 13.7 | ³ A ₂ (F) | | |
| [Ni ₂ Cl ₆ (L ⁺ CH ₂ Cl) ₂] | Purple | 20.8 | ³ T ₁ (P) | Five-coordinate, chloro- bridged, dimeric complex | |
| | | 5.2 | | | |
| | | 10.7 | | | |
| | | 14.8 ^g | | | |
| | | 17.8 sh | | | |
| | | 19.8 | | | |

^a L⁺CH₂Cl = *N*-chloromethyl-Dabconium, (CH₂Cl)N⁺(CH₂CH₂)₃N. ^b Values reported are absorption maxima from diffuse reflectance spectra at room temperature; sh is shoulder. ^c Pure, or as a crystalline solution with the isomorphous [ZnCl₃(L⁺CH₂Cl)] complex. ^d Reference 3. ^e Midpoint of ill-resolved doublet. ^f Reference 6. ^g Very sharp, weak band. ^h Reference 9.

by Stucky.⁵ Accordingly, the assignments of the observed transitions, listed in Table II, follow those of [NiCl₃(H₂O)(L⁺CH₂Cl)], whose entire spectrum at liquid nitrogen temperature had been fitted very satisfactorily to the energy level diagram calculated by Ciampolini⁶ for Ni(II) in a trigonal-bipyramidal configuration of five equivalent dipoles.

The blue-gray complex of simple formula 3NiCl₂ · 2(L⁺CH₂Cl)Cl is assigned the structural formula [NiCl₃(L⁺CH₂Cl)₂]₂[NiCl₄] on the basis of its d-d electronic spectrum (Figure 2c) and vibrational infrared spectrum. In this complex salt the cation [NiCl₃(L⁺CH₂Cl)₂]⁺ is the same trigonal-bipyramidal entity present in the chloride and perchlorate complex salts discussed above, and the NiCl₄²⁻ anion is as usual tetrahedral. In fact, both the color and the d-d electronic spectrum of [NiCl₃(L⁺CH₂Cl)₂]₂ · [NiCl₄] can be reproduced by mixing [NiCl₃(L⁺CH₂Cl)₂]Cl with the NiCl₄²⁻ anion (for example as the tetraethylammonium salt) in a 2:1 molar ratio.

The deep purple complex of simple formula NiCl₂ · (L⁺CH₂Cl)Cl, obviously a structural isomer of the blue, pseudotetrahedral [NiCl₃(L⁺CH₂Cl)], has a magnetic moment of 3.45 BM and a d-d electronic spectrum (Figure 2d) characteristic of five-coordinate Ni(II)^{1,4,6,7} even though not clearly diagnostic of its exact stereochemistry. The pseudotetrahedral [NiCl₃(L⁺CH₂Cl)] can change to a five-coordinate geometry only by dimerization *via* halogen bridging as shown schematically in Figure 1b. Dimerization of this type has been observed⁵ for the tetrahedral anion NiCl₄²⁻, which under special conditions forms a five-coordinate chloro-bridged dimer, Ni₂Cl₈⁴⁻, whose structure has been confirmed by a three-dimensional X-ray study.⁸ The logical formulation of the purple isomer of composition NiCl₂ · (L⁺CH₂Cl)Cl as a chloro-

bridged dimeric species, [Ni₂Cl₆(L⁺CH₂Cl)₂], is supported by the position of its d-d absorption bands which appear midway between those of [NiCl₃(L⁺CH₂Cl)₂]⁺ and Ni₂Cl₈⁴⁻ (Figure 2e). Such a formulation is further supported by the presence, in the far-infrared spectrum, of a very strong, broad, asymmetric absorption near 250 cm⁻¹, assigned to the Ni-Cl stretching modes. This absorption, similar to that observed for Ni₂Cl₈⁴⁻, very likely arises from the overlap of Ni-Cl stretching vibrations involving terminal as well as bridging Cl atoms.

The purple dimer [Ni₂Cl₆(L⁺CH₂Cl)₂] is far more easily obtained than the blue monomer [NiCl₃(L⁺CH₂Cl)] and is generally more stable. In fact, the blue monomer readily transforms into the purple dimer in the presence of appropriate solvents and sometimes even when dry and pure. On the other hand, the reverse transformation, purple dimer → blue monomer, has never been observed to occur. Unfortunately, it has not been possible to find conditions suitable for the measurement of the difference in enthalpy of the blue and purple isomers.

