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## The Donor Properties of Positively Charged Ligands. Metal Complexes of the $\beta$ -Aminoethyltrimethylammonium and $\gamma$ -Aminopropyltrimethylammonium Cations

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Metal coordination compounds of the cation ligands  $\beta$ -aminoethyltrimethylammonium,  $[(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_2\text{NH}_2]$  ( $\beta\text{-L}^+$ ), and  $\gamma$ -aminopropyltrimethylammonium,  $[(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{NH}_2]$  ( $\gamma\text{-L}^+$ ), have been prepared. The complexes are electrolytes of the type  $[\text{M}(\text{L}^+)_6](\text{ClO}_4)_6$  for  $\text{M} = \text{Co}(\text{II})$  and  $\text{Ni}(\text{II})$ , and  $[\text{M}(\text{L}^+)_4](\text{ClO}_4)_6$  for  $\text{M} = \text{Cu}(\text{II})$ ,  $\text{Zn}(\text{II})$ ,  $\text{Cd}(\text{II})$ , and  $\text{Pd}(\text{II})$ . They were characterized by their conductivity, magnetic susceptibility, and visible and infrared spectra. The  $\text{p}K_a$  of the ligand acid perchlorate salts were also determined and found to be 6.91 and 8.82 for the ( $\beta\text{-L}^+$ ) and ( $\gamma\text{-L}^+$ ), respectively.

### Introduction

A very large number and variety of metal coordination compounds of neutral or negatively charged (anionic) ligands have been prepared and extensively studied. In contrast, no planned work has as yet been reported on the coordinating ability of positively charged species, although as early as 1932 it had been observed by Drew<sup>1</sup> that such cations as partially protonated polyamines can act as ligands toward metal ions in aqueous solution. The nitrosyl complexes, of which a rather large number have been reported in recent years,<sup>2,3</sup> may be considered to be coordination compounds of the positively charged species  $\text{NO}^+$ . However, the instability of the  $\text{NO}^+$  species when not coordinated, together with the fact that the complexes are usually prepared by reaction of a suitable metal derivative with the (neutral)  $\text{NO}$  gas, places the nitrosyl complexes in a separate class.<sup>3a</sup> The substitution products of some transition metal carbonyls with the *N*-methylpyridinium<sup>4</sup> and the protonated cycloheptatriene<sup>5</sup> cations are indeed complexes of positively charged ligands, in which the bonding to the metal is assumed to be of the  $\pi$  type.

The interest of studying the coordinating ability of positive ion ligands toward metal ions is manifold. New aspects of the electronic interaction between the coordinate bond and the rest of the ligand may become apparent if a positive charge in place of a negative charge is located in a known position in the ligand. In those cases where a strong interaction between the charged and the ligating atom is possible, a drastic change of ligating ability is to be expected and the complexes, if formed, may then be of an unusual type. Also the metal complexes of positive ion ligands would

in most cases be cations of unusually high charge. For instance, whereas the highest charge so far obtained for a nonpolymeric cationic species is +4, a six-coordinated complex of a monodentate, single-charge positive ion ligand would have a formal charge of +8 for divalent and +9 for trivalent metal ions. Of course, by opportunely choosing a cation ligand of higher charge, it may be possible to prepare complex metal cations of much higher formal charge. The interest of preparing and studying salts of this type is not restricted to purely chemical problems, but may well extend to biochemistry because of the important role of highly charged water-soluble species in biochemical reactions.<sup>6</sup>

For the present investigation, two simple positive ion ligands were chosen, namely the  $\beta$ -aminoethyltrimethylammonium cation,  $[(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_2\text{NH}_2]$  ( $\beta\text{-L}^+$ ), and its analog  $\gamma$ -aminopropyltrimethylammonium cation,  $[(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{NH}_2]$  ( $\gamma\text{-L}^+$ ), in which the positive group (a substituted ammonium ion) and the ligating group (a primary amine) are separated by an aliphatic chain of two and three methylene groups, respectively. The stronger the influence of the positive charge on the donor properties of the amino group, the more these cationic ligands will depart from the well-known behavior of donor primary amines. Thus the study of the coordination compounds of these ligands will give us some basic, though far from complete, information on the possibilities of obtaining stable metal complexes with various positive ion ligands.

