these results with polymethacrylate to say which system shows the greater binding at these concentrations. A value of 0.4 has been obtained by Oth and Doty[7] for polymethacrylate at lower sodium ion concentrations. This suggests that the binding of polymethacrylate is slightly smaller than that by polyacrylate for a given sodium ion concentration. This would be consistent with the observation that acrylic resins form stronger complexes than methacrylic resins.[8]

Binding of Other Alkali Metals.—Dialysis experiments were also carried out on buffered (*p*H 9, 0.0025 M $Na_2B_4O_7$) solutions of 0.0107 "N" PMA and 1.9×10^{-5} M $[Ru(phen)_3](ClO_4)_2$ in 0.050 M LiCl, KCl, RbCl, CsCl and $(CH_3)_4NCl$, respectively. The same experiment was performed using NaCl instead of the other chlorides and the NaCl concentration was varied from 0.02 to 0.10 M. A comparison of the binding of a particular monovalent cation with that of the sodium ion was then possible by observing the concentration of sodium ion necessary to give the same effect as the 0.050 M solution of the cation. This comparison is valid regardless of whether the observed distribution of complex is caused by the Donnan effect, by competitive binding of the complex or both. Within experimental error it was found that the 0.050 M alkali halides all correspond to 0.050 M NaCl. The binding of $(CH_3)_4N^+$ is appreciably less as evidenced by the observation that 0.050 M $(CH_3)_4N^+$ is only as effective as is 0.026 M Na^+. Thus the binding tendencies of the monovalent cations with PMA^- are

$$Li^+ \sim Na^+ \sim K^+ \sim Rb^+ \sim Cs^+ > (CH_3)_4N^+$$

This is in agreement with the observation of Wall and Doremus[9] that sodium and potassium ions are bound to the same extent to polyacrylate ion. However, this does not agree with the small differences in the binding of lithium and sodium ions with polyacrylate reported by Hutschneker and Deuel[10] nor to the differences observed with polymethacrylate.[11] Failure to detect a difference in binding in our experiments may result from the technique used not being sensitive enough to show up such small differences. It is also of interest to note that the alkali metal ions are differentiated by ion-exchange resins.[12]

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[7] A. Oth and P. Doty, *J. Phys. Chem.*, **56**, 43 (1952).

[8] H. P. Gregor, L. B. Luttinger and E. M. Loebl, *ibid.*, **59**, 366 (1955).

[9] F. T. Wall and R. H. Doremus, THIS JOURNAL, **76**, 1557 (1954).

[10] K. Hutschneker and H. Deuel, *Helv. Chim. Acta*, **39**, 1038 (1956).

[11] H. P. Gregor and M. Frederick, *J. Polymer Sci.*, **23**, 451 (1957); H. P. Gregor, D. H. Gold and M. Frederick, *ibid.*, **23**, 467 (1957).

[12] R. Kunin and R. L. Myers, "Ion Exchange Resins," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 22–25; H. P. Gregor, M. J. Hamilton, R. J. Oza and F. Bernstein, *J. Phys. Chem.*, **60**, 263 (1956).

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Hydrolytic Tendencies of Metal Chelate Compounds. III. Oxometal Ions[1]

BY S. CHABEREK, JR., R. L. GUSTAFSON, R. C. COURTNEY AND A. E. MARTELL

RECEIVED MARCH 14, 1958

The hydrolysis of a variety of metal chelate compounds of VO(IV), ZrO(IV), UO_2(VI) and MO_2(VI) ions has been studied potentiometrically to determine relative tendencies toward the formation of hydroxo metal chelates. These ions have relatively high affinity for oxygen donor atoms and form the more stable metal chelate systems with ligands containing basic oxygens such as those found in polyphenols and hydroxy acids. Hydrolytic tendencies increase in the order VO(IV) < ZrO(IV) < UO_2(VI) < MoO_2(VI). The most stable soluble aqueous systems are found with Tiron (disodium pyrocatechol-3,5-disulfonate) as a ligand.

