

Positively Charged Ligands. The Donor Properties
of the 1,1,4-trimethylpiperazinium(+1) CationA.S.N. Murthy, J.V. Quagliano, and L.M. Vallarino¹

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The 1,1,4-trimethylpiperazinium(+1) cation (L^+), which has a tertiary N-atom available for coordination, acts as a ligand in a number of transition metal complexes of the type $[MX_3(L^+)]$, where $M = Co^{II}$, Ni^{II} , Cu^{II} , and Zn^{II} , and $X = Cl, Br, \text{ and } I$. However, the donor properties of this cation are relatively weak, and under slightly different conditions the salts $(L^+)_2[CoCl_4]$ and $(L^+)_2[MnX_4]$ ($X = Cl, Br, I$) are formed. With traces of water present in the reaction mixture, protonation of the N-tertiary atom occurs, and salts of the type $(LH^{2+})[MX_4]$ are obtained ($M = Mn^{II}, Ni^{II}, Cu^{II}$; $X = Cl, Br$).

Introduction

Coordination compounds of monodentate tertiary amines with the metal ions of the second half of the transition series are relatively scarce and it has been generally accepted that aliphatic tertiary N-atoms are poorer donors toward metal ions than are secondary and primary N-atoms.² In general, tertiary amino-groups coordinate more readily if they are incorporated in a polydentate chelating ligand,³ but even then the ligand field strength of tertiary N-atoms appears to be lower than that of secondary and primary N-atoms. Since the pK_a values of related amines usually vary in the reverse order (tertiary N > secondary N > primary N), it is reasonable to assume that steric hindrance of the bulky and flexible substituents is an important factor which prevents coordination of the tertiary amines to metal ions. Recent studies on the metal complexes of quinuclidine (Figure 1a), whose cage-like structure minimizes the steric hindrance of the tertiary N-atom, confirm this assumption.⁴ However, even with quinuclidine one serious experimental difficulty remains: the basicity of the tertiary N-atom is so high that in solutions containing hydrolyzable metal ions the salts of the protonated quinuclidinium cation are often formed rather than the complexes of quinuclidine itself. Thus it appears that the coordination of a monodentate tertiary N-donor

ligand to a metal ion should be favored when the steric hindrance of the ligand is reduced and its basicity is lowered. Both requirements are met by the positively charged ligands obtained by monoquaternization of the cage-like ditertiary amine DABCO (Figure 1b) and in fact these ligands coordinate readily to metal ions, forming a variety of stable complexes with unusual structures and stereochemistries.⁵

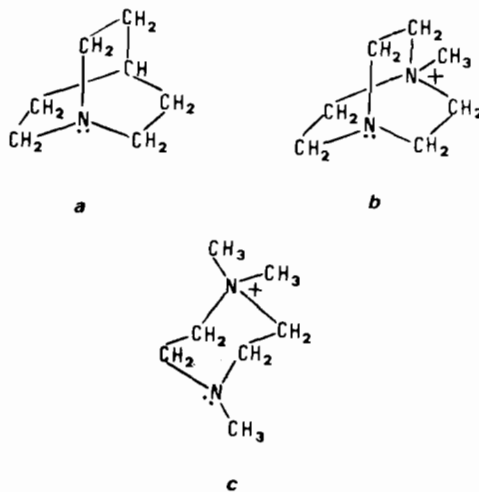


Figure 1. a, Quinuclidine b, N-methyl-DABCO-nium; c, 1,1,4-trimethylpiperazinium.

Our investigation has now been extended to consider positively charged tertiary N-donor ligands in which both steric hindrance and basicity are only slightly less favorable to coordination than those of the monoquaternized DABCO ligands—for example, the 1,1,4-trimethylpiperazinium cation (Figure 1c). This paper reports the reaction between the halides of this cation and the halides of the d^5 to d^{10} metal ions, Mn^{II} through Zn^{II} (except for Fe^{II}) which are known to have closely related acceptor properties.