### Experimental

**Preparation of the Ligands.**  $\beta$ -Aminoethyltrimethylammonium Perchlorate.  $[(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_2\text{NH}_2](\text{ClO}_4)$ .—This compound was prepared by the following procedure. The commercially available amine,  $(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{NH}_2$ , was further purified by fractional distillation and then acetylated with acetic anhydride in benzene solution. The crude acetylamine was methylated with methyl iodide in acetone solution at 0° and the product was recrystallized from ethanol. The acetyl group was next hydrolyzed by refluxing with concentrated  $\text{HCl}$  in methanol solution. The excess acid and some iodine present as an impurity were removed

(6) For instance, F. A. Loewus, F. H. Westheimer, and B. Vennesland, *J. Am. Chem. Soc.*, **75**, 5018 (1953).

(1) H. D. K. Drew, *J. Chem. Soc.*, 2328 (1932).

(2) J. C. Bailar, Jr., Ed., "Chemistry of the Coordination Compounds," Reinhold Publishing Co., New York, N. Y., 1956, p. 531.

(3) J. Lewis, *Sci. Progr.*, **47**, 506 (1959).

(3a) NOTE ADDED IN PROOF.—The occurrence of the hydrazinium(+1) ion as a ligand in the compound  $(\text{N}_2\text{H}_5)_2\text{Zn}(\text{SO}_4)_2$  has been established by X-ray analysis by C. K. Prout and H. M. Powell, *J. Chem. Soc.*, 4177 (1961).

(4) B. Moore and G. Wilkinson, *Proc. Chem. Soc.*, 61 (1959).

(5) A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *Chem. Ind. (London)* 553 (1961).

TABLE I  
 FORMULAS AND SOME PROPERTIES OF THE METAL COMPLEXES OF  
 $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{NH}_2]^+(\beta\text{-L}^+)$  AND  $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_3\text{NH}_2]^+(\gamma\text{-L}^+)$

Compound	Color	M.p., <sup>a</sup> °C.	$\mu_{\text{eff}}^b$	(e <sup>-</sup> ) <sup>c</sup>	$\Delta M^{\text{d,e}}$	mmole l. <sup>-1</sup> (CH <sub>3</sub> CN soln.)
[Co( $\beta\text{-L}^+$ ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Pink	219–220	5.15	(3)	827	1.438
[Ni( $\beta\text{-L}^+$ ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Light blue	234	3.43	(2)	805	1.320
[Cu( $\beta\text{-L}^+$ ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Blue	191	1.76	(1)	688	1.165
[Zn( $\beta\text{-L}^+$ ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	White	239–240	0	(0)	698	1.153
[Cd( $\beta\text{-L}^+$ ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	White	>255	0	(0)	...	...
[Pd( $\beta\text{-L}^+$ ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Yellow	205	0	(0)	480	1.878
[Co( $\gamma\text{-L}^+$ ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Pink	196	4.60	(3)	852	1.542
[Ni( $\gamma\text{-L}^+$ ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Light blue	~248	2.85	(2)	832	1.306
[Cu( $\gamma\text{-L}^+$ ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Blue	173	2.06	(1)	683	1.094
[Zn( $\gamma\text{-L}^+$ ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	White	252–254	0	(0)	683	1.626

<sup>a</sup> With decomposition. <sup>b</sup> Bohr magnetons. <sup>c</sup> Unpaired electrons. <sup>d</sup> Molar conductivity, ohm<sup>-1</sup> cm.<sup>2</sup> mole<sup>-1</sup>. <sup>e</sup> Values of ( $\beta\text{-L}^+$ )(ClO<sub>4</sub>) and [Ni(CH<sub>3</sub>CN)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> were 159 and 305 at  $6 \times 10^{-3}$  and  $10^{-3}$  M, respectively.

by treatment with excess K<sub>2</sub>CO<sub>3</sub>. The neutralization mixture was treated with absolute ethanol to cause separation of the inorganic salts, and from the filtered ethanol solution, upon concentration, the crystalline [(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]Cl was obtained. The perchlorate was obtained from the chloride by metathesis with LiClO<sub>4</sub> in absolute ethanol solution. The product, [(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>](ClO<sub>4</sub>), was a very hygroscopic white powder.