This investigation was undertaken to study the nature of the reactions of incompletely coördinated metal chelate compounds and is an extension of investigations already reported on the hydrolysis of metal ions containing no oxo groups. A review of the literature showed that very little work had been reported on the hydrolysis of metal chelates of oxo metal ions. Although the dioxouranium (VI) ion is known to undergo simultaneous hydrolysis and polymerization,[2,3] the reactions seemed to be very complex. It was shown recently by Cabell[4] that aminopolycarboxylic acid ligands containing large numbers of donor groups form uranyl complexes which contain only one metal ion in the complex anion. On the other hand, potentiometric and spectrophotometric measurements reported by Feldman, Havill and Neuman[5] with such ligands as malate, citrate and tartrate, indicated the formation of polynuclear chelates containing hydroxyl ions or oxo ions as coördinating links between two or more uranyl groups. They interpreted their data on the basis of transitions from binuclear to ternuclear uranyl chelates of α-hydroxy acids.

Experimental

The experimental method consisted of potentiometric titrations of the ligand in the absence of and in the presence of the metal ions being studied in accordance with the detailed procedure previously described.[6] The temperature was regulated at 25 ± 0.1°, and the ionic strength was maintained relatively

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[1] This paper reports work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C.

[2] S. Ahrland, S. Hietanen and L. G. Sillen, *Acta Chem. Scand.*, **8**, 1907 (1954).

[3] J. Sutton, *J. Chem. Soc.*, 5275 (1949).

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[5] (a) I. Feldman, J. R. Havill and W. F. Neuman, THIS JOURNAL, **76**, 4726 (1954); (b) W. F. Neuman, J. R. Havill and I. Feldman, *ibid.*, **73**, 3593 (1951).

[6] A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback and H. Hyytiainen, *ibid.*, **79**, 3036 (1957).

TABLE I

Metal ion	Ligand	Type formula of ligand	Equilibrium quotient	Log *K*	Remarks
VO(IV)	EDTA	H_4A	$[VOA]/[VO][A]$	18.77,[a] 20°	....
VO(IV)	HEDTA	H_3AOH	$[VOAOH]/[VO][AOH]$	..	....
VO(IV)	HEDDA	$H_2A(OH)_2$	$[VOA(OH)_2]/[VO][A(OH)_2]$	..	....
			$[VOA(OH)_2]/[VO[OH]A(OH)_2][H^+]$[b]	5.5	....
VO(IV)	HIMDA	H_2AOH	$[VOAOH]/[VO][AOH]$	..	....
			$[VOAOH]/[VO[OH]AOH][H^+]$[b]	5.7	....
VO(IV)	2-HxG	$HA(OH)_2$	Indeterminate	..	Ppt. above *p*H 4.5
VO(IV)	PDS	$A(OH)_2$	$[VOAO_2]/[VO][AO_2]$	17.2	....
			$[VOAO_2]/[VO[OH]AO_2][H^+]$	5.1	....
VO(IV)	DNS	$A(OH)_2$	$[VOAO_2]/[VO][AO_2]$	17.4	
			$[VOAO_2]/[VO[OH]AO_2][H^+]$	6.0	
VO(IV)	5-SSA	H_2AOH	$[VOAO]/[VO][AO]$	14.8	....
			$[VOAO]/[VO[OH]AO][H^+]$	5.7	....
ZrO(IV)	EDTA	H_4A	Indeterminate	..	Ppt. below *p*H 5.1
ZrO(IV)	HEDTA	H_3AOH	$[ZrOAOH]/[ZrO][AOH]$	..	....
ZrO(IV)	HEDTA	$H_2A(OH)_2$	$[ZrOA(OH)_2]/[ZrO][A(OH)_2]$	..	....
			$[ZrOA(OH)_2]/[ZrO[OH]A(OH)_2][H^+]$	7	....
ZrO(IV)	PDS	$A(OH)_2$	$[ZrOAO_2]/[ZrO][AO_2]$	..	....
ZrO(IV)	DNS	$A(OH)_2$	Little or no chelation	..	Ppt. above *p*H 3
ZrO(IV)	2-HxG	$HA(OH)_2$	$[ZrOA(OH)_2]/[ZrO][A(OH)_2]$	..	....
			$[ZrOA(OH)_2]/[ZrO[OH]A(OH)_2][H^+]$[b]	3.9	....
			$[ZrO[OH]A(OH)_2]/[ZrO[OH]_2A(OH)_2][H^+]$[b]	8.5	....
ZrO(IV)	HIMDA	H_2AOH	$[ZrOAOH]/[ZrO[OH]AOH][H^+]$[b]	5.3	....
ZrO(IV)	CIT	H_3AOH	$[ZrOAOH]/[ZrO[OH]AOH][H^+]$[b]	6.0	....
ZrO(IV)	5-SSA	H_2AOH	(Little or no chelation)	..	Ppt. through
ZrO(IV)	NTA	H_3A	(Little or no chelation)	..	entire *p*H
ZrO(IV)	HEN	AOH	(Little or no chelation)	..	range
UO_2(VI)	HEDTA	H_3AOH	UO_2AOH formed	..	....
			UO_2AO formed	..	Ppt. above *p*H 9
UO_2(VI)	2-HxG	$HA(OH)_2$	$UO_2A(OH)_2$ formed	..	Ppt above *p*H 9
UO_2(VI)	PDS	$A(OH)_2$	$(UO_2AO_2)_3(OH)_2$ probably formed	..	....
UO_2(VI)	DNS	$A(OH)_2$	UO_2AO_2 formed	..	....
UO_2(VI)	5-SSA	H_2AOH	$[UO_2AOH]/[UO_2][AOH]$	3.89[c]	$\mu = 0.015$

