on the donor nitrogens. Correlations with basicity and with Hammett substituent constants both indicate this, and it is corroborated to some extent by the nmr chemical shifts of the ligand protons. This conclusion is unexpected, since the function of the metal ion in promoting decarboxylation is to serve as a positive center to attract electrons from the substrate, and more basic ligands should decrease the charge on the metal ion. A tentative explanation is suggested from the examination of Mn–N overlap integrals. More basic ligands would be more tightly bound to the metal. If the enhancement of catalytic ability were due to delocalization into the ligand π-system of the negative charge which develops on the oxygen of the substrate during reaction, then the more basic ligands would be the best enhancers.

The rates of zinc catalysis are not easily correlated with the electron availability on the ligand nitrogens, nor can the same argument that was made involving overlap integrals of manganese be used for zinc. The rates do seem well correlated, however, with the energies of the lowest $\pi \rightarrow \pi^*$ transitions of the ligands. Based on previous explanations of similar phenomena, it is possible to argue that low-lying excited states tend to mix with the ground state as the transition state is approached. The free energy of activation would thus be decreased in complexes containing lower lying excited states.

Transition Metal Complexes with the Tetradentate Ligand 3,3',3''-Triaminotripropylamine: Stability Constants
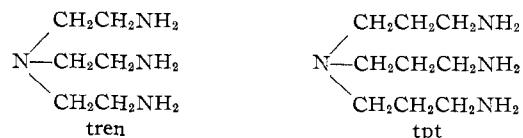
By A. DEI, P. PAOLETTI,[1] AND A. VACCA

The four basicity constants of 3,3',3''-triaminotripropylamine (tpt) and the formation constants of its complexes with Co(II), Ni(II), Cu(II), and Zn(II) have been determined by potentiometric titration in 0.1 M KCl at 25°. The calculation of the constants and the relative standard deviations was carried out on the IBM 1620 computer, using a FORTRAN program based on the generalized least-squares procedure of "pit mapping" due to Sillén. The following values of the protonation constants of the ligand have been obtained: $\log K_1 = 10.511$, $\log K_{12} = 9.824$, $\log K_{13} \approx 9.129$, and $\log K_{14} = 5.615$. In addition to normal complexes $M(tpt)^{2+}$, Co(II) and Cu(II) give at high pH hydroxo complexes $M(tpt)(OH)^+$. Ni(II) and Cu(II) also form a protonated complex $M(Htpt)^{3+}$. The formation constants of the above complexes have been calculated: $\log K_1 = 6.360, 8.702, 13.117$, and 10.702, for Co(II), Ni(II), Cu(II), and Zn(II), respectively; $\log K(ML^{2+} + OH^- \rightleftarrows ML(OH)^+) = 2.990$ and 3.991 for M = Co and Cu, respectively; and $\log K(M^{2+} + HL^+ \rightleftarrows MHL^{3+}) = 5.27$ and 10.757 for M = Ni and Cu, respectively. The stability constants of the normal complexes are compared with the corresponding values, from the literature, for 2,2',2''-triaminotriethylamine (tren) and 3,3'-diaminodipropylamine (dpt). The lower stability of the tpt complexes compared with those of tren (4.0–6.5 log units) seems to be due to the greater strain present in six-membered chelate rings.

Introduction

2,2',2''-Triaminotriethylamine (tren) is able to form metal complexes with different stereochemistry. For example, in a thermochemical study[2] it was shown that in aqueous solution Co(II) forms a high-spin five-coordinated complex $Co(tren)(H_2O)^{2+}$. Structural investigation of the solid complexes of general formula $M(tren)(NCS)_2$ showed that although the Ni(II) complex is octahedral,[3] the Cu(II)[4] and Zn(II)[5] complexes have a trigonal-bipyramidal configuration. Furthermore the visible spectrum of the complex $Co(tren)(NCS)_2$ has been interpreted on the basis of a

five-coordinated structure.[6] These results are in agreement with the findings of a calorimetric investigation of two series of polyamine complexes;[7] that is, for Cu(II), Zn(II), and Co(II) the five-coordinated configuration is favored, while for Mn(II), Fe(II), and Ni(II) the octahedral configuration is more stable.

