then the equilibrium constant for reaction 1 can be calculated. The probable value is 7×10^2; this corresponds to a free energy change of -4 kcal./mole. Values of ΔH, -12 kcal./mole, and ΔS, -34 e.u., for reaction 1 were calculated from the activation parameters for the forward and reverse reactions.

Studies on the reaction of *trans*-Pt(NH$_3$)$_4$Cl$_2^{2+}$ and NH$_3$ in dilute unbuffered NH$_3$ indicate that the products include 50% or less Pt(NH$_3$)$_5$Cl^{3+}. Moreover, the change in absorbance at 318 mμ of reaction mixtures does not give linear first- or second-order kinetic plots. Sufficiently detailed studies to ascertain the nature of the products of the reaction were not performed. However, it seems clear that the previous kinetic study on this system[2] at best reflects the total rate of two or more concurrent or consecutive processes. The most probable side reaction is hydrolysis (eq. 3). Kinetic

$$\text{\textit{trans}-Pt(NH}_3)_4\text{Cl}^{2+} + \text{OH}^- \rightarrow \text{\textit{trans}-Pt(NH}_3)_4\text{ClOH}^{2+} + \text{Cl}^- \tag{3}$$

data on reaction 3 at 25° in the pH range 10–11 are not available, but examination of related data does suggest hydrolysis would compete with the slow replacement of chloride by ammonia (in the absence of Pt(NH$_3$)$_4^{2+}$).[5,13]

Zvyagintsev and Shubochkina also reported rate data on other reactions of dihalotetraammine complexes with ammonia and pyridine.[2] In view of the present study all of these data need review. The reactions with pyridine are less likely to be subject to a competing hydrolysis reaction, since the pyridine reactions are faster and pyridine is a much weaker base than ammonia. However, if their data are accurate, it still seems likely that a platinum(II)-catalyzed process will provide an alternate route to products.

(13) A. A. Grinberg and Yu. N. Kukushkin, *Zh. Neorgan. Khim.*, **6**, 1095 (1961).

Metal Chelates of Triethylenetetraminehexaacetic Acid[1]

By T. A. Bohigian, Jr., and A. E. Martell

Potentiometric studies of the interaction between the decadentate chelating agent triethylenetetraminehexaacetic acid (TTHA) and various metal ions are described. Evidence is given for the formation of Th(IV) chelates having a 1:1 ratio of Th(IV) to ligand, Cu(II), Co(II), Ni(II), and La(III) chelates with 1:1 and 2:1 molar ratios of the respective metal ions to ligand, and chelates containing 1:1, 2:1, and 3:1 molar ratios of Mg(II) and Ca(II) ions to ligand. Formation constants are calculated and probable coordinate bonding of the 1:1, 2:1, and 3:1 chelates is deduced.

One of the objectives of coordination chemists has been to synthesize chelating agents which have the highest possible affinities toward metal ions. A survey of published stability constants in collections such as the tables of stability constants by Sillén and Martell[2] reveals that the achievement of high stability has been developed about as far as seems possible with the synthesis and investigation of ethylenediaminetetraacetic acid and a number of analogous compounds and derivatives.

It has been noted, however, that some of the metal chelates of diethylenetriaminepentaacetic acid are considerably more stable than those of EDTA, especially for the more highly charged ions. It would seem, therefore, that further extension of the EDTA structure

to the analogous substituted tetramine, the decadentate ligand triethylenetetraminehexaacetic acid shown in formula I, is of interest because of the possibility of further increasing the affinity of the ligand for metal ions of $+3$ and $+4$ charge. Further, because of the presence of ten coordinating groups, this ligand would provide some interesting possibilities for the formation of polynuclear complexes with metals of lower charge or relatively low coordination number. A potentiometric investigation of the interaction between TTHA and various metal ions was therefore carried out to determine the nature and extent of these reactions. The metal chelates of Ca(II), Mg(II), Cu(II), Co(II), Ni(II), La(III), and Th(IV) ions were studied in varying ratios of metal ion to ligand.

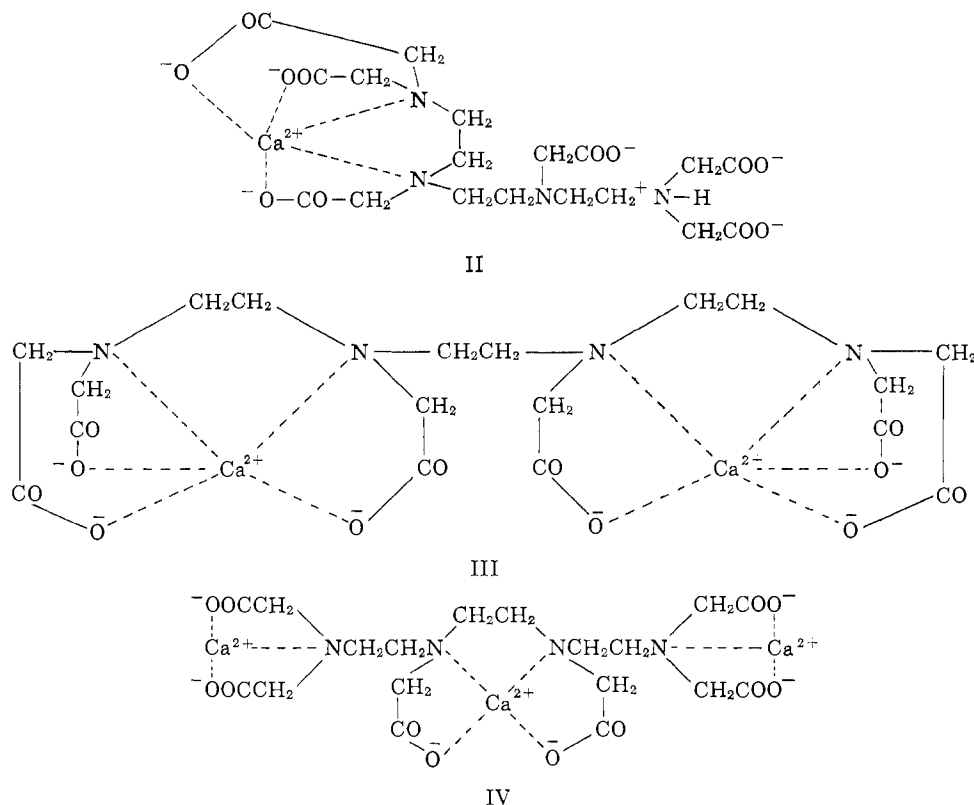While this work was in progress Grimes, *et al.*,[3]

