

## THE DONOR PROPERTIES OF POSITIVELY CHARGED LIGANDS. METAL COMPLEXES OF THE N-ALKYLTRIETHYLENEDIAMINIUM CATION

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As part of a study of the donor properties of positively charged ligands, triethylenediamine (tred) was methylated and the reactions of the resulting *N*-methyl(tred)ium cation (abbreviated as  $L^+$ ), with a number of metal salts were investigated. It was found that transition metal halides reacted with  $L^+$  halides to form compounds of the type  $M(L^+)X_3$  ( $M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Pd^{II}, Pt^{II}$ ;  $X = Cl^-, Br^-,$  or  $I^-$ ), and that  $L^+NO_3^-$  formed similar compounds,  $M(L^+)(NO_3)_3$ , with some metal nitrates. From the reaction of  $L^+ClO_4^-$  with metal perchlorates, the following compounds were obtained:  $Co(L^+)_2(ClO_4)_4$ ,  $M(L^+)_4(ClO_4)_6$  ( $M = Ni^{II}, Cu^{II}$ ) and  $Ag(L^+)_4(ClO_4)_5$ . Many of these compounds are insoluble in organic solvents, so that a complete structural investigation could not be carried out. However, the magnetic and spectral properties of the solids, as well as the conductivities and solution spectra of the soluble compounds, indicate that the  $L^+$  cation is coordinated to the metal. This formulation is further supported by the following observations: the dipositive cation, *N,N'*-dimethyl(tred)ium ( $L^{2+}$ ), and the quinuclidinium cation ( $L_q^+$ ), do not form compounds with metal nitrates and perchlorates, and with metal halides form only the usual tetrachlorometallates, such as  $(L^{2+})[CoCl_4]$  and  $(L_q^+)[CoCl_4]$ .

### EXPERIMENTAL

**Starting Materials.** The triethylenediamine, tred, was obtained from the Houdry Chem. Co. A sample of quinuclidine was very kindly provided by Dr. S. Elkin, Temple University, Philadelphia. The hydrated metal salts were dried in an oven at  $100^\circ$  before use. The anhydrous metal salts were used without further purification, except  $NiI_2$  which was repeatedly washed with chloroform to remove traces of iodine.

*Preparation of Organic Intermediates*

*N-methyl(tred)ium iodide, (L<sup>+</sup>)I<sup>-</sup>*. The amine, tred, (15 g) was dissolved in 50 ml cold acetone and treated dropwise with 15 ml of CH<sub>3</sub>I, at room temperature, with mechanical stirring. A white solid separated, was filtered off, washed with acetone and dried in an oven at 80°. The product was recrystallized from hot absolute ethanol, and had a m.p. 220°. *Anal.* Calcd. for C<sub>7</sub>H<sub>15</sub>N<sub>2</sub>I: N, 11.04; I, 49.98. Found: N, 10.92; I, 49.88. The compound is very soluble in water, ethanol, methanol, dichloromethane, nitromethane and acetonitrile; insoluble in the other common solvents.

*N-methyl(tred)ium, (L<sup>+</sup>), chloride, bromide and nitrate* were prepared by passing a solution of the iodide (3 g in 50 ml distilled water) through a column of Dowex-1X8 (100–200 mesh) in the Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> form respectively. The rate of elution was eight drops per min. The effluents, free of iodide ion (Pd<sup>II</sup> test), were evaporated to dryness on a steam bath and the residues were recrystallized from hot ethanol and dried in an oven at 100°. The compounds were white hygroscopic powders. *Anal.* Calcd. for (L<sup>+</sup>)Cl<sup>-</sup>, C<sub>7</sub>H<sub>15</sub>N<sub>2</sub>Cl: N, 17.23; Cl, 21.82. Found: N, 17.01; Cl, 21.76. Calcd. for (L<sup>+</sup>)Br<sup>-</sup>, C<sub>7</sub>H<sub>15</sub>N<sub>2</sub>Br: N, 13.52; Br, 38.60. Found: N, 13.50; Br, 38.46. Calcd. for (L<sup>+</sup>)NO<sub>3</sub><sup>-</sup>, C<sub>7</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>: N, 22.21. Found: N, 21.98.

*N-methyl(tred)ium perchlorate, (L<sup>+</sup>)ClO<sub>4</sub><sup>-</sup>*, was prepared by mixing a saturated ethanol solution of the iodide with a saturated ethanol solution of LiClO<sub>4</sub> (excess). The product separated out as a white hygroscopic powder. *Anal.* Calcd. for C<sub>7</sub>H<sub>15</sub>N<sub>2</sub>O<sub>4</sub>Cl: N, 12.37. Found: N, 12.30.

*N,N'-dimethyl(tred)ium iodide, (L<sup>2+</sup>)I<sub>2</sub>*, was prepared by treating an ethanol solution of tred with CH<sub>3</sub>I (1:2 molar ratio) at room temperature. The product, which separated immediately as white crystals, was filtered off, washed with ethanol and dried in an oven at 100°. *Anal.* Calcd. for (L<sup>2+</sup>)I<sub>2</sub>: N, 7.08; I, 64.12. Found: N, 7.06; I, 64.09.

