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Pseudo-Tetrahedral Complexes of the Tertiary Amine Quinuclidine with Some Transition Metal Ions

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The direct reaction of the monodentate tertiary amine, quinuclidine, $N(CH_2CH_2)_3CH$ = Q, with the chlorides of Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) in ethanol–diethylether solution yields a series of crystalline complexes of formula $[MCl_2Q_2]$. *On the basis of d–d electronic spectra, vibrational spectra, magnetic properties, and X-ray powder diffraction patterns these complexes are assigned a pseudo-tetrahedral geometry with* C_{2v} *symmetry. The ligand field strength of quinuclidine is discussed in comparison to that of sterically hindered substituted pyridines.*

Introduction

Tertiary aliphatic amines have traditionally been considered to be "poor ligands" toward transition metal ions [1], especially those of the first transition series which tend to attain six-coordination with donor atoms of moderate-to-weak ligand field strength. In fact, although it has been known for some time that tertiary N-donor atoms coordinate fairly readily when present in a polydentate chelating ligand [2], only relatively recently it has been pointed out [3] that transition metal complexes of monodentate tertiary aliphatic amines can be formed under appropriate conditions. Our studies of the donor properties of positively charged tertiary amine ligands [4–6] – in particular those obtained by monoquaternization of the ditertiary cage-like diamine, DABCO (Fig. 1a) – have shown that these ligands coordinate very readily to the d^5 to d^{10} divalent ions of the first transition series – Mn(II) through Zn(II). Furthermore, the metal complexes thus formed were remarkably stable and displayed an unusual tendency to form both four-coordinate pseudo-tetrahedral species with C_{3v} symmetry [4] and five-coordinate species with D_{3h} symmetry [5]. For the five-coordinate complexes of the DABCO-nium ligands, it was difficult to estimate the relative importance of steric and electronic factors in determining this unusual coordination number. Therefore, it appeared worthwhile to investigate for comparison the donor properties of the mono-tertiary amine quinuclidine toward these same metal ions. Quinuclidine has exactly the same steric requirements as the mono-protonated DABCO-nium cation-ligand (Fig. 1c) but differs from it very markedly in the availability of the lone pair on the N-donor atom, as shown by the enormous difference in basicity (pK_A of $[\text{quinuclidine–H}]^+ \cong 11$ [7]; pK_A of $[\text{DABCO–H}_2]^{++} \cong 3$ [4, 7b].

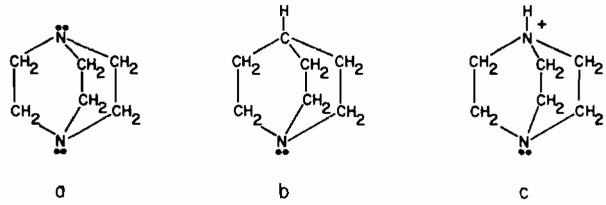

Figure 1. *a*, DABCO; *b*, quinuclidine; *c*, mono-protonated DABCO-nium cation-ligand.

Experimental

Quinuclidine, $N(CH_2CH_2)_3CH$, was obtained from its hydrochloride (Aldrich Chemical Co.) by neutralization with NaOH in concentrated aqueous solution, followed by extraction with diethylether. The ether solution was first dehydrated over KOH pellets, then over alumina (Woelm, neutral, grade 1), and finally it was evaporated to dryness under reduced pressure at 0 °C. Quinuclidine was obtained (90% yields) as colorless crystals, m.p. 157 °C (in sealed capillary); reported for quinuclidine, 158 °C [8]. The infrared spectrum, shown in Fig. 3, agrees with that reported by Bruesch and Guthard [9].

Preparation of the Metal Complexes, $[MCl_2Q_2]$, *M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II)*

An ethanol–ether solution of quinuclidine and an ethanol–ether solution of the metal halide were

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TABLE I. Some Properties of Metal Complexes of Quinuclidine.

