tirely ascribable to the activation energy difference. This near-identity of the frequency factors (and thus entropies of activation) offers support for the assumption of identical mechanisms.

Finally, one must note the differences in the reactions of $Coen_2CO_3^+$ ion[3] and $Coen_2C_2O_4^+$. The sensitivity of the carbonato species to acid decomposition must arise from a major difference in mechanism. It has been suggested by experiments using H_2O^{18} that the initial process in the acid decomposition of $Co(NH_3)_4CO_3^+$ is probably C–O bond cleavage,[21] and one would expect $Coen_2CO_3^+$ to show similar behavior. Unfortunately, no comparable data are available for the $Coen_2C_2O_4^+$–OH^- reaction. However, the possibility exists that in the mono-oxalato decomposition, the initial step is metal–oxygen bond fission; such a mechanism would provide a basis for the contrast in behavior observed with the two carbonato species.

Financial support of this work has been generously provided by the U. S. Atomic Energy Commission through Contract No. AT(30-1)-1578 with the University of Buffalo.

[21] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **75**, 4099 (1953); J. P. Hunt, A. C. Rutenberg, and H. Taube, *ibid.*, **74**, 268 (1952).

CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Some Metal Chelates of Ethylenediaminetetraacetic Acid, Diethylenetriaminepentaacetic Acid, and Triethylenetetraminehexaacetic Acid[1,2]

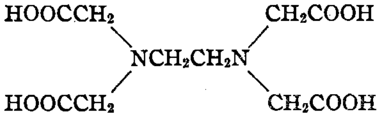
BY ROBERT E. SIEVERS AND JOHN C. BAILAR, JR.

Received September 18, 1961

The properties and structural characteristics of some metal chelates of ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, and triethylenetetraminehexaacetic acid are reported. For chelates of 33 different metal ions, a correlation is observed between the charge/size ratio of the metal ion and the degree of covalency in the metal–oxygen bond. The infrared spectra of chelates of metal ions having charge/size ratios larger than 3.6 exhibit carbonyl absorption maxima in the 1625 to 1650 cm.$^{-1}$ region, but in complexes where the ratio is below 3.6 the maxima occur between 1590 and 1615 cm.$^{-1}$. A Th(IV) complex, in which diethylenetriaminepentaacetic acid apparently functions as an octodentate ligand, was isolated. Syntheses of binuclear Mo(V) complexes of diethylenetriaminepentaacetic acid and triethylenetetraminehexaacetic acids are reported.

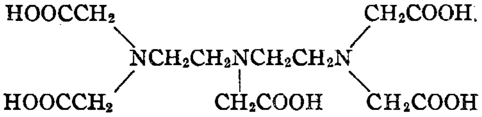
Introduction

This study is concerned with some of the properties and structural characteristics of metal chelates of the polyaminocarboxylic acids shown in I–III.



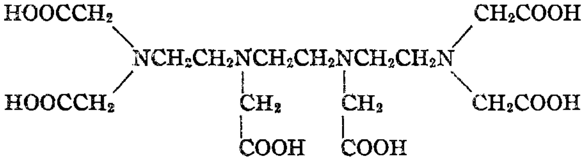
$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$

(I) H_4EDTA



$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)_2$

(II) H_5DTPA



$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)_2$

(III) H_6TTHA

Earlier studies[3–9] of the infrared spectra of metal complexes of EDTA have revealed some very interesting phenomena. It was learned that the asymmetric stretching frequency of the carbonyl group varies considerably in structure IV

---

[1] Based upon a portion of a dissertation submitted by Robert E. Sievers in August, 1960 in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

[2] This research was supported in part by the Socony-Mobil Corporation, whose assistance is gratefully acknowledged.

[3] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953).

[4] D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 716 (1956).

[5] T. Moeller, F. A. J. Moss, and R. H. Marshall, *ibid.*, **77**, 3182 (1955).

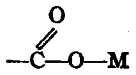
[6] M. L. Morris and D. H. Busch, *ibid.*, **78**, 5178 (1956).

[7] S. Kirschner, *ibid.*, **78**, 2372 (1956).

[8] D. T. Sawyer and P. J. Paulsen, *ibid.*, **80**, 1597 (1958).

[9] D. T. Sawyer and P. J. Paulsen, *ibid.*, **81**, 816 (1959).

as M is changed.



(IV)

When M is a proton, as in H_4EDTA, carbonyl absorption occurs near 1700 cm.$^{-1}$; but if M is a potassium ion, *e.g.* in K_4EDTA, the absorption occurs at 1595 cm.$^{-1}$. In metal–EDTA complexes, absorption maxima are found near 1650 cm.$^{-1}$ when M is Co(III), and at 1600 cm.$^{-1}$ in the case of the Cd(II) complex.

It was suggested that these variations can be accounted for in terms of the nature of the O–M bond.[3] If the bond is primarily ionic, as in the potassium salt, the possibilities for carboxylate resonance are at a maximum. This results in partial single bond character in the carbonyl group and a lower stretching frequency than ordinarily observed for a C=O group. If the covalency of the O–M bond is increased, carboxylate resonance is partially blocked and the frequency is shifted to higher wave numbers. It follows that the location of the carbonyl band can be taken as a measure of the covalent character of the metal–oxygen bond.

In addition to furnishing information about the nature of bonding, infrared evidence has been useful in structure determinations.[3–11] Since the –COOH group absorbs in a different region than a carboxyl group coördinated to a metal ion, it often is possible to detect the existence of such groups in the presence of each other. Furthermore, it is possible in certain instances to detect an uncoördinated $-COO^-$ group in the presence of coördinated carboxyl groups. In the latter case, the technique is restricted to those complexes in which there is a large covalent contribution in the metal–oxygen bond.[6] In complexes in which the bonding is primarily ionic, the absorption of the –COOM group occurs in the same region as the uncoördinated $-COO^-$ group, so it is not possible to distinguish between these two cases.