*N,N'-dimethyl(tred)ium (L<sup>2+</sup>) chloride, bromide, nitrate and perchlorate* were prepared by ion-exchange, similarly to the corresponding *N-methyl(tred)ium* salts, and were obtained as white hygroscopic powders. *Anal.* Calcd. for (L<sub>2</sub><sup>+</sup>)Cl<sub>2</sub>: N, 13.16; Cl, 33.3. Found: N, 13.1; Cl, 33.1. Calcd. for (L<sub>2</sub><sup>+</sup>)Br<sub>2</sub>: N, 9.28; Br, 52.95. Found: N, 9.26; Br, 52.94. Calcd. for (L<sub>2</sub><sup>+</sup>)(NO<sub>3</sub>)<sub>2</sub>: N, 21.07. Found: N, 21.16. Calcd. for (L<sub>2</sub><sup>+</sup>)(ClO<sub>4</sub>)<sub>2</sub>: N, 8.22. Found: N, 8.3.

*N-n-butyl(tred)ium (L<sub>a</sub><sup>+</sup>) and N-iso-butyl(tred)ium (L<sub>b</sub><sup>+</sup>) iodides, and N-tert-butyl(tred)ium (L<sub>c</sub><sup>+</sup>) bromide and iodide* were prepared similarly to *N-methyl(tred)ium iodide*, and were obtained as white powders. *Anal.* Calcd. for (L<sub>a</sub><sup>+</sup>)I<sup>-</sup>,

$(L_b^+)I^-$  and  $(L_c^+)I^-$ : N, 9.47; I, 42.88. Found: for  $(L_a^+)I^-$ : N, 9.52; I, 43.2; for  $(L_b^+)I^-$ : N, 9.6; I, 43.0; for  $(L_c^+)I^-$ : N, 9.6; I, 42.8. Calcd. for  $(L_c^+)Br^-$ : N, 11.26; Br, 32.1. Found: N, 11.1; Br, 32.0.

*N-methylquinuclidinium iodide*,  $(L_q^+)I^-$ , prepared similarly to *N-methyl-(tred)ium iodide*, was obtained as a white powder. Anal. Calcd. for  $C_8H_{16}NI$ : N, 5.53; I, 50.17. Found: N, 5.4; I, 50.1.

#### Preparation of Metal Complexes

The complexes prepared are listed in Table I, together with their colors, melting points, magnetic moments and molar conductivities. Anhydrous solvents were used in all preparations.

The complexes  $Ni(L^+)X_3$  ( $X = Cl, Br, I$ ) were prepared by the dropwise addition of a saturated ethanol solution of anhydrous nickel halide to an ethanol solution of the ligand halide (mole ratio 1:1). The products separated immediately as well formed crystals, were filtered, washed with ethanol and dried in an oven at  $100^\circ$ .

The complexes  $Mn(L^+)Cl_3$ ,  $Fe(L^+)Cl_3$  and  $Cu(L^+)Cl_3$ , prepared similarly to the  $Ni^{II}$  halide complexes, were obtained as powders. The complexes  $Co(L^+)X_3$  ( $X = Cl, Br, I$ ) were also prepared in a similar manner, but the reaction mixture was cooled in an ice-bath. The powdery compounds were dried *in vacuo* over  $P_4O_{10}$ .

The complexes  $Pd(L^+)Cl_3$  and  $Pt(L^+)Cl_3$  were prepared by mixing an ethanol solution of the ligand with an ethanol solution of  $Li_2[PdCl_4]$  and  $Li_2[PtCl_4]$ , respectively, in a 1:1 mole ratio. The complexes which separated out immediately were isolated and dried at  $100^\circ$ .

The complexes  $Co(L^+)(H_2O)(NO_3)_3$  and  $Ni(L^+)(H_2O)(NO_3)_3$  were prepared by mixing the hydrated metal nitrate with the ligand nitrate (mole ratio 1:2) in ethanol solution. After the solution was heated at  $60-70^\circ$  for about 10 min, crystals separated. These were filtered off, washed with ethanol and dried at  $70^\circ$ . The complex  $Cu(L^+)(H_2O)(NO_3)_3$  was prepared similarly, but the reaction mixture was concentrated under reduced pressure at room temperature, to avoid decomposition.

The  $Co(L^+)(NO_3)_3$ ,  $Ni(L^+)(NO_3)_3$  and  $Cu(L^+)(NO_3)_3$  complexes were prepared by heating the corresponding aquo-complexes,  $M(L^+)(H_2O)(NO_3)_3$ , for 30 min at about  $120, 180$  and  $125^\circ$ , respectively. Upon exposure to moisture these anhydrous complexes reformed the parent aquo-complexes.