Complex[a]	Color	d–d Electronic Absorption Maxima[b] (kK)	M–Cl Stretching Frequencies (cm^{-1})	Analytical Data[d]			
				%Metal		%Chlorine	
				Found	Calcd.	Found	Calcd.
$[FeCl_2Q_2]$	white	4.9, 7.0	325, 285	15.8	16.00	20.1	20.35
$[CoCl_2Q_2]$	blue	6.0(sh), 7.3, 9.3, 16.3[e]	335, 294	16.6	16.73	20.0	20.14
$[NiCl_2Q_2]$	blue–violet	9.3(sh), 10.7, 11.9, 17.3[f]	330, 280	16.6	16.68	20.0	20.15
$[CuCl_2Q_2]$	golden–brown	11.5, 12.8	305, 275	17.7	17.80	19.9	19.88
$[ZnCl_2Q_2]$	white		307, 285	18.2	18.24	19.5	19.81

[a] Q = quinuclidine, $N(CH_2CH_2)_3CH$. [b] Reported values are midpoints of absorption bands in chlorobenzene solutions containing quinuclidine (0.1*M*). Spectra of solid complexes as hexachlorobutadiene mulls agree within experimental error. [c] Spectra as Nujol mulls. [d] Also, % nitrogen:calcd for $[CoCl_2Q_2]$, 7.95; found 7.9. Calcd. for $[NiCl_2Q_2]$, 7.95; found 7.8. Calcd. for $[CuCl_2Q_2]$, 7.85; found, 7.6. [e] With ill-resolved peaks at 15.6, 16.3, and 17.00 kK. [f] With ill-resolved peaks at 17.0 and 18.9 kK.

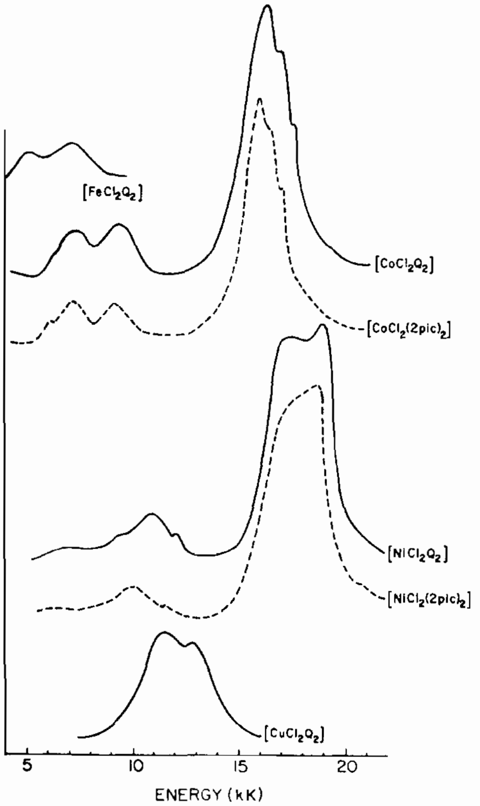

Figure 2. d–d Electronic absorption spectra of the pseudotetrahedral complexes $[MCl_2Q_2]$ and $[MCl_2(2\text{-pic})_2]$ in chlorobenzene solution with 0.1*M* added ligand.

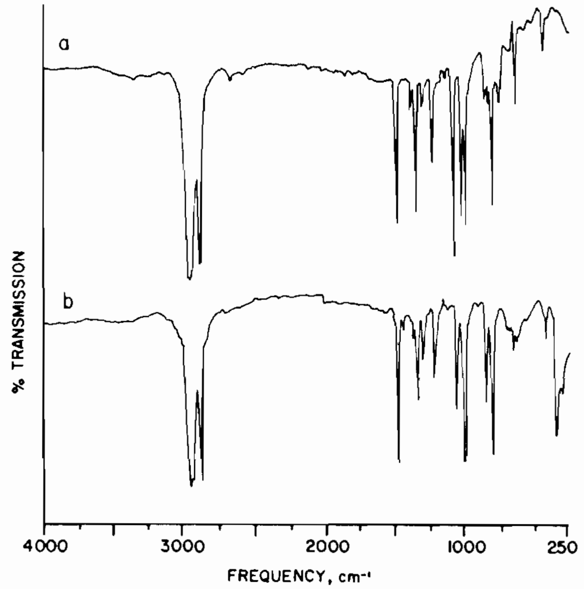

Figure 3. Vibrational spectrum of: *a*, quinuclidine, and *b*, the complex $[CoCl_2Q_2]$ (Nujol and hexachlorobutadiene mulls).