[a] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954). [b] The hydrolysis is interpreted as resulting in the coördination of a hydroxyl ion with the metal, but it also may be interpreted as the dissociation of an alkyl or aryl hydroxyl of the ligand and coördination of the alkoxy or aryloxy ion with the metal. [c] T. R. Foley and R. S. Anderson, THIS JOURNAL, **71**, 909 (1949).

constant by using a medium of 0.10 *M* potassium nitrate. Carbonate-free potassium hydroxide was employed for the titrations and carbon dioxide-free nitrogen was passed slowly through the experimental solution. The *p*H was measured by a Beckman Model G *p*H meter fitted with extension glass and calomel electrodes. The *p*H meter was calibrated against a standard buffer to determine hydrogen ion concentration.

Materials.—Reagent grade salts of all metals were employed, the chlorides being used in each case except for UO_2(VI), which was obtained as the nitrate. Standardization of the metal solutions consisted of precipitation of the hydrous oxide followed by ignition to the oxide, except in the case of the vanadyl salt which was standardized by titration with sodium hydroxide in the presence of excess disodium salt of EDTA according to the method of Schwarzenbach.[7] Samples of ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), N,N'-dihydroxyethylethylenediaminediacetic acid (HEDDA), N-hydroxyethyliminodiacetic acid (HIMDA), nitrilotriacetic acid (NTA) and N,N-dihydroxyethylglycine (2-HxG) were obtained through the courtesy of Versenes, Incorporated, Framingham, Massachusetts. 5-Sulfosalicylic acid (5-SSA) and 1,8-dihydroxynaphthalene-3,6-disodium sulfonate (DNS) were purchased from Eastman Kodak Company and disodium pyrocatechol-3,5-disulfonate (PDS) was purchased from the LaMotte Chemical Products Corp.

Titrations of the metal ions with various ligands listed above were carried out for the most part with a 1:1 ratio of ligand to metal ion. In certain instances when a bidentate ligand produced a chelate which was insufficiently stable to prevent precipitation from aqueous solution in the intermediate *p*H range, systems containing 2:1 ratios of ligand to metal ion also were investigated. In general, however, systems in which the metal ion was considered completely coordinated were avoided in this investigation.

Results

Potentiometric titration curves of the various metals and ligands investigated are given in Figs. 1–4. In many cases the tendency for hydrolysis of the metal ion was so great that no appreciable interaction was observable from the titration curves. In such cases the curves usually are not given in Figs. 1–4. The results of these investigations, the formulas of the metal chelates formed and the equilibrium constants calculated from potentiometric data are summarized in Table I.

Discussion

VO(IV) Chelates.—The chemical properties of the vanadyl ion often have been compared with those of Cu(II). Thus the color and coördination requirements of VO(IV) and Cu(II) seem to be quite similar. The hydrolytic tendencies of these two ions seem to be quite different, a fact which is no doubt due in large part to the presence of the oxo group on VO(IV). In general, the data obtained in this research indicate that the vanadyl ion does

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(7) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 331 (1948).