**N,N,N-Trimethylethylenediammonium Perchlorate**, [(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.— $\beta$ -Aminoethyltrimethylammonium perchlorate (0.5 g.) was dissolved in 20 ml. of methanol and treated with a 30% solution of perchloric acid until the pH was about 2–3. On standing white crystals separated, which were filtered off and dried over phosphoric anhydride. The product had a melting point of 270° dec.

*Anal.* Calcd. for [(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>: C, 19.81; H, 5.31; N, 9.24. Found: C, 19.77; H, 5.42; N, 9.14.

**$\gamma$ -Aminopropyltrimethylammonium Perchlorate**, [(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.—The starting material, (CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub> (practical grade), was purified by fractional distillation at 100 mm., collecting the steady boiling fraction at 75°; lit. 134° (760 mm.), 70–80° (128–130 mm.), and 44–45° (20 mm.). The distillate had a refractive index ( $n_D^{25}$  1.42) identical with the values reported for the pure amine, and the melting points of the dihydrochloride (183–184°) and of the picrate (211°) also agreed with the literature. The preparation of [(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>](ClO<sub>4</sub>) from the purified amine was carried out essentially as described for the ethylene analog, but the product of the acetylation, (CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>NHC(O)CH<sub>3</sub>, was purified by fractional distillation, collecting the fraction at 120–125° (3 mm.); lit. 154–158° (19–23 mm.) and 142–143° (10 mm.). The refractive index ( $n_D^{25}$  1.458) agreed with the reported value. Purification of the acetyl derivative was necessary because the methyl iodide adduct (next step) could not be easily purified by recrystallization as in the case of the ethylene analog. The final product was a hygroscopic white powder.

**N,N,N-Trimethyltrimethylenediammonium Perchlorate**, [(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.—This compound was prepared similarly to the ethylene analog except that 60% perchloric acid was used and the pH was adjusted to 6–8. A white crystalline product (m.p. 196–197°) formed on prolonged cooling and was filtered off and dried over phosphoric anhydride.

*Anal.* Calcd. for [(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>: C, 22.72; H, 5.72; N, 8.83. Found: C, 23.15; H, 5.87; N, 8.48.

**Preparation of the Complexes.**—The compounds prepared, together with some of their physical properties, are listed in Table I. The complexes were generally prepared by mixing alcohol (ethanol or methanol) solutions of the hydrated metal perchlorates with an alcohol solution of the ligand in the molar ratio about 1:5 for the [ML<sub>4</sub>]<sup>2+</sup> complexes and about 1:7 for the [ML<sub>6</sub>]<sup>3+</sup> complexes. The concentration of the solutions and the alcohol used as solvent were chosen in each case to give the best results. The products separated rapidly from the reaction mixture, were filtered off, washed repeatedly with anhydrous ethanol,

and dried under vacuum over P<sub>4</sub>O<sub>10</sub>. The palladium(II) complex of [(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>] was prepared by mixing a methanol solution of Li<sub>2</sub>PdCl<sub>4</sub> with a methanol solution of the ligand containing an excess of LiClO<sub>4</sub>. The crude product was recrystallized from hot water containing some ligand and LiClO<sub>4</sub>, filtered, washed with ethanol, and dried over P<sub>4</sub>O<sub>10</sub> under vacuum.

**Characterization of the Complexes. Analyses.**—Carbon, hydrogen, and nitrogen were determined by microanalyses, metals by titration with EDTA<sup>7</sup> or electrodeposition. The analytical data are listed in Table II.