Experimental Section

Preparation of the Ligands. The 1,1,4-trimethyl-

(1) To whom correspondence should be addressed.
(2) * The Chemistry of Coordination Compounds. » J.C. Bailar, Ed., Reinhold Publishing Corp., New York, N.Y., (1956), p. 62.
(3) (a) F.G. Mann and H.R. Watson, *J. Chem. Soc.*, 2772 (1958), and references therein. (b) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 6, 262 (1967). (c) S.F. Pavkovic and D.W. Meek, *Inorg. Chem.*, 4, 20 (1965). (d) D.W. Meek, *Inorg. Chem.*, 4, 250 (1965). (e) D.W. Meek, S.A. Ehrhardt, *Inorg. Chem.*, 4, 250 (1965). (f) D.W. Meek, S.A. Ehrhardt, *Inorg. Chem.*, 4, 584 (1965).
(4) V.L. Goedken, J.V. Quagliano, and L.M. Vallarino, *Inorg. Chem.*, in press.

(5) (a) J.V. Quagliano, A.K. Banerjee, V.L. Goedken, and L.M. Vallarino, *J. Am. Chem. Soc.*, 92, 482 (1970). (b) V.L. Goedken, J.V. Quagliano, and L.M. Vallarino, *Inorg. Chem.*, 8, 2331 (1969).

piperazinium(+1) iodide, $[(\text{CH}_3)_2\text{N}^+(\text{CH}_2\text{CH}_2)_2\text{N}-\text{CH}_3]\text{I}^-$, was prepared by the dropwise addition of methyl iodide to a chilled and stirred acetone solution of 1,4-dimethylpiperazine (mole ratio 1:1). The colorless precipitate which formed was filtered off, washed with acetone and then with diethylether, and recrystallized from hot ethanol. *Anal.* Calcd for $\text{C}_7\text{H}_{17}\text{N}_2\text{I}$: I, 49.54. Found: 48.9. The corresponding chloride and bromide were prepared from the iodide by ion-exchange in aqueous solution, using Dowex 1 X-8 resin in the chloride and bromide forms. The effluents were evaporated to dryness and the products recrystallized from hot ethanol. *Anal.* Calcd for $\text{C}_7\text{H}_{17}\text{N}_2\text{Cl}$: Cl, 21.52; N, 17.01. Found: Cl, 21.2; N, 17.5. Calcd for $\text{C}_7\text{H}_{17}\text{N}_2\text{Br}$: Br, 38.20; N, 13.39. Found: Br, 38.3; N, 13.4.

Preparation of the Complexes $[\text{MX}_3(\text{L}^+)]$. $[\text{CoCl}_3(\text{L}^+)]$, $[\text{CoBr}_3(\text{L}^+)]$, $[\text{CoI}_3(\text{L}^+)]$, $[\text{NiCl}_3(\text{L}^+)]$, $[\text{NiBr}_3(\text{L}^+)]$, $[\text{NiI}_3(\text{L}^+)]$, $[\text{ZnCl}_3(\text{L}^+)]$, $[\text{ZnBr}_3(\text{L}^+)]$, and $[\text{ZnI}_3(\text{L}^+)]$. The ligand salts $(\text{L}^+)\text{X}$, and the corresponding metal salts, MX_2 , were separately dissolved in a mixture of ethanol (50%), nitromethane (40%), and triethylorthoformate (10%). These solutions were heated to boiling for a few minutes to remove all traces of water, and the hot solution of the ligand was added dropwise and with stirring to the hot solution of the metal salt. Some of the complexes precipitated immediately as crystalline powders; others separated as well-formed crystals after the reaction mixture was heated just below boiling for about 10 min. and then cooled in a refrigerator for several hours. The products thus obtained were filtered off, washed repeatedly with small volumes of the solvent-mixture, and dried *in vacuo*. In most cases the products were analytically pure. If purification was necessary, the original products were recrystallized by dissolving them in hot nitromethane, diluting the filtered solution with twice the volume of anhydrous ethanol, and cooling in a refrigerator overnight. It should be noted that the mole ratio of $(\text{L}^+)\text{X}$ and MX_2 has little or no influence in the preparation of these $[\text{MX}_3(\text{L}^+)]$ complexes, provided the solutions are rigorously anhydrous.

$[\text{CuCl}_3(\text{L}^+)]$. A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmole) in 95% ethanol was treated with an excess of $(\text{L}^+)\text{Cl}$ (1.5 mmoles) in 95% ethanol. The yellow-tan amorphous precipitate which formed at once became bright yellow and crystalline after the reaction mixture was heated for 10 min at 70-75°C. The product was filtered, washed with hot anhydrous ethanol and recrystallized as described for the other $[\text{MX}_3(\text{L}^+)]$ complexes.