We have presently initiated a study of the complexes formed in aqueous medium by a ligand similar to tren but which has a longer aliphatic chain, namely, 3,3',3''-triaminotripropylamine (tpt). This ligand has

$$
\begin{array}{cc}
\begin{array}{l}
\quad CH_2CH_2NH_2 \\
\diagup \\
N{-\!\!-}CH_2CH_2NH_2 \\
\diagdown \\
\quad CH_2CH_2NH_2 \\
\quad\quad tren
\end{array}
&
\begin{array}{l}
\quad CH_2CH_2CH_2NH_2 \\
\diagup \\
N{-\!\!-}CH_2CH_2CH_2NH_2 \\
\diagdown \\
\quad CH_2CH_2CH_2NH_2 \\
\quad\quad tpt
\end{array}
\end{array}
$$

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(2) P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

(3) D. Hall and M. D. Woulfe, *Proc. Chem. Soc.*, 346 (1958); S. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

(4) P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc.*, **89**, 724 (1967).

(5) P. C. Jain, E. C. Lingafelter, and P. Paoletti, *ibid.*, **90**, 519 (1968).

(6) M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6**, 1261 (1967).

(7) P. Paoletti and M. Ciampolini, *ibid.*, **6**, 64 (1967).

not previously been the subject of a thermodynamic investigation. The present work reports results permitting the identification of the species present in solution and the calculation of formation constants, both ligand basicity constants and complex stability constants. From previous studies[8,9] it is possible to predict that tpt will be more basic than tren but will form less stable complexes. On the other hand, it is not possible to say *a priori* if the greater bulk of the propylene chain will favor or not the formation of complexes with a coordination number lower than six.

Experimental Section

Materials.—Solutions of metal chlorides were prepared and stored as previously described.[8] Nitrogen was purified by passing it over pyrophoric copper at 100°.

tpt·4HCl·0.5H$_2$O was prepared as described by Mann and Pope.[10] The yield from this reaction was extremely low. All attempts to obtain tpt by other methods, for example, by catalytic reduction of tris-β-cyanoethylamine, proved futile. An aqueous solution of the free base was obtained by passing a solution of the hydrochloride through a column filled with Amberlite IRA 400 anion-exchange resin. The water was removed by distillation and the base was then distilled under vacuum. A sample of the distillate, titrated with standard HCl, proved to be 100.0% pure.

A 0.1 *M* KOH solution was prepared by diluting BDH concentrated KOH with CO$_2$-free water and was stored in a flask of neutral Jena glass. A few crystals of BaCl$_2$ were added to this solution to indicate any possible contamination due to CO$_2$. The strength of the solution was checked before every measurement and the maximum variations observed were of the order of 0.5%. An approximately 0.25 *M* solution of tpt was prepared using CO$_2$-free water, and it was then standardized by potentiometric titration against standard HCl. The titer of this solution was checked prior to every measurement using a method described in the section on calculations. The solution was stored in a neutral glass flask, connected directly to a piston buret and furnished with a soda lime tube.

Emf Measurements.—The apparatus for the potentiometric titrations has already been described elsewhere.[11] The standard potential of the electrode, $E°$, was measured, as previously described,[11] every morning and afternoon, and it was checked before every measurement by a method described in the section on calculations.

For the determination of basicity constants the thermostated cell contained about 110 ml of a 0.1 *M* KCl solution containing *ca.* 0.1 mmol of tpt and 0.5 mmol of HCl. When complex formation constants were being determined, the cell contained in addition to the above varying quantities (0.04–0.10 mmol) of metal chloride. The solutions were titrated with 0.1 *M* KOH using a piston buret graduated to 0.01 ml. Potentiometric curves were not obtained for metal/ligand mole ratios greater than 1 because hydroxide precipitation occurred before an appreciable amount of the complex had been formed.

Equilibrium was attained almost instantaneously in all systems, except in the case of Ni(II) where it was necessary to wait 10 min after each addition before a stable potential was obtained.