The red complex of simple formula NiCl₂ · 2(L⁺CH₂Cl)Cl · H₂O has a d-d electronic spectrum (Figure 2b) identical with that of the red, trigonal-bipyramidal complex of *N*-methyl-Dabconium, [NiCl₃(H₂O)(L⁺CH₂Cl)]. The vibrational spectrum shows the absorptions characteristic of both coordinated and "free" *N*-chloromethyl-Dabconium as well as those attributable to coordinated water ($\nu(\text{OH}_2)$ 3485 cm⁻¹ vs. 3318 vs; $\delta(\text{OH}_2)$ 1638 s; $\rho(\text{OH}_2)$ 640 m, br). Deuteration of the complex causes the expected isotopic shifts for these absorptions (Figure 3). Thus, the red compound is formulated as [NiCl₃(H₂O)(L⁺CH₂Cl)] · (L⁺CH₂Cl)Cl, with the coordination entity having a five-coordinate, trigonal-bipyramidal stereochemistry. A very unusual feature of this complex is the pattern of the infrared absorption arising from the antisymmetric and symmetric OH stretching vibrations. For most aquo complexes of metals, even those containing a single H₂O

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

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

(7) V. L. Goedken, L. M. Vallarino, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **92**, 303 (1970).

(8) F. K. Ross and G. D. Stucky, *J. Amer. Chem. Soc.*, **92**, 4538 (1970).

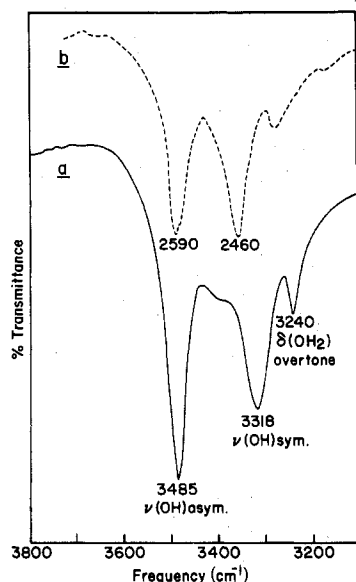


Figure 3. Infrared absorptions due to the stretching vibrations of coordinated water in $[\text{NiCl}_3(\text{H}_2\text{O})(\text{L}^+\text{CH}_2\text{Cl})] \cdot (\text{L}^+\text{CH}_2\text{Cl})\text{Cl}$ (solid line) and its deuterated analog (dashed line).

molecule, the OH stretching absorption appears as a broad band, which occasionally shows two ill-resolved maxima. In contrast, the OH stretching modes of $[\text{NiCl}_3(\text{H}_2\text{O})(\text{L}^+\text{CH}_2\text{Cl})] \cdot (\text{L}^+\text{CH}_2\text{Cl})\text{Cl}$ give rise to two narrow, sharp, and well-resolved peaks (Figure 3) separated by about 160 cm^{-1} —a separation greater by 55 cm^{-1} than that of water vapor and as large as that observed for dilute solutions of water in mixed solvents such as $\text{CCl}_4\text{-CH}_3\text{NO}_2$ or $\text{CCl}_4\text{-CH}_3\text{CN}$. In these solutions the H_2O molecules are believed to exist as monomers and to be hydrogen bonded to the base, CH_3NO_2 or CH_3CN , through only one of the H atoms. Thus, it is reasonable to assume that in the complex $[\text{NiCl}_3(\text{H}_2\text{O})(\text{L}^+\text{CH}_2\text{Cl})] \cdot (\text{L}^+\text{CH}_2\text{Cl})\text{Cl}$ the H_2O molecule is hydrogen bonded to the tertiary nitrogen atom of the “free” Dabconium ligand (Figure 1c) rather than to the “free” Cl^- ion. This kind of hydrogen bonding might then explain why water adds so readily and reversibly to $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})_2]\text{Cl}$ but does not add to the dimer $[\text{Ni}_2\text{Cl}_6(\text{L}^+\text{CH}_2\text{Cl})_2]$ or to the monomer $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})]$, neither of which contains a “free” Dabconium ligand available for hydrogen bonding.