Protonated carboxyl groups ordinarily can be detected in the presence of either ionically or covalently coördinated carboxyl groups. Therefore, it is advantageous to isolate complexes in protonated form rather than as the alkali metal salts. This decreases the uncertainty encountered in some of the previous studies in the assignment of absorption bands and in the interpretation of the spectra.

Experimental[12]

For reasons mentioned previously, the crystalline complexes were isolated in the acid form in preference to the sodium salt form. In some instances sodium salts crystallize preferentially even from acidic solutions. This was circumvented by preparing the complexes in the absence of alkali metal ions. Strongly coördinating anions also were avoided in most instances. Sirupy or glassy products often resulted upon concentration of aqueous solutions of the complexes, so mixed solvent systems were used to effect crystallization.

The Fe(III) and Ni(II) complexes were dried in vacuo over phosphorus(V) oxide. The rest of the compounds were dried over anhydrous calcium chloride at reduced pressure.

Preparation of Ligands.—H_4EDTA was prepared by the acidification of an aqueous solution of reagent grade $Na_2H_2EDTA \cdot 2H_2O$ (Hach Chemical Co.) with concentrated hydrochloric acid. Commercial grade H_5DTPA (Geigy Chemical Corp.) was purified by recrystallization from a minimum volume of hot water.

Triethylenetetraminehexaacetic acid was made by the procedure of Bersworth,[13] which involves the alkaline condensation of formaldehyde, sodium cyanide, and an amine. The triethylenetetramine (Carbide and Carbon Chemicals Co.) employed in this synthesis was purified by fractional distillation at reduced pressure. The crude alkaline reaction product was purified by passing it through an ion-exchange column containing Dowex 50W-X8 resin (acid cycle). H_6TTHA crystallized upon dropwise addition of the eluate to absolute ethanol. Frost has reported[14] that the compound can be recrystallized from water, but our efforts to do this resulted only in sirupy or glassy products.

Anal. Calcd. for $C_{18}H_{30}N_4O_{12}$: C, 43.72; H, 6.12; N, 11.33. Found: C, 43.60; H, 6.17; N, 11.10.

Monohydrogen aquo(ethylenediaminetetraacetato) aluminate(III), gallate(III), indate(III), and thallate(III).—The methods used to prepare these complexes are similar to those reported by Saito and Terrey.[15] Recrystallization of the Al(III) complex was accomplished by acidifying an aqueous solution with perchloric acid and adding acetone until a white precipitate appeared. A stringy, amorphous product is obtained if acidification is omitted. Although the analyses of the Ga(III) and In(III) complexes deviate appreciably from the calculated values, potentiometric titration curves indicated that the desired compounds were obtained.

Anal. Calcd. for $H[Al(C_{10}H_{12}N_2O_8)(H_2O)]$: C, 35.93; H, 4.52; N, 8.38. Found: C, 35.16; H, 4.75; N, 7.59.

Anal. Calcd. for $H[Ga(C_{10}H_{12}N_2O_8)(H_2O)]$: C, 31.86; H, 4.01; N, 7.43. Found: C, 27.72; H, 4.08; N, 6.56.

Anal. Calcd. for $H[In(C_{10}H_{12}N_2O_8)(H_2O)]$: C, 28.46; H, 3.58; N, 6.64. Found: C, 22.54; H, 3.76; N, 5.91.

Anal. Calcd. for $H[Tl(C_{10}H_{12}N_2O_8)(H_2O)]$: C, 23.47;

---

(10) D. T. Sawyer and J. M. McKinnie, *J. Am. Chem. Soc.*, **82**, 4191 (1960).

(11) F. P. Dwyer and F. L. Garvan, *ibid.*, **82**, 4823 (1960).

(12) The authors wish to thank P. McMahon, C. Juan, J. Nemeth, and their staffs, who helped with the infrared and ultraviolet spectra and the elemental analyses.

(13) F. C. Bersworth, U. S. Patent 2,407,645 (Sept. 17, 1946).

(14) A. E. Frost, *Nature*, **178**, 322 (1956).

(15) K. Saito and H. Terrey, *J. Chem. Soc.*, 4701 (1956).

H, 2.95; N, 5.48. Found: C, 23.34; H, 2.88; N, 5.81.

Monohydrogen (diethylenetriaminepentaacetato-8) thorate(IV) monohydrate[16]—A solution of 27.6 g. (0.05 mole) of thorium(IV) nitrate tetrahydrate dissolved in 100 ml. of water was added to a solution of 19.65 g. (0.05 mole) of H_5DTPA in 800 ml. of water. The resulting solution was evaporated on a steam cone until the volume was reduced to 100 ml. When 600 ml. of acetone was added, a white crystalline solid formed; yield, 29 g. (90%). The crude product was recrystallized from a mixture of 200 ml. of water and 300 ml. of acetone.

Anal. Calcd. for $H[Th(C_{14}H_{18}N_3O_{10})] \cdot H_2O$: C, 26.29; H, 3.31; N, 6.57; Th, 36.30. Found: C, 23.23; H, 3.47; N, 6.28; Th, 37.77.

Monohydrogen (diethylenetriaminepentaacetato) zirconate(IV) trihydrate.—A freshly prepared solution of 16.1 g. (0.05 mole) of zirconium(IV) oxychloride octahydrate in 100 ml. of water was added to 800 ml. of a solution containing an equimolar quantity of H_5DTPA (19.65 g.). The resulting clear solution became hazy upon heating at 80° for 1 hr. The solution was concentrated to a volume of approximately 100 ml. and 1 g. of what appeared to be a polymeric substance was removed by filtration. The clear filtrate was acidified with 3 ml. of concentrated perchloric acid, and when 500 ml. of acetone was added a white precipitate formed. The precipitate was separated by filtration and washed with acetone.

Anal. Calcd. for $H[Zr(C_{14}H_{18}N_3O_{10})] \cdot 3H_2O$: C, 31.45; H, 4.71; N, 7.86; Zr, 17.06. Found: C, 31.61; H, 4.72; N, 8.07; Zr, 17.57.