**Conductivity measurements** were made at 25° using closed type cells as previously described.<sup>8</sup> All measurements were made on freshly prepared solutions as soon as thermal equilibrium had been attained (about 25 min.). The solvent was Spectro grade acetonitrile with a specific conductivity of  $9.02 \times 10^{-7}$  ohm<sup>-1</sup> cm.<sup>-1</sup>. The values of the molar conductivities are listed in Table I.

**Magnetic susceptibility measurements** were made by the Gouy<sup>9,10</sup> method on finely powdered samples at room temperature, and the values of the magnetic moments,  $\mu_{\text{eff}}$ , calculated from the magnetic susceptibilities, are listed in Table I.

**Electronic spectra** in the range 3600 to 15,000 Å. were taken on a Cary Model 14 spectrophotometer using Spectro grade N,N-dimethylformamide and acetonitrile as solvents. Nujol mulls were used for solid spectra.

**Infrared spectra** in the range 2.5–38  $\mu$  were measured with a Perkin-Elmer Model 221 spectrophotometer equipped with grating sodium chloride and cesium bromide interchanges, using both Nujol mulls and KBr disks. Great care was taken in preparing and examining the samples, as the bands in the NH stretching region appear to be very sensitive to moisture, which causes shifts and changes in contour. Table III lists the observed absorption frequencies of interest with their assignments.

**Melting or decomposition temperatures** were determined on a Fisher-Johns (hot stage) melting point apparatus.

**pH titrations** employed a Beckman Model G pH meter and a silver, silver chloride electrode *vs.* a glass electrode with a recommended pH range of 0–11. From the titration data of H<sub>2</sub>L<sup>2+</sup> with NaOH, the acid dissociation constants of the acid perchlorate salts of the ligands were determined by use of the equation

$$K_a = \frac{[\text{H}^+][\text{L}^+]}{[\text{HL}^{+2}]}$$

(7) F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," D. Van Nostrand Co., Inc., New York, N. Y., 1957.

(8) P. G. Simpson, A. Vinciguerra, and J. V. Quagliano, *Inorg. Chem.*, **2**, 282 (1963).

(9) B. N. Figgis and J. Lewis, "The Magnetochemistry of Complex Compounds," Chapter 6 of "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 400.

(10) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956.

TABLE II  
ANALYTICAL DATA FOR THE COMPLEXES OF  
[(CH<sub>3</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub>]<sup>+</sup>: n = 2, (β-L<sup>+</sup>); n = 3, (γ-L<sup>+</sup>)

Compound	Carbon, %		Hydrogen, %		Metal, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
[Co(β-L <sup>+</sup> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>8</sub>	24.44	24.55	6.16	6.16	4.00	3.80
[Ni(β-L <sup>+</sup> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>8</sub>	24.45	24.53	6.16	6.01	3.98	3.82
[Cu(β-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	22.39	22.07	5.64	5.86	5.92	6.29
[Zn(β-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	22.35	22.27	5.63	5.78	6.08	6.18
[Cd(β-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	21.41	21.23	5.39	5.14	10.02	10.13
[Pd(β-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	21.18	20.91	5.51	5.32	9.88	10.15
[Co(γ-L <sup>+</sup> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>8</sub>	27.75	27.44	6.60	6.40	3.78	3.69
[Ni(γ-L <sup>+</sup> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>8</sub>	27.76	27.49	6.60	6.52	3.77	3.91
[Cu(γ-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	25.53	25.49	6.07	5.96	5.63	5.55
[Zn(γ-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	25.49	25.58	6.06	5.92	5.78	5.65

giving

$$K_a = \frac{[H^+]\{C_{OH^-} + [H^+]\}}{C_{HL^{+2}} - \{C_{OH^-} + [H^+]\}}$$

as a valid approximation in the region of partial neutralization. All symbols in this expression have their usual meaning.<sup>11</sup> The pK<sub>a</sub> value of each point of the titration was determined and the over-all average (discarding values far from the average) was used. The calculated values agreed within 0.02 pK<sub>a</sub> unit with those from graphical (titration midpoint) determinations.