The interrelationships among the various Ni(II) complexes of the *N*-chloromethyl-Dabconium ligand are summarized in Figure 4.

Solution Equilibria among Four-, Five-, and Six-coordinate Ni(II) Complexes Containing the *N*-Chloromethyl-Dabconium Ligand. All metal complexes of the Dabconium ligands so far investigated, once isolated in the crystalline state, are insoluble in all noncoordinating solvents. This lack of solubility may be attributed to the high lattice energy arising from the electrostatic attractions between the positively charged quaternized N atoms of the Dabconium ligands and neighboring Cl ligands, or “free” Cl^- ions, in the crystal lattice. It was observed, however, that under appropriate conditions some Ni(II) complexes containing Dabconium ligands exist also in nitromethane solution, although in a metastable state with respect to precipitation of the crystals. The time interval during which these complexes remain in solution depends on various factors, such as the quaternizing group R of the Dabconium ligand, the concentration of the ligand chloride

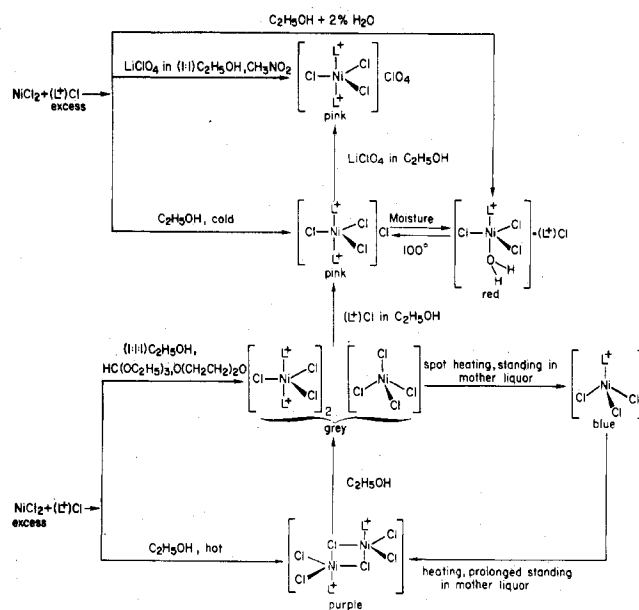


Figure 4. Relationships among the Ni(II) complexes of the *N*-chloromethyl-Dabconium ligand, L^+ .

and nickel(II) chloride, and the temperature of the solution. When the quaternizing group R is CH_2Cl , the complexes remain in solution long enough to permit a spectroscopic structural study of the NiCl_2 -*N*-chloromethyl-Dabconium chloride system over a range of temperatures.

The most favorable conditions are achieved by rapidly adding an approximately $10^{-2} M$ solution of NiCl_2 in ethanol-nitromethane (30:70 mixture) to a 50-fold excess of *N*-chloromethyl-Dabconium chloride in ethanol-nitromethane (5:95 mixture). The small amount of ethanol is necessary initially to bring the NiCl_2 into solution and prevent its precipitation in the presence of nitromethane, and the large excess of Dabconium ligand is required to minimize the effect on the equilibrium of the competing ligand $\text{C}_2\text{H}_5\text{OH}$ and ensure that virtually all Ni(II) will be present in solution as Dabconium complexes.

The d-d electronic spectrum of the solution, measured at different temperatures (Figure 5), shows the presence of four major complex species—the tetrahedral $[\text{NiCl}_4]^{2-}$ anion (blue), the pseudotetrahedral nonionic $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})]$ (blue), the trigonal-bipyramidal cation $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})_2]^+$ (deep pink), and an octahedral species (green) of unidentified composition. The $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})]$ and $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})_2]^+$ species in solution were identified by comparison with the diffuse reflectance and transmission (mull) spectra of the corresponding crystalline compounds. At higher temperatures, 80–60°, the solution is blue, and a major portion (about 75–80%) of the Ni(II) is present as the pseudotetrahedral, nonionic $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})]$; together with some tetrahedral $[\text{NiCl}_4]^{2-}$. The solution gradually becomes purple upon cooling, and at 20° it contains approximately a 50:50 mixture of pseudotetrahedral $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})]$ and trigonal-bipyramidal $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})_2]^+$. As the temperature is lowered below –30°, the pink color gradually fades while a pale green color appears, and the spectrum now shows absorptions characteristic of Ni(II) in an octahedral environment.