The experimental values of the emf have not been corrected for liquid junction potentials or for the potential drift of the electrode during the measurements. Preliminary acid–base titrations, carried out using the same experimental conditions, showed that the magnitude of the correction due to these effects

was negligible in the pH range 3–11, since it was of the same order of magnitude as the experimental error of the potentiometer (0.2 mV).

The ionic product for water was determined in 0.1 *M* KCl as described in a previous publication;[11] the value found (pK_w = 13.78) is in excellent agreement with the literature value.[12]

Results

The concentration conditions (concentration of metal ion, ligand, and acid; $-\log$ [H$^+$] and $\bar{n}$ intervals) for all of the systems are shown in Table I. Some of the titration curves (with metal/ligand mole ratios close to 1) are shown in Figure 1.

TABLE I

EXPERIMENTAL DETAILS OF THE
POTENTIOMETRIC MEASUREMENTS[a]

| Curve	Ion	Initial concn, m*M*			Range	
		MCl$_2$	tpt	HCl	$-\log$ [H$^+$]	$\bar{n}$
1[b]	H$^+$		0.895	4.922	2.9–10.6	
2			0.881	4.478	3.0–10.6	
3			0.891	5.024	2.8–10.6	
4	Co^{2+}	0.697	0.927	4.509	3.1–8.9	0.0–0.6
5		0.455	0.940	4.554	3.1–10.7	0.0–1.0
6[b]		0.880	0.977	5.226	2.9–8.9	0.0–0.5
7		0.908	0.984	5.105	2.9–8.9	0.0–0.5
8[b]	Ni^{2+}	0.752	0.915	4.517	3.1–10.8	0.0–1.0
9		0.757	0.904	4.403	3.1–10.8	0.0–1.0
10		0.437	0.920	4.513	3.1–10.8	0.0–1.0
11[b]	Cu^{2+}	0.871	0.921	4.933	2.9–10.7	0.0–1.0
12		0.821	0.882	4.768	2.9–10.6	0.0–1.0
13		0.447	0.929	4.554	3.1–10.7	0.0–1.0
14	Zn^{2+}	0.872	0.953	4.671	3.1–8.1	0.0–0.9
15[b]		0.790	0.926	4.509	3.1–10.8	0.0–1.0
16		0.423	0.910	4.430	3.1–10.8	0.0–1.0

[a] Reference 13. [b] Shown in Figure 1.
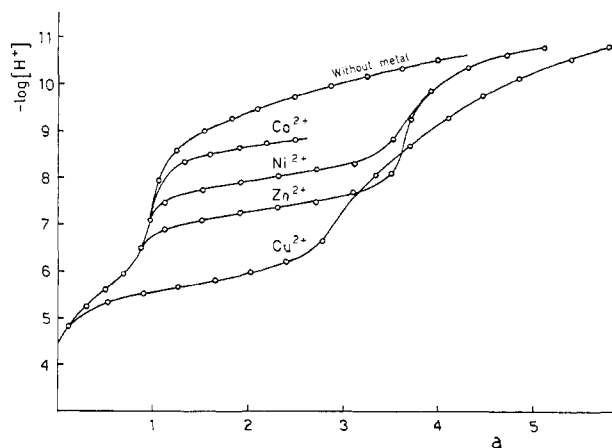
Figure 1.—Illustration of the titration curves 1, 6, 8, 11, and 15 of Table I: $-\log$ [H$^+$] = ($E°$ − E)/59.154. *a* represents the number of moles of KOH added per mol of tpt after the excess of HCl over the molar ratio HCl/tpt = 4 was neutralized; open circles, experimental points; solid lines, values calculated from the equilibrium constants reported in Table II.

In the case of Co(II) the precipitation of the hydroxide prevents the completion of the titration curve when the metal/ligand mole ratio is close to 1, but complete curves were obtained using a lower relative concentration of the cobalt salt.

(8) A. Vacca, D. Arenare, and P. Paoletti, *Inorg. Chem.*, **5**, 1384 (1966).

(9) P. Teyssiè, G. Anderegg, and G. Schwarzenbach, *Bull. Soc. Chim. Belges*, **71**, 177 (1962).

(10) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 489 (1926).

(11) P. Paoletti, J. H. Stern, and A. Vacca, *J. Phys. Chem.*, **69**, 3759 (1965).