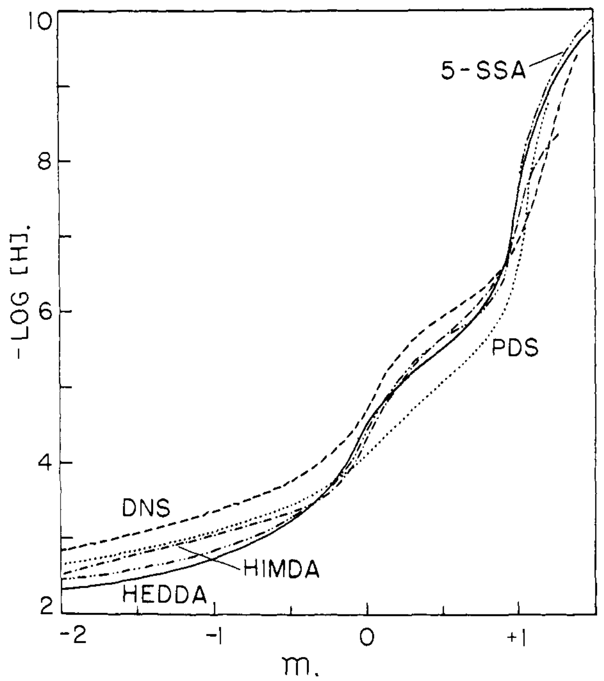

Fig. 1.—Potentiometric titration of 1:1 VO(IV) chelates of HEDDA, HIMDA, PDS, DNS and 5-SSA. Value of zero on abscissa correspond to completion of formation of normal aquo chelate. Portions of curves to right of zero represent formation of hydroxo complexes. m = moles of base added per gram-ion of metal present.

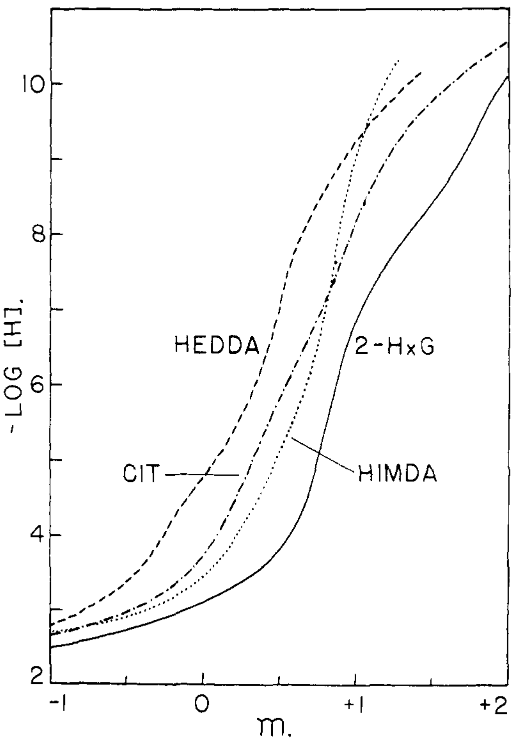

Fig. 2.—Potentiometric titration of 1:1 ZrO(IV) chelates of HEDDA, HIMDA, 2-HxG and CIT. Units of m on abscissa indicate moles of base added per gram-ion of metal present beyond the amount required to form the normal chelate compound.

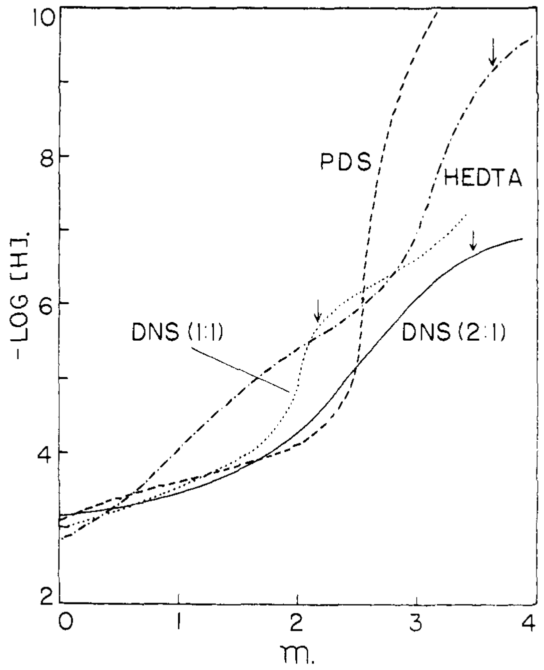

Fig. 3.—Potentiometric titration of 1:1 UO_2(VI) chelates of PDS, DNS and HEDTA and 2:1 chelate of DNS. Arrows indicate appearance of a solid phase; m = moles of base added per gram-ion of metal present.