$\text{CuBr}_2 \cdot (\text{L}^+)\text{Br}$. A dark-brown complex of this composition was obtained as follows. A hot solution of CuBr_2 (1.5 mmoles) in a mixture of ethanol (50%), nitromethane (40%), and triethylorthoformate (10%), was added dropwise and with stirring to a hot solution of $(\text{L}^+)\text{Br}$ (1 mmole) in the same mixed solvent. The reaction mixture was heated just below boiling for about 10 min, and the dark brown crystalline precipitate thus obtained was filtered, washed with hot anhydrous ethanol, and dried *in vacuo*. If the CuBr_2 and L^+Br solutions are not both carefully de-

hydrated before mixing, the product formed contains variable quantities of the dark brown salt $(\text{LH}^{++})\text{[CuBr}_4]$, which can be identified by its characteristic infrared spectrum.

Some Properties of the $[\text{MX}_3(\text{L}^+)]$ Complexes. Colors, magnetic moments and analytical data of the $[\text{MX}_3(\text{L}^+)]$ complexes are given in Table I. The crystalline Co^{II} , Zn^{II} , and Cu^{II} complexes are not affected by exposure to atmospheric moisture. The crystalline Ni^{II} complexes, on the other hand, are very hygroscopic and rapidly decompose in moist air to give a green sticky substance.

All the $[\text{MX}_3(\text{L}^+)]$ complexes are insoluble in non-polar solvents and dissolve with solvation in polar solvents. The solution behavior of the $[\text{CoX}_3(\text{L}^+)]$ complexes in nitromethane is rather interesting. The $d-d$ spectra of saturated solutions ($\sim 10^{-3} M$) of $[\text{CoX}_3(\text{L}^+)]$ show the presence of a pseudo-tetrahedral species of C_{3v} symmetry, very close in crystal field parameters to the crystalline complexes. For the bromo-complex, for example, the absorption maxima in KCl and the molar absorptancies are: 6.9(60), 16.1(480), 14.9(660), 14.8(720). These solution species, however, are identical to those present in the solutions of the tetrahalocobaltate(II) anions,⁶ and have been identified as the solvates $[\text{CoX}_3(\text{CH}_3\text{NO}_2)]^-$. Thus, the $[\text{CoX}_3(\text{L}^+)]$ complexes, when dissolved in nitromethane, undergo a solvation reaction: $[\text{CoX}_3(\text{L}^+)] + \text{CH}_3\text{NO}_2 \rightleftharpoons [\text{CoX}_3(\text{CH}_3\text{NO}_2)]^- + \text{L}^+$, which is completely shifted to the right at $10^{-3} M$ concentration. This explains the electrical conductivity of the solutions (Δ_M in $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$: $[\text{CoCl}_3(\text{L}^+)]$, 80; $[\text{CoBr}_3(\text{L}^+)]$, 89; $[\text{CuCl}_3(\text{L}^+)]$, 82), whose values are characteristic of 1:1 electrolytes.

Preparation of the Salts $(\text{L}^+)_2[\text{MX}_4]$. The Mn^{II} derivatives were obtained by adding a hot solution of MnX_2 (1 mmole) to a hot solution of the ligand (2-3 mmoles). The same mixed solvent was used as in the preparation of the $[\text{MX}_3(\text{L}^+)]$ complexes of Co^{II} , Ni^{II} , and Zn^{II} . The crystalline products were filtered, washed repeatedly with the solvent mixture, and dried *in vacuo*.

The salt $(\text{L}^+)_2[\text{CoCl}_4]$ was prepared by adding CoCl_2 (1 mmole) to $(\text{L}^+)\text{Cl}$ (2-3 mmoles), both reactants being dissolved in a mixture of ethanol (90%) and water (10%). The resulting purplish solution was heated to boiling and treated dropwise with a small quantity of triethylorthoformate. The pale blue precipitate (shiny leaflets) which formed after a few minutes was filtered, washed with anhydrous ethanol, and dried *in vacuo*.

The analytical data of the salts $(\text{L}^+)_2[\text{MX}_4]$ are given in Table II.

