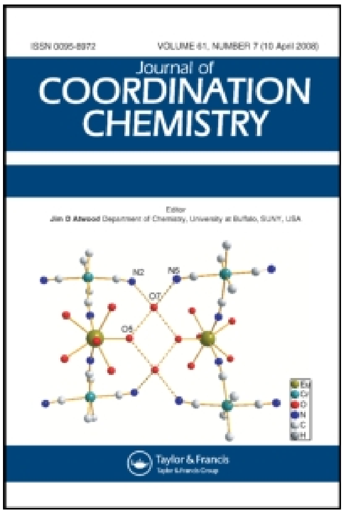

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NEW MULTIDENTATE LIGANDS. XXV.† THE COORDINATION CHEMISTRY OF DIVALENT METAL IONS WITH DIGLYCOLIC ACID, CARBOXYMETHYLTARTRONIC ACID AND DITARTRONIC ACID

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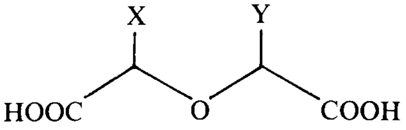
Potentiometric determinations of protonation constants and metal binding constants of the ether polycarboxylate ligands diglycolic, carboxymethyltartronic, and ditartronic acid are reported. The magnitudes of the equilibrium constants are discussed in terms of the functional groups present. Competition between ditartronic acid and nitrilotriacetic acid (NTA) for calcium(II) demonstrates that the ether polycarboxylates are particularly effective as sequestering agents in weakly to moderately acid solutions.

INTRODUCTION

The three ligands diglycolic, carboxymethyltartronic and ditartronic acids are the lower members of a series of organic ligands containing ether and carboxylate groups, which are capable of forming reasonably stable and soluble complexes of divalent metal ions in acqueous solution. These chelating agents are of interest for certain applications (*e.g.* detergent builders, water conditioning, *etc.*) because they do not contain nitrogen or phosphorus. They are also of interest as rudimentary models for natural ligands such as humic and fulvic acids, which derive much of their coordinating ability from ether and carboxylate groups. Of the three, only diglycolic acid has been studied previously as a coordinating ligand. Formulas **1-3** illustrates the close structural relationship between these ligands.



Diglycolic acid derivatives

1 diglycolic acid: X = H, Y = H (DG)
2 carboxymethyltartronic acid: X = H, Y = COOH (CMT)
3 ditartronic acid; X = COOH, Y = COOH (DT)

This purpose of this research is to determine the coordinating tendencies of these interesting ligands.

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† Part XXIV: C. Susemihl and A.E. Martell, *Inorg. Chim. Acta*, in press.
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EXPERIMENTAL

Potentiometric measurements were carried out on aqueous solutions containing 0.100 M KCl as supporting electrolyte and at 25.00 ± .01°. The potentiometric measurements were made with a Beckman Research pH meter fitted with E-2 glass and calomel electrodes, and calibrated with standard HCl to read – logarithm hydrogen ion concentration directly. The concentrations of ligands were generally 2-5 millimolar and 0.100 M KOH, prepared from CO_2-free Dilut-It concentrate, was employed as the added base. The computations of protonation constants were carried out using the FORTRAN program PKAS[1] while the stability constants were computed using the FORTRAN program BEST.[2]

RESULTS AND DISCUSSION

Protonation Reactions

The protonation constants obtained in this study are presented in Table I. It is believed that for the conditions stated, these constants are accurate to the third decimal place because the pH meter was calibrated in the acid region with standard acid solution and the resulting fit obtained indicated unusually high precision. For comparison, the latest recommended[3] literature values for diglycolic (DG) acid protonation constants are 3.92 and 2.80, while the protonation constants for carboxymethyltartronic (CMT) and ditartronic (DT) acids had not been measured. It is clear that in each case log K_1 and log K_2 differ by about 1.1 log units, indicating a considerably higher difference than would be predicted on statistical grounds, so that most of the effect can be considered to be due coulombic interactions between the donor groups. Similar differences are observed for successive protonation constants for the ligands containing additional carboxylate groups, with some variation in the magnitudes of the decreases observed. A straightforward discussion based on first principles is clouded by the existence of additional microspecies present in solution corresponding to the intermediate protonation steps (Table II). These considerations are consistent with a successive protonation scheme which is relatively simple for DG, since only a single microspecies is involved at each level of protonation. However in CMT, the first protonation occurs on the tartronic group, with some microspecies contribution from the glycolic group, while the second protonation is represented nearly totally by a microspecies which possesses a proton and a carboxylate on both sides of the oxo bridge. In DT, after the second protonation, the protons reside on the opposite sides of the molecule. However out of 19 microspecies possible, 13 internally hydrogen bonded structures are possible. The final two protonations are involved in breaking the bifurcated structures. It is also important to note that even in DG, the second protonation involves the breaking of a stabilizing $-COOH\ldots{}^{-}OOC$-hydrogen bond.