(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1020.

(2) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes, Section II, Organic Ligands," The Chemical Society, London, 1964.

(3) J. H. Grimes, A. J. Huggard, and S. P. Wilford, *J. Inorg. Nucl. Chem.*, **25**, 1225 (1963).

reported formation of diprotonated, monoprotonated, mononuclear, and binuclear chelates of TTHA and the alkaline earth ions. The present work differs from theirs in that a detailed quantitative study is made of the possible formation of ternuclear complexes of magnesium and calcium and in the extension of equilibrium studies to interesting TTHA chelate systems involving lanthanum, thorium, and some representative transition metal ions.

Experimental

Triethylenetetraminehexaacetic acid (TTHA) was obtained through the courtesy of the Dow Chemical Co., Midland, Mich. The purity of the compound was established by nitrogen analysis and potentiometric titration. The results of these two criteria checked exactly with the theoretical values. Solutions of Cu(II), Co(II), Ni(II), Mg(II), Ca(II), and Th(IV) were prepared from the respective nitrate salts. The Cu(II), Co(II), and Ni(II) solutions were standardized by titration with standard disodium salt of ethylenediaminetetraacetic acid, with murexide as an indicator.[4] The Mg(II) and Ca(II) solutions were standardized by titration with standard disodium EDTA, with Eriochrome-schwarz T as an indicator.[4] The Th(IV) solution was standardized gravimetrically by ignition to ThO_2. A stock solution of lanthanum nitrate was prepared from reagent grade lanthanum oxide and was standardized by ignition to the oxide.

The experimental method consisted of potentiometric titration of the hexabasic acid TTHA in the absence and presence of the metal ion being investigated. A Radiometer Model pH M4 pH meter fitted with extension glass and saturated calomel electrodes was calibrated to determine hydrogen ion concentrations by titration against standard acid, base, and an acetic acid–acetate buffer using the known concentration constant for our experimental conditions as given by Harned and Owen.[5] Measurements were made at a temperature of 25° and at a constant ionic strength of 0.1 M in KNO_3. The ligand concentration in all titrations was 2×10^{-3} M. With the exception of Th(IV), all metal ions studied were titrated in both 1:1 and 2:1 molar ratios of metal ion to ligand. In addition, systems containing Ca(II) and Mg(II) were also titrated in 3:1 and 10:1 molar ratios of metal ion to ligand.

Results

The neutralization of the free ligand TTHA occurs in three steps, as is shown by the titration curve in Figure 1, which has a weak inflection at $a = 3$ (where a is the moles of base added per mole of ligand present in the experimental solution) and a stronger inflection at $a = 4$. The first step, requiring three equivalents of

$$\underset{I}{\overset{\overset{\displaystyle 1 \quad\quad 2 \quad\quad 3 \quad\quad 4}{HOOCCH_2 \quad H \quad\ H \quad\ H \quad\ H \ CH_2COOH}}{\underset{{}^-OOCCH_2}{\diagdown}\,^+NCH_2CH_2N^+CH_2CH_2N^+CH_2CH_2N^+\diagup\underset{CH_2COO^-}{}\underset{CH_2COO^-}{}\diagdown CH_2COO^-}}$$

base, is the reaction of the neutral (uncharged) form of the ligand, I, to give a trinegative anion with protons in positions 1, 2, and 4 or 1, 3, and 4. The next neutralization step occurs at higher pH and results in the removal of the proton from one of the basic nitrogen atoms near the center of the polyamine chain, at positions 2 and 3, since the formation of a tetraanion

(4) G. Schwarzenbach, "Die Komplexometrische Titration," Ferdinand Enke, Stuttgart, 1955, pp. 62, 63, 78, 79, 82.

(5) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Co., New York, N. Y., 1950, p. 523.
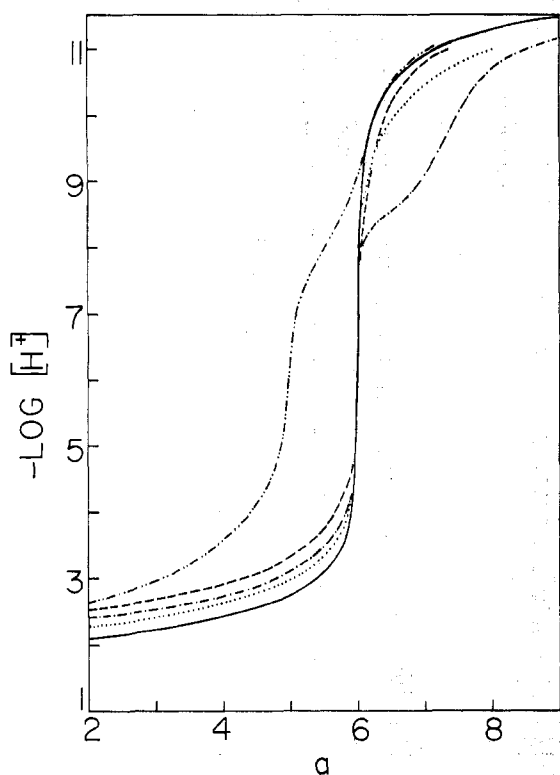