Dihydrogen (diethylenetriaminepentaacetato-6) ferrate(III).—Iron(III) nitrate nonahydrate (20.2 g., 0.05 mole) was dissolved in 100 ml. of water and an equimolar quantity of crystalline H_5DTPA (19.65 g.) was added. The solution was heated, and after all of the H_5DPTA had dissolved, the temperature was maintained at 70° while 30 ml. of ethanol was added. The solution was allowed to cool slowly, whereupon yellow crystals formed. The crystals were filtered and washed with small amounts of water and then with ethanol; yield, 16.8 g. (75%).

Anal. Calcd. for $H_2[Fe(C_{14}H_{18}N_3O_{10})]$: C, 37.68; H, 4.52; N, 9.42; Fe, 12.52. Found: C, 37.62; H, 4.80; N, 9.38; Fe, 12.50.

Trihydrogen (diethylenetriaminepentaacetato) nickelate (II) monohydrate.—A sample of H_5DTPA was partially dissolved in 200 ml. of water. An equimolar quantity (5.93 g.) of powdered nickel(II) carbonate was added slowly. After evolution of carbon dioxide had subsided, the blue-green solution was boiled until the volume was reduced to 70 ml. When the solution had cooled to 70°, 15 ml. of ethanol was added. The solution was cooled in an ice-bath and blue-green crystals formed.

Anal. Calcd. for $H_3[Ni(C_{14}H_{18}N_3O_{10})] \cdot H_2O$: C, 35.92; H, 4.95; N, 8.98; Ni, 12.54. Found: C, 35.81; H, 5.35; N, 9.81; Ni, 11.96.

Monohydrogen tetraaquo-μ-(diethylenetriaminepentaacetato-3,5) dinickelate(II) trihydrate.—Powdered nickel(II) carbonate was added in small increments, totaling 11.86 g. (0.1 mole), to 19.65 g. (0.05 mole) of H_5DTPA partially dissolved in 200 ml. of water. The solution was boiled for 10 min., then cooled and placed in a vacuum desiccator. After several days a semi-crystalline blue-green solid formed on the surface of the solution.

Anal. Calcd. for $H[Ni_2(C_{14}H_{18}N_3O_{10})(H_2O)_4] \cdot 3H_2O$: C, 26.57; H, 5.26; N, 6.64; Ni, 18.55. Found: C, 26.69; H, 5.13; N, 7.00; Ni, 18.32.

Trihydrogen (diethylenetriaminepentaacetato) cuprate(II) monohydrate.—An equimolar quantity of freshly prepared copper(II) hydroxide was added to 19.65 g. (0.05 mole) of H_5DTPA dissolved in 800 ml. of water. The volume of the solution was reduced to 60 ml. by evaporation on a steam cone. The temperature of the solution was maintained at 70° while 35 ml. of ethanol was added. Blue crystals separated as the solution slowly cooled; yield, 18 g. (76%). Crystals up to 2 cm. in length were obtained upon recrystallization from water by slow evaporation.

Anal. Calcd. for $H_3[Cu(C_{14}H_{18}N_3O_{10})] \cdot H_2O$: C, 35.56; H, 4.90; N, 8.88; Cu, 13.43. Found: C, 35.46; H, 4.84; N, 8.84; Cu, 13.23.

Monohydrogen aquo-μ-(diethylenetriaminepentaacetato-3,4) dicuprate(II).—One-tenth mole of freshly prepared copper(II) hydroxide was added to 19.65 g. (0.05 mole) of H_5DTPA in 800 ml. of water. The mixture was boiled until the volume was reduced to 400 ml. The temperature of the solution was maintained at 65° while 400 ml. of ethanol was added. The water–ethanol solution was allowed to cool slowly, whereupon well defined blue crystals formed; yield, 18.2 g. (68%). The product was recrystallized from hot water.

Anal. Calcd. for $H[Cu_2(C_{14}H_{18}N_3O_{10})(H_2O)]$: C, 31.46; H, 3.96; N, 7.86; Cu, 23.78. Found: C, 32.54; H, 4.27; N, 7.74; Cu, 22.48.

Trihydrogen dioxotetrahydro-μ-(diethylenetriaminepentaacetato) dimolybdate(V).—An acidic stock solution of molybdenum(V) was prepared by the reduction of molybdenum(VI) oxide with mercury. Fifty g. of mercury and 8.64 g. (0.06 mole) of molybdenum(VI) oxide were suspended in 300 ml. of 3 *M* hydrochloric acid. The mixture was shaken for 48 hr. and filtered. The filtrate was stored in a stoppered bottle over a small amount of mercury.

One hundred ml. of the stock solution was added to a solution of 11.78 g. (0.03 mole) of H_5DTPA in 650 ml. of water. The solution was distilled down to 50 ml. at reduced pressure in order to remove some of the hydrochloric acid. The solution was diluted to 100 ml. and ethanol was added until a slight turbidity appeared. Orange crystals formed when the solution was cooled in an ice-bath. The product was recrystallized from a minimum volume of hot water.

Anal. Calcd. for $H_3[Mo_2O_2(OH)_4(C_{14}H_{18}N_3O_{10})]$: C, 24.61; H, 3.69; N, 6.15; Mo, 28.08. Found: C, 24.74; H, 4.06; N, 6.03; Mo, 28.02.

Trihydrogen dioxotrihydroxo-μ-(triethylenetetraminehexaacetato) dimolybdate(V) tetrahydrate.—The molybdenum(V) stock solution (105 ml.) was added to 3.47 g. (0.007 mole) of H_6TTHA dissolved in 20 ml. of water. The solution was distilled at reduced pressure until the

---

[16] In the name and formula of a complex, it seems desirable to employ some system to indicate the number of donor groups through which a multidentate ligand is attached to the metal ion. The arabic figure 8 indicates that the diethylenetriaminepentaacetato group is octodentate. This notation will be used only when there is evidence for a particular "dentate number." Evidence for the structures given is discussed later in this paper. A thorough study of the structures by other means is desirable since infrared evidence is only indicative.