The complex  $Co(L^+)_2(ClO_4)_4$  was prepared by mixing hydrated  $Co^{II}$  perchlorate and ligand perchlorate (mole ratio 1:2) in acetone. After the solution was concentrated under reduced pressure at  $40^\circ$ , a crystalline product separated and was dried over  $P_4O_{10}$  *in vacuo*. The complex  $Ni(L^+)_4(ClO_4)_6$  was prepared similarly (mole ratio 1:6), but prolonged warming of the solution at  $40^\circ$  was necessary to

TABLE I

FORMULAS AND SOME PROPERTIES OF THE COMPLEXES

Compound <sup>a</sup>	Color	M.p., °C <sup>b</sup>	$\mu_{eff}$ , B.M.	$\Lambda_M^c$	Geometry <sup>c</sup>
Mn(L <sup>+</sup> )Cl <sub>3</sub>	White	300	5.59	d	
Fe(L <sup>+</sup> )Cl <sub>3</sub>	Cream	187	4.86	65	
Co(L <sup>+</sup> )Cl <sub>3</sub>	Blue	300	4.51	50	Td.
Ni(L <sup>+</sup> )Cl <sub>3</sub>	Deep blue	300	3.65	20	Td.
Cu(L <sup>+</sup> )Cl <sub>3</sub>	Bright yellow	262	1.90	25	
Pd(L <sup>+</sup> )Cl <sub>3</sub>	Yellow	250	Diamag.	d	Sq.pl.
Pt(L <sup>+</sup> )Cl <sub>3</sub>	Yellow-brown	265	Diamag.	d	Sq.pl.
Ni(L <sup>+</sup> )(H <sub>2</sub> O)Cl <sub>2</sub>	Red	>300	3.69	d	
Co(L <sup>+</sup> )Br <sub>3</sub>	Blue	>300	4.51	40	Td.
Ni(L <sup>+</sup> )Br <sub>3</sub>	Deep blue	>300	3.66	41	Td.
Ni(L <sup>+</sup> )(H <sub>2</sub> O)Br <sub>3</sub>	Deep violet	>300	3.69	d	
Co(L <sup>+</sup> )I <sub>3</sub>	Light green	260	4.52	70	Td.
Ni(L <sup>+</sup> )I <sub>3</sub>	Dark brown	265	3.50	d	Td.
Co(L <sup>+</sup> )(NO <sub>3</sub> ) <sub>3</sub>	Purple-red	238	4.60	74	Oh.
Ni(L <sup>+</sup> )(NO <sub>3</sub> ) <sub>3</sub>	Light green	265	3.22	d	Oh.
Cu(L <sup>+</sup> )(NO <sub>3</sub> ) <sub>3</sub>	Pale blue	235	1.92	d	
Co(L <sup>+</sup> )(H <sub>2</sub> O)(NO <sub>3</sub> ) <sub>3</sub>	Purple-red	238	4.60	d	Oh.
Ni(L <sup>+</sup> )(H <sub>2</sub> O)(NO <sub>3</sub> ) <sub>3</sub>	Green	265	3.20	d	Oh.
Cu(L <sup>+</sup> )(H <sub>2</sub> O)(NO <sub>3</sub> ) <sub>3</sub>	Pale blue	235	1.96	d	
Co(L <sup>+</sup> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>4</sub>	Green-blue	235	4.50	d	Td.
Ni(L <sup>+</sup> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>4</sub>	Pale green	242	3.42	d	Oh.
Cu(L <sup>+</sup> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>4</sub>	Pale green-blue	240	1.76	d	
Ag(L <sup>+</sup> ) <sub>4</sub> (ClO <sub>4</sub> ) <sub>5</sub>	White	280	Diamag.	d	
Co(L <sub>2</sub> <sup>+</sup> )I <sub>3</sub>	Blue-green	292d	4.54	45	Td.
Ni(L <sub>2</sub> <sup>+</sup> )I <sub>3</sub>	Brown	298d	3.30	58	Td.
Co(L <sub>3</sub> <sup>+</sup> )I <sub>3</sub>	Blue-green	>300	4.72	32	Td.
Ni(L <sub>3</sub> <sup>+</sup> )I <sub>3</sub>	Brown	300d	3.25	48	Td.
Co(L <sub>6</sub> <sup>+</sup> )Br <sub>3</sub>	Blue	>300	4.70	27	Td.
Ni(L <sub>6</sub> <sup>+</sup> )Br <sub>3</sub>	Deep blue	>300	3.67	29	Td.
Co(L <sub>6</sub> <sup>+</sup> )I <sub>3</sub>	Blue-green	280d	4.70	34	Td.
Ni(L <sub>6</sub> <sup>+</sup> )I <sub>3</sub>	Brown	295d	3.10	65	Td.
(L <sup>2+</sup> )[MnCl <sub>4</sub> ]	White	300	5.80	d	Td.
(L <sup>2+</sup> )[CoCl <sub>4</sub> ]	Blue	>300	4.63	d	Td.
(L <sup>2+</sup> )[NiCl <sub>4</sub> ]	Blue	>300	3.67	d	Td.
(L <sup>2+</sup> )[CuCl <sub>4</sub> ]	Bright yellow	263	1.89	d	
(L <sup>2+</sup> )[PdCl <sub>4</sub> ]	Yellow-brown	270d	Diamag.	d	Sq.pl.
(L <sup>2+</sup> )[CoBr <sub>4</sub> ]	Blue	250d	4.70	d	Td.
(L <sup>2+</sup> )[CuBr <sub>4</sub> ]	Deep violet	>300	1.90	d	Td.
(L <sub>q</sub> <sup>+</sup> ) <sub>2</sub> [CoI <sub>4</sub> ]	Pale green	280d			Td.
(L <sub>q</sub> <sup>+</sup> ) <sub>2</sub> [NiI <sub>4</sub> ]	Brownish red	>300			Td.