Figure 1.—Potentiometric titration of Ca(II)–TTHA chelates at 25° in 0.1 M KNO_3 with the following molar ratios of metal ion to ligand: ———, ligand alone; . . . . . ., Ca (1:1); - - - - - - - -, Ca (2:1); —·—·—, Ca (10:1). Ligand concentration (T_L) = 2.0×10^{-3} M; a = moles of base added per mole of ligand.

protonated in the 1 and 4 positions would have the least mutual electrostatic repulsion between the protonated amino groups.

Combination of the triprotonated ligand with one Ca(II) ion per mole results in the displacement of two protons in the pH range 4–6, with a definite inflection in the curve at $a = 5$ (Figure 1), probably corresponding to the formation of a protonated metal chelate, II, which then dissociates at somewhat higher pH. With a 2:1 molar ratio of Ca(II) ion to ligand, it is seen that the buffer region corresponding to the second dissociation is lowered, indicating that the second metal ion combines with the protonated chelate II to give a binuclear complex indicated by III.

When there is a large excess of metal ion, interaction with the ligand is seen to be stronger, as the result of the formation of a binuclear complex III, a ternuclear complex IV, or higher polynuclear complexes. From the analogous potentiometric titration curves for Mg(II) (not shown), it may be deduced that the reactions of the Mg(II) ion with TTHA in 1:1, 2:1, 3:1, and 10:1 molar ratios of metal ion to ligand are similar to those described for the Ca(II) ion. Neutralization of the ligand in the presence of a threefold molar concentration of Ca(II) ion results in considerable further lowering of the buffer region of the second dissociation steps, indicating the possible formation of a ternuclear complex IV. The analogous 3:1 Mg–TTHA curve also showed this type of interaction. A superposition of the 1:1 Mg(II) and Ca(II) curves shows a deeper depression of the $-\log$ [H^+] values for Ca(II), thus indicating that the interaction between the ligand

and the Ca(II) ion is similar to but stronger than that with the Mg(II) ion. This observation is in accord with the behavior of analogous ligands, such as EDTA and DTPA.

Interaction of TTHA with a molar equivalent of Cu(II) ion, illustrated in Figure 2, results in the formation of a protonated metal chelate, as evidenced by a steep inflection at $a = 5$. There is a subsequent dissociation step, the pK value of which ($\sim$8) is lowered from that of pK_6 of the free ligand because of the combination of the metal ion with adjacent coordinating groups. In the presence of two moles of the Cu(II),

the two metal ions to form a binuclear chelate compound. Above pH 8 the complex disproportionates to give a precipitate of La(OH)$_3$ plus an aqueous solution containing the more stable chelate compound formed from the 1:1 mixture. Drifting to lower pH values was observed in the buffer region where La(OH)$_3$ precipitation occurs.

The potentiometric titration curve for the 1:1 Th–TTHA chelate compound has a single steep inflection at $a = 6$ and no subsequent hydrolysis step, indicating that the complex formed is extremely stable. Addition of base to greater than 1:1 ratios of Th(IV)

II

III

IV

it is seen that all of the available protons on the ligand are neutralized in a single step and a binuclear chelate is formed. This system has a sharp inflection at $a = 6$. Results similar to the Cu(II) case are obtained when Co(II) is titrated with TTHA in 1:1 and 2:1 molar ratios of metal ion to ligand.

Interaction of 2 moles of Ni(II) ion with TTHA yields a curve similar to the Cu(II) and Co(II) cases. The 1:1 Ni–TTHA titration curve again shows evidence of the formation of a protonated chelate, but the subsequent dissociation step is not well defined as in the case of Cu(II) and of Co(II).

When La(III) ion is combined with TTHA in an equivalent molar ratio, a very sharp inflection is noted in the potentiometric titration curve at an a value of 6 (Figure 2). This indicates formation of a stable 1:1 chelate.

In the presence of two moles of La(III) per mole of the ligand, both La(III) ions are bound (i.e., the solution is free of precipitate) up to a pH of 8, indicating that the donor groups of the ligand are shared between

ion to ligand results in precipitation of the excess Th(IV), indicating that stable binuclear chelates are not formed in this case.

Calculations

All equilibrium constants reported in this investigation were calculated using 10–15 data points taken from the entire buffer region of interest in each case; the data are presented in Table I.

Acid Dissociation Constants.—Calculation of the first three acid dissociation constants of TTHA was carried out by means of a modification of the method outlined by Carlson, *et al.*[6] The dissociation constants thus determined are given in Table II.

The single step dissociation constant corresponding to $a = 3$–4 was calculated algebraically in the usual way. The dissociation constants corresponding to the two overlapping dissociation steps from $a = 4$ to 6 were determined by the graphical method of Schwarzen-

(6) G. A. Carlson, J. P. McReynolds, and F. H. Verhoek, *J. Am. Chem. Soc.*, **67**, 1335 (1945).

Figure 2.—Potentiometric titration of Cu(II), La(III), and Th(IV) chelates of TTHA at 25° in 0.1 M KNO$_3$ with the following molar ratios of metal ion to ligand: ——·——, Cu (1:1); ......, Cu (2:1); ————, La (1:1); —·—·—, La (2:1); ———, Th (1:1); T_L = 2.0 × 10^{-3} M.