TABLE I

INFRARED ABSORPTION PEAKS FOR METAL-POLYAMINOCARBOXYLATE CHELATES[a]

Spectrum	Compound	O-H	COOH	COOM	CH_2COOH	C-N
A	$H[Al(EDTA\text{-}5)(H_2O)]$	3400sh	1730sh	1650s	1230w	1097m
B	$H[Ga(EDTA\text{-}5)(H_2O)]$	3100sh	1740m	1650s	1233w	1100m
C	$H[In(EDTA\text{-}5)(H_2O)]$	3400sh	1690sh	1600s	1233w	1091s
D	$H[Tl(EDTA)(H_2O)]$	3440sh	...	1610s	1220m 1244m	1092s 1116m
E	$H[Th(DTPA\text{-}8)] \cdot H_2O$	3300m	...	1600s	...	1085w
F	$H[Zr(DTPA)] \cdot 3H_2O$	3420sh	1725sh	1650s	...	1085w
G	$H_2[Fe(DTPA\text{-}6)]$	...	1730m	1650s	1218sh	1096w
H	$H_3[Ni(DTPA)] \cdot H_2O$	3190m 3390m	1735m	1602s	1235m	1100w
I	$H[Ni_2(DTPA\text{-}3,5)(H_2O)_4] \cdot 3H_2O$	3280s	...	1590s	...	1094w
J	$H_3[Cu(DTPA)] \cdot H_2O$	3330w	1765w 1733m 1690sh	1605s 1573s	1210m 1247w	1088m
K	$H[Cu_2(DTPA\text{-}3,4)(H_2O)]$	3410w	1732w	1597s	1210w	1116w
L	$H_3[Mo_2O_2(OH)_4(DTPA)]$	3310m	1724w	1630s	1230sh	1080w
M	$H_3[Mo_2O_2(OH)_3(TTHA)] \cdot 4H_2O$	3400m	1745w	1640s	1250sh	1075w

[a] Abbreviations used in this table: s, strong; m, medium; w, weak; sh, shoulder. Frequencies are given in wave numbers, cm.$^{-1}$.

residual volume reached 70 ml. The temperature of the concentrated orange solution was maintained at 70° while 140 ml. of ethanol was added. As the solution cooled, 4.9 g. of orange crystals separated (84%, based on the amount of H_6TTHA used). The product was recrystallized from 150 ml. of hot water.

Anal. Calcd. for $H_3[Mo_2O_2(OH)_3(C_{18}H_{24}N_4O_{12})] \cdot 4H_2O$: C, 25.78; H, 4.57; N, 6.68; Mo, 22.89. Found: C, 25.62; H, 4.44; N, 6.56; Mo, 23.60.

Infrared Spectra.—Infrared spectra were obtained with a Perkin–Elmer Model 21 double beam recording spectrophotometer, using Nujol suspensions between rock salt plates.

Ultraviolet Spectra.—Ultraviolet absorption measurements were made with a Cary recording spectrophotometer, Model 14M. Mole ratio studies were conducted in a manner similar to that described by Pecsok and Sawyer.[17] The metal/ligand ratio was determined for the molybdenum(V) complexes of H_5DTPA and H_6TTHA.

Potentiometric Titrations.—A Beckman Model G *p*H meter, equipped with glass and saturated calomel electrodes, was used for *p*H measurements. The measurements were made in an apparatus designed to exclude carbon dioxide. Samples of crystalline complexes were weighed and dissolved in freshly boiled demineralized water. The ionic strength of each solution was adjusted to 0.1 with potassium nitrate and the solution then was titrated with a standard solution of 0.1 *N* potassium hydroxide (carbonate-free).

Results and Discussion

Infrared spectra over the range from 600 to 4000 cm.$^{-1}$ were obtained for the metal chelates. In Table I, assignments are given for absorption bands which are of diagnostic value in the study of structures and the nature of bonding in the complexes.[18]

Stretching vibrations of the O–H group appear as broad bands of medium intensity in the 3100 to 3500 cm.$^{-1}$ region. Absorption at 1075–1116 cm.$^{-1}$ is attributed tentatively to the C–N group, and that at 1210–1250 cm.$^{-1}$ to the $-CH_2COOH$ group.[19] The region of the spectra deserving closest examination is that lying between 1550 and 1750 cm.$^{-1}$. In this region absorption by the carbonyl group in –COOH, –COOM, and $-COO^-$ occurs.

As previously mentioned, the position of the carbonyl peak in the infrared spectra of EDTA complexes has been employed extensively as an indication of the nature of bonding in the metal–oxygen link. The positions of the carbonyl peak maxima arising from the –COOM group in EDTA, DTPA, and TTHA complexes are shown in Table II. The position of the carbonyl band probably is influenced by several factors, but two are particularly apparent: the charge and the size of the metal ion. High charge and small size appear to enhance the covalency of the metal–oxygen bond.

An interesting correlation is observed when the charge to size ratio (q/r) of the metal ion is compared with the position of the carbonyl peak maximum for each of the complexes. When q/r is

---

(17) R. L. Pecsok and D. T. Sawyer, *J. Am. Chem. Soc.*, **78**, 5496 (1956).

(18) The spectra are reproduced in full in R. E. Sievers, Doctoral Dissertation, University of Illinois, 1960.

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 171, 258.