(12) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 634.

For Fe(II) and Mn(II) all attempts to obtain titration curves failed owing to the precipitation of the hydroxides before an appreciable amount of the complex had been formed.

Calculations

All of the equilibrium constants reported in this study have been obtained from data points on three different titration curves: 83–160 points were used for each system.[13] In calculating the equilibrium constants we have followed the method of "pit mapping" proposed by Sillén.[14] Each point on a titration curve represents a state of equilibrium between different species of general formula $H_pM_qL_r$ (where M = metal and L = ligand). The charges have been omitted for clarity. For details on this symbolism see ref 8. The concentration of the species $H_pM_qL_r$ is given by the equation $[H_pM_qL_r] = \beta_{pqr}[H]^p[M]^q[L]^r$, where β_{pqr} is the formation constant of the species under consideration, and [H], [M], and [L] are the concentrations at equilibrium of the hydrogen ion, the metal ion, and the free ligand. Let us consider the mass balance equations

$$T_M = [M] + \sum q\beta_{pqr}[H]^p[M]^q[L]^r \qquad (1)$$

$$T_L = [L] + \sum r\beta_{pqr}[H]^p[M]^q[L]^r \qquad (2)$$

where T_M and T_L are the total concentrations of metal and ligand present. If arbitrary values are assigned to the constants β_{pqr}, eq 1 and 2 become two nonlinear equations in the unknown [M] and [L] since [H] is known from the potentiometric measurements. Values of [M] and [L] which satisfy the equations are calculated by the reiterative method of Newton–Raphson.[15] In particular systems, for example in the absence of metal ion (basicity constants) or in cases where protonated or hydroxo complexes were absent, the calculations were speeded up by suitable simplifications. Using values obtained in this way a value of T_H is calculated

$$T_H = [H] + \sum p\beta_{pqr}[H]^p[M]^q[L]^r \qquad (3)$$

It is then possible to calculate the volume of KOH using the relationship: $vol_{calcd} = (H_0 - T_HV)/C_{KOH}$ (where H_0 = number of millimoles of acid added, V = volume in milliliters of the solution in the cell, and C_{KOH} = KOH titer). The calculated volume is compared with the actual volume added, vol_{exptl}. If the agreement for all N points on the curve is not satisfactory, the values of β_{pqr} can be varied in turn so as to minimize the sum of the squares of the residuals

$$U = f(\beta_{pqr}) = \sum_{i=1}^{N} (vol_{exptl} - vol_{calcd})_i^2$$

The search of the minimum of the function U is carried out using Sillén's "pit mapping" procedure.[14] The calculations were performed on an IBM 1620 computer using an appropriate FORTRAN program (LG/2). After each cycle, the computer gave the refined values of the constants, the relative standard deviations, and the value of U. In addition, as a measure of the closeness of fit, the standard deviation on the titer, σ_{vol}, which is calculated from the standard formula

$$\sigma_{vol} = \sqrt{U/(N - n)}$$

was also printed out by the computer. The program stops the calculations when the values for the constants calculated in two successive cycles differ by less than a small preestablished amount.

In general the calculation of the complex formation constants was commenced assuming that the only complex present was $M(tpt)^{2+}$. Later, other complexes were tried in turn. Of course, the number of possible species $H_pM_qL_r$ which could be chosen is very large. However, many species could be discarded immediately owing to their very improbable existence in a chemical sense for the considered systems. In addition by an inspection of the residuals calculated for the curves under consideration, it was possible to anticipate the types of complexes (hydroxo, protonated, or polynuclear complexes) most probable for a particular system. When one of these conceivable new complexes was included and considered by the program, one of the following descriptions usually was observed: (a) the value of the constant converges in the successive cycles to a satisfactory limit with a small relative standard deviation, and at the same time the error-square sum decreases; (b) the constant of the new species, through a progressive decrease, becomes negative, while the agreement with experiment is not improved appreciably; (c) a positive value of the constant is obtained, which is, however, smaller than three times the corresponding standard deviation. If case a occurred, the new constant was retained for subsequent calculation. In cases b and c it was discarded, and the corresponding species was assumed to be unimportant.