Preparation of the Salts $(\text{LH}^{++})[\text{MX}_4]$. The Mn^{II} derivatives were obtained directly from $(\text{L}^+)\text{X}$ and MnX_2 , under conditions similar to those described for the preparation of the $[\text{MX}_3(\text{L}^+)]$ complexes of Co^{II} , Ni^{II} , and Zn^{II} . The Ni^{II} chloride derivative was obtained from $(\text{L}^+)\text{Cl}$ and NiCl_2 in a manner similar to that described for the preparation of $(\text{L}^+)_2[\text{CoCl}_4]$. Analytical data are given in Table II.

(6) S. Buffagni and T.M. Dunn, *J. Chem. Soc.*, 5105 (1961).

Table I. Colors, Magnetic Moments, and Analytical Data of Metal Complexes Containing the Coordinated 1,1,4-Trimethylpiperazinium(+1) Cation.

Compound ^a	Color	Magnetic Moment (μ_{eff} (B.M.))	Metal %		Halide %		Nitrogen %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
[CoCl ₃ (L ⁺)]	blue	4.54	20.01	19.9	36.17	36.0	9.52	9.8
[CoBr ₃ (L ⁺)]	blue	4.64	13.77	13.6	56.03	55.8	6.54	6.7
[CoI ₃ (L ⁺)]	dark green	4.60	10.39	10.3	67.13	67.3		
[NiCl ₃ (L ⁺)]	blue	3.83	19.71	20.0	36.14	35.5	9.52	9.7
[NiBr ₃ (L ⁺)]	blue	3.80	13.56	13.5	56.05	56.2	6.55	6.7
[NiI ₃ (L ⁺)]	dark brown	3.69	10.32	10.5	66.95	67.1		
[CuCl ₃ (L ⁺)]	yellow	1.95	21.26	21.7	35.58	35.46	9.37	9.6
CuBr ₂ ·(L ⁺)Br ^b	dark brown	1.98	14.69	14.4	55.27	55.4	6.48	6.7
[ZnCl ₃ (L ⁺)]	colorless	diam.	21.72	22.0	35.40	35.3	9.31	9.8
[ZnBr ₃ (L ⁺)]	colorless	diam.	15.05	15.3	55.19	55.4		
[ZnI ₃ (L ⁺)]	colorless	diam.	11.36	11.4	65.94	66.4		

^a L⁺ = 1,1,4-trimethylpiperazinium(+1), [CH₃N(CH₂CH₂)₂N⁺(CH₃)₂]. ^b The coordination formula of this compound has not been established.

Table II. Colors and Analytical Data of Some Halometallates(II) of the 1,1,4-Trimethylpiperazinium(+1) Cation and Its Protonated(+2) Derivative.

Compound ^a	Color	Calcd.	Metal %		Calcd.	Halide %	
			Found	Found		Found	Found
(L ⁺) ₂ [MnCl ₄]	greenish	12.07		12.2	31.15		30.8
(L ⁺) ₂ [MnBr ₄]	greenish	8.69		8.8	30.91		55.8
(L ⁺) ₂ [CoCl ₄]	light blue	12.83		12.8	56.04		31.1
(LH ²⁺) ₂ [MnCl ₄]	greenish	16.80		17.1	43.37		43.0
(LH ²⁺) ₂ [NiCl ₄]	turquoise	17.84		17.9	42.99		43.3

^a L⁺ = [CH₃N(CH₂CH₂)₂N⁺(CH₃)₂]; LH²⁺ = [(CH₃)HN⁺(CH₂CH₂)₂N⁺(CH₃)₂].

Several other salts of the type (LH²⁺)[MX₄], where M = Mn^{II}, Co^{II}, Ni^{II}, and X = Cl, Br, were prepared as follows. A solution of the (L⁺)X salt (1 mmole) in ethanol (50%) - nitromethane (50%) was treated with several drops of conc. halogen acid and added to a solution of the metal halide (about 1.5 mmole) in the same solvent. Immediately, or after gentle warming and concentration, the crystalline (LH²⁺)-[MX₄] salts precipitated, and were identified by analyses (metal and halogen), infrared spectra, and *d-d* electronic spectra.