dried over 4-A molecular sieves for several days, until all traces of water were removed. It is important to point out that water should be removed by use of molecular sieves. Dehydration with dimethoxypropane, triethylorthoformate, or similar "dehydrating agents" was unsuccessful because products contaminated with derivatives of the protonated quinuclidinium cation were obtained. The anhydrous metal halide solution was then added dropwise and with stirring to a large excess of the quinuclidine solution at room temperature. The $[MCl_2Q_2]$ complex precipitated immediately as a microcrystalline product provided sufficient ether was present; if not, more ether was added to induce precipitation. The complex was filtered off and dried *in vacuo*. If purification was required, the product was recrystallized by dissolving it in chlorobenzene containing "free" quinuclidine (about 10^{-2} *M*) and diluting the filtered, clear solution with hexane.

The complexes were prepared and handled in a dry box, since all but the Cu(II) complex are extremely

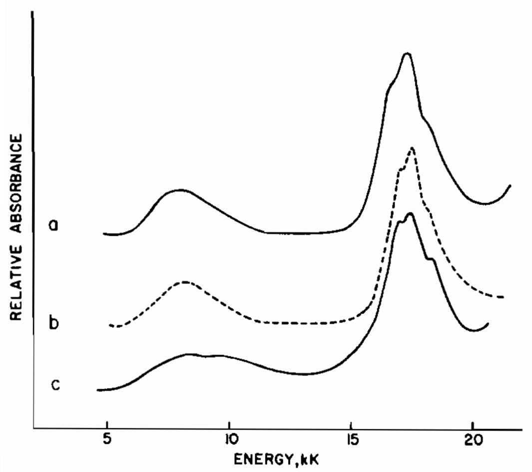

Figure 4. d–d Electronic absorption spectra of: *a*, $[CoQ_4](ClO_4)_2$ in chlorobenzene solution with 0.2*M* added quinuclidine; *b*, $[Co(2\text{-pic})_4](ClO_4)_2$ in chlorobenzene solution with 0.2*M* added 2-picoline; *c*, solid $[Co(2\text{-pic})_4](ClO_4)_2$ as hexachlorobutadiene mull. The strong absorption centered at 17.85 kK is assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ transition and the weaker absorption centered at 8.26 kK is assigned to the $^4A_2 \rightarrow {}^4T_1(F)$ transition of tetrahedrally coordinated Co(II).

sensitive to atmospheric moisture. In addition, the Fe(II) complex was prepared and handled in an oxygen-free atmosphere to prevent immediate oxidation. Analyses and some physical properties of the complexes are listed in Table I. The d–d electronic spectra are shown in Fig. 2 and a representative vibrational spectrum is shown in Fig. 3.

Preparation of $[CoQ_4](ClO_4)_2$ *in Solution*

A sample of the pink crystalline complex $[Co(3,4\text{-dimethylpyridine})_6](ClO_4)_2$ (a potential source of anhydrous Co(II) perchlorate) was added to a 0.2*M* solution of quinuclidine in chlorobenzene which had been dried for one week over molecular sieves. The crystalline starting material, although completely insoluble in chlorobenzene alone, dissolved slowly in the chlorobenzene–quinuclidine mixture giving a purple–blue solution (Co(II), about 10^{-4} *M*) whose d–d electronic spectrum is shown in Fig. 4a. When exposed to moist air the solution discolored immediately and a flocculent brownish–green precipitate formed. A sample of $[Co(3,4\text{-dimethylpyridine})_6](ClO_4)_2$ was similarly dissolved in a 0.2*M* solution of 2-methylpyridine (2-picoline) in chlorobenzene. The d–d electronic spectrum of the purple–blue solution thus obtained (again, Co(II), about 10^{-4} *M*) was identical to that of a dichloromethane–2-picoline solution obtained from an analyzed crystalline sample of $[Co(2\text{-picoline})_4](ClO_4)_2$, and was also almost identical to its mull spectrum [10]. Solutions having identical d–d electronic spectra were similarly obtained, for both quinuclidine and 2-picoline, using as the starting material the crystalline violet complex $[Co(2\text{-methylpyridine-N-oxide})_5](ClO_4)_2$.