TABLE I
POTENTIOMETRIC EQUILIBRIUM MEASUREMENTS OF TTHA SYSTEMS[a]
μ = 0.10 (KNO$_3$); 25°; T_L = 2.0 × 10^{-3} M

	Free TTHA				1:1 Mg–TTHA				1:1 Ca–TTHA		
a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$
0.20	2.715	3.67	6.448	0.08	2.677	5.27	8.945	0.17	2.701	4.79	6.113
0.51	2.804	3.72	6.561	0.61	2.841	5.32	9.051	0.69	2.865	4.89	6.477
0.82	2.916	3.82	6.854	1.12	3.044	5.37	9.148	1.21	3.081	5.00	7.081
1.08	3.096	3.93	7.275	1.54	3.277	5.42	9.229	1.57	3.293	5.10	7.715
1.23	3.101	4.03	8.014	1.90	3.549	5.48	9.510	1.78	3.455	5.20	8.018
1.39	3.186	4.14	8.555	2.22	3.851	5.58	9.462	1.99	3.605	5.25	8.146
1.54	3.282	4.24	8.838	2.42	4.067	5.68	9.608	2.20	3.796	5.31	8.260
1.70	3.394	4.34	9.018	2.62	4.320	5.79	9.735	2.40	3.998	5.36	8.368
1.80	3.475	4.45	9.180	2.83	4.587	5.89	9.892	2.61	4.191	5.41	8.483
2.01	3.655	4.50	9.241	3.04	4.837	5.95	9.970	2.82	4.387	5.46	8.595
2.22	3.872	4.60	9.367	3.25	5.035	6.05	10.096	3.03	4.562	5.51	8.647
2.37	4.049	-.71	9.475	3.51	5.222			3.23	4.718	5.62	8.789
2.53	4.250	4.82	9.586	3.66	5.327			3.39	4.806	5.72	8.956
2.74	4.578	4.91	9.674	3.82	5.424			3.49	4.892	5.82	9.140
2.89	4.901	5.02	9.767	3.97	5.527			3.60	4.963	5.95	9.363
3.00	5.171	5.12	9.855	4.13	5.634			3.75	5.067	6.03	9.602
3.15	5.520	5.22	9.946	4.28	5.753			3.91	5.166		
3.31	5.851	5.33	10.023	4.40	5.850			4.06	5.272		
3.36	5.918	5.48	10.148	4.54	5.998			4.22	5.392		
3.41	6.014	5.59	10.229	4.73	6.294			4.32	5.479		
3.46	6.093	5.74	10.339	4.85	6.552			4.42	5.573		
3.51	6.172	5.90	10.447	4.96	7.142			4.53	5.686		
3.57	6.265			5.06	8.194			4.63	5.819		
3.62	6.354			5.22	8.821			4.68	5.899		

	2:1 Mg–TTHA		2:1 Ca–TTHA		3:1 Mg–TTHA		3:1 Ca–TTHA		2:1 Cu–TTHA		2:1 Ni–TTHA
a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$
4.02	5.265	4.00	5.011	4.01	5.154	4.29	5.051	1.45	2.196	1.40	2.102
4.23	5.364	4.16	5.106	4.24	5.245	4.46	5.162	1.97	2.662	1.91	2.105
4.38	5.456	4.33	5.220	4.46	5.336	4.62	5.306	2.49	2.355	2.45	2.822
4.59	5.537	4.50	5.342	-.69	5.436	4.74	5.422	3.01	2.419	2.69	2.896
4.69	5.649	4.61	5.446	4.91	5.544	4.85	5.569	3.53	2.519	3.80	2.355
5.05	5.824	4.72	5.573	5.17	5.673	4.96	5.765	3.79	2.578	3.78	2.452
5.16	5.908	4.78	5.647	5.50	5.944	5.02	5.880	4.05	2.644	3.98	2.495
5.26	6.008	4.85	5.754	5.67	6.178	5.08	5.982	4.31	2.714	4.23	2.551
5.36	6.114	4.95	5.950	5.84	6.539	5.13	6.081	4.57	2.800	4.36	2.564
5.47	6.265	5.06	6.206	6.01	7.666	5.25	6.320			4.54	2.648
5.52	6.346	5.27	6.473			5.30	6.464				
5.57	6.440	5.28	6.745								
5.62	6.542	5.40	6.996								
5.68	6.659	5.51	7.296								
5.73	6.823	5.62	7.558								
5.78	6.991	5.74	7.926								
5.83	7.196	5.85	8.331								
5.88	7.458	5.96	8.822								
5.95	7.764										
5.99	8.202										

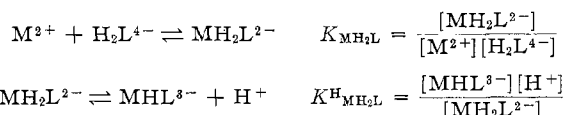|	2:1 Co–TTHA		1:1 La–TTHA		2:1 La–TTHA
a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$	a	$-\log[\text{H}^+]$
1.44	2.201	1.57	2.479	1.78	2.581
1.96	2.055	1.89	2.518	2.35	2.447
2.48	2.318	2.81	2.560	2.64	2.496
3.00	2.390	2.53	2.607	2.95	2.585
3.26	2.451	2.85	2.660	3.22	2.657
3.58	2.475	3.17	2.718	3.51	2.699
3.78	2.585	3.49	2.704	3.80	2.686
4.04	2.580	3.81	2.864	4.08	2.790
4.30	2.644	4.13	2.954	4.37	2.652
4.56	2.737				

[a] T_L = total analytical concentration of ligand in all forms.