TABLE II

INFRARED PEAK MAXIMA FOR THE CARBONYL GROUP IN –COOM

Peak maxima, 1625–1650 cm.$^{-1}$ (appreciable covalency in metal–carboxylate bond)					Peak maxima, 1590–1610 cm.$^{-1}$ (primarily ionic bonding)				
M	Ref. or spectrum	Ionic rad.,[20] Å.	q/r	Peak max., cm.$^{-1}$	M	Ref. or spectrum	Ionic rad., Å.	q/r	Peak max., cm.$^{-1}$
Mo(VI)	10			1630	Th(IV)	E	1.10	3.6	1600
Mo(V)	L			1630	In(III)	C	0.92	3.3	1600
	M			1640	Tl(III)	D	1.05	2.9	1610
V(IV)	10	0.61	6.5	1630	Y(III)	21	1.06	2.8	1600
Zr(IV)	F	0.87	4.6	1650	Sm(III)	21	1.13	2.7	1600
Fe(III)	G	0.67	4.5	1650	Nd(III)	5	1.15	2.6	1600
Cr(III)	11	0.65	4.6	1650	Ce(III)	10	1.18	2.5	1600
Rh(III)	11	0.69	4.4	1643	Bi(III)	10	1.20	2.5	1610
Co(III)	6	0.65	4.6	1650	Ni(II)	H	0.78	2.6	1602
Al(III)	A	0.57	5.3	1650		I			1590
Ga(III)	B	0.62	4.8	1650	Cu(II)	J			1605
V(III)	10			1630		K			1597
Pd(II)	4	0.50	4.0	1625	Co(II)	9	0.82	2.4	1600
Pt(II)	4	0.52	3.9	1635	Zn(II)	9	0.83	2.4	1600
					Mn(II)	9	0.91	2.2	1600
					Cd(II)	9	1.03	1.9	1595
					Hg(II)	9	1.12	1.8	1595
					Pb(II)	9	1.32	1.5	1600
					Mg(II)	8	0.78	2.6	1610
					Ca(II)	8	1.06	1.9	1605
					Sr(II)	8	1.27	1.6	1595
					Ba(II)	8	1.43	1.4	1590

larger than 3.6, carbonyl absorption maxima occur in the 1625 to 1650 cm.$^{-1}$ region; but when q/r is less than 3.6, the maxima occur between 1590 and 1615 cm.$^{-1}$. This relationship appears to hold for EDTA and DTPA complexes of 33 metal ions of widely varying size, charge, and number of d electrons. The choice of wave number ranges for dividing the compounds into two groups is arbitrary; nonetheless the extent of the correlation is impressive. No exceptions have been observed in metal–EDTA and DTPA complexes in which it clearly is established that only tertiary nitrogen atoms, carboxyl groups, or water molecules are coördinated to the metal ion. When groups such as Cl^-, Br^-, or OH^- occupy positions in the coordination sphere, deviations in the position of the carbonyl band may occur.[22]

The degree of ionic character in a bond depends upon differences in the electronegativity of the bonded atoms. A refinement of q/r may be taken as a measure of the electronegativity of a cation. A cation having a large charge and small radius should be in a better position to compete with an electronegative ligand for the electrons of the coordinate bond than a cation having a smaller q/r ratio.[23] As seen in Table II, covalency in the metal–carboxylate bond is indicated only in cases where q/r is large.

Aluminum(III), Gallium(III), Indium(III), and Thallium(III) Complexes of EDTA.—Saito and Terrey[15] prepared crystalline compounds which may be formulated as either H[M(EDTA-5)·(H_2O)] or H[M(EDTA-6)]·H_2O. In the first case the water molecule is an integral part of the complex and the remaining five coördination positions are occupied by quinquedentate EDTA. Alternatively, EDTA may function as a sexadentate ligand. It was not possible to discriminate between the alternatives on the basis of potentiometric titration data.

Infrared data obtained for these compounds indicate, in at least three of the four complexes, that EDTA is quinquedentate. The spectrum of the gallium(III) complex shows two clearly defined peaks in the 1600–1750 cm.$^{-1}$ region. One peak of medium intensity occurs at 1740 cm.$^{-1}$ and is attributed to the presence of an uncomplexed

---

(20) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 140.

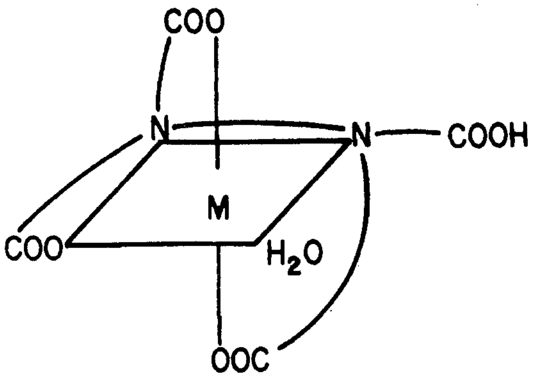
(21) T. Moeller and E. P. Horwitz, *J. Inorg. & Nuclear Chem.*, **12**, 49 (1959).

(22) Carbonyl frequencies near 1600 cm.$^{-1}$ were reported for $KH_2[Rh(EDTA)Br_2]$ and $KH_2[Rh(EDTA)Cl_2]$ in ref. 11. The Al(III) and Th(IV)-EDTA complexes described in ref. 10 were isolated at *p*H 9 and in actuality may be hydroxo complexes.

(23) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 86.

–COOH group. A stronger peak at 1650 cm.$^{-1}$ is assigned to the remaining three complexed carboxyl groups. The spectra of the aluminum(III) and indium(III) complexes contain strong peaks at 1650 and 1600 cm.$^{-1}$, respectively, which are assigned to –COOM groups. Each of these peaks has a shoulder at a somewhat higher wave number which is believed to arise from an uncomplexed carboxyl group. Absorption is very broad and poorly defined in the 1550–1750 cm.$^{-1}$ region in the spectrum of the thallium(III) complex. In view of the breadth of the carbonyl peak, the presence of an uncomplexed –COOH group can be neither confirmed nor ruled out in this case. Tentative assignment of peaks in the 1220–1244 cm.$^{-1}$ region to the $-CH_2COOH$ group, however, tends to indicate that there are uncomplexed carboxyl groups in all of the compounds in question.