### Results and Discussion

The reaction of β-aminoethyltrimethylammonium perchlorate, (β-L<sup>+</sup>)(ClO<sub>4</sub>), and its propyl analog, (γ-L<sup>+</sup>)(ClO<sub>4</sub>), with the perchlorate salts of some transition metal ions and zinc(II) yielded coordination compounds of the general formulas [M<sup>II</sup>(L<sup>+</sup>)<sub>4</sub>](ClO<sub>4</sub>)<sub>6</sub> and [M<sup>II</sup>(L<sup>+</sup>)<sub>6</sub>](ClO<sub>4</sub>)<sub>8</sub>. These complex salts have a remarkable thermal stability, decomposing without explosion in the range 150–250°, and in the solid state are stable to air and only moderately sensitive to moisture. They are insoluble in solvents of low polarity, very slightly soluble in alcohols, and relatively soluble in acetonitrile and N,N-dimethylformamide. Water hydrolyzes them rapidly and completely. In general the metal complexes of γ-L<sup>+</sup> are more soluble in alcohols than those of β-L<sup>+</sup> and this probably accounts for the greater difficulty in obtaining pure complexes of the former.

The magnetic moments of the solid cobalt(II) and nickel(II) complexes (Table I) are in the range expected for spin-free octahedral configurations.<sup>9,10</sup> The complexes of β-L<sup>+</sup> have values at the high end, and those of γ-L<sup>+</sup> at the low end of this range. The difference, despite the difficulty of obtaining very accurate values for the magnetic moments of compounds with such high molecular weight, is significant and indicates that the γ-aminopropyltrimethylammonium cation has the greater ability to share effectively with the metal ion the electron pair of the donor amino group, thereby partially "quenching" the orbital contribution to the magnetic moment.<sup>12</sup> In other words, for the complexes of β-L<sup>+</sup> the d<sub>e</sub>-d<sub>γ</sub> separations are less than the inter-electronic repulsions, whereas for the complexes of γ-L<sup>+</sup> the d<sub>e</sub>-d<sub>γ</sub> separations are greater than the inter-electronic repulsions but smaller than spin coupling

TABLE III

SOME SIGNIFICANT INFRARED ABSORPTION FREQUENCIES<sup>a,b</sup>  
(CM.<sup>-1</sup>) OF THE POSITIVE ION LIGAND COMPLEXES

Compound	N-H stretching	NH <sub>2</sub> scissors	NH <sub>2</sub> rocking
(β-L <sup>+</sup> )(ClO <sub>4</sub> )	3350 s, vb	1587 m, b	
(Hβ-L <sup>+</sup> )(ClO <sub>4</sub> ) <sub>2</sub>	3230 vb	1597	
[Co(β-L <sup>+</sup> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>8</sub>	3320 b	1594	576 m, b
	3238 b		
[Ni(β-L <sup>+</sup> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>8</sub>	3331	1591	590–500 <sup>c</sup>
	3283	1560 sh?	
	3210 b		
[Cu(β-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	3303 s	1593	664 m
	3265 s		
	3173 sh		
[Zn(β-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	3338	1590 s	554 m, b
	3271		
[Pd(β-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	3302 s	1577 s (asym.)	
	3250 s		
[Cd(β-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	3327 s	1601 m	
	3284 s		
	3241 s		
(γ-L <sup>+</sup> )(ClO <sub>4</sub> )	3350 vb	1600 s, b	
[Co(γ-L <sup>+</sup> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>8</sub>	3365 s, vb	1590 vb	576 sh
	3245 sh		
[Ni(γ-L <sup>+</sup> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>8</sub>	3360 s, vb	1590 vb	610–510 <sup>c</sup>
	3240 sh		
	3157 sh?		
[Cu(γ-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	3304 s	1610 m, b	665 m
	3270 s	1590 m, b	
	3170		
[Zn(γ-L <sup>+</sup> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>6</sub>	3312 b	1588 s, b	566 m, sh
	3270 sh		
	3160 sh?		