<sup>a</sup> L<sup>+</sup> = *N*-methyl(tred)ium, L<sub>2</sub><sup>+</sup> = *N*-*n*-butyl(tred)ium, L<sub>3</sub><sup>+</sup> = *N*-isobutyl(tred)ium, L<sub>6</sub><sup>+</sup> = *N*-*tert*-butyl(tred)ium, L<sup>2+</sup> = *N,N*-dimethyl(tred)ium, L<sub>q</sub><sup>+</sup> = *N*-methylquinuclidinium. <sup>b</sup> With decomposition. <sup>c</sup> Ohm<sup>-1</sup>cmole<sup>-1</sup>cm<sup>2</sup>, at 25°, for 10<sup>-3</sup> M solutions in nitromethane. <sup>d</sup> Insoluble in nitromethane. <sup>e</sup> Oh. = octahedral, Td. = tetrahedral, Sq.pl. = square planar.

obtain a pure product. The Cu(L<sup>+</sup>)<sub>4</sub>(ClO<sub>4</sub>)<sub>6</sub> and Ag(L<sup>+</sup>)<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub> complexes precipitated immediately as powders, upon mixing acetone solutions of the metal and ligand perchlorates. They were dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

The Co<sup>II</sup> and Ni<sup>II</sup> complexes of (L<sub>2</sub><sup>+</sup>), (L<sub>3</sub><sup>+</sup>) and (L<sub>6</sub><sup>+</sup>) were obtained by

mixing an ethanol solution of the metal halide with an ethanol solution of the corresponding ligand halide (mole ratio about 1:2). The products separated immediately as powders, were filtered off, washed with ethanol and dried *in vacuo* over  $P_4O_{10}$ .

*Preparation of the Tetrahalometallates of  $(L^{2+})$  and  $(L_q^+)$ .* The compounds  $(L^{2+})[MnCl_4]$ ,  $(L^{2+})[CoCl_4]$ ,  $(L^{2+})[NiCl_4]$ ,  $(L^{2+})[CuCl_4]$  and  $(L^{2+})[PdCl_4]$  were prepared by adding an ethanol solution of  $MnCl_2$ ,  $CoCl_2$ ,  $NiCl_2$ ,  $CuCl_2$  or  $Li_2[PdCl_4]$  to a hot ethanol solution of  $(L^{2+})Cl_2$  (mole ratio about 1.5:1). After heating the mixture at  $70^\circ$  for a few minutes, the products separated as powders and were filtered rapidly from the hot solutions. They were washed with hot ethanol and dried at  $90^\circ$ . The compounds  $(L^{2+})[CoBr_4]$  and  $(L^{2+})[CuBr_4]$  were prepared similarly, but the reaction mixture was heated on a steam bath for about one h to insure complete reaction of the nearly insoluble  $(L^{2+})Br_2$ . No products were obtained by mixing  $(L^{2+})(NO_3)_2$  and  $(L^{2+})(ClO_4)_2$  with metal nitrates and perchlorates, respectively, under various conditions. The compounds  $(L_q^+)_2[CoI_4]$  and  $(L_q^+)_2[NiI_4]$  were prepared by mixing  $CoI_2$  and  $(L_q^+)I$  (mole ratio 1:2) in ethanol, and heating the mixture at  $60^\circ$  for a few minutes. The  $Co^{II}$  compound separated at once, whereas the  $Ni^{II}$  compound was obtained by dilution of the ethanol solution with ethyl ether.

*Sensitivity to Moisture.* The crystalline, deep blue  $[Ni(L^+)Cl_3]$  and  $[Ni(L^+)Br_3]$  complexes readily absorbed atmospheric moisture, with change in color to brick red and dark violet, respectively. The hydrated complexes, after drying over  $KOH$ , had compositions corresponding to  $Ni(L^+)(H_2O)X_3$ . When heated at  $100^\circ$  for 10 min the water was lost and the parent compounds reformed. Similarly, the solid complexes  $M(L^+)(NO_3)_3$  ( $M = Ni^{II}, Co^{II}, Cu^{II}$ ) gave the corresponding aquo-complexes  $M(L^+)(H_2O)(NO_3)_3$  when exposed to atmospheric moisture. All other complexes were somewhat sensitive to moisture, but no well defined aquo-complexes were isolated.

*Solubility.* All metal complexes are insoluble in aliphatic and aromatic hydrocarbons, carbon tetrachloride, chloroform, dichloromethane, nitrobenzene, chlorobenzene, dioxane, tetrahydrofuran, ether, acetone, dimethylformamide and alcohols.

Nitromethane and acetonitrile dissolve the complexes of the type  $M(L^+)X_3$  ( $M = Co^{II}, Ni^{II}, Cu^{II}$ ;  $X = Cl, Br, I$ ) and, to a lesser extent,  $M(L_q^+)X_3$ ,  $M(L_b^+)X_3$  and  $M(L_c^+)X_3$  ( $M = Co^{II}, Ni^{II}$ ;  $X = Br, I$ ). Nitromethane and acetonitrile dissolve  $Co(L^+)(NO_3)_3$ , and acetonitrile also dissolves  $Ni(L^+)(NO_3)_3$ . Nitromethane, acetonitrile and ethanol dissolve the quinuclidinium salts,  $(L_q^+)_2[MI_4]$  ( $M = Co^{II}, Ni^{II}$ ).