Characterization of the Complexes

The complexes were characterized by analyses, vibrational spectra, d–d electronic spectra in the solid state (hexachlorobutadiene mulls or diffuse reflectance) and in chlorobenzene solution, X-ray powder diffraction spectra, and magnetic susceptibilities at room temperature (μ_{eff} for $[CoCl_2Q_2]$, 4.50 B.M.; for $[NiCl_2Q_2]$, 3.53 B.M.). Details of the procedures were described elsewhere [4].

Results and Discussion

In the presence of a large excess of quinuclidine the chlorides of Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) react to form complexes of stoichiometry $MCl_2 \cdot 2Q$ which can be isolated from ethanol–ether solutions as micro-crystalline powders. The reaction is straightforward but requires very careful precautions to eliminate all traces of water from the reactants, the solvents, and the surrounding atmosphere. If moisture is present the quinuclidine complexes either fail to form or are obtained contaminated with varying amounts of hydrolysis side-products.

The $MCl_2 \cdot 2Q$ complexes of Fe(II), Co(II), Ni(II), and Zn(II) have identical X-ray powder patterns, as well as nearly superimposable vibrational spectra, and therefore may be considered to constitute an isostructural series. For the bright blue Co(II) complex and also for the violet–blue Ni(II) complex, the magnetic moments (4.50 B.M. and 3.53 B.M., respectively) and d–d electronic spectra (Table I and Fig. 2) are clearly diagnostic of a high-spin pseudo-tetrahedral geometry approaching C_{2v} symmetry [1]. The Co(II) and Ni(II) complexes can therefore be formulated as the non-ionic species $[CoCl_2Q_2]$ and $[NiCl_2Q_2]$, and a similar structure can be assigned to the isomorphous Fe(II) and Zn(II) complexes. The blue complex $[CoCl_2Q_2]$ is apparently identical to that recently obtained by a somewhat different procedure by Hilliard and Yoke [2b]. Although the gold-colored complex $CuCl_2 \cdot 2Q$ has an X-ray powder pattern that differs somewhat from those of the other $[MCl_2Q_2]$ complexes, its vibrational spectrum is still very similar and its d–d electronic spectrum (Fig. 2) is compatible with that expected for Cu(II) in a pseudo-tetrahedral environment of two Cl and two N donor atoms. Thus the Cu(II) complex may also be assigned a structure similar to other members of this series, although somewhat distorted as expected for a d^9 metal ion. It is interesting that the complex $[CuCl_2Q_2]$ is obtained from ethanol–ether solutions as described in the Experimental Section, whereas from butanol solution Yoke and coworkers isolated a complex of formula $[CuCl_2Q]$ [3b]. This appears to be another example of the directing influence of the solvent on the synthesis of metal complexes.

The crystalline complexes of Co(II), Ni(II), Cu(II), and Zn(II) are quite stable in a dry atmosphere but hydrate very rapidly in the presence of moisture. The iron(II) complex, $[FeCl_2Q_2]$, is also extremely sensitive to atmospheric oxidation. This behavior of $[FeCl_2Q_2]$ contrasts with that of the moderately stable complex $[FeCl_2(quinoline)_2]$ [12], and very likely arises from an initial hydrolysis of the quinuclidine ligand by traces of moisture to form the protonated quinuclidinium cation and readily oxidizable hydroxo-derivatives of Fe(II).