TABLE II
EQUILIBRIUM CONSTANTS OF TTHA AND ITS METAL CHELATES

Metal ion	Ratio [metal]/[ligand]	Reaction	Log K	
H$^+$		H$^+$ + L^{6-} ⇌ HL^{5-}	10.19	$K_1{}^H$
		H$^+$ + HL^{5-} ⇌ H$_2$L^{4-}	9.40	$K_2{}^H$
		H$^+$ + H$_2$L^{4-} ⇌ H$_3$L^{3-}	6.16	$K_3{}^H$
		H$^+$ + H$_3$L^{3-} ⇌ H$_4$L^{2-}	4.16	$K_4{}^H$
		H$^+$ + H$_4$L^{2-} ⇌ H$_5$L^{-}	2.95	$K_5{}^H$
		H$^+$ + H$_5$L^{-} ⇌ H$_6$L	2.42	$K_6{}^H$
Mg^{2+}	1:1	Mg^{2+} + H$_2$L^{4-} ⇌ MgH$_2$L^{2-}	2.81	$K_{\text{MgH}_2\text{L}}$
	1:1	Mg^{2+} + HL^{5-} ⇌ MgHL^{3-}	7.55	K_{MgHL}
	1:1	Mg^{2+} + L^{6-} ⇌ MgL^{4-}	8.43	K_{MgL}
	2:1	MgL^{4-} + Mg^{2+} ⇌ Mg$_2$L^{2-}	5.5	$K_{\text{Mg}_2\text{L}}$
	3:1	Mg$_2$L^{2-} + Mg^{2+} ⇌ Mg$_3$L	5.32	$K_{\text{Mg}_3\text{L}}$
Ca^{2+}	1:1	Ca^{2+} + H$_2$L^{4-} ⇌ CaH$_2$L^{2-}	3.76	$K_{\text{CaH}_2\text{L}}$
	1:1	Ca^{2+} + HL^{5-} ⇌ CaHL^{3-}	8.23	K_{CaHL}
	1:1	Ca^{2+} + L^{6-} ⇌ CaL^{4-}	9.89	K_{CaL}
	2:1	CaL^{4-} + Ca^{2+} ⇌ Ca$_2$L^{2-}	4.32	$K_{\text{Ca}_2\text{L}}$
	3:1	Ca$_2$L^{2-} + Ca^{2+} ⇌ Ca$_3$L	4.00	$K_{\text{Ca}_3\text{L}}$
Cu^{2+}	2:1	2Cu^{2+} + L^{6-} ⇌ Cu$_2$L^{2-}	27.6	
Co^{2+}	2:1	2Co^{2+} + L^{6-} ⇌ Co$_2$L^{2-}	28.0	
Ni^{2+}	2:1	2Ni^{2+} + L^{6-} ⇌ Ni$_2$L^{2-}	29.5	
La^{3+}	1:1	La^{3+} + L^{6-} ⇌ LaL^{3-}	23.1	
	2:1	2La^{3+} + L^{6-} ⇌ La$_2$L	26.9	
Th^{4+}	1:1	Th^{4+} + L^{6-} ⇌ ThL^{2-}	>>27	

bach.[7] The dissociation constants thus determined (Table II) are in fairly good agreement with those of Frost[8] and Grimes.[3]

For the 1:1 Mg(II) and Ca(II) systems, where two protonated metal chelates, MH$_2$L and MHL, are formed in the region a = 2–5 (Figure 1), the equilibria involved are

$$M^{2+} + H_2L^{4-} \rightleftharpoons MH_2L^{2-} \qquad K_{\text{MH}_2\text{L}} = \frac{[MH_2L^{2-}]}{[M^{2+}][H_2L^{4-}]}$$

$$MH_2L^{2-} \rightleftharpoons MHL^{3-} + H^+ \qquad K^H_{\text{MH}_2\text{L}} = \frac{[MHL^{3-}][H^+]}{[MH_2L^{2-}]}$$

From the usual mass balance and electroneutrality relationships the following equations may be obtained

$$[HL^{5-}] = \frac{T_{OH} + [H^+] - [OH^-] - 3T_M + \dfrac{[H^+]}{K^H_{\text{MH}_2\text{L}}}[T_{OH} + [H^+] - [OH^-] - 2T_M]}{Y - 3X + \dfrac{Y[H^+]}{K^H_{\text{MH}_2\text{L}}} - \dfrac{2X[H^+]}{K^H_{\text{MH}_2\text{L}}}} \qquad (1)$$

$$K_{\text{MH}_2\text{L}} = \frac{[3T_M - 3[HL^{5-}]]X - T_{OH} - [H^+] + [OH^-] + [HL^{5-}]Y K^H_2}{[HL^{5-}]^2[H^+]X} \qquad (2)$$

where T_M is the total concentration of metal ion species and T_{OH} is the total concentration of base added. Also

$$X = 1 + \sum_{i=1}^{n-1} \frac{[H^+]^i}{\prod\limits_{Z=2}^{i+1} K^H_Z} \qquad \text{where } n = 4$$

$$Y = 3 + \sum_{i=1}^{n-1} \frac{(n-i)[H^+]^i}{\prod\limits_{Z=2}^{i+1} K^H_Z} \qquad \text{where } n = 3$$

where K^H_n represents the corresponding dissociation constant of the ligand. A series of values was assumed