*Analyses.* Halogens were determined by the Volhard method. The metals  $Co$ ,  $Ni$ ,  $Cu$  were determined by titration with EDTA,  $Ag$  by titration with  $SCN^-$ ,  $Pt$  by combustion, and  $Pd$  by combustion followed by reduction with  $H_2$ . Nitrogen

TABLE II  
ANALYTICAL DATA

Compound	Metal, %		Halogen, %		N, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
[Mn(L <sup>+</sup> )Cl <sub>3</sub> ]			36.90	36.69	9.71	9.67
[Fe(L <sup>+</sup> )Cl <sub>3</sub> ]			36.70	36.49	9.68	10.00
[Co(L <sup>+</sup> )Cl <sub>3</sub> ]	20.15	19.94	36.40	36.28	9.58	9.60
[Ni(L <sup>+</sup> )Cl <sub>3</sub> ]	20.08	19.88	36.40	36.24	9.60	9.62
[Cu(L <sup>+</sup> )Cl <sub>3</sub> ]	21.30	21.19	35.70	36.66	9.43	9.42
[Pd(L <sup>+</sup> )Cl <sub>3</sub> ]	31.37	31.15			8.23	8.19
[Pt(L <sup>+</sup> )Cl <sub>3</sub> ]	45.54	45.59			6.53	6.41
[Ni(L <sup>+</sup> )(H <sub>2</sub> O)Cl <sub>2</sub> ]	18.93	18.90	34.31	34.14	9.04	9.08
[Co(L <sup>+</sup> )Br <sub>3</sub> ]	13.80	13.65	56.30	56.24	6.58	6.45
[Ni(L <sup>+</sup> )Br <sub>3</sub> ]	13.80	13.67	56.30	56.21	6.58	6.52
[Ni(L <sup>+</sup> )(H <sub>2</sub> O)Br <sub>2</sub> ]	13.24	13.20	54.05	53.97	6.31	6.32
[Co(L <sup>+</sup> )I <sub>3</sub> ]	10.36	10.26	67.17	67.17	4.95	4.90
[Ni(L <sup>+</sup> )I <sub>3</sub> ]	10.36	10.26	67.17	66.96	4.95	4.96
[Co(L <sup>+</sup> )(NO <sub>3</sub> ) <sub>3</sub> ]	15.78	15.66			18.80	18.57
[Ni(L <sup>+</sup> )(NO <sub>3</sub> ) <sub>3</sub> ]	15.79	15.68			18.80	18.71
[Cu(L <sup>+</sup> )(NO <sub>3</sub> ) <sub>3</sub> ]	16.87	16.62			18.60	18.50
[Co(L <sup>+</sup> )(H <sub>2</sub> O)(NO <sub>3</sub> ) <sub>2</sub> ]	15.05	14.85			17.95	17.88
[Ni(L <sup>+</sup> )(H <sub>2</sub> O)(NO <sub>3</sub> ) <sub>2</sub> ]	15.06	14.91			17.96	17.74
[Cu(L <sup>+</sup> )(H <sub>2</sub> O)(NO <sub>3</sub> ) <sub>2</sub> ]	16.12	16.09			17.75	17.71
[Co(L <sup>+</sup> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	8.29	8.10			7.88	7.69
[Ni(L <sup>+</sup> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	5.05	4.96			9.63	9.57
[Cu(L <sup>+</sup> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	5.40	5.27			9.59	9.70
[Ag(L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>5</sub>	9.68	9.70			9.20	8.96
[Co(L <sub>a</sub> <sup>+</sup> )I <sub>3</sub> ]	9.69	9.68	62.55	61.70	4.60	4.44
[Ni(L <sub>a</sub> <sup>+</sup> )I <sub>3</sub> ]	9.65	9.55	62.57	63.00	4.60	4.53
[Co(L <sub>b</sub> <sup>+</sup> )I <sub>3</sub> ]	9.69	9.70	62.55	62.20	4.60	4.69
[Ni(L <sub>b</sub> <sup>+</sup> )I <sub>3</sub> ]	9.65	9.70	62.57	62.50	4.60	4.66
[Co(L <sub>c</sub> <sup>+</sup> )Br <sub>3</sub> ]	12.60	12.58	51.26	51.35	5.99	6.12
[Ni(L <sub>c</sub> <sup>+</sup> )Br <sub>3</sub> ]	12.56	12.60	51.28	51.40	5.99	6.10
[Co(L <sub>c</sub> <sup>+</sup> )I <sub>3</sub> ]	9.69	9.62	62.55	62.60	4.60	4.71
[Ni(L <sub>c</sub> <sup>+</sup> )I <sub>3</sub> ]	9.65	9.73	62.57	62.60	4.60	4.68
(L <sup>2+</sup> )[MnCl <sub>4</sub> ]			41.87	41.75	8.26	8.21
(L <sup>2+</sup> )[CoCl <sub>4</sub> ]	17.18	16.84	41.38	39.96	8.17	7.90
(L <sup>2+</sup> )[NiCl <sub>4</sub> ]	17.14	17.30	41.40	41.60	8.17	8.20
(L <sup>2+</sup> )[CuCl <sub>4</sub> ]	18.29	18.24	40.83	40.76	8.06	8.04
(L <sup>2+</sup> )[PdCl <sub>4</sub> ]	27.32	27.37			7.17	7.11
(L <sup>2+</sup> )[CoBr <sub>4</sub> ]	11.31	11.29	61.40	61.50	5.38	5.40
(L <sup>2+</sup> )[CuBr <sub>4</sub> ]	12.09	12.09	60.86	60.90	5.33	5.29
(L <sub>q</sub> <sup>+</sup> ) <sub>2</sub> [CoI <sub>4</sub> ]	7.20	7.01	62.00	61.64	3.42	3.45
(L <sub>q</sub> <sup>+</sup> ) <sub>2</sub> [NiI <sub>4</sub> ]	7.17	6.96	62.03	62.07	3.42	3.41