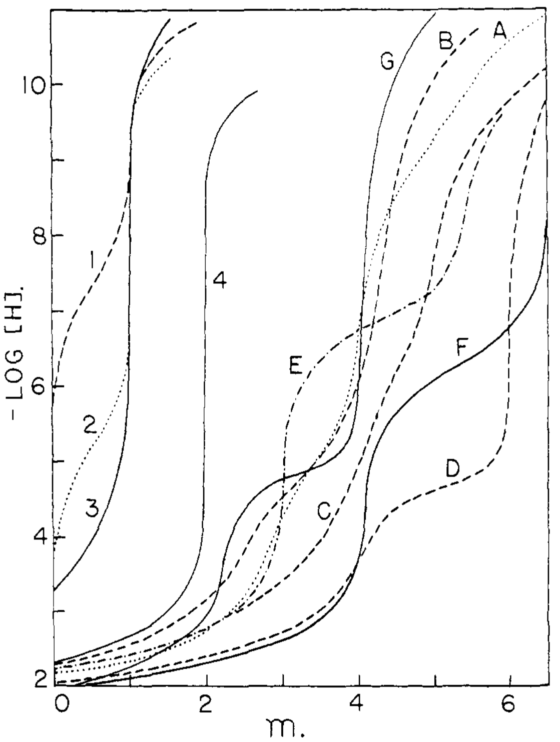

Fig. 4.—Potentiometric titration of (1:1) MoO_2(VI) chelates of A, PDS; B, DNS; C, NTA; D, 5-SSA; E, Na_2-EDTA; F, NaHEDTA. Curves 1, 2, 3 and 4 represent ligand titration data for PDS, DNS, NTA and 5-SSA, respectively, while curve G represents titration of MoO_2Cl_2. m = no. of moles of base added per gram-ion of metal present.

not form 1:1 complexes with simple diamines which are stable in aqueous solution at intermediate and high *p*H. The more stable complexes listed in Table I are those of EDTA and HEDTA, both of which are formed in acid solution and do not undergo hydrolysis at higher *p*H. With ligands containing fewer donor groups, such as HEDDA and HIMDA, there seem to be two definite hydrolysis steps with *pK* values of 5.5 and 5.7, respectively. The hydroxo complexes thus formed may contain a hydroxyl ion bound directly to the metal or may contain alkoxide linkages derived from the hydroxyethyl groups of the ligand as in the case of similar complexes of Cu(II)[6] and Fe(III).[7] It is impossible to distinguish between these alternative structures with data presently available. With ligands having only oxygen donors, vanadyl ion forms stable complexes in which protons are dissociated from all groups attached directly to the metal. This is true, for example, for the vanadyl chelates of PDS, DNS and 5-SSA. These compounds undergo further hydrolysis with *pK* values of 5.1, 6.0 and 5.7, respectively. Reasons for the observed differences in these *pK* values are not yet obvious with the data available. However, it is interesting to note that all of the *pK* values for hydrolysis of vanadyl chelates lie between 5 and 6.

ZrO(IV) Chelates.—The tendency of the ZrO^{+2} ion to form stable chelate compounds in aqueous solution seems to depend on the presence of hydroxyalkyl or hydroxyaryl groups in the ligand. Thus stable chelates are formed with ligands containing one or more hydroxyethyl groups, such as HEDTA and HEDDA. It is interesting to note that these metal complexes seem to be quite normal in that protons are not displaced from the hydroxyethyl groups in the formation of the initial metal chelate compound. The HEDDA chelate undergoes further hydrolysis with a *pK* value of 7 to give a complex in which an additional hydroxyl group probably is bound directly to the metal ion. Other aliphatic complexing agents which form stable aqueous zirconyl chelates are 2-HxG, HIMDA and CIT. The latter two ligands form chelates which undergo further hydrolysis steps with *pK* values of 5.3 and 6.0, respectively. The 2-HxG chelate of the ZrO(IV) ion undergoes a two step hydrolysis with *pK* values of 3.9 and 8.5. It is impossible to state whether the hydroxo complexes are all coördinated directly to the metal ion or whether there is some involvement of a displacement reaction in which the hydroxyethyl proton is removed. The chelate compounds obtained are probably tautomeric mixtures of various forms involving both types of interaction.