One of the possible structures in which EDTA functions in a quinquedentate manner is shown in structure V. This is the same structure that was established for $H_2[Ni(EDTA\text{-}5)(H_2O)]$ by an X-ray study.[24] For the sake of clarity, methylene linking groups are omitted in the structures and represented by curved lines linking the donor groups.



(V)

Thorium(IV) and Zirconium(IV) Complexes of DTPA.—A thorium(IV) complex having the formula $H[Th(DTPA\text{-}8)]\cdot H_2O$ can be crystallized from an acidic aqueous solution. The potentiometric titration curve for this compound (Fig. 1) shows two buffer regions. The first buffer region occurs at *p*H 3.5–4.5 and corresponds to the neutralization of an acidic proton. At $a = 1$ there is a sharp inflection point. A second buffer region appears at *p*H 8–9.5. This second buffer region may arise from the neutralization of a proton from a coördinated water molecule, or from the introduction of a hydroxo group into the coördination sphere of the thorium(IV) ion. The infrared spectrum indicates that the latter is the correct explanation, as shown below.

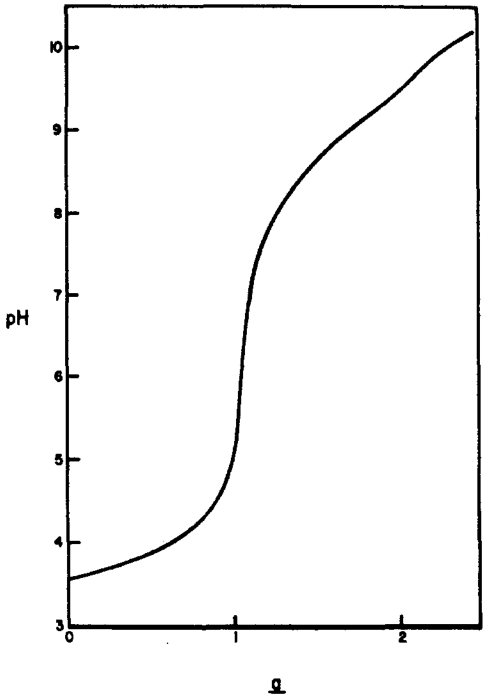
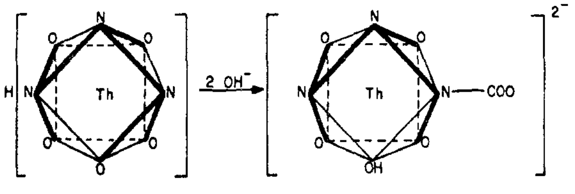


Fig. 1.—Potentiometric titration of $H[Th(DTPA\text{-}8)]\cdot H_2O$. Concn. of metal complex = 1.0×10^{-3} *M*; temp., 30°; a = moles of KOH added per mole of complex; μ = 0.1 (KNO_3).

The infrared spectrum of the crystalline complex shows a single peak in the 1550–1750 cm.$^{-1}$ region. This peak occurs at 1600 cm.$^{-1}$ and is attributed to carboxyl groups which are coördinated to the thorium(IV) ion. The absence of absorption at higher wave numbers indicates that no uncomplexed –COOH groups are present. The spectrum, however, does not preclude the presence of uncomplexed $-COO^-$ groups, since they absorb in the same region as carboxyl groups which are coördinated to the thorium(IV) ion (at *ca.* 1600 cm.$^{-1}$). Nevertheless, it may be reasoned that the proton in the complex is associated with the most basic group available. If there were an uncomplexed $-COO^-$ group in the structure, it undoubtedly would be the most basic group. Since the –COOH group is absent, it is concluded that all of the carboxyl groups are coördinated and that DTPA is octodentate in the acid complex. As the *p*H is increased to 8–9, a hydroxo group replaces one of the carboxyl groups, thus forming a septidentate complex (VI → VII).

---

[24] G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 556 (1959).



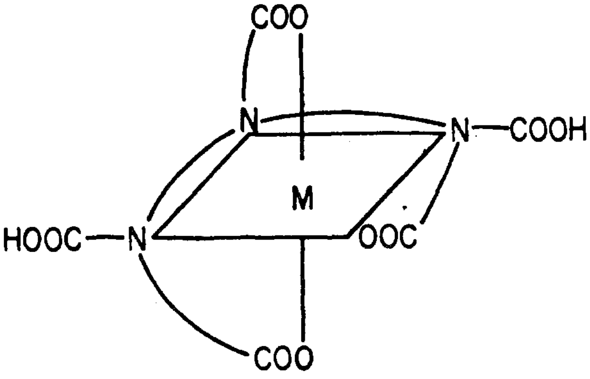
(VI) (VII)

The structures are shown for the octo- and septidentate complexes as Archimedean antiprisms, but other geometrical arrangements are also possible. In structures VI and VII, curved lines linking the nitrogen atoms and carboxyl groups are omitted in an effort to simplify the representation. The heavy lines indicate the edges of the antiprism along which the ligand forms chelate rings. The oxygen atoms in these two structures represent carboxyl groups. The octodentate complex contains seven fused five-membered rings, which accounts for its remarkably high hydrolytic stability.[25]

The infrared and potentiometric titration data are not as conclusive for the zirconium(IV)–DTPA complex as for the thorium(IV) complex. It has been reported[26] that the *p*H behavior of the zirconium(IV) complex of DTPA depends upon the make-up of the zirconium(IV) stock solution. When a dilute stock solution of zirconium(IV) chloride was used, an insoluble, partially chelated species was observed over the entire *p*H range. When a more concentrated stock solution was employed, a complex was formed which was water-soluble between *p*H 5 and 9.

A soluble complex having the formula $H[Zr(DTPA)]\cdot 3H_2O$ was isolated in the present work. The infrared spectrum of this compound shows a broad peak at 1650 cm.$^{-1}$. There is a very slight shoulder at 1725 cm.$^{-1}$, but it is not clear whether this should be considered indicative of an uncomplexed –COOH group. No well-defined peak is apparent in the second region (1210–1250 cm.$^{-1}$) associated with absorption by the carboxylic acid group. It is probable that all, or at least the majority, of the carboxyl groups are coördinated in this complex.