The $[MCl_2Q_2]$ complexes dissolve readily but with extensive solvation in good-donor solvents such as alcohols, dimethylsulfoxide, nitromethane, and dimethylformamide; in water the complexes decompose completely – quinuclidine is protonated and insoluble hydroxo-metal derivatives precipitate. The complexes $[MCl_2Q_2]$ are also readily soluble in aliphatic halocarbons such as dichloromethane and chloroform. However, these solutions are not stable as the solvents slowly quaternize the N-atom of quinuclidine; in dichloromethane, for example, ionic species of the type $[\overset{+}{Q}CH_2Cl][MCl_3Q]$ and $[\overset{+}{Q}CH_2Cl]_2[MCl_4]$ are formed. In chlorobenzene, on the other hand, the $[MCl_2Q_2]$ complexes dissolve sparingly but without dissociation, solvation, or quaternization of the ligand, as shown by the very close similarity between the d–d spectra of the solutions and those of the solid complexes. In very dilute chlorobenzene solution some dissociation takes place with precipitation of the insoluble metal chloride, but this can prevented by the addition of an excess of quinuclidine to the solution.

Because the $[MCl_2Q_2]$ complexes are very difficult to obtain pure and are so easily decomposed under atmospheric conditions, it was necessary to assess the purity of each sample after preparation and again at intervals during its investigation. Fortunately, the vibrational spectra of the $[MCl_2Q_2]$ complexes, and in particular the high energy region between 3500 and 2500 cm^{-1}, are extremely sensitive to the presence of any hydrolysis side-product which would contain $\overset{+}{N}$–H groups or OH^- groups or both, and thus served as a reliable check of their purity. For the pure $[MCl_2Q_2]$ complexes, the spectra are virtually identical throughout the series from Fe(II) to Zn(II) and consist of many intense absorptions arising from the vibrations of coordinated quinuclidine. The pattern of these absorptions closely resembles that of "free" quinuclidine (Fig. 3), indicating that the symmetry of this rigid cage-like ligand is not appreciably altered by coordination of the N atom to a metal ion.

An interesting feature in the vibrational spectra of the $[MCl_2Q_2]$ complexes is the presence, in the low-energy region, of two strong absorptions arising from the antisymmetric and symmetric M–Cl stretching modes. The actual frequency values of these absorptions listed in Table I follow a well-defined trend, parallel to that of the tetrahedral crystal field stabilization energies for these d^6 to d^{10} metal ions. A similar trend of the M–Cl stretching frequencies has been observed for the closely related pseudo-tetrahedral complexes of formula $[M(L^+)Cl_3]$, where L^+ is a monoquaternized DABCO-nium ligand [4], and also for the tetrahedral tetrachlorometallate anions, $[MCl_4]^{2-}$ [13].

This trend therefore appears to be characteristic for a series of isostructural tetrahedral complexes of these metal ions. It may be noted that for each metal ion the M–Cl stretching modes occur at increasingly higher frequencies in going from $[MCl_4]^{2-}$, to $[MCl_3(L^+)]$ and $[MCl_2Q_2]$. A similar shift has been observed for the pseudo-tetrahedral Co(II) and Zn(II) pyridine complexes, $[MCl_3(py)]^-$ and $[MCl_2(py)_2]$, which also have C_{3v} and C_{2v} symmetry, respectively [14]. These frequency shifts may be attributed chiefly to the successive replacement of a negatively charged chloro-ligand by the nitrogen atom of a positively charged or neutral ligand, resulting in an increase of effective positive charge on the central M(II) ion and hence in a higher force constant of the M–Cl bonds.