It is interesting to note that in the case of polymeric oxozirconium(IV) ion, as is true of other metal ions, the chelate formed with PDS is stable whereas the analogous compound of DNS is not. In the latter case, little or no reaction takes place and the metal is precipitated above *p*H 3. The analogous ligand, 5-SSA, is also a poor chelating agent for the ZrO(IV) ion.

The zirconyl ion also was found to have very little affinity for ligands containing basic amino groups such as hydroxyethylethylenediamine and for a number of ligands capable of forming only a small number of chelate rings. The number of stable aqueous zirconyl chelates which have been observed to hydrolyze in aqueous solution is insufficient to allow correlation of *pK* values for the hydrolysis steps with the structure of the ligand.

UO_2(VI) Chelates.—While the interactions of a large number of ligands with the uranyl ion were investigated, only a few ligands were found to form stable 1:1 complexes in aqueous solution. Thus, ligands such as HIMDA, 2-HxG and 5-SSA form relatively unstable metal chelate compounds which disproportionate above *p*H 4 or 5 to give insoluble substances containing the metal ion. Ligands with a larger number of donor groups, however, such as EDTA and HEDTA form more stable uranyl complexes which do not precipitate until the *p*H is raised to relatively high values. In both cases, 4 moles of base are required per mole of metal chelate formed. Thus the uranyl–HEDTA complex involves coördination of the metal with the hydroxyethyl group in such a way that the proton is displaced to give an alkoxide type of linkage. The direct displacement of the proton from the hydroxyalkyl group is believed to occur in this case in view of the fact that four moles of base are required in the first step of the neutralization reaction.

The most interesting type of uranyl chelate compounds studied in this investigation are the 1:1 compounds formed from diphenols such as DNS and PDS. The uranyl-DNS 1:1 chelate forms with the neutralization of two moles of base per mole of metal ion. The reaction product is somewhat unstable, however, and disproportionates to give a solid above *p*H 6. With a ratio of ligand to metal ion of 2:1, a similar reaction takes place with further utilization of base until the *p*H reaches a value of around 6.5 to 7, whereupon a solid appears. The initial step of the reaction seems to involve two moles of base per mole of metal ion and may correspond to the initial step observed in the formation of the 1:1 chelate compounds. However, further interaction occurs with the utilization of more base, and the combination of the initial chelate with a second mole of ligand is thus believed to take place. The 1:1 uranyl 5-SSA chelate is analogous to the 1:1 DNS chelate in that 3 moles of base are required for the formation of the initial metal chelate. Further addition of base, however, results in precipitation of a solid phase. The 5-SSA and DNS chelates therefore are believed to be analogous.

Perhaps the most interesting of the uranyl chelates thus far investigated is the 1:1 compound formed with PDS. This complex involves the utilization of approximately $2^2/_3$ moles of base per mole of metal ion with the development of a deep reddish brown color. Although equilibrium is reached slowly and the compound formed is obviously a polymer, there is no precipitation even at the highest *p*H values. A tentative formula of the complex formed is given in Table I. However, further studies now in progress indicate that this reaction is quite complex, involving overlapping chelate formation of either a ternuclear compound or some multiple having the same composition.

It is interesting to note that Feldman, *et al.*,[5a] observed inflections in the *p*H range 5–8 when the ratio of moles of base added to moles of UO_2(VI) salt was equal to 1 $^2/_3$ plus the number of carboxyl groups present in the ligand in the cases of the 1:2 chelates of lactate, citrate, tartrate and malate. There is no evidence at this point, however, indicating that the reactions observed in this paper, and those of Feldman, *et al.*,[5a] represent the same, or even related, phenomena.