Sometimes it was found that residuals calculated for similar curves showed patterns of very small positive and negative deviations. On the other hand, no better agreement could be reached either by varying the values of the constants or by introducing new species.

The titer of tpt and the potential E° were checked at the beginning of each titration. As mentioned in the Experimental Section, the solutions being investigated contained excess HCl (about 5.5 times the amount of amine) which was titrated with varying amounts of KOH. The computer found values of T_L and E° giving the best agreement between the calculated and experimental volumes for that part of the curve where free acid is still present. In the calculation of the

(13) All of the data taken from the potentiometric curves of Table I and used in the calculations of the constants (488 data points) have been deposited as Document No. 9834 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $2.50 for photoprints, or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(14) L. G. Sillén, *Acta Chem. Scand.*, **16**, 159 (1962); **18**, 1085 (1965); N. Ingri and L. G. Sillén, *Arkiv Kemi*, **23**, 97 (1964).

(15) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1956, p 492.

constants the values of T_L and $E°$ obtained in the way just described were used. The titer obtained in this way for the tpt solution tended to vary with time, and after a few days it reached a value that was 0.3% less than the initial analytical titer. The agreement between the values of $E°$ found using this method and those found before and after the titration was on the average ±0.4 mV.

The percentages of the species present were calculated for all curves, and relative distribution diagrams are shown in Figures 2–5. The full lines show percentages relative to total metal, while the broken lines show percentages relative to total ligand.

Discussion

Basicity Constants.—The basicity constants for 3,3′,3″-triaminotripropylamine are shown in Table II. Comparison with the corresponding constants for tren, determined by Schwarzenbach at 20° in 0.1 M KCl[16] and later corrected to 25°[17] (log K_1 = 10.14, log K_{12} = 9.43, and log K_{13} = 8.41) shows that (a) the amine groups are more basic in tpt than in tren and (b) the tertiary nitrogen is largely protonated in tpt, while in tren it is not. This is obviously due to smaller electrostatic repulsion exerted by the three positive poles which are further from the tertiary nitrogen in tpt than in tren. As a consequence it is possible to obtain a solution which contains essentially the wholly protonated species H_4tpt^{4+} below pH 4.

An examination of the basicity constants leads to the conclusion that the first three stages of protonation involve the three equivalent primary nitrogen atoms. It is thus easy to understand why it is not possible to obtain solutions containing only a mono- or diprotonated species. On the other hand, it is possible to obtain only the species H_3tpt^{3+} for values of pH close to 7, and this species is presumed to be symmetrically protonated on three primary nitrogen atoms.

Complexes of Co(II).—The formation constants for the complexes $Co(tpt)^{2+}$ and $Co(tpt)(OH)^+$ are shown in Table II. In a first calculation carried out assuming the presence of only one complex species $Co(tpt)^{2+}$, the agreement between the experimental and calculated titers was within a standard deviation of 0.053 ml and log K_1 = 6.367. The introduction of the hydroxo complex lowered the value of σ_{vol} to 0.011 ml, but the value of the constant for the normal complex (see Table II) is only decreased by a very small amount. This appears to be the first known case in which a cobalt(II) polyamine complex undergoes hydrolysis in solution. Assuming the formation of a protonated complex $Co(Htpt)^{3+}$ does not give better agreement and the program calculated a negative value for its constant. From the distribution diagram (Figure 2), obtained using the refined constants, it is seen that the normal complex $Co(tpt)^{2+}$ never exists alone but is always found together with free metal ion or with the hydroxo complex. Furthermore, in the
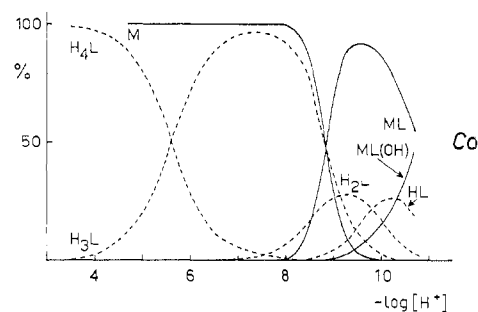
(16) J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 963 (1950).
(17) P. Paoletti and M. Ciampolini, *Ric. Sci. Suppl.*, **33** (II-A), 405 (1963).

