THE STABILITY CONSTANTS
OF ETHYLENEDIPHOSPHINETETRAACETATE COMPLEXES*

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The stability constants of complexes formed by the anions of ethylenediphosphinetetraacetic acid and the metal ions Cu(I), Ag(I), Ca(II), Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pb(II) and La(III) were determined by various methods (mainly potentiometry and UV-VIS spectrophotometry), followed by data treatment using standard computer programs. The type and stability of the complexes formed depend mostly on the relative affinity of the particular metal ion for the two donor groups of the ligand. Unlike EDTA, the ligand is highly selective for soft metal ions, whose complexes are very stable even in strongly acidic aqueous solutions.

In the previous paper in this series[1], the synthesis and characterization of tetrasodium ethylenediphosphinetetraacetate (Na_4L) as a structural analogue of EDTA was described. The stability of metal complexes of this ligand, containing a combination of soft and hard donor atoms is of interest both theoretically and in connection with potential applications, *e.g.* as a selective analytical reagent. This work was carried out to determine the stability constants of complexes with a representative series of metal ions whose properties change continuously from typically hard to typically soft ions.

EXPERIMENTAL

Materials

The tetrasodium salt[1] was purified by conversion[2] to $H_4L.2\ HBr$, which was recrystallized twice from freshly distilled azeotropic HBr. Under argon, a 20% aqueous solution of the pure bis--hydrobromide was neutralized carefully with 20% aqueous NaOH to pH 8·0 and added drop-wise to an excess of absolute methanol with vigorous stirring. The precipitated tetrasodium salt was filtered off, washed thoroughly with methanol and dried *in vacuo*. The product with the composition $Na_4L.H_2O$ was free of bromide and contained $99·8 \pm 0·3\%$ total phosphorus in the tervalent form.

As a source of metal ions, acidified solutions of metal perchlorates were prepared from *p.a.* metal oxides or carbonates and a slight excess of Merck *p.a.* perchloric acid. The metal content was determined by standard volumetric or gravimetric methods and the excess acid by titration with a base according to the Gran method[3]. Tetrakis(acetonitrile)copper(I) perchlorate[4] was used as a source of Cu(I). Acetonitrile was purified by standard method followed by fractional distillation. Metal amalgams of 0·5—8% (w/w) concentration were prepared by electrolysis of metal perchlorate solutions in an apparatus enabling storage and transfer into the electrode under inert gas[5]. Vacuum redistilled mercury "for polarography" was used throughout.

Procedure

All the stability constants were determined at $25 \pm 0.1°C$ and $I = 0.1$ (NaClO$_4$ unless stated otherwise). The experimental procedures were as follows:

Potentiometric measurements were arranged as titrations and changes in the potential of the indicator electrode(s) were registered as a function of added titrant. In every system, equilibrium establishment was checked by reverse titrations. The solution was placed in a 70 ml vessel equipped with a jacket, joints for electrodes, a salt bridge, a burette and an inlet and outlet for pure argon which was pre-saturated with the solvent vapour. The titrant was added from a calibrated burette; typically, a total of 5 ml of the titrant was added in 20—50 data points with a precision of 0·002 ml. Potentials were measured on a Radiometer PHM 64 instrument readable to 0·1 mV (0·001 pH). The following measuring cells were used: *1*) Radiometer glass G 203 C and saturated calomel K 401 electrodes, which were separated by a salt bridge containing 0·1M-NaClO$_4$ for systems where interference could be expected from Cl$^-$. The cell was calibrated[6] in terms of $-\log[\text{H}^+]$ by the titration of HClO$_4$ and CH$_3$COOH with a NaOH solution and checked using a standard phthalate buffer of pH 4·010 before each titration. The precision of $-\log[\text{H}^+]$ was better than 0·005 units. *2*) A cell consisting of a silver Radiometer P 104 electrode (or a metal amalgam electrode) and a K 401 electrode separated by a salt bridge; the immersible metal amalgam electrode was of the J-type with a working surface of about 60 mm^2. The cell was calibrated as follows: first, the liquid junction potential was measured as a function of $-\log[\text{H}^+]$ in the whole acidity range studied: the metal electrode was replaced by a hydrogen electrode and the potential at a number of perchloric acid, acetic acid or sodium hydroxide concentrations was determined. The E_j values for a given acidity were found from the difference between the measured and theoretical potential values calculated assuming complete dissociation of perchloric acid, using the recommended values of the dissociation constant of acetic acid and the ion product of water[7]. These differences, amounting to at most 9·2 mV at $-\log[\text{H}^+] = 1.3$, were further used as a correction to the potential of the metal electrode. The cell could then be calibrated to give the metal ion concentration: the potential of the metal (amalgam) electrode was measured at various ion concentrations with sufficient perchloric acid to eliminate hydrolysis. Values of the standard potentials obtained in this manner between $c_M = 0.02$ and $5 . 10^{-5}$M differ by less than 1·0 mV provided that oxygen was rigorously excluded.