The gradual change from four- to five- to six-coordination, which occurs when the temperature of the solution is lowered from +80 to –30°, reverses when the temperature is raised from –30 to +80°. Thus, even though the

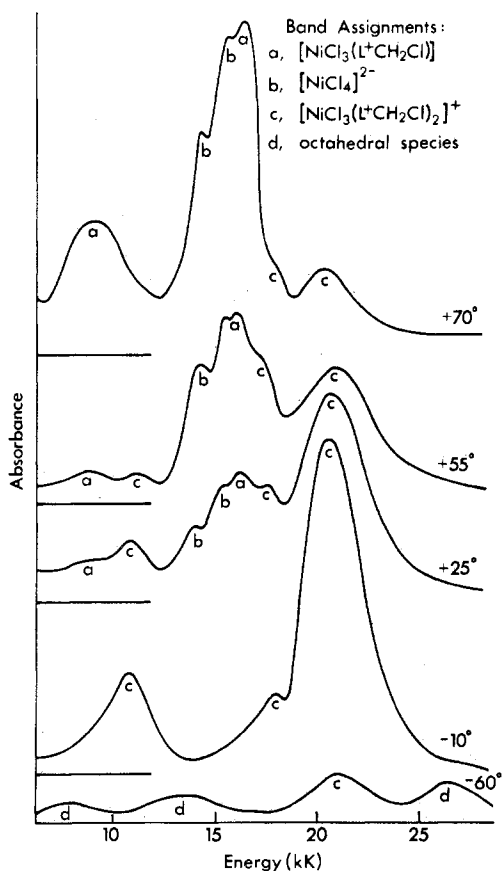


Figure 5. d-d electronic spectra of a nitromethane solution of NiCl_2 and $(\text{L}^+\text{CH}_2\text{Cl})\text{Cl}$ at various temperatures.

solution is supersaturated with respect to each individual complex species, the interconversion of the various species in solution is reversible, and to each temperature corresponds a well-defined equilibrium mixture of various species.

At about 0° , virtually all $\text{Ni}(\text{II})$ is present as the five-coordinate species $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})_2]^+$; the molar extinction coefficients of the absorptions at 20.5 and 17.8 kK were then calculated to be 125 and 36, respectively. On this basis, the extinction coefficient of the highest energy band (16.4 kK) of the pseudotetrahedral species $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})]$ was estimated to be about 175, in good agreement with the expected value. The absorption bands of the octahedral species formed at low temperature occur at approximately 8, 14, and 26 kK and have molar extinction coefficients between 5 and 10. From the estimated value of the average ligand field, it seems reasonable to assume that this low-temperature octahedral species results from the coordination of an oxygen donor ligand, either an ethanol or a nitromethane molecule, to the five-coordinate $[\text{NiCl}_3(\text{L}^+\text{CH}_2\text{Cl})_2]^+$ cation.

It is well known that nickel(II) often exhibits equilibria between two or more complex species in solution.^{9,10} Usually these equilibria involve either substitution reactions among species of the same coordination number and stereochemistry, or dissociation-association reactions between six- and four-coordinate species. The complexes of $\text{Ni}(\text{II})$ with Dabconium ligands represent an unusual example of an equilibrium involving four-, five-, and six-coordinate species—with the five-coordinate, trigonal-

bipyramidal species being the most stable within a well-defined although narrow temperature interval. This result is very significant in our studies of positively charged ligands, as it offers the first opportunity to evaluate the electronic effects of the positively charged ligands in the absence of the effects of crystalline lattice energy.