was determined by a semi-micro Dumas method; analytical data are listed in Table II.

**Magnetic Susceptibility** measurements were made by the Gouy method. The magnetic moments,  $\mu_{eff}$ , of the solid complexes are listed in Table I.

**Electronic Spectra.** Solution (transmission) spectra were taken with a Cary Model 14 recording spectrophotometer, using nitromethane as the solvent. Solid (reflectance) spectra were taken with a Beckmann Model DU quartz spectrophoto-

TABLE III

SPECTRA OF TETRAHEDRAL  $\text{Co}^{\text{II}}$  AND  $\text{Ni}^{\text{II}}$  COMPLEXES

Compound	Absorption Maxima <sup>a</sup> , (cm <sup>-1</sup> · 10 <sup>-3</sup> )			
<i>Nitromethane solutions</i>				
[Co(L <sup>+</sup> )Cl <sub>2</sub> ]	14.7 (570)	15.4 (520)	15.7 (470)	16.9 (505)
[Co(L <sup>+</sup> )Br <sub>2</sub> ]	14.5 (605)	14.8 (570)	15.6 (350)	16.1 (395)
[Co(L <sub>c</sub> <sup>+</sup> )Br <sub>2</sub> ]	14.4 (600)	14.8 (580)		16.1 (380)
[Co(L <sup>+</sup> )I <sub>2</sub> ]	13.6 (940)	14.3 (550)	15.0 (365)	
[Co(L <sub>a</sub> <sup>+</sup> )I <sub>2</sub> ]	13.6 (980)	14.3 (560)	15.0 (380)	
[Co(L <sub>b</sub> <sup>+</sup> )I <sub>2</sub> ]	13.6 (950)	14.3 (590)	15.0 (390)	
[Co(L <sub>c</sub> <sup>+</sup> )I <sub>2</sub> ]	13.6 (1010)	14.3 (560)	15.0 (370)	
[Ni(L <sup>+</sup> )Cl <sub>2</sub> ]	8.9 (30)	10.2 sh	16.9 (123)	
[Ni(L <sup>+</sup> )Br <sub>2</sub> ]	8.4 (50)	15.7 (195)	16.3 sh	
[Ni(L <sup>+</sup> )I <sub>2</sub> ]	8.2 (40)	14.0 (150)		
<i>Solids (reflectance)</i>				
[Co(L <sup>+</sup> )Cl <sub>2</sub> ]	15.1 (1.00)	16.7 (0.97)		
[Co(L <sup>+</sup> )Br <sub>2</sub> ]	14.7 (1.00)	15.4 (1.00)	17.9 sh	
[Co(L <sup>+</sup> )I <sub>2</sub> ]	13.8 (1.00)	14.5 sh	15.2 (0.39)	
[Co(L <sup>+</sup> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	14.8 sh	15.6	16.9 sh	
[Ni(L <sup>+</sup> )Cl <sub>2</sub> ]	8.9 (0.78)	10.2 sh	16.1 (1.00)	
[Ni(L <sup>+</sup> )Br <sub>2</sub> ]	8.8 (0.83)		16.0 (1.00)	
[Ni(L <sup>+</sup> )I <sub>2</sub> ]	8.3 (0.8)	14.3 (1.00)		

<sup>a</sup> Numbers in parentheses are molar extinction coefficients for solution (transmission) spectra and relative absorbancies for solid (reflectance) spectra.

TABLE IV

SPECTRA OF OCTAHEDRAL  $\text{Ni}^{\text{II}}$  COMPLEXES

Compound	Absorption Maxima <sup>a</sup> , $\text{cm}^{-1} \cdot 10^3$				
	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_2/\nu_1$
$[\text{Ni}(\text{L}^+)(\text{NO}_3)_2] \begin{cases} \text{b} \\ \text{c} \end{cases}$	8.9 (0.25)	11.5 sh	14.7 (0.66)	25.6 (1.00)	1.65
	9.3 (16)	13.16 sh	15.5 (30)	25.6 (64)	1.67
$[\text{Ni}(\text{L}^+)(\text{H}_2\text{O})(\text{NO}_3)_2] \begin{cases} \text{b} \\ \text{c} \end{cases}$	8.8 (0.33)	11.4 sh	14.7 (0.66)	25.0 (1.00)	1.66
	9.3 (14)	13.0 sh	15.5 (26)	25.5 (50)	1.67
$[\text{Ni}(\text{L}^+)_2(\text{ClO}_4)_2](\text{ClO}_4)_4^{\text{b}}$	8.8 (0.22)	11.5 sh	15.1 (0.60)	25.6 (1.00)	1.71

<sup>a</sup> Numbers in parentheses are relative absorbancies for solid (reflectance) spectra, and molar extinction coefficients for solution (transmission) spectra. <sup>b</sup> Diffuse reflectance spectrum. <sup>c</sup> Transmission spectrum in acetonitrile.

meter, equipped with a diffuse reflectance attachment, using  $\text{MgCO}_3$  as the reference. The absorption maxima of the complexes are listed in Tables III and IV.