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. *Raman Spectra* of solid samples were recorded between 600 and 150 cm⁻¹ with a Cary 81 Spectrophotometer using an exciting radiation of 6328 Å (LASER source). *d-d Electronic Spectra* of solid samples were recorded with a Cary Model 14 Spectrophotometer (30,000-4,000 cm⁻¹ range) equipped with a diffuse reflectance attachment. Transmission spectra were obtained in nitromethane solutions. *X-ray Powder Diffractographs* were taken using nickel-filtered Cuα radiation. *Magnetic Susceptibilities* were measured by the Gouy method on powdered samples at room temperature. Diamagnetic corrections from Pascal's Tables were used in the calculation of μ_{eff} .

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

Results and Discussion

The reaction between the halides of the 1,1,4-trimethylpiperazinium cation (L⁺), and the corresponding halides of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} yields three different types of compounds, [MX₃(L⁺)], (L⁺)₂[MX₄], and (LH²⁺)[MX₄], depending on the metal ion M, the halide X, and to some extent also on the experimental conditions. It is convenient to consider each type of compound separately.

The Complexes [MX₃(L⁺)]. The complexes of this type, listed in Table I, are obtained directly by the reaction of the 1,1,4-trimethylpiperazinium halide with the metal halide, under the conditions described in the Experimental Section. For the complexes of Co^{II} and Ni^{II}, the magnetic moments (Table I) and the *d-d* electronic spectra (Table III) clearly indicate a pseudo-tetrahedral stereochemistry. Furthermore, the characteristic splittings of the ⁴A₂(F)→⁴T₁(F) transition in the Co^{II} complexes and of the ³T₁(F)→³T₂(F) transition in the Ni^{II} complexes, show that the ligand field environment has a symmetry approaching C_{3v}.⁷ These complexes, therefore, may be considered to have mononuclear formulas, [CoX₃(L⁺)] and [NiX₃(L⁺)], similar to those of the corresponding complexes of the monoquaternized DABCO-nium ligands.^{5a} The infrared spectra further confirm this structural formulation. In the spectrum of the « free » ligand salts, the stretching vibrations of the -CH₃ group attached to the tertiary N-atom appear as two medium-strong bands at 2810 and 2780 cm⁻¹, in agreement with the well-known pattern of the >N-CH₃ functional

Table III. *d-d* Electronic Spectra of the Crystalline Complexes $[MX_3(L^+)]$.

Complex ^a	Absorption Maxima ^b (kK) and Assignments			
	⁴ A ₂ (T ₁ ,F)		⁴ A ₂ (F)→ ⁴ E(T ₁ ,F)	⁴ E(T ₁ ,P), ⁴ A ₂ (T ₁ ,P)
$[CoCl_3(L^+)]$	5.1 ^c		5.6	15.6
$[CoBr_3(L^+)]$	4.7 ^c		7.0	15.3
$[CoI_3(L^+)]$	4.4 ^c		6.5	14.0
	³ E(T ₂ ,F)	³ A ₁ (T ₂ ,F)	³ E(T ₁ ,F)→ ³ A ₂ (F)	³ E(T ₁ ,P), ³ A ₂ (T ₁ ,P)
$[NiCl_3(L^+)]$	4.7 ^c	6.2	9.2	16.0 ^d
$[NiBr_3(L^+)]$	4.7 ^c	5.9	8.6	15.0
$[NiI_3(L^+)]$	4.6 ^c	5.9	8.3	14.3

^a (L⁺) = $[CH_3N(CH_2CH_3)_2N^+(CH_3)_2]$. ^b The reported values are midpoints of absorption bands of diffuse reflectance spectra. ^c Partly overlaid by vibrational absorptions of the (L⁺) ligand. ^d With well resolved peaks at 17.2 and 14.7 kK.

Table IV. Metal-halogen Stretching Frequencies (cm⁻¹) of $[MX_3(L^+)]$ Complexes.