MoO_2(VI).—In the reaction of a MoO_2(VI) salt with various ligands such as EDTA, HEDTA, 5-SSA and DNS, the titration data showed very little difference between the metal ion alone and metal solutions containing ligand. In all cases there is no evidence from the potentiometric data that any reactions other than simple formation of the molybdate ion occurred along with neutralization of free ligand as base was added to the solution. In the case of PDS (Tiron), however, there was a definite *p*H effect indicating the formation of a stable chelate between some electropositive molybdenum species, such as MoO_2^{+2}, with one or more moles of ligand. The inflection corresponding to the formation of the molybdate anion in the case of the other titrations occurred at the same position in the presence of Tiron. Before definite conclusions can be drawn concerning the extent and the nature of the interaction of MoO_2(VI) with this ligand, it will be necessary to study the interaction by measuring other properties of this system such as ultraviolet absorption spectra.

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Hydrolytic Tendencies of Metal Chelate Compounds. IV. Dimerization of Copper(II) Chelates[1]

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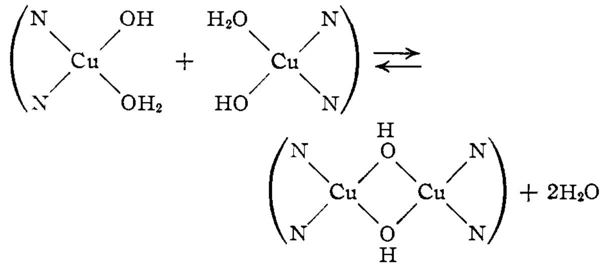
RECEIVED APRIL 7, 1958

The interactions of N-hydroxyethylethylenediamine (HEN), N,N'-dihydroxyethylethylenediamine (2-HEN), 1,3-diaminopropane (DAP), diethylenetriamine (DIEN) and triethylenetetramine (TRIEN) with equivalent amounts of Cu(II) ion were investigated over the entire *p*H range. Chelate formation constants, chelate hydrolysis constants and chelate olation constants are reported for the chelate compounds formed with bidentate ligands, and hydrolysis constants are reported for the 1:1 Cu(II) chelates of DIEN and TRIEN. Hydrolytic tendencies of the chelates decrease with an increase in the number of donor groups in the ligands, while olation reactions occur with only the diamine chelates to form binuclear compounds.

In a recent publication[2] in which the hydrolytic tendencies of a large number of copper(II) chelates were compared, it was shown that the degree of formation of soluble hydroxo complexes generally increases with decreasing metal chelate stability, increasing charge of the central metal ion and decreasing number of donor groups associated with the ligand. Thus the Cu(II) chelate of ethylenediamine readily forms hydroxo complexes, while no measurable hydrolysis can be detected for the analogous chelate of ethylenediaminetetraacetic acid.

Since the formation of a monohydroxo complex may be considered to be the first step in dimer formation, which proceeds according to the reaction



it would seem logical to assume that the same general rules apply also to dimer formation as well.

In order to provide a comparison between analogous Cu(II) chelates having different numbers of free aquo positions attached to the metal ion, the interactions of Cu(II) nitrate with N-hydroxyethylethylenediamine (HEN), N,N'-dihydroxyethylethylenediamine (2-HEN), 1,3-diaminopropane(DAP), diethylenetriamine(DIEN) and triethylenetetramine (TRIEN) were investigated. While DAP may function only as a bidentate chelating agent, the analogous chelates of HEN and 2-HEN could possibly act as tri- or tetradentate donors, provided that the hydroxyethyl groups take part in chelation. DIEN and TRIEN are normally considered to function as tri- and tetradentate ligands, respectively.

Experimental

Reagents.—A solution of J. T. Baker Analyzed Reagent cupric nitrate was standardized both by thiosulfate titration and by the method of Schwarzenbach[3] in which standard disodium ethylenediaminetetraacetate was employed as a titrant with murexide as an indicator in ammoniacal solution. Results obtained by the two methods agreed within three parts per thousand. Samples of diethylenetriamine, triethylenetetramine, 1,3-diaminopropane, N-hydroxyethylethylenediamine and N,N'-dihydroxyethylethylenediamine were purified by fractional distillation and were then isolated as the corresponding hydrochlorides. Standardization of the aqueous solutions of these chelating agents was effected by means of potentiometric titration with standard carbonate-

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[1] This paper reports work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C.

[2] A. E. Martell, S. Chaberek, Jr., R. C. Courtney, H. Hyytiainen and S. J. Westerback, THIS JOURNAL, **79**, 3036 (1957).

[3] G. Schwarzenbach, "Die komplexometrische Titration," Ferdinand Enke, Stuttgart, 1955, p. 68.