Iron(III) Complex of DTPA.—Evidence obtained by a potentiometric titration of an iron(III)–DTPA system indicates that DTPA functions either as a quinque- or a sexadentate ligand toward the ferric ion.[27] The infrared spectrum of the crystalline complex $H_2[Fe(DTPA\text{-}6)]$ exhibits two distinct peaks in the carbonyl region. The peak of moderate intensity at 1730 cm.$^{-1}$ indicates the presence of one or more uncomplexed carboxylic acid groups. The more intense peak at 1650 cm.$^{-1}$ arises from the coördinated carboxyl groups which are present. Relative peak areas suggest that the ratio of complexed to uncomplexed carboxyl groups is 3:2. This is consistent with the conclusion that DTPA is sexadentate in this complex. One of the several possible sexadentate structures is shown in VIII (where M = Fe(III)).



(VIII)

Mono- and Binuclear Nickel(II) and Copper(II) Complexes of DTPA.—Evidence obtained by potentiometric and spectrophotometric procedures indicates that DTPA is capable of forming binuclear complexes, as well as simple 1:1 compounds. It has been shown[28] that the visible absorption spectra of copper(II)–DTPA solutions having a metal:ligand ratio less than 1:1 have an absorption maximum at *ca.* 660 mμ. In the visible spectra of solutions in which the ratio is greater than 1:1, the maxima are shifted to 740 mμ. Potentiometric titration data[28,29] indicate that DTPA also forms a binuclear complex with nickel(II).

The infrared spectra of crystalline mono- and binuclear nickel(II) and copper(II) complexes were obtained in the present work. The infrared spectrum of the mononuclear complex, $H_3[Ni(DTPA)]\cdot H_2O$, is similar to that shown for the sexadentate iron(III)–DTPA complex. Peaks which are attributed to absorption by –COONi and –COOH groups occur at 1602 and 1735 cm.$^{-1}$. The peak area ratio is roughly 3:2 and suggests

---

[25] R. F. Bogucki and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 4170 (1958).

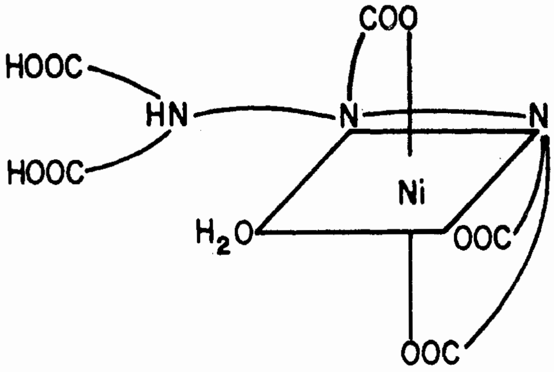
[26] B. I. Intorre and A. E. Martell, *ibid.*, **82**, 358 (1960).

[27] J. Vandegaer, S. Chaberek, Jr., and A. E. Frost, *J. Inorg. & Nuclear Chem.*, **11**, 210 (1959).

[28] S. Chaberek, Jr., A. E. Frost, M. A. Doran, and N. J. Bicknell, *ibid.*, **11**, 184 (1959).

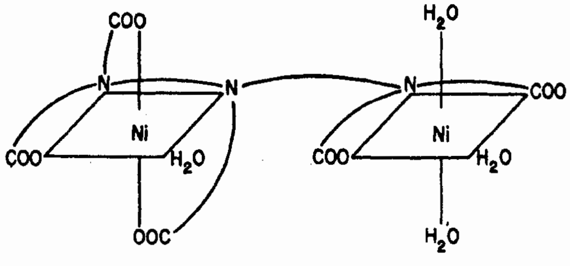
[29] G. Anderegg, P. Nageli, F. Muller, and G. Schwarzenbach, *Helv. Chim. Acta*, **42**, 827 (1959).

that the complexed carboxyl groups may be present in greater numbers than the uncomplexed groups. If this is the case, a sexadentate structure, such as in VIII (where M = Ni(II)), or the quinquedentate structure, IX, are considered to be the most likely structural possibilities. In other structures in which DTPA is quinquedentate, the coördinated carboxyl groups outnumber the uncoördinated ones.



(IX)

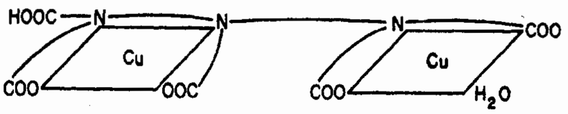
The spectrum of the binuclear nickel(II)–DTPA complex exhibits only a single peak in the carbonyl region, thus indicating that uncoördinated carboxyl groups are absent. In the absence of uncoördinated carboxylic acid groups, a structural arrangement is proposed in which DTPA acts as a quinquedentate ligand toward one nickel ion and is attached to the other as a tridentate group. An example of such an arrangement is seen in X.



(X)

The spectrum of $H_3[Cu(DTPA)]\cdot H_2O$ shows two principal peaks in the carbonyl region. Fine structure is present in each of the peaks, making it impractical to attempt structural interpretations based on the spectrum. A sample of the complex was recrystallized repeatedly with no observed change in its spectrum, so the fine structure is believed to be characteristic of the compound rather than arising from impurities.

The spectrum of the binuclear copper(II) complex $H[Cu_2(DTPA\text{-}3,4)(H_2O)]$ shows a well defined peak at 1732 cm.$^{-1}$ which is characteristic of absorption by a carboxylic acid group. The rest of the donor groups doubtless are coördinated if a coördination number of four is assumed for each of the copper(II) ions. A plausible structure in which DTPA functions as a tridentate–quadridentate ligand is shown in XI.