Complex	Infrared ^a	Raman ^b
$[CoCl_3(L^+)]$	325, 305	^c
$[NiCl_3(L^+)]$	323, 293	^c
$[CuCl_3(L^+)]$	298, 275	274
$[ZnCl_3(L^+)]$	305, 280 (sh)	283
$[ZnBr_3(L^+)]$	^d	182

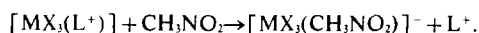
^a Nujol mulls. ^b Finely powdered samples. ^c Sample decomposed by exciting radiation. ^d Below limit of instrument used.

group.⁸ In the spectra of the $[MX_3(L^+)]$ complexes, on the other hand, these absorptions shift to higher frequencies and become indistinguishable from those of the $>\dot{N}(CH_3)_2$ group—thus showing that the lone electron pair of the tertiary N-atom of the ligand has become involved in bonding (to a metal ion). The infrared spectra of the $[CoX_3(L^+)]$ and $[NiX_3(L^+)]$ complexes also differ markedly from that of the «free» ligand in the 1600-250 cm⁻¹ region, which is the most sensitive to changes in conformation. The resulting spectral pattern is characteristic of the coordinated 1,1,4-trimethylpiperazinium cation-ligand in these pseudo-tetrahedral complexes $[MX_3(L^+)]$, and can serve as a sensitive diagnostic tool in their identification. It is also significant that the far-infrared spectra of the $[CoCl_3(L^+)]$ and $[NiCl_3(L^+)]$ complexes show two absorptions arising from the antisymmetric and symmetric M-Cl stretching modes, as expected for a -MCl₃ group of C_{3v} symmetry.⁹

The colorless Zn^{II} complexes and the bright yellow Cu^{II}-chloride complex, whose infrared spectra are virtually identical with those of the corresponding Co^{II} and Ni^{II} complexes, are also assigned a pseudo-tetrahedral mononuclear structure, $[MX_3(L^+)]$, with C_{3v} symmetry. This formulation is further supported by the *d-d* spectrum of the Cu^{II} chloride complex, which is very similar to that of the analogous DABCO-nium complex.^{5a} It is significant that $[CuCl_3(L^+)]$ forms crystalline solutions with $[ZnCl_3(L^+)]$ in virtually all

proportions, even though the X-ray powder patterns of the two individual complexes are similar but not identical.

The $[MX_3(L^+)]$ complexes dissolve slightly in nitromethane, but the *d-d* spectra and electrical conductivity of the solutions indicate that the original species have undergone solvation according to the schematic equation:



The crystalline $[MX_3(L^+)]$ complexes have good thermal stability; they melt with charring in the range 180-200°C., somewhat higher than the halide salts of the «free» ligand. The sensitivity of the complexes to moisture varies with the metal ion—the Co^{II} and Zn^{II} complexes are virtually unaffected atmospheric moisture, whereas the Ni^{II} complexes are very hygroscopic.

The $[MX_3(L^+)]$ complexes of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} constitute an isostructural series of inorganic «zwitter-ions», in which the quaternized N-atom of the L⁺ ligand represents the positive end, while the -MX₃ moiety represent the negative end. Undoubtedly the ionic interactions between oppositely charged sites of adjacent «zwitter-ions» in the crystal lattice greatly contributes to the overall stability of the crystalline complexes $[MX_3(L^+)]$ and also accounts for their generally low solubility in non-donor solvents. This and our previous investigations clearly indicate that when coordination of a positively charged ligand to a negatively charged acceptor results in the formation of an uncharged «zwitter-ion» complex, the formation of such a complex is greatly favored.⁵

The Salts (L⁺)₂[MX₄]. The light-blue compound of empirical formula $CoCl_2 \cdot 2(L^+)Cl$, obtained by reaction of CoCl₂ with (L⁺)Cl in ethanol-water solution, was identified as the (L⁺)₂[CoCl₄] salt by its *d-d* electronic spectrum and low-energy infrared spectrum, which show the absorptions characteristic of the tetrahedral $[CoCl_4]^{2-}$ anion. The higher energy region of the infrared (vibrational) spectrum shows a medium multiple absorption at about 2820 cm⁻¹, which identifies the presence of a non-coordinated $>\dot{N}-CH_3$ group⁸ in the L⁺ cation. It is interesting to note that the contours of this -CH₃ stretching absorption band,

(8) J.T. Braunholtz, E.A.V. Ebsworth, F.G. Mann, and N. Sheppard, *J. Chem. Soc.*, 2780 (1956).