Figure 2.—Distribution diagram for the system Co^{2+}–tpt. The percentages have been calculated from the data of curve 5 in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.
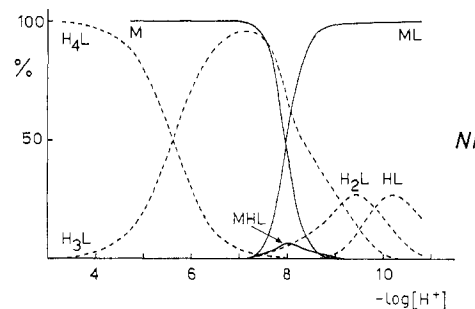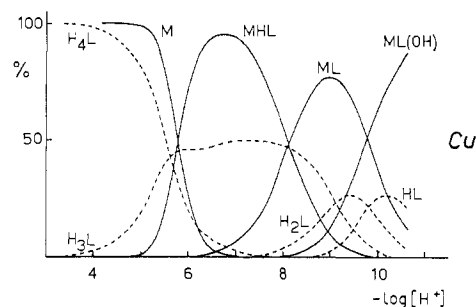

Figure 3.—Distribution diagram for the system Ni^{2+}–tpt. The percentages have been calculated from the data of curve 10 in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

Figure 4.—Distribution diagram for the system Cu^{2+}–tpt. The percentages have been calculated from the data of curve 13 in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

range of pH in which complexes are formed, the mono- and diprotonated forms of the ligand are also present in appreciable quantities.

Complexes of Ni(II).—Nickel(II) and tpt form a normal complex and a protonated complex $Ni(Htpt)^{3+}$ (Table II). The interpretation of the experimental data simply on the basis of a single complex $Ni(tpt)^{2+}$ gives a fairly good fit (log K_1 = 8.710 and σ_{vol} = 0.017 ml). The inclusion of new species does not lead to better agreement except in the case of $Ni(Htpt)^{3+}$. As was observed in the case of cobalt, the introduction of a second species did not lead to an appreciable change in the constant for the normal complex; however,

Table II

Basicity Constants of 3,3',3''-Triaminotripropylamine (tpt) and
Stability Constants of Its Metal Complexes in 0.1 M KCl at 25.0°[a]

Ion	Reaction	Log K	
H^+	$H^+ + tpt \rightleftharpoons Htpt^+$	10.511 ± 0.004	K_1
	$H^+ + Htpt^+ \rightleftharpoons H_2tpt^{2+}$	9.824 ± 0.007	K_{12}
	$H^+ + H_2tpt^{2+} \rightleftharpoons H_3tpt^{3+}$	9.129 ± 0.006	K_{13}
	$H^+ + H_3tpt^{3+} \rightleftharpoons H_4tpt^{4+}$	5.615 ± 0.009	K_{14}
Co^{2+}	$Co^{2+} + tpt \rightleftharpoons Co(tpt)^{2+}$	6.360 ± 0.004	K_1
	$Co(tpt)^{2+} + OH^- \rightleftharpoons Co(tpt)(OH)^+$	2.990 ± 0.036	$K_{Co(tpt)(OH)}$
Ni^{2+}	$Ni^{2+} + tpt \rightleftharpoons Ni(tpt)^{2+}$	8.702 ± 0.004	K_1
	$Ni^{2+} + Htpt^+ \rightleftharpoons Ni(Htpt)^{3+}$	5.27 ± 0.10	$K_{Ni(Htpt)}$
Cu^{2+}	$Cu^{2+} + tpt \rightleftharpoons Cu(tpt)^{2+}$	13.117 ± 0.009	K_1
	$Cu^{2+} + Htpt^+ \rightleftharpoons Cu(Htpt)^{3+}$	10.757 ± 0.008	$K_{Cu(Htpt)}$
	$Cu(tpt)^{2+} + OH^- \rightleftharpoons Cu(tpt)(OH)^+$	3.991 ± 0.020	$K_{Cu(tpt)(OH)}$
Zn^{2+}	$Zn^{2+} + tpt \rightleftharpoons Zn(tpt)^{2+}$	10.702 ± 0.003	K_1