<sup>a</sup> s, strong; m, medium; w, weak; sh, shoulder; b, broad; v, very. <sup>b</sup> The first two columns are for KBr disks and the third for Nujol mulls. <sup>c</sup> The band is overlaid by the stronger ClO<sub>4</sub> band at 623 cm.<sup>-1</sup> and appears as an unsymmetrical contour of the ClO<sub>4</sub> band in the region indicated.

effects.<sup>9</sup> Further information can be drawn from the electronic spectra of these complexes in the solid state. The observed absorptions are typical of the octahedral configurations of the Ni(II) and Co(II) ions and show an appreciable shift to lower frequencies from the complexes of γ-L<sup>+</sup> to those of β-L<sup>+</sup>. In fact the Ni(II) complex of γ-L<sup>+</sup> absorbs at 27,000 (ν<sub>3</sub>), 17,100 (ν<sub>2</sub>), and ~10,000 cm.<sup>-1</sup> (ν<sub>1</sub>), thus closely resembling [Ni(CH<sub>2</sub>-NH<sub>2</sub>)<sub>6</sub>]<sup>2+</sup> (ν<sub>1</sub> = 10,000, ν<sub>2</sub> = 16,700, and ν<sub>3</sub> = 27,200 cm.<sup>-1</sup>),<sup>13</sup> whereas the β-L<sup>+</sup> complex absorbs at 26,000

(11) H. Irving and J. M. M. Griffiths, *J. Chem. Soc.*, 213 (1954).

(12) J. Lewis, *Sci. Progr.*, **50**, 419 (1962).

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( $\nu_3$ ), 16,500 ( $\nu_2$ ), and 10,100  $\text{cm}^{-1}$  ( $\nu_1$ ). A similar shift is observed for the Co(II) complexes, although the intensity of their bands at about 20,000  $\text{cm}^{-1}$  is too low to permit accurate assignment. The spectra of the solid Cu(II) complexes show the same trend, the complex of  $\gamma\text{-L}^+$  having a broad band at 16,200  $\text{cm}^{-1}$  and that of  $\beta\text{-L}^+$  at 15,000  $\text{cm}^{-1}$ .

The infrared absorptions of the ligand salts and of the metal complexes in the solid state were assigned by comparison with the values reported<sup>14,15</sup> for aliphatic amines. The frequencies of the most significant bands, namely the NH stretching, the  $\text{NH}_2$  scissors, and the  $\text{NH}_2$  rocking vibrations, are reported in Table III. For the metal complexes of aliphatic amines, it has been shown that the NH stretching frequencies decrease as the strength of the coordinate bond increases,<sup>16,17</sup> and a similar behavior is to be expected for the complexes of  $\beta\text{-L}^+$  and  $\gamma\text{-L}^+$ . Thus, the NH stretching vibrations of these complexes, which appear as well-defined and relatively strong bands, rather broad because of hydrogen bonding, indicate that the bond stability varies in the order  $\text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$ , following the Irving-Williams<sup>18</sup> series for these divalent metal ions. The other absorption bands in the sodium chloride region are of little interest in relation to the coordinating ability of the ligands. However, it may be worthwhile to note that the frequencies of the NH deformation vibration in the 1600  $\text{cm}^{-1}$  region are rather high, although both the positive charge on the ammonium ion and the coordination of the amine group to the metal might be expected to lower their value. In the CsBr region, the  $\text{ClO}_4$  deformation vibration at about 623  $\text{cm}^{-1}$  and the  $\text{NH}_2$  rocking mode at 600–550  $\text{cm}^{-1}$  could be assigned with confidence. The  $\text{NH}_2$  rocking frequencies vary with the metal ion, increasing with the strength of the coordinate bond in the order of the Irving-Williams series. The remaining bands in this region of the spectra were too broad and weak to permit valid assignments, and it was therefore not possible to identify the metal-to-nitrogen stretching frequency.