Although the vibrational spectra were most sensitive in assessing the purity of the $[MCl_2Q_2]$ complexes, the d–d electronic spectra (Fig. 2 and Table I) provided the most diagnostic information on their structure and also on the donor properties of the quinuclidine ligand. For each metal complex, the electronic spectrum of the solid as hexachlorobutadiene mull is identical to that of a chlorobenzene solution, either alone or with added "free" quinuclidine. Thus only two quinuclidine ligands coordinate to the chlorides of these metal ions even in the presence of a large excess (1:100 mol ratio) of ligand. In this respect, quinuclidine behaves similarly to the well-known α-substituted pyridines (α-picoline, and the α,β- and α,γ-lutidines) which even in solutions of the pure liquid ligand form only complexes of the type $[CoCl_2(ligand)_2]$ and $[NiCl_2(ligand)_2]$. The similarity between quinuclidine and the α-substituted pyridines becomes even more striking if one compares the d–d electronic spectra of $[CoCl_2Q_2]$ and $[NiCl_2Q_2]$ with those of the corresponding complexes of, for example, 2-picoline. As Fig. 2 clearly shows, these spectra are almost identical – and yet quinuclidine is a highly basic (pK_A = 10.65) [7] aliphatic sigma-donor ligand, whereas 2-picoline is moderately basic (pK_A = 5.97) [15] and is a typical aromatic N-heterocyclic ligand also capable of π-interactions with a metal ion. It was tempting to explain the similarity of these spectra by assuming that in each case the somewhat polarizable chloro-ligands so adapt their electronic contribution to compensate for minor differences in the donor properties of their partner N-donor ligands. To elucidate this point, chlorobenzene solutions containing the ionic tetrahedral species $[CoQ_4](ClO_4)_2$ and $[Co(2\text{-pic})_4](ClO_4)_2$ were prepared. Again, as illustrated in Fig. 4, the spectra of the two complexes containing the $[CoN_4]$ chromophore are virtually identical, thus showing that indeed quinuclidine and 2-picoline have practically the same ligand field strengths although they differ vastly in basicity and in the electronic character of their N-donor atoms. From the energy of the observed absorptions of the $[CoQ_4]^{2+}$ and $[Co(2\text{-pic})_4]^{2+}$ species, the 10 Dq and B values of quinuclidine and 2-picoline are calculated to be 485 cm^{-1} and 770 cm^{-1}, respectively. Thus quinuclidine and α-picoline occupy a position slightly higher than that of the NCS^- ion in the spectrochemical series of tetrahedral Co(II).

The formation of the $[CoQ_4]^{2+}$ complex ion in solution indicates that there is no insurmountable steric hindrance to the tetrahedral coordination of four quinuclidine ligands to a metal ion. Thus, no serious steric hindrance would be expected for "mixed" chloroquinuclidine five-coordinate species of the type $[NiCl_2Q_3]$ or $[NiCl_3Q_2]^-$, similar to the trigonal bipyramidal complexes formed under analogous conditions by the mono-quaternized DABCO-nium ligands. However, a careful spectroscopic investigation of a chlorobenzene solution of $[NiCl_2Q_2]$, in the presence of a very large excess of free quinuclidine, showed no evidence for a five-coordinate species in the temperature range between +60° and −10 °C. Even if only a small quantity of such a species were formed it should be easily detected since the characteristic intense absorptions of high-spin five-coordinate Ni(II) occur in regions of the spectrum not obscured by absorptions of the tetrahedral species.

Conclusions

This study of the donor properties of quinuclidine toward transition metal ions leads to some very interesting conclusions. First, quinuclidine is not a "poor" ligand; in fact, from the view-point of ligand field strength it is virtually identical with the substituted pyridines – and these are among the "best" tertiary N-donor ligands. The experimental difficulty in obtaining the transition metal complexes of quinuclidine, and the lack of stability of the complexes themselves in the presence of atmospheric moisture, arise not from an intrinsically poor donor ability of the N-atom of quinuclidine toward metal ions, but rather from its exceptionally great tendency to act as an electron pair donor toward the proton of water or toward any other suitable electrophile – for example, the "$\overset{+}{C}H_2Cl$" group of the solvent dichloromethane. The basicity of quinuclidine (pK_A = 10.65) is greater than that of 2-picoline (pK_A = 5.97) by a factor of about 10^5. Thus, it is not surprising that in the presence of even minute traces of water, and of metal ions which can assist in an hydrolysis process by forming insoluble hydroxo-derivatives, quinuclidine should tend to protonate rather than coordinate as an uncharged ligand.

Another interesting observation arising from our study is that quinuclidine does not show especially stringent steric requirements, since four quinuclidine ligands can be accommodated around Co(II) in the tetrahedral complex cation $[CoQ_4]^{2+}$. It is therefore reasonable to assume that there should be no forbidding steric hindrance to the formation of five-coordinate, trigonal bipyramidal quinuclidine complexes such as $[MCl_3Q_2]^-$ or $[MCl_2Q_3]$. Our failure to observe any such species, under conditions similar to those which favor the five-coordinate complexes of the equally bulky DABCO-nium cations, lends support to the view that these positively charged ligands favor five-coordination owing chiefly to electronic rather than steric factors.

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