Depending on the type of metal ion involved, the following arrangements were used for data accumulation.

Method A. Titration of mixtures of the ligand and a metal ion with a base and then with an acid: $-\log[\text{H}^+]$ alone is measured.

Method B. The titration of a metal ion solution with a solution of Na$_4$L and then back-titration with the metal ion solution; $-\log[\text{M}^{n+}]$ alone is measured.

Method C. As sub *A*, $-\log [H^+]$ and $-\log [M^{n+}]$ are measured simultaneously; complementary titrations of an acidified metal ion solution with an Na_4L solution and *vice versa*.

Method D. Competition titrations arranged as *C* but with a second metal ion M′ present in a suitable concentration depending on the expected stability constant ratio; $-\log [H^+]$ and $-\log [M'^{n+}]$ measured simultaneously.

Method E-polarography. Experimental details are essentially the same as described previously[8]. The half-wave potentials were determined to 1 mV. The dependence of the half-wave potential on $-\log [H^+]$ and on the concentration of mercury (II) and of the ligand was measured in individually prepared solutions.

Spectrophotometry. A Unicam SP 800 instrument was used for orientative measurements and a single-beam VSU-2 (Zeiss, Jena) spectrophotometer for precise determination of the absorbance. After careful selection and matching of the cells, the VSU-2 instrument was calibrated with potassium dichromate solutions. A precision of 0·003 A was achieved in the region $A = 0\cdot07 - 0\cdot65$ where all the measurements were then carried out.

Method F. Distribution of a metal between L^{4-} and another ligand (1,10-phenanthroline). Mixtures containing the metal ion, Na_4L and phenanthroline hydrochloride in $0\cdot01M$ Britton–Robinson buffer of pH 7·5 and $I = 0\cdot1$ (Cl⁻) were prepared, sealed under argon and equilibrated at 25°C for 5 days (Fe) or 6 months (Ni). Control experiments always involved mixing the reagents in the reverse order. The absorbance of the solutions was then measured in the region where maximal changes occur.

Method G. Replacement of two metal ions, Co and Ni, in the L^{4-} complex. Samples prepared at $I = 0\cdot1$ (NaClO₄) were equilibrated for 4 months.

Solubility — method H. Nickel(II) dimethylglyoximate prepared from nickel(II) perchlorate and dimethylglyoxime in dilute ammonia was recrystallized from chloroform. The product was sealed under argon with Na_4L solutions of various concentrations and equilibrated for 4 weeks with occasional shaking. After filtration, the visible spectrum of the solution was measured and the concentration of nickel was determined by adding excess Na_4L and calculation using the known molar absorptivity of the NiL_2^{6-} complex.

Data Treatment

The potentiometric data were treated by the program, MINIQUAD (ref.[9]). Stability constants of the hydroxocomplexes, used for correction, were taken from the literature[7]. Criteria for model selection and refinement were the same as discussed previously[10], which is essentially in agreement with the authors of the program[11]. Models including all the components present, *i.e.* protonated or mixed complexes where competition reactions were studied, were tested in all cases.

In the evaluation of the polarographic data, initial estimates of the model and stability, obtained as described previously[8], were refined by the POLAG program[12]. The data treatment was considerably simplified as a result of the presence of a single dominant complex.

The SQUAD program[13] was used for handling the spectrophotometric data. Criteria for model selection followed from preliminary matrix analysis of the data[14] which gave the number of absorbing species involved in the equilibrium.

The solubility data were evaluated by simple application of the material balance equations for the three components present. No mixed complexes were detected.

All calculations involving statistical programs were carried out on an ICL 4-72 computer.