(9) «Low-Frequency Vibrations of Inorganic and Coordination Compounds», J.R. Ferraro, Plenum Press, New York, 1971, p. 134-137 and references therein.

as well as the entire pattern of the spectrum of $(L^+)_2[CoCl_4]$ between 4000 and 300 cm^{-1} , are similar to but not identical with those of the halide salts of the L^+ cation. The observed differences in the infrared spectra of $(L^+)_2[CoCl_4]$ and $(L^+)X$, where $X = Cl, Br, I$, obviously arise from differences in the conformation of the flexible 1,1,4-trimethylpiperazinium cation due to the effect of the different counter-ions. Accordingly, it may be expected and it is indeed found that the spectra of the tetrahalomanganate(II) salts, $(L^+)_2[MnX_4]$, where $X = Cl, Br$, are identical to that of $(L^+)_2[CoCl_4]$ in the entire 4000-250 cm^{-1} range.

The Salts $(LH^{2+})[MX_4]$. It is well known that the aquo-complexes of the divalent metal ions of the first transition series are appreciably hydrolyzed even at room temperature, the extent of hydrolysis generally increasing as the temperature rises. It is not surprising, therefore, that in hot solutions containing traces of water the hydrogen ion concentration due to hydrolysis of the metal ions may reach levels sufficient to cause protonation of a tertiary N-atom of a ligand. Under these conditions, the tetrahalometallate(II) salts of the protonated 1,1,4-trimethylpiperazinium cation, (LH^{2+}) , may separate from solution. This indeed happens for Mn^{II} chloride, bromide, and iodide, Ni^{II} chloride, and Cu^{II} chloride and bromide. The salts thus obtained (Table II), which have the general formula $(LH^{2+})[MX_4]$ and contain the well-known tetrahedral tetrahalometallate(II) anions of these metals, are identical to those prepared directly by reaction of the metal halides with the halides of the protonated (LH^{2+}) cations. In all these tetrahalometallate salts, the protonated 1,1,4-trimethylpiperazinium cation has a very characteristic infrared absorption spectrum, somewhat different from that of its simple halide salts. Thus it appears that the conformation and hence the infrared spectrum of the (LH^{2+}) cation in its crystalline salts is again strictly related to the formula and stereochemistry of the counterion.¹¹ The presence of a single sharp $\overset{+}{N}-H$ stretching absorp-

(10) F. Basolo, *Coord. Chem. Rev.*, 3, 213 (1968) and references therein.

tion at 2740 cm^{-1} further indicates that in these salts hydrogen bonding must also have a very regular distribution throughout the crystal lattice.^{5a}

Conclusions

The positively charged tertiary amine 1,1,4-trimethylpiperazinium, a potential monodentate N-donor ligand of moderate basicity ($pK_A = 4.3$), readily coordinates to divalent transition metal ions forming a series of isostructural complexes $[MX_3(L^+)]$, in which the central metal has coordination number four and a pseudo-tetrahedral stereo-chemistry with C_{3v} symmetry. The $d-d$ electronic spectra of the Co^{II} and Ni^{II} complexes show that the ligand field strength of the 1,1,4-trimethylpiperazinium cation-ligand is extremely close to that of other tertiary N-donor ligands—whether neutral such as quinuclidine ($pK_A = 10.6$) or positively charged such as the monoquaternized DABCO cations ($pK_A = 2.7$). In fact, for the Co^{II} complexes, the energy splitting of the ${}^4T_1(F)$ term into an A and an E component, which is a direct measure of the difference in Dq values between the halide X and the ligand L, is exactly the same (about 2300 cm^{-1} for the bromo-complexes) for quinuclidine, 1,1,4-trimethylpiperazinium(+1), or N-methyl-DABCO-nium(+1). The overall coordinating ability of the 1,1,4-trimethylpiperazinium cation-ligand, however, is rather different from that of the N-methyl-DABCO-nium cation-ligand. Unlike this latter, which readily forms five-coordinate metal complexes of the type $[MX_3(H_2O)(L^+)]$ and $[MX_3(L^+)_2]X$, the 1,1,4-trimethylpiperazinium ligand does not favor five-coordination even under carefully controlled conditions. Also, 1,1,4-trimethylpiperazinium occasionally acts as a non-coordinated cation even in the presence of potential metal-ion acceptors, a behavior which has not been observed for the DABCO-nium cation-ligands.

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