As mentioned previously, the metal complexes of  $\beta\text{-L}^+$  and  $\gamma\text{-L}^+$ , with the exception of the Pd(II) complex, are easily decomposed by water and wet solvents. Also, as shown by their electronic spectra in solution, they undergo a more or less extensive solvolysis in nearly all organic liquids in which they dissolve. For this reason solution studies of their spectra were not carried out and it was also difficult to find a medium for conductivity measurements. For conductivity, acetonitrile appeared to be the only suitable solvent. In fact, the solution spectra of the complexes in acetonitrile are fairly close to those of the solids in position, contour, and relative intensity of the bands, but differ from the spectra of the acetonitrile complexes of the

metal perchlorates, particularly in relative intensity and contour. It therefore appears that no appreciable solvolysis occurs in acetonitrile, as might be expected owing to its weak donor character. The conductivity values of the complexes of the positive ion ligands in acetonitrile are reported in Table I. It would have been interesting to compare the conductivities of these high-charge electrolytes with those of other salts in the same solvent. Unfortunately, only very scarce data are available for conductivities in acetonitrile and they are limited to salts of low-charge ions, because the salts of high-charge polynuclear ions are generally insoluble in this solvent. A comparison between the conductivity values obtained experimentally and those calculated for completely solvolyzed complexes may be of interest. Using the minimal values of 150 and 300  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-2}$  for the conductivities of the positive ion ligand and  $\text{M}(\text{ClO}_4)_2$ , respectively, in acetonitrile at the experimental concentrations, one would expect an apparent conductivity of 1200 and 900  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  for the completely dissociated 8:1 and 6:1 electrolytes, respectively. The experimental values (Table I) are appreciably lower. The conductivity of the Pd(II) complex is close to that expected by interpolation for a 4:1 electrolyte and suggests ion pair formation.

In order to compare the basicity of the two cation ligands with one another and with that of similar amines, the acid dissociation constants of the acid perchlorate salts,  $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{NH}_3](\text{ClO}_4)_2$  and  $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_3\text{NH}_3](\text{ClO}_4)_2$ , were determined. It was found that the propyl analog has  $\text{p}K_a = 8.82$ , corresponding to the lower end of the range of  $\text{p}K_{\text{BH}^+}$  for aliphatic amines, whereas the ethyl analog has a value lower by about two units,  $\text{p}K_a = 6.91$ , and close to the  $\text{p}K_{\text{BH}_2^{2+}}$  of diprotonated ethylenediamines.<sup>11</sup> This appreciable difference between the  $\text{p}K_a$  values of the ethyl and propyl analogs, arising from the presence in the latter of one additional  $-\text{CH}_2-$  group interposed between the  $-\text{NH}_3^+$  and the  $(\text{CH}_3)_3^+\text{N}-$  groups, finds a parallel in the value of  $\text{p}K_a$  reported for a number of polyamine acid salts.<sup>19</sup>

### Conclusions

The metal complexes of the  $\gamma\text{-L}^+$  and  $\beta\text{-L}^+$  ligands are analogous, in their stoichiometry and steric configurations, to those of short-chain, aliphatic primary amines. In fact, the six-coordinated Co(II) and Ni(II) complexes have octahedral spin-free configurations, the complexes of Zn(II) and Cd(II) are four-coordinated, and the Pd(II) complex is square-planar. It may be deduced that in compounds of this type the positive charge on the tetrasubstituted ammonium group does not basically alter the donor properties of the primary amino group toward metal ions. However, the influence of the positive charge and of the number of methylene groups interposed between it and the primary amino group is clearly shown in the  $\text{p}K_a$  values of the acid perchlorate salts of the two ligands. Thus, the value of  $\text{p}K_a$  for the propyl analog, 8.82, is fairly close

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to the value of aliphatic monoamines, whereas the value of  $pK_a$  for the ethyl analog, 6.91, corresponds to an acidity a hundred times greater and falls in the range of methyl-substituted, diprotonated ethylenediamines. Consequently, since the donor tendency of an amino group toward a metal ion can be expected, in the absence of steric hindrance, to run parallel to its basic strength, the propyl analog should be a better complexing agent than the ethyl analog. The electronic spectra of the nickel(II) complexes indicate that in fact the  $\gamma$ - $L^+$  ligand has a field strength very close to that of methylamine, whereas the  $\beta$ - $L^+$  ligand is much weaker and in the spectrochemical series occupies a position about halfway between a primary amine and water. That the propyl complexes were actually the more difficult to isolate may simply be explained by their greater solubility.