Conductivity measurements were made at 25° using spectrograde nitromethane as the solvent (Table I).

## RESULTS

**Halocomplexes.** The reaction between  $L^+$  halides and the anhydrous metal halides yields compounds of the general formula  $M(L^+)X_3$  ( $M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Pd^{II}$  and  $Pt^{II}$ ,  $X = Cl, Br$ , or  $I$ ). These are crystalline solids, stable to dry air, readily decomposed by moisture and water, and insoluble in organic solvents except nitromethane and acetonitrile. The magnetic and spectral properties of the solid  $Co^{II}$  and  $Ni^{II}$  complexes indicate an essentially tetrahedral stereochemistry for the central metal ion. The complex  $Cu(L^+)Cl_3$  has a magnetic moment and an electronic spectrum which suggest a largely distorted tetrahedral configuration, similar to that of the  $[CuCl_4]^{2-}$  ion. Finally, the diamagnetic  $Pd^{II}$  and  $Pt^{II}$  complexes may be assigned a square planar configuration.

In nitromethane solution, the  $M(L^+)X_3$  compounds have a slight electrical conductivity,  $\Lambda_M = 20-50 \text{ ohm}^{-1}\text{mole}^{-1}\text{cm}^2$  in  $10^{-3} M$  solution at  $25^\circ$ , which is much lower than the value expected for either a 1:1 ( $\Lambda_M = 90-100 \text{ ohm}^{-1}\text{mole}^{-1}\text{cm}^2$ ) or a 1:2 electrolyte under the same conditions. This slight conductivity very likely results from partial solvolysis of a non-ionic species. This is consistent with the electronic spectra of the  $Co^{II}$  and  $Ni^{II}$  complexes in nitromethane, since the species present in these solutions are still tetrahedral, although their absorption bands are slightly shifted as compared with the solids. On the basis of this evidence, it is reasonable to assign to the  $M(L^+)X_3$  complexes the monomeric, non-ionic formula  $[M(L^+)X_3]$ . The two alternative possible structures,  $(L^+)_2[M_2X_6]$  and  $[M_2(L^+)_2X_4]X_2$  (both with a double halogen bridge connecting the two  $M$  atoms) appear unlikely, as they would be expected to give rise to higher values of the molar conductivity.

When exposed to moisture, the  $[Ni(L^+)Cl_3]$  and  $[Ni(L^+)Br_3]$  complexes take on one molecule of water to form the compounds  $Ni(L^+)(H_2O)Cl_3$  and  $Ni(L^+)(H_2O)Br_3$ , which are insoluble in organic solvents. The infrared spectra of these hydrated compounds and their deuterated analogues,  $Ni(L^+)(D_2O)Cl_3$  and  $Ni(L^+)(D_2O)Br_3$ , show that water is coordinated, and their visible reflectance spectra are similar to those of the polymeric  $[Ni(2\text{-picoline})Cl_2]_n$  and  $[Ni(3\text{-picoline})Br_2]_n$ , which have been assigned a distorted octahedral structure. The magnetic moments of both  $Ni(L^+)(H_2O)Cl_3$  and  $Ni(L^+)(H_2O)Br_3$  are rather high ( $\mu_{eff.} = 3.69 \text{ B.M.}$ ) as compared with the usual range for octahedral  $Ni^{II}$  ( $\mu_{eff.} < 3.3 \text{ B.M.}$ ), but it is significant that the polymeric octahedral  $[NiCl_2]_n$  has  $\mu_{eff.} = 3.9 \text{ B.M.}$  It is interesting that whereas  $H_2O$  and  $D_2O$  vapors react rapidly with  $[Ni(L^+)Cl_3]$  and  $[Ni(L^+)Br_3]$  to form the aquo-complexes, the vapors of other donor solvents, such as methanol, ethanol, acetone and acetonitrile, have no effect.