(7) G. Schwarzenbach, A. Willi, and R. O. Bach, *Helv. Chim. Acta*, **30**, 1303 (1947).
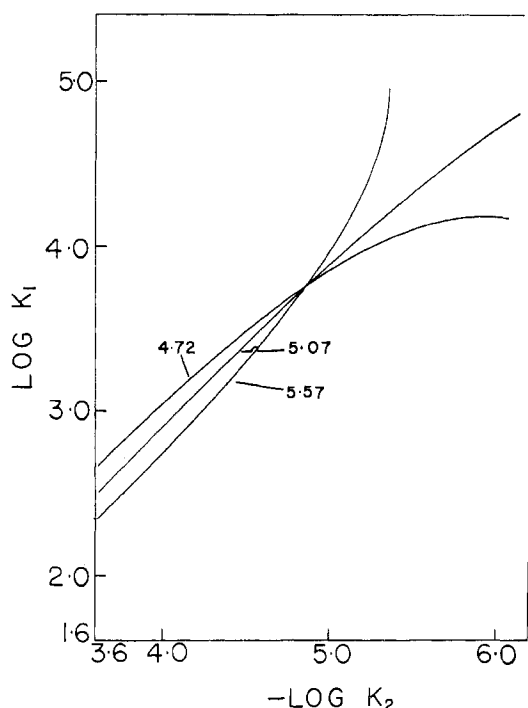(8) A. E. Frost, *Nature*, **178**, 322 (1956).

Figure 3.—Graphical solution for stepwise equilibrium constants, K_{CaH_2L} and $K^H_{CaH_2L}$; numbers on curves indicate $-\log$ [H$^+$] values.

for $K^H_{MH_2L}$ and corresponding values for K_{MH_2L} were calculated from eq. 2. The resulting values of K_{MH_2L} were plotted against the assumed values of $K^H_{MH_2L}$ to give the intersecting lines shown in Figure 3. The different lines obtained from different points on one titration curve all intersect at one point as shown in Figure 3 for the 1:1 Ca–TTHA system. This indicates the existence of a set of unique values for K_{MH_2L} and $K^H_{MH_2L}$ which will satisfy the assumed two-step reaction at any point along the titration curve between $a = 2$ and 5. Values for log K_{MH_2L} and K_{MHL} (obtained from the equation $K_{MHL} = (K_{MH_2L})(K^H_{MH_2L})/K^H_2$) are listed in Table II.

Values for K_{MHL} were also determined by a one-step calculation involving the equilibrium

$$M^{2+} + HL^{5-} \rightleftharpoons MHL^{3-} \qquad K_{MHL} = \frac{[MHL^{3-}]}{[M^{2+}][HL^{5-}]}$$
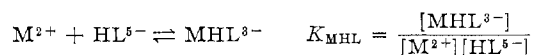
The final expression obtained from the mass balance and electroneutrality relationships is

$$K_{MHL} = \frac{T_M - [HL^{5-}]X}{[HL^{5-}]^2 X}$$

where

$$[HL^{5-}] = \frac{2T_L - T_{OH} - [H^+] + [OH^-]}{Y'}$$

$$Y' = \sum_{i=1}^{n-1} \frac{i[H^+]^i}{i+1 \prod_{z=2} K^H_z}$$

where $n = 3$, X is as defined above, with $n = 3$, and T_L is the total concentration of ligand species.

Values obtained for K_{MHL} using this method (log K_{MgHL} = 7.55, log K_{CaHL} = 8.29) were essentially the same as those determined by the overlap method.

In a similar fashion the following equations were obtained for the formation of the 1:1 La:TTHA chelate compound

$$K_{ML} = \frac{T_M - [L^{6-}]X'}{[L^{6-}]^2 X'}$$

where

$$[L^{6-}] = \frac{5T_L - T_{OH} - [H^+] + [OH^-]}{Y''}$$

$$Y'' = \sum_{i=1}^{n} \frac{i[H^+]^i}{i \prod_{z=1} K^H_z}$$

$$X' = 1 + \sum_{i=1}^{n} \frac{[H^+]^i}{i \prod_{z=1} K^H_z}$$

where $n = 5$ for Y'' and X'.

Mathematical treatment of the 1:1 Cu–, Co–, and Ni–TTHA systems has been attempted by using the same method as was described above for Mg(II) and Ca(II). A unique intersection was not obtained for these systems, thus showing that this mathematical treatment did not lend itself to these systems. The one-step method for determining K_{MHL} described for Mg and Ca was also attempted, but constants were not obtained. Further mathematical treatment of these systems is in progress.

K_{ML} was calculated for the 1:1 Mg and Ca systems between $a = 5$ and $a = 6$ using the equilibria

$$MHL^{3-} \xrightarrow{K^H_{MHL}} ML^{4-} + H^+$$
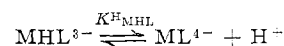
K^H_{MHL} was determined in the usual manner and utilized in calculating K_{ML} by the equation

$$K_{ML} = \frac{(K^H_{MHL})(K_{MHL})}{K^H_1} \qquad (3)$$

Values of K_{M_2L} for Mg and Ca were obtained from the 2:1 curves in the region $a = 4$ to $a = 6$ by use of the equilibrium expressions

$$M^{2+} + L^{6-} \rightleftharpoons ML^{4-} \qquad K_{ML} = \frac{[ML^{4-}]}{[M^{2+}][L^{6-}]} \qquad (4)$$

$$ML^{4-} + M^{2+} \rightleftharpoons M_2L^{2-} \qquad K_{M_2L} = \frac{[M_2L^{2-}]}{[M^{2+}][ML^{4-}]} \qquad (5)$$
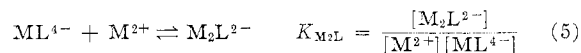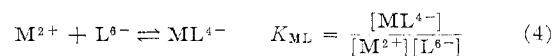
With the usual mass balance and electroneutrality relationships the following expression for K_{M_2L} was obtained