It is reasonable to assume that in solution the stabilization of the unusual five-coordinate species results from the perturbation of the N-donor atom of the Dabconium ligand by the positive charge of the quaternized N atom, rather than by limitations imposed by the bulk of the Dabconium ligands. This assumption is supported by the observation that solutions containing nickel(II) chloride and the uncharged ditertiary amine Dabco, or the similarly shaped monotertiary amine quinuclidine (Figure 1d) show no evidence for the presence of a five-coordinate species in the $+80$ to -60° temperature range. At room temperature, these solutions are blue-violet and contain only the pseudotetrahedral $[\text{NiCl}_2\text{L}_2]$ species;¹¹ on cooling to about -20° the solutions become green and show the characteristic absorptions of octahedral $\text{Ni}(\text{II})$. If an intermediate five-coordinate species of the type $[\text{NiCl}_3\text{L}_2]^-$ were formed, even in relatively small concentrations, its characteristic highest energy absorption could certainly be detected, since it would occur in a region free from absorptions of either tetrahedral or octahedral species, and moreover it would have a high molar absorptivity. Now the steric requirements of both Dabco and quinuclidine are virtually identical with those of the monoquaternized Dabconium ligands, so their marked difference in donor properties most likely arises from the decreased availability of the lone pair of the Dabconium ligands, as a result of electronic interaction with the positively charged, quaternized N atom. The dramatic decrease in $\text{p}K_a$ values—from 10.6 for quinuclidine and 8.6 for Dabco to about 2.9–3.3 for the monoquaternized Dabconium ligands^{2,4}—is another manifestation of this same effect.

Conclusions

The variation of the electron-withdrawing character of the quaternizing groups of the Dabconium cations affects to some extent the stoichiometry and geometry of the crystalline complexes formed with $\text{Ni}(\text{II})$, although no definite trend was observed. The different structures of the crystalline complexes appear to result from a fine balance of several factors, with slight variations in lattice energy playing a determining role. In the solid state the complexes of the Dabconium ligands with nickel(II) chloride have a pronounced tendency to form four- and five-coordinate species. The five-coordinate species are usually obtained from four-coordinate pseudotetrahedral complexes by addition of a fifth ligand such as a molecule of water or ammonia or an additional Dabconium ligand. In the absence of a suitable fifth ligand, five-coordination can be achieved through dimerization of two tetrahedral species *via* halogen bridging. In these complexes, the tendency to form five-coordination appears to be a result of the diminished availability of the nitrogen lone pair of the monoquaternized Dabconium ligands. The electronic requirements of the metal are then satisfied by the formation of a fifth coordinate covalent bond. Six-coordination is not observed for the solid complexes but does occur in solutions at low temperature, probably through coordination of a solvent molecule.

(9) C. Furlani and G. Morpurgo, *Z. Phys. Chem.*, **28**, 93 (1961).

(10) E. Scaife and K. P. Wood, *Inorg. Chem.*, **6**, 358 (1967).

(11) V. L. Goedken, L. M. Vallarino, and J. V. Quagliano, submitted for publication.

This series of Ni(II) complexes represents a specific example in which four-, five-, or six-coordination is in turn favored by a balance of factors such as relative crystal field stabilization energy, entropy, enthalpy (as demonstrated by the temperature dependence of the equilibria in solution), lattice, and solvation effects. Examples of this type are rare under normal laboratory conditions, but should be considerably more common in systems subjected to high temperatures and pressures. The wide variation in coordination numbers and topological arrangement of coordination polyhedral observed in minerals of transition metal ions is probably due to their formation under conditions of high temperature and pressure where equilibria among many coordination numbers were possible.¹² It is thus suggested that the complexes of Dabconium cations represent merely a special example of a broadly occurring natural phenomenon.

Experimental Section

N-Chloromethyl-Dabconium Chloride, $[N(CH_2CH_2)_3N^+CH_2Cl]Cl^-$. A solution of 10 g of Dabco in 100 ml of a 1:1 acetone-dichloromethane mixture was allowed to stand at room temperature for several days. The white crystalline product which separated slowly was filtered, washed with acetone, and recrystallized by dissolving it in hot ethanol and then diluting the filtered solution with acetone. The product was dried *in vacuo*. *Anal.* Calcd for $[C_7H_{14}N_2Cl]Cl$: N, 14.20; Cl (ionic), 17.98. Found: N, 14.2; Cl (ionic), 17.8. The other alkyl-Dabconium halides listed in Table I were prepared in a similar manner. For details and analytical data, see ref 13.

Preparation of the Complexes. Anhydrous metal chlorides and anhydrous reagent grade solvents were used in the preparation of the complexes.