**Nitrate complexes.** The reaction between  $L^+NO_3^-$  and the hydrated metal nitrates yielded complexes of the type  $M(L^+)(H_2O)(NO_3)_3$ , where  $M = Co^{II}, Ni^{II}$  and  $Cu^{II}$ , insoluble in organic solvents. The infrared spectra of these com-



pounds show the absorptions typical of coordinated water, and the presence of both coordinated and free  $\text{NO}_3$  groups. The magnetic moments and electronic spectra indicate an octahedral configuration for the  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  compounds; the  $\text{Cu}^{\text{II}}$  complex very likely has a tetragonally distorted octahedral structure. These aquo-complexes lose water on heating and the resulting compounds have the formula  $\text{M}(\text{L}^+) (\text{NO}_3)_3$ ; in turn, these rapidly reform the parent aquo-complexes when exposed to moisture. Both the stereochemistry and the average ligand field strength of the complexes remain unchanged upon loss of  $\text{H}_2\text{O}$ . For the anhydrous compounds, the infrared spectra show the presence of only coordinated nitrate groups in the (solid)  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  complexes, whereas both coordinated and free  $\text{NO}_3$  are present in the  $\text{Cu}^{\text{II}}$  complex. The  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  compounds also differ from the insoluble  $\text{Cu}^{\text{II}}$  compound in that they are moderately soluble in nitromethane and acetonitrile. The slight electrical conductivity of the  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  complexes may be considered to result from partial solvolysis.

It seems reasonable to formulate the anhydrous  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  nitrate complexes as monomeric, non-ionic octahedral species of the type  $[\text{M}(\text{L}^+) (\text{NO}_3)_3]$ , containing both mono- and bi-dentate  $\text{NO}_3$  groups. On the other hand, the anhydrous  $\text{Cu}^{\text{II}}$  complex, which is insoluble and still contains free  $\text{NO}_3^-$ , very likely has a polymeric formula with  $\text{NO}_3$  bridges. For the aquo-complexes, both a monomeric formula with bidentate  $\text{NO}_3$  groups,  $[\text{M}(\text{L}^+) (\text{H}_2\text{O}) (\text{NO}_3)_2] (\text{NO}_3)$  or a polymeric formula with  $\text{NO}_3$  bridges are possible, although for the  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  compounds the monomeric formula appears more likely in view of the ease of the reaction,  $\text{M}(\text{H}_2\text{O}) (\text{L}^+) (\text{NO}_3)_3 \rightleftharpoons \text{M}(\text{L}^+) (\text{NO}_3)_3 + \text{H}_2\text{O}$ .

**Perchlorate Complexes.** The following compounds were obtained from the reaction of  $\text{L}^+ \text{ClO}_4^-$  and metal perchlorates:  $\text{CoL}^+_2 (\text{ClO}_4)_4$ ,  $\text{Ni}(\text{L}^+)_4 (\text{ClO}_4)_6$ ,  $\text{Cu}(\text{L}^+)_4 (\text{ClO}_4)_6$  and  $\text{Ag}(\text{L}^+)_4 (\text{ClO}_4)_5$ . These compounds are all insoluble in organic solvents, so that their investigation was limited to the solid state. From the magnetic moment and electronic spectrum, the  $\text{Co}^{\text{II}}$  compound is shown to be tetrahedral and the  $\text{Ni}^{\text{II}}$  compound octahedral, thus indicating that in these complexes some of the  $\text{ClO}_4$  groups are coordinated. It was not possible to find support for this conclusion in the infrared spectra, because the regions of absorption of monodentate  $\text{ClO}_4$  are obscured by the very strong absorptions of the free  $\text{ClO}_4^-$  ion. However, it seems reasonable to formulate these compounds as  $[\text{Co}(\text{L}^+)_2 (\text{ClO}_4)_2] (\text{ClO}_4)_2$  and  $[\text{Ni}(\text{L}^+)_4 (\text{ClO}_4)_2] (\text{ClO}_4)_4$ . The average ligand field strength of the  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  complexes, as shown by their visible spectra, is that expected for a tetrahedral  $\text{Co}^{\text{II}}$  with 2 N and 2 O ligating atoms, and for octahedral  $\text{Ni}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  with 4 N and 2 O.

**Comparison of the Behavior of  $(\text{L}^+)$  and  $(\text{L}^{2+})$  towards Metal Salts.** As discussed in the previous sections, the general properties and behavior of the compounds obtained from the reaction of N-methyl(tred)ium,  $\text{L}^+$ , salts with metal salts indicate that  $\text{L}^+$  is coordinated, that is, it acts as a positively charged ligand toward metal ions. However, the possibility that some compounds may be salts of

the free  $L^+$  cation was taken into consideration. Two organic cations which closely resemble  $L^+$  in size, shape and chemical constitution, namely *N,N'*-dimethyl-(tred)ium,  $L^{2+}$ , and *N*-methyl-quinuclidinium,  $L_q^+$ , were prepared and the reactions of their salts with a number of metal salts were investigated. Under the same experimental conditions used in the preparation of  $(L^+)$ -metal compounds, the  $L^{2+}$  halides reacted with divalent metal halides to form tetrahalometallate salts,  $(L^{2+})[M^{II}X_4]$ ; similarly,  $L_q^+I^-$  reacted with  $CoI_2$  and  $NiI_2$  to give  $(L_q^+)_2[CoI_4]$  and  $(L_q^+)_2[NiI_4]$ . On the other hand, no reaction was observed between the nitrate and perchlorate salts of  $L^{2+}$  and the metal nitrates and perchlorates. The different results obtained with  $L^+$  as compared with  $L^{2+}$  and  $L_q^+$  show that  $L^{2+}$  and  $L_q^+$  behave simply as cations, whereas  $L^+$ , in which one of the N atoms is still free to act as a donor atom, behaves as a (positively charged) ligand toward metal ions, forming stable metal complexes.

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