$$K_{M_2L} = \frac{\dfrac{T_L + [L^{6-}]X'}{[M^{2+}]} - 1}{[M^{2+}] - 2[L^{6-}]X'} \qquad (6)$$
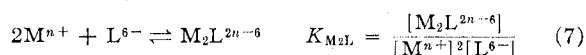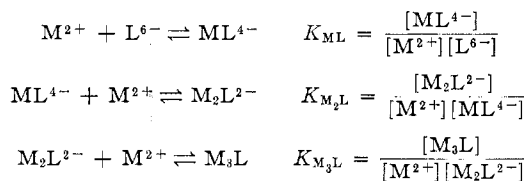
where

$$[L^{6-}] = \frac{4T_L - T_{OH} - [H^+] + [OH^-]}{4X' - Y'''}$$

$$[M^{2+}] = \frac{2[L^{6-}]X'}{1 - K_{ML}[L^{6-}]}$$

$$Y''' = 4 + \sum_{i=1}^{n} \frac{(n - i + 1)[H^+]^i}{\prod\limits_{z=1}^{II} K^H_z}$$

where $n = 3$. X' is defined as above with $n = 4$. For equilibria involving the Ca(II) ion, these equations were modified to take into account the presence of the CaHL^{3-} species. The value for K_{ML} obtained from eq. 3 was used in these calculations and the value for K_{MHL} obtained previously was used in the Ca(II) case.

The following equilibria and equations apply to the binuclear chelate compounds formed by La(III), Co(II), Cu(II), and Ni(II)

$$2M^{n+} + L^{6-} \rightleftharpoons M_2L^{2n-6} \qquad K_{M_2L} = \frac{[M_2L^{2n-6}]}{[M^{n+}]^2[L^{6-}]} \qquad (7)$$

The equation obtained for K_{M_2L} is

$$K_{M_2L} = \frac{T_M - 2[L^{6-}]X'}{8[L^{6-}]^3 X'^2} \qquad (8)$$

where

$$[L^{6-}] = \frac{3T_L - T_{OH} - [H^+] + [OH^-]}{Y''}$$

Y'' is defined as above, with $n = 3$; X' is defined as above, with $n = 3$.

The equilibria and equations for the formation of the ternuclear Mg(II) and Ca(II) complexes are

$$M^{2+} + L^{6-} \rightleftharpoons ML^{4-} \qquad K_{ML} = \frac{[ML^{4-}]}{[M^{2+}][L^{6-}]}$$

$$ML^{4-} + M^{2+} \rightleftharpoons M_2L^{2-} \qquad K_{M_2L} = \frac{[M_2L^{2-}]}{[M^{2+}][ML^{4-}]}$$

$$M_2L^{2-} + M^{2+} \rightleftharpoons M_3L \qquad K_{M_3L} = \frac{[M_3L]}{[M^{2+}][M_2L^{2-}]}$$

The expression obtained for K_{M_3L} is

$$K_{M_3L} = \frac{[M_3L] - K_{ML}[M_3L][L^{6-}]}{2T_L^2 - 4[M_3L]T_L + 5T_L[L^{6-}]X' + 2[M_3L]^2 - 5[M_3L][L^{6-}]X' + 2[L^{6-}]^2X'^2}$$

where X' and $[L^{6-}]$ are as described above and

$$K_{M_2L}[M_3L]^2 + [M_3L](2K_{ML}[L^{6-}] - 2K_{M_2L}T_L - 3K_{M_2L}[L^{6-}]X' - 1) = [L^{6-}]X' - T_L - K_{M_2L}T_L^2 - 3K_{M_2L}T_L[L^{6-}]X' - 2K_{M_2L}[L^{6-}]^2X'^2 + [L^{6-}]^2X'K_{ML} + 2T_LK_{ML}[L^{6-}]$$

Values for K_{ML} from eq. 3 and K_{M_2L} from eq. 6 were used in these calculations.

The equilibrium constants for the combination of the ligand with protons and metal ions, calculated in accordance with the above relationships, are given in Table II.

Discussion

Acid Dissociation Constants.—It is interesting to note that the first low pH three-equivalent buffer region must involve the dissociation of protons from an ammonium group as well as from two carboxyl groups.

This unusual situation is ascribed to the influence of two adjacent positive ammonium groups in decreasing the proton affinity of the central basic nitrogen atoms. This depression in the pK of the $\equiv$N$^+$H group is so great that the ionization of the first of these groups is comparable to that of the carboxyl groups in this ligand. In view of this lowered proton affinity of the basic nitrogen groups, it is apparent that one or more of the negative carboxylate groups present can compete somewhat with the amino group when the ligand is in the binegative form, so that a number of tautomeric species would be present in solution. Two of these possible forms are illustrated by the microscopic equilibrium
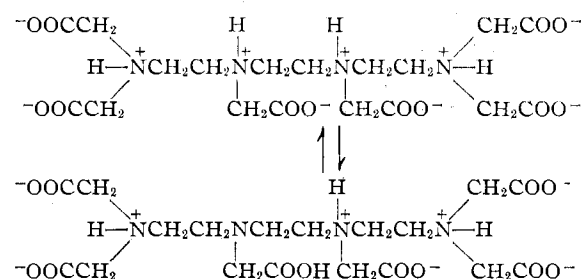
The determination of the microscopic equilibrium constant for this reaction would be very difficult because of the number of functional groups present in the ligand. However, a similar microscopic constant has been reported for the next lower analog, diethylenetriaminepentaacetic acid (DTPA), on the basis of the relative intensities of infrared –COO$^-$ and –COOH bands of the aqueous solute.[9]

The next dissociation probably occurs so as to produce the ligand species having positive nitrogens at the ends of the polyamine chain, with protons at positions 1 and 4 (formula I). The other possibility is a species in which the protons are on alternate nitrogen atoms. Although some of this form no doubt is present, the weak coulombic repulsion between the positive nitrogen atoms would tend to make it less stable.