$[NiCl_3(L^+CH_2Cl)_2]_2[NiCl_4]$. A solution of $NiCl_2$ in a 1:1 mixture of ethanol and triethyl orthoformate was added to a solution of ligand chloride in the same solvent (Ni:ligand mole ratio 4:1). The flocculent blue-gray precipitate that formed immediately was filtered, washed several times with ethanol-triethyl orthoformate, and dried *in vacuo*. *Anal.* Calcd for $(C_7H_{14}N_2Cl)_4Ni_3Cl_{10}$: Ni, 14.97; Cl(except C bonded), 30.14; N, 9.52. Found: Ni, 14.8; Cl, 30.1; N, 9.4. In the preparation of this complex the solutions should be at room temperature. If the solutions are warmed prior to mixing or if the blue-gray precipitate is heated within its mother liquor, the blue $[NiCl_3(L^+CH_2Cl)]$ or the deep-purple $[Ni_2Cl_6(L^+CH_2Cl)_2]$ may form. Also, the blue-gray precipitate if washed with ethanol alone immediately converts to the purple $[Ni_2Cl_6(L^+CH_2Cl)_2]$, while $NiCl_2$ passes into solution.

$[Ni_2Cl_6(L^+CH_2Cl)_2]$. Well-formed, small crystals of this complex were obtained by adding a hot solution of ligand chloride in a 1:1 mixture of ethanol-nitromethane to a hot solution of $NiCl_2$ in the same solvent (Ni:ligand mole ratio 1.5:1). As the solution cooled to room temperature, the purple crystals separated slowly. The precipitate was filtered, washed several times with ethanol, and dried *in vacuo*. The complex is stable to the atmosphere. *Anal.* Calcd for $(C_7H_{14}N_2Cl)_2NiCl_4$: Ni, 17.98; Cl(except C bonded), 32.58; N, 8.57. Found: Ni, 17.8; Cl, 32.7; N, 8.6. The magnetic moment at 25° is $\mu_{eff} = 3.45$ BM.

$[NiCl_3(L^+CH_2Cl)_2]Cl$. A cold, saturated solution of $NiCl_2$ in ethanol was added to a cold, nearly saturated solution of the ligand chloride in nitromethane (Ni:ligand mole ratio 1:3). A flocculent gray precipitate formed immediately, which on stirring redissolved to give a purple solution. From this purple solution, on standing at room temperature, a pink crystalline precipitate formed slowly. It was filtered, washed several times with nitromethane, and dried *in vacuo*. *Anal.* Calcd for $(C_7H_{14}N_2Cl)_2NiCl_4$: Ni, 11.23; Cl(except

C bonded), 27.10; N, 10.70. Found: Ni, 11.0; Cl, 27.3; N, 10.5. The magnetic moment at 25° is $\mu_{eff} = 3.64$ BM. The pink $[NiCl_3(L^+CH_2Cl)_2]Cl$ is very sensitive to atmospheric moisture, which transforms it to the red $[NiCl_3(H_2O)(L^+CH_2Cl)] \cdot (L^+CH_2Cl)Cl$.

$[NiCl_3(L^+CH_2Cl)_2]ClO_4$. A saturated solution of $NiCl_2$ in a 1:1 mixture of ethanol-nitromethane was added to a nearly saturated solution of ligand chloride (Ni:ligand mole ratio 1:4) and $LiClO_4$ (large excess) in the same solvent. A purplish solution resulted, from which upon standing at room temperature a pink crystalline precipitate formed. It was filtered, washed repeatedly with the ethanol-nitromethane mixture, and dried *in vacuo*. *Anal.* Calcd for $(C_7H_{14}N_2Cl)_2NiCl_3(ClO_4)$: Ni, 9.98; Cl(except C and O bonded), 18.09. Found: Ni, 9.6; Cl, 17.7.