[a] Uncertainty limits associated with all values are twice the standard deviations.
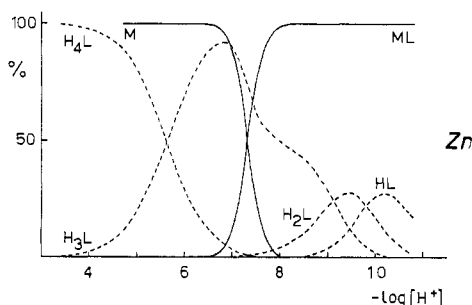

Figure 5.—Distribution diagram for the system Zn^{2+}-tpt. The percentages have been calculated from the data of curve 16 in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

Figure 6.—Stability constants of the complexes ML^{2+} (where L = tpt, dpt, or tren) plotted vs. the atomic number of the metal. For tren and dpt complexes the values are taken from ref 16 and 8, respectively.

σ_{vol} improved to 0.009 ml. In fact, the protonated complex must be considered as a species of secondary importance since the extent of formation in our measurements never exceeded 6% (see Figure 3). From the distribution diagram it is also seen that for pH 9 all of the nickel(II) is present in the form of the normal complex.

Complexes of Cu(II).—When equivalent amounts of metal and ligand are present (curves 11 and 12 in Table I and Figure 1) the titration curves show a jump at $a = 3$ suggesting the possible formation of a monoprotonated copper complex. Consequently both the normal and the protonated complexes were introduced from the start in the calculation of the constants. With this assumption the values $\sigma_{vol} = 0.329$, $\log K_1 = 13.304$, and $\log K_{Cu(Htpt)} = 10.755$ were obtained. The agreement was definitely not good, especially in the high pH range. This led us to consider the formation of a hydroxo complex $Cu(tpt)(OH)^+$ and this in turn led to a greatly improved fit with $\sigma_{vol} = 0.007$. The refined constants are shown in Table II and it appears that only the constant of the normal complex has been affected appreciably by the introduction of the hydroxo complex. Metal complex formation with tpt occurs even at pH 5, and while it is possible to obtain the protonated or hydroxo complexes alone in solution, the normal complex is always present together with one of the above two (Figure 4). Unlike
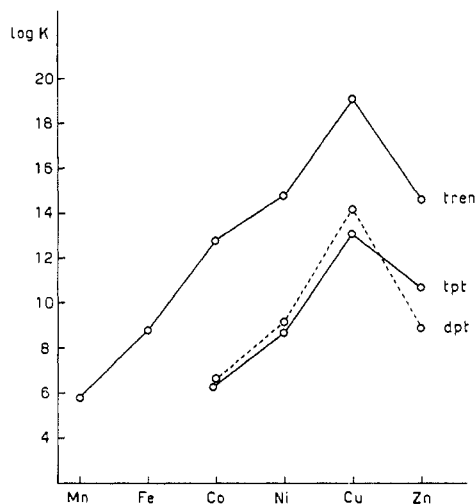
the nickel(II) compound the copper protonated complex is very stable and the reaction $Cu^{2+} + H_3tpt^{3+} \rightarrow Cu(Htpt)^{3+} + 2H^+$ is favored, sharply reducing the concentration of the triprotonated ligand in solution (Figure 4).

Complexes of Zn(II).—Zinc forms only the normal complex with tpt. Attempts to improve the excellent agreement between the experimental and calculated titers obtained upon the assumption of only one normal complex formed ($\sigma_{vol} = 0.007$ ml) proved fruitless. It is noteworthy that this complex is particularly stable, being actually more stable than the corresponding nickel complex (Table II). It is thus surprising that zinc does not form a protonated complex like nickel and that there is no hydroxo species such as occurs in other zinc–polyamine systems. In the series of metal ions investigated this is the only case in which the metal is completely present as the normal complex even at pH 8 (see Figure 5).

Conclusions

In Figure 6 the values of log K for the formation of the normal complexes with tpt, tren,[16] and dpt[8] are plotted against the atomic number of the metal ion.