RESULTS AND DISCUSSION

The choice of experimental methods for determining stability constants in this case is of extreme importance because of the "hybrid" character[15] of the ligand. With EDTA, methods involving mutual displacement of protons, metal ions and a second ligand mostly suffice for the determination of the stability constants. The presence of soft and hard donor atoms in L^{4-} leads, however, to at least two differences from EDTA: greater selectivity of the ligand and, primarily, the consequences of back π-donation $P \leftarrow M$ from the soft metal ions. With respect to the mechanism of ligand protonation[2], this effect can be expected to be partly independent of the acidity and consequently not measurable by classical proton-metal displacement methods. Therefore, at least two independent methods are necessary: one, indicative for changes in the carboxyl group environment, most conveniently measurement of $-\log[H^+]$, and, second, preferably measurement of $-\log[M^{n+}]$ wherever possible. When two experimental methods are used for the determination of the same stability constant, some convention concerning the error in the constant must be adopted. The situation is unambiguous in treatment of the $-\log[H^+]$ and $-\log[M^{n+}]$ data using the MINIQUAD program which gives the standard deviation pertinent to the whole set of data. When the data from two or more methods were treated separately, the standard deviation of the mean, given in the work was calculated by standard formulae for the propagation of errors assuming unit weights for the individual constants.

The stability constants for the complexes and necessary experimental details are given in Table I. The given set of constants represents the "best model" chosen using the criteria cited.

Depending on the stability of their complexes, the metal ions studied can be clearly divided into three types. This division depends primarily on the soft or hard character of the metal ion and not on its charge or size.

The first group includes the typically hard metal ions Ca(II), Mn(II), Zn(II) and La(III). The weak interaction of these metal ions with the ligand involves only the carboxyl groups of the ligand. The 1 : 1 complexes formed are capable of adding two protons. According to the protonation constant values, it is probable that this protonation involves two free (i.e. uncoordinated) carboxyl groups in a 1 : 1 complex. Further protonation is associated with decomposition of the complex. With these metal ions, no 2 : 1 or 1 : 2 complexes could be detected in the concentration range studied.

Metal ion, M	p	q	r	log $\beta(\sigma)$	Method	Conc. range studied $-\log$ (mol l^{-1})	No of titrations (data points)
H$^{+\ a}$	0	1	1	5·97 (1)	A	L 2·3—3	3 (212)
	0	1	2	10·50 (2)		H 1·3—13	
	0	1	3	14·17 (2)			
	0	1	4	16·79 (2)			
Ca(II)	1	0	1	3·20 (2)	A	L 2·5—3	6 (241)
	1	1	1	8·58 (3)	D(M' = Zn)	Ca 2·3—3·3	
	1	2	1	12·80 (5)		Zn 2·5—3	
						H 2—12	
Mn(II)	1	0	1	2·92 (2)	as Ca	as Ca	7 (290)
	1	1	1	8·47 (4)			
	1	2	1	12·46 (6)			
La(III)	1	0	1	4·84 (4)	as Ca	as Ca	6 (228)
	1	1	1	9·70 (2)			
	1	2	1	13·15 (4)			
Zn(II)	1	0	1	3·69 (1)	A, B, C	L 2·5—3	8 (314)
	1	1	1	8·54 (2)		Zn 2·3—3·3	
	1	2	1	12·65 (3)		H 2—12	
Cd(II)	1	0	1	6·27 (7)	A, B, C, E	L 2·8—3·6	A—C 8 (271)
	1	1	1	10·13 (9)		Cd 2·5—4	E (36)
	1	2	1	14·05 (5)		H 2—12	
	2	1	0	10·38 (5)			
Pb(II)	1	0	1	6·67 (2)	A, B, C	as Cd	8 (288)
	1	1	1	10·08 (9)			
	1	2	1	13·28 (6)			
	2	1	0	9·77 (6)			
Fe(II)	1	2	0	16·44 (2)	A, F^b	L 2·2—4	A 2 (109)
	1	2	2	27·51 (3)		Fe 2·5—4	F 11 (21)^c
	1	2	4	35·41 (6)		phen 3·3—3·7	
	1	2	6	41·30 (9)		H 1·3—12	
Co(II)	1	2	0	22·54 (2)	A, G	L 2·1—3	A 2 (113)
	1	2	2	32·71 (4)		Co 2·4—3·3	G 9 (26)^{c,d}
	1	2	4	40·15 (6)		Ni 2·5—3·4	
	1	2	6	45·72 (7)		H 1·3—12	

TABLE I
(*Continued*)