$[NiCl_3(H_2O)(L^+CH_2Cl)] \cdot (L^+CH_2Cl)Cl$. A solution of $NiCl_2$ in ethanol was added to a solution of ligand chloride in ethanol containing 2% water (Ni:ligand mole ratio 1:2.5). The red precipitate, which formed slowly, was filtered, washed once with ethanol, and dried *in vacuo*. *Anal.* Calcd for $(C_7H_{14}N_2Cl)_2NiCl_4 \cdot H_2O$: Ni, 10.83; Cl(except C bonded), 26.17; H_2O , 3.32. Found: Ni, 10.6; Cl, 25.9; H_2O , 3.4. This compound was always obtained with 1 mol of ligand chloride in the lattice and apparently would not form unless a sufficiently large excess of ligand chloride is present in the reaction mixture. When heated at 110° the red compound sharply loses water to form the pink $[NiCl_3(L^+CH_2Cl)_2]Cl$.

$[NiCl_3(L^+CH_2Cl)]$. A solution of the ligand chloride in a 1:1:1 mixture of ethanol, triethyl orthoformate, and dioxane was added at once to a solution of $NiCl_2$ in this same solvent (Ni:ligand ratio 2:1). A blue-gray powdery precipitate of $[NiCl_3(L^+CH_2Cl)_2]_2 \cdot [NiCl_4]$ formed immediately. This precipitate, still in its mother liquor, was spot-heated on a microflame and a bright blue color appeared locally. The flame was removed immediately and the blue-gray precipitate changed slowly to the blue $[NiCl_3(L^+CH_2Cl)]$. The blue precipitate was filtered, washed once with the ethanol-triethyl orthoformate-dioxane mixture, and dried *in vacuo*. *Anal.* Calcd for $(C_7H_{14}N_2Cl)NiCl_3$: Ni, 16.99; Cl(except C bonded), 32.95. Found: Ni, 17.1; Cl, 33.1. The desired blue complex $[NiCl_3(L^+CH_2Cl)]$ was obtained pure in only about 20% of the attempts. Otherwise, the blue complex either is not formed at all or is obtained mixed with the blue-gray $[NiCl_3(L^+CH_2Cl)_2]_2 \cdot [NiCl_4]$ or with the deep-purple $[Ni_2Cl_6(L^+CH_2Cl)_2]$ or with both. In the presence of its mother liquor, the blue $[NiCl_3(L^+CH_2Cl)]$ transforms completely into the deep-purple dimer $[Ni_2Cl_6(L^+CH_2Cl)_2]$. Once isolated in the solid state, however, the blue complex is fairly stable in the absence of moisture.

A crystalline solution of $[NiCl_3(L^+CH_2Cl)]$ and $[ZnCl_3(L^+CH_2Cl)]$ was obtained easily as follows. A solution of ligand chloride in a 1:1 mixture of ethanol and nitromethane was added dropwise and with stirring to a hot solution of the nickel(II) and zinc(II) chlorides in the same solvent. A fluffy blue precipitate formed at once which on stirring for 30 min at 70° became heavy and crystalline. The precipitate was filtered, washed with the ethanol-nitromethane mixture, and dried *in vacuo*. As a crystalline solution with the isomorphous Zn(II) complex, the blue $[NiCl_3(L^+CH_2Cl)]$ is not sensitive to atmospheric moisture, nor does it not show any tendency to transform into the purple dimer $[Ni_2Cl_6(L^+CH_2Cl)_2]$.

Characterization of the Complexes. The complexes were characterized by analyses, vibrational and d-d electronic spectra, magnetic susceptibilities, and X-ray powder diffraction spectra. Details of the procedure were described elsewhere.²

Registry No. L^+CH_2Cl , 36273-11-7; $[NiCl_3(L^+CH_2Cl)]$, 36273-12-8; $[Ni_2Cl_6(L^+CH_2Cl)_2]$, 36273-13-9; $[NiCl_3(L^+CH_2Cl)_2]Cl$, 36273-14-0; $[NiCl_3(L^+CH_2Cl)_2]ClO_4$, 36273-15-1; $[NiCl_3(L^+CH_2Cl)_2][NiCl_4]$, 36273-16-2; $[NiCl_3(H_2O)(L^+CH_2Cl)](L^+CH_2Cl)Cl$, 36182-32-8.

Acknowledgment. This research was supported in part by the National Science Foundation under Grant No. NSF GP-22700.

(12) P. Moore, private communication.

(13) V. L. Goedken, Ph.D. Thesis, Florida State University, 1968.