(XI)

Molybdenum(V) Complexes of DTPA and TTHA.–The aquated molybdenum(V) species is readily oxidized by air to molybdenum(VI) in neutral or basic solutions, but the formation of polyaminocarboxylate chelates stabilizes the molybdenum ion in the pentavalent oxidation state. The crystalline complexes are easily isolated and are stable indefinitely in air, and the neutral solutions of the complexes resist air oxidation at 90° over a period of several days. If solutions of the complexes are made strongly basic, insoluble hydrolysis products result.

Mole ratio studies, similar to that described by Pecsok and Sawyer,[17] were conducted in order to determine the metal:ligand ratio in molybdenum(V) complexes of DTPA and TTHA. The results are plotted in Figure 2. The initial concentration of molybdenum(V) in every case is 4.00×10^{-4} *M*. The ultraviolet absorbance, measured at 297 mμ, is plotted against the molar concentration of the ligand.

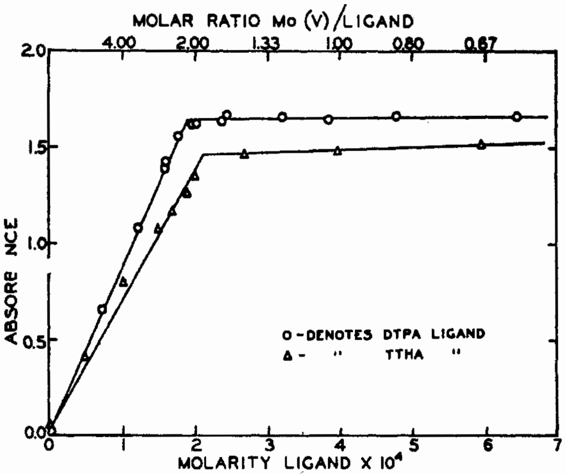


Fig. 2.—Molar ratio continuous variations plot of Mo(V)–DTPA system. The absorbances of a series of solutions containing an initial Mo(V) concentration of 4.00×10^{-4} *M* are plotted *vs.* DTPA concentration at *p*H 8.0.

Both plots show a steady increase in absorbance until the metal–ligand ratio reaches approximately 2:1. Further increases in the ligand concentration do not alter the absorbance appreciably. The observed discontinuity occurs at a metal: ligand ratio of 2.10 in the case of the DTPA complex and at 1.94 for the TTHA complex. The plots indicate that binuclear molybdenum complexes of DTPA and TTHA are formed.

Crystalline binuclear molybdenum(V) complexes of DTPA and TTHA were synthesized and their infrared spectra examined. As seen in Table I, the spectra show peaks which are indicative of uncoördinated –COOH groups. The ratio of coördinated to uncoördinated carboxyl groups appears to be large in both cases.

Since uncoördinated carboxyl groups were detected in the DTPA complex, a tridentate–quinquedentate structural arrangement for this compound (similar to that shown for Ni in X) is eliminated from consideration. The best structural choices appear to be those in which DTPA functions either as a tridentate–quadridentate or as a tridentate–tridentate ligand.

Similar structures may be proposed for the binuclear Mo(V)–TTHA complex. Structures in which one or both ends of the TTHA group function in a quinquedentate manner are considered unlikely in view of the infrared spectral evidence for the presence of at least one uncoördinated carboxylic acid group. A quadridentate–quadridentate or tridentate–quadridentate structural arrangement appears to be likely for this complex.

Potentiometric titration curves were obtained for the binuclear molybdenum(V) complexes of DTPA and TTHA. The curves showed that each of the complexes contains three acidic protons per molecule. The complexes are tentatively formulated as $H_3[Mo_2O_2(OH)_4(DTPA)]$ and $H_3[Mo_2O_2(OH)_3(TTHA)]\cdot 4H_2O$. Since the coördination number of Mo(V) is not well established, the number of oxo and hydroxo groups coördinated to the metal ion is uncertain.

Acknowledgment.—The authors wish to thank Professor T. Moeller for his kind interest in this work.

Notes

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND

Six-Coördinate Mercury(II)

By Richard L. Carlin, James Roitman, Mary Dankleff, and John O. Edwards

Received October 25, 1961

We wish to report the synthesis of four new complexes of mercury(II), all of which exhibit the unusually high coördination number of six. These complexes also are unusual in that, in each case, the donor atom is oxygen; the low stability of most oxygen donors to mercury(II) is well-known. The complexes, all of them white, are of the form $[HgL_6](ClO_4)_2$, where L is one of the following: pyridine N-oxide,[1] dimethyl sulfoxide, tetrahydrothiophene oxide, and thioxane oxide. The complexes of several of these ligands with salts of the transition metals have been reported earlier.[1–4]

The structure of each of these complexes involves either octahedral or distorted octahedral[5] coördination about the central mercury atom; earlier workers[6] have suggested that mercury(II) has the coördination number of six in aqueous solution. The fact that four different ligands form compounds of the correct stoichiometry $Hg(ClO_4)_2\cdot 6L$ is indicative of the fact that the complexes are not of the form $[HgL_n](ClO_4)_2$, where n is less than six and with the remaining $6-n$ ligands uncoördinated but in the lattice, for we would not expect this behavior to be general for such varied ligands.

Comparison of X-ray powder patterns of [Ni-

---

(1) R. L. Carlin, *J. Am. Chem. Soc.*, **83**, 3773 (1961).

(2) F. A. Cotton and R. Francis, *ibid.*, **82**, 2986 (1960).

(3) D. W. Meek, D. K. Straub, and R. S. Drago, *ibid.*, **82**, 6013 (1960).

(4) R. Francis and F. A. Cotton, *J. Chem. Soc.*, 2078 (1961).

(5) L. E. Orgel, *ibid.*, 4186 (1958).

(6) (a) C. L. van Panthaleon van Eck, Thesis, Leiden, 1958; (b) P. K. Gallagher and E. L. King, *J. Am. Chem. Soc.*, **82**, 3510 (1960).