Metal ion, M	p q r	$\log \beta(\sigma)$	Method	Conc. range studied $-\log (\text{mol } l^{-1})$	No of titrations (data points)
Ni(II)	1 2 0	22·24 (1)	A, F[e], H[f]	L 1·7—2·8	A 2 (114)
	1 2 2	31·22 (2)		Ni 2·4—3·1	F 11 (21)[c]
	1 2 4	38·24 (3)		phen 2·5—2·9	H (8)
	1 2 6	43·60 (3)		H 1·3—12	
Hg(II)	1 2 0	38·85 (9)	A, E	L 2·5—3·5	A 2 (110)
	1 2 2	49·4 (1)		Hg 2·2—3·9	E (47)
	1 2 4	57·5 (1)		H 1·3—12	
	1 2 6	63·7 (2)			
Cu(I)[g]	1 1 0	7·41 (2)	B, C	L 1·8—3·6	B 2 (163)
	2 1 0	10·94 (4)		Cu 2·2—3·5	C 4 (190)
	1 1 1	12·34 (3)		CH_3CN 0·7	
	1 1 2	16·38 (3)		H 1·3—12	
	1 1 3	19·72 (4)			
Ag(I)	1 1 0	9·36 (3)	B, C	L 1·8—3·6	B 2 (174)
	2 1 0	14·83 (9)		Ag 2·2—3·5	C 4 (211)
	1 1 1	13·85 (4)		H 1·3—12	
	1 1 2	17·44 (4)			
	1 1 3	19·89 (4)			
	2 1 1	18·8 (1)			
	2 1 2	22·2 (1)			

[a] See[1]; [b] $\log \beta_{Fe(phen)_3} = 21·15$ (see[16]); [c] No of solutions (wavelengths); [d] measured at $c_{Co} \leq 2c_L$; $CoNiL_2$ present at $c_{Co} > 2c_L$; [e] $\log \beta_{Ni(phen)_3} = 24·80$ (see[17]); [f] for Ni (dmg)$_2$, $K_s = 10^{-23.66}$ (see[18]); [g] in 0·2M-CH_3CN to stabilize the free Cu(I).

The d^{10} metal ions of a transient type between soft and hard fall into the second group: Cd(II) and Pb(II). The somewhat higher stability constant values indicate that the predominant character of the metal ion—carboxyl group interaction is supported by a weak phosphorus—metal interaction, probably only through $\sigma(P \rightarrow M)$ donation. The coordination of phosphorus is not, however, strong enough to exist separately: in an acidic solution of pH < 2, where COO—M bonds are broken, the Cd and Pb complexes are completely dissociated. In this group, the further M_2L complexes were detected; their limited solubility and slow precipitation somewhat complicated the measurements. As in the first group, no ML_2 complexes are formed.

Typically soft metal ions and transition metal ions with incompletely filled d-shells comprise the third group which is characteristic for the studied ligand. These metal ions include Cu(I), Ag(I), Hg(II), Fe(II), Co(II) and Ni(II) and form stable, water-soluble complexes which are not decomposed even in strong mineral acids (unless $c_H > c$. 6M and even higher for Hg). This behaviour is caused by the fact that the metal–ligand interaction is realized primarily (and almost exclusively) through $P-M$ bonding which is not affected by protons unless the formation of phosphonium salts[2] begins to be a competitive factor. Divalent metal ions form ML_2^{6-} complexes which are protonated quite separately and independently of the ML_2 unit, presumably at uncoordinated carboxyl groups. The basicity of the individual carboxyl groups is affected only slightly by the metal ion, evidently through an inductive effect alone. It is interesting to note that only the stepwise addition of always two protons simultaneously by the two ligands can be detected from pH-titration of the ML_2 complex, in agreement with the formal equivalence of the ligands. Comparison of the behaviour of HgL_2, CoL_2 and NiL_2 with that of the complexes of monophosphines[8,10] indicates that the stability results primarily from the chelate effect of the PCH_2CH_2P group. On the other hand, the stability of the Cu(I) complexes is comparable to that of monophosphines[10] which indicates that no chelate structures are formed with Cu(I).

Consequently, the univalent ions yield 2 : 1 (metal–ligand) and 1 : 1 complexes, which are not decomposed in strong acid medium and are presumably also protonated at the free carboxyl groups. After correcting the values of the stability constants of the Cu(I) complexes for the acetonitrile complex[4], $Cu(CH_3CN)_2^+$, ($\log \beta_2 = 4.35$), similar values for Cu and Ag are obtained, which is in agreement with the proposed structural analogy between these two sets of complexes.

In summary, the stability constants of metal–ethylenediphosphinetetraacetate complexes are generally in agreement with the expected selective behaviour of the ligand. The most important result seems to be the high stability of the complexes of soft metal ions even in strongly acidic aqueous solutions where only a very limited number of complexes can exist.

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