As expected, even though tpt is more basic than tren, it forms less stable complexes with the difference between the formation constants varying between 6.5 log units for cobalt(II) and 4 log units for zinc(II). The reason for this large destabilization must be that the tpt complexes have six-membered chelate rings, and it is well known that these are less stable than analogous five-membered rings. The complexes M-$(tpt)^{2+}$ are, with the exception of that of zinc(II), slightly less stable than those of dpt. This is surprising considering that dpt has one less donor amine group.

Thus it may be suspected that only three nitrogen atoms in tpt were involved in coordination (two primary and one tertiary), but in this case the values of the equilibrium constants for

$$M(tpt)^{2+} + H^+ \rightleftharpoons M(Htpt)^{3+}$$
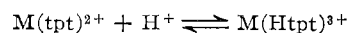
should be very close to the first basicity constant of the free amine. However, the value observed for nickel(II) (log K = 7.1) is too low to justify such a hypothesis, while for copper(II) (log K = 8.2) no conclusions may be drawn.

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Mass Spectral Studies of Metal Chelates. II. Mass Spectra and Appearance Potentials of Acetylacetonates of Trivalent Metals of the First Transition Series

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The mass spectra are reported for the tris acetylacetonates of Ti, V, Cr, Mn, Fe, Co, and Al as well as the appearance potentials of $M(acac)_3^+$ and $M(acac)_2^+$ derived from these compounds. The results are not in agreement with theoretical calculations and electronic spectra of these molecules.

Introduction

A number of papers dealing with the mass spectrometric investigation of metal acetylacetonates have recently been published.[1-4] These studies are potentially useful in elucidating bonding and molecular and electronic structure of these compounds. In this paper we report a systematic study of the mass spectra of the acetylacetonates of trivalent metals of the first transition series and the appearance potentials of ions derived therefrom. Also studied were acetylacetone and aluminum tris(acetylacetonate). The lack of reproducibility between mass spectra of acetylacetonates of Mn, Cr, Fe, and Co in previous studies[1,3] is explained with the help of the appearance potential measurements and different conditions of introduction of the compounds into the ionization chamber.

Although appearance potentials have been determined for many organometallic compounds,[5,6] little effort has been made to interpret the results in terms of the electronic structures of these compounds. For carbonyl compounds, for example, Winters and Kiser[6] have simply commented that on ionization the electron is removed from an orbital localized largely on the metal atom.

For metal acetylacetonates, molecular orbital calculations have been published.[7-10] These calculations have helped toward a better though still controversial interpretation of the electronic spectra. Barnum[7] has obtained good agreement between calculated and observed energies. Because of difficulties in determining the effect of substituents on the energy of the excited states of a molecule, Price[11] has stated that "the simpler changes which occur in ionization potentials are easier to assess and can be regarded as being a first step in elucidating those which occur in absorption bands." Consequently, it is hoped that the results presented in this paper will result in more thorough theoretical calculations and lead to a better interpretation of the electronic spectra of these compounds.

(1) C. G. MacDonald and J. S. Shannon, *Australian J. Chem.*, **19**, 1545 (1966).
(2) J. Macklin and G. Dudek, *Inorg. Nucl. Chem. Letters*, **2**, 403 (1966).
(3) S. Sasaki, Y. Itagakki, T. Kwokawa, K. Nakanishi, and A. Kasahara, *Bull. Chem. Soc. Japan*, **40**, 76 (1967).
(4) C. Reichert, J. B. Westmore, and H. D. Gesser, *Chem. Commun.*, 782 (1967).
(5) R. W. Kiser, M. A. Krassoi, and R. J. Clark, *J. Am. Chem. Soc.*, **89**, 3653 (1967), and references therein.
(6) R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **4**, 157 (1965).
(7) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); **22**, 183 (1961).
(8) J. P. Fackler, F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).
(9) K. DeArmand and L. S. Forster, *Spectrochim. Acta*, **19**, 1393 (1963).
(10) L. S. Forster, *J. Am. Chem. Soc.*, **86**, 3001 (1964).
(11) R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc.* (London), **A258**, 459 (1960).