This reaction is similar to the third dissociation of EDTA, in that the affinity of the proton for the basic nitrogen atom is considerably reduced by its proximity to another positive protonated nitrogen atom only two carbons away. The resulting pK value (6.16) is very close to that of EDTA under the same conditions. The remaining dissociation constants (pK_5 and pK_6) are about normal (p$K \sim 10$) for aliphatic ammonium groups, since the dissociating groups are far enough apart that coulombic repulsive interactions tending to lower pK_5 are minimized.

Formation Constants.—On the basis of the equilibrium constants calculated for the formation of protonated chelates of Mg(II) and Ca(II), II is proposed for these complexes. An alternative arrangement in which the calcium ion is coordinated to the two central nitrogen atoms is less probable since this would require a positive charge on a nitrogen atom adjacent to a nitrogen atom coordinated to the metal ion, rather

(9) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 309 (1963).

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than on the second nitrogen atom removed. Also, in order to coordinate the Ca(II) ion at five or six positions, the alternate arrangement of ligand donor groups would require that the Ca(II) ion be coordinated to three nitrogen atoms and only two or three negative carboxyl groups. Since such complexes are usually considered to have relatively low stability, II is favored for the monoprotonated complexes.

The most probable coordinate bonding of all the binuclear complexes found in this investigation is III, since it involves the maximum coordination of both metal ions with negative carboxylate groups.

The formation constants for the ternuclear chelates of Ca(II) and Mg(II), illustrated by formula IV, are the first reported stability constants for a ternuclear metal chelate known to the authors. The relatively low stability of this chelate, as evidenced by log $(K_{ML} \cdot K_{M_3L}K_{M_3L})/3 \ll \log K_{ML}$, is to be expected in view of the smaller number of coordinating groups, especially negative coordinating groups, available per metal ion. This type of effect is also clearly seen in the comparison of the stabilities of the mono- and binuclear chelates of La(III). Since a basic nitrogen atom would have very little affinity for the ions of Ca(II), Mg(II), La(III), and Th(IV), the coordination of a basic nitrogen atom in their complexes is conceivable only if there is contribution to the stability from an adjacent negative carboxylate group. Thus the alternatives for the

1:1 La(III) complexes are penta- and heptacoordination. In view of the stability of this complex, therefore, heptacoordination is favored. On this basis it is clear why the 1:1 complex has only a slight tendency to go over to a binuclear complex analogous to III. Since some of the coordinate bonds in a heptacoordinated mononuclear complex must be broken to form the binuclear complex, it is clear that the latter would not be much more stable than the mononuclear heptacoordinated complex.

Similar arguments may be used to indicate that the very stable Th(IV) TTHA chelate must be nona- or decadentate. This complex is considerably more stable than that of DTPA, which has been shown to hydrolyze at higher pH to give a monohydroxo species. This higher stability reflects higher coordination and hence must involve an additional nitrogen atom plus one or more of the carboxylate groups attached to that nitrogen atom. Also, it is known that the primary stability contributions of the polyaminopolycarboxylic acids come from the negative charges of the carboxylate groups. To achieve higher stability than that of the Th(IV)–DTPA chelate, the TTHA chelate must involve the coordination of one more carboxylate group than the number coordinated in the former.[9] Thus it seems that all six carboxylate groups, and by inference all four nitrogens, of TTHA must be coordinated to the Th(IV) ion, giving a decadentate complex.

Transition Metal Complexes Derived from Octafluorocyclohexa-1,3-diene[1]

By R. L. HUNT[2] and G. WILKINSON

The interaction of octafluorocyclohexa-1,3-diene with octacarbonyldicobalt gives a complex of stoichiometry $Co_2(CO)_6C_6F_6$ which has been shown to have a cyclic fluorocarbon group bridging the metal atoms and bound to them by an acetylenic type bond. With di-π-cyclopentadienylnickel a π-cyclopentadienyl π-allyl complex is obtained, while the product with dicarbonylchlororhodium is an olefin complex.

Introduction

There are comparatively few π-complexes in which perfluoroolefins are bound to transition metal atoms: these are perfluorocyclohexadienetricarbonyliron[3] and its derivative,[4] the π-allylic ion $[C_6F_9Fe(CO)_3]^-$,[4] some recently reported perfluorocyclopentadiene complexes,[5] and a number of complexes derived from perfluorobut-2-yne.[6] We now describe further complexes

obtained from octafluorocyclohexa-1,3-diene. This olefin is not particularly reactive toward metal carbonyls without bridging carbonyl groups, and at temperatures below 175° or under ultraviolet radiation no reaction occurs with $Fe(CO)_5$, $Ni(CO)_4$, $Mn_2(CO)_{10}$, and $Mo(CO)_6$; further, there appears to be no reaction with $PdCl_2$, $PtCl_2$, or square complexes of the type L_2PdCl_2. However, interactions occurred with $Co_2(CO)_8$, $(\pi\text{-}C_5H_5)_2Ni$, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, $[\pi\text{-}C_5H_5Ni(CO)]_2$, and $[Rh(CO)_2Cl]_2$.

Experimental

Materials.—Analyses are by the Microanalytical Laboratory, Imperial College. Octafluorocyclohexa-1,3-diene was provided by Professor J. C. Tatlow, University of Birmingham, to whom we are indebted for generous gifts of this material. Octacarbon-

(1) This research has been supported in part by the United States Air Force under Grant AF EOAR 64-75, European Office of Aerospace Research.

(2) National Science Foundation Postdoctoral Fellow.

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(6) R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 2699 (1964), and other references therein.