It might have been expected that the difference in ligating ability between  $\beta$ - $L^+$  and  $\gamma$ - $L^+$  would also be reflected in the frequency of the NH stretching and the

$NH_2$  rocking vibrations of the complexes, since these infrared modes are sensitive to the strength of the coordinate bond. Failure to observe this difference may be ascribed to the balancing effects of the increased strength of the coordinate bond and of the decreased withdrawal of electrons from the N-H bond, as the positive charge is farther removed from the donor amino group.

The results of this research show that the presence of a positive charge on a ligand does not in itself seriously prevent the formation of a coordinate bond to metal ions. It is therefore to be expected that, by an appropriate choice of multiple-charge cation ligands capable of chelation or  $\pi$ -bonding, a large variety of new complex metal cations can be formed, of higher charge and greater stability than those reported here.

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## Electron Transfer through Mediators Coordinated to Cobalt by Nitrogen Atoms<sup>1</sup>

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The chromium(II) reduction of a number of cobalt(III) ammine complexes containing ligands coordinated by nitrogen has been examined. The ligands studied include urethane, methyl glycinate, benzocaine, ethyl nicotinate and isonicotinate, and ethyl 4-aminobutyrate. The complexes are reduced at a rate fifty to a thousand times faster than complexes containing similar ligands attached to cobalt through oxygen. Since the possibility of adjacent attack no longer exists in the case of these substituted amines, reduction through ligands of low conductivity can be studied and is found to fall off rapidly as the number of  $-CH_2-$  groups in the transfer path increases. The decrease is not related to the steric consequences of the increase in ligand size, a factor that has also been studied. The introduction of a group of low conductivity but containing atoms with electrons available for reductant bonding results in the lowering of the free energy of activation by 3 kcal./mole from that for the chromium(II) reduction of the parent hexaamminecobalt(III) ion.

### Introduction

The use of carboxylic acids as mediators in electron-transfer reactions is limited by the fact that reduction by attack at some remote site on the ligand, to be measurable, must proceed at a rate equal to or greater than reaction *via* the adjacent carboxyl. Since the specific rate of adjacent attack is approximately  $0.15 M^{-1} \text{ sec.}^{-1}$  at room temperature (taking the value of the chromium(II) reduction of acetatopentaamminecobalt(III) ion as an example<sup>3</sup>), this value effectively represents the lower limit of measurement, at least with chromium(II) ion as reductant. In contrast, the specific rate for the Cr(II) reduction of hexaamminecobalt(III) ion at 25° is  $9 \times 10^{-5} M^{-1} \text{ sec.}^{-1}$ , fifteen

hundred times as slow.<sup>4</sup> The possibility of substituted amines as mediators is immediately suggested, for just as electron transfer is slow through the coordinated  $NH_3$  group because of the lack of unpaired electrons on the nitrogen, adjacent attack in the amine-N complexes should be negligible. This paper reports the study of the rates of reduction of some pentaammine complexes containing substituted amines in the sixth coordination position about the cobalt.

### Experimental

**Materials.**—Methyl aminoacetate (methyl glycinate), ethyl 4-aminobutyrate, and the esters of the nicotinic acids were obtained from the acids *via* the respective acid chlorides. The ester hydrochlorides were freed from HCl by treating an ether suspension with either sodium hydroxide or barium hydroxide, drying the ether solution of the ester over magnesium sulfate, and removing the ether at a low temperature in the absence of

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