TABLE I
Protonation Constants of Diglycolic Acid, Carboxymethyltartronic Acid and Ditartronic Acid (25.0°, $\mu = 0.100$ M)

		pK_a's (log protonation constants)[a]			
Ligand	Log K_1	Log K_2	Log K_3	Log K_4	σ fit[b]
DG	3.937	2.817			0.0005
CMT	4.409	3.250	1.72		0.0005
DT	4.710	3.659	2.328	1.27	0.0034

[a] $\log K_n = [H_nL]/[H^+][H_{n-1}L]$. [b] $\sigma_{fit} = \left\{ \sum_{i=1}^{N} (pH_i^{obs} - pH_i^{calc})^2/(N-1) \right\}^{1/2}$ where N = number of potentiometric equilibrium points

TABLE II

Protonated Forms of Diglycolic Acid, Carboxylmethyltartronic Acid and Ditartronic Acid[a]

	DG			CMT			DT		
Degree of Protonation	Total	Unique	Favored Species	Total	Unique	Favored Species	Total	Unique	Favored Species
1	3	2	1	6	2,2,1,1	3	9	4,3,2	5
2	1	1		6	2,2,1,1	3	19	8,4,4,2,1	13
3				1	1		10	4,4,2	6
4							1	1	

[a] Total: the number of discrete microspecies possible; Unique: the number of microspecies in each unique set (numbers represent number of indistinguishable species in each set). Favored species: the number of microspecies allocated higher probability because of hydrogen bonding between adjacent carboylate groups.

TABLE III

Stability Constants of Diglycolic Acid with Metal Ions at 25.0°, $\mu = 0.100$ M

Metal Ion	Log K_{ML}[a]	Log K^H_{ML}[b]	ρ Fit[c]	Log $\frac{[MHL]}{[M][HL]}$	Log K_{ML} Glycolic[d]	Glutartic[d]
Ca^{2+}	3.36	1.94	0.001	1.36	1.11	1.06
Mg^{2+}	1.61	2.0	0.002	-0.33	0.92	1.08
Sr^{2+}	2.52	2.4	0.002	0.98	0.80	
Cu^{2+}	3.97	1.39	0.006	1.42	2.31	2.40
Ni^{2+}	2.81	1.97	0.002	0.84	1.69	1.6
Co^{2+}	2.74	2.28	0.005	1.08	1.68	2.20
Zn^{2+}	3.65		0.008			1.6
Mn^{2+}	2.54		0.006			1.13
Cd^{2+}	3.21	1.75	0.006	1.02	1.47	2.00
Pb^{2+}	4.41	1.45	0.002	1.93	2.01	2.8
Sn^{2+}	5.56		0.007	—		
Fe^{2+}	2.48	2.09	0.003	0.63	1.33	

[a] $K_{ML} = [ML]/[M][L]$. [b] $K^H_{ML} = [MHL]/[ML][H^+]$. [c] See Table I. [d] Refs. 3 and 4.

TABLE IV

Stability Constants of Carboxymethyltartronic Acid with Metal Ions at 25.0°, $\mu = 0.100$ M.

Metal Ion	Log K_{ML}[a]	Log $K^H{}_{ML}$[a]	Log $K^{HL}{}_{MHL}$	σ fit[b]	Tartronic acid[c]
Ca^{2+}	4.62	2.65	2.86	0.002	2.27
Mg^{2+}	2.77	3.07	1.43	0.002	2.17
Sr^{2+}	3.79	2.91		0.004	
Cu^{2+}	5.20	3.01	3.80	0.002	5.34
Ni^{2+}	3.84	2.89		0.003	
Co^{2+}	3.87	2.81	2.27	0.002	3.25
Zn^{2+}	4.87	2.42	2.88	0.002	3.22
Mn^{2+}	3.76	2.84		0.002	
Cd^{2+}	4.49	2.67	2.75	0.002	2.85
Pb^{2+}	6.04	2.02		0.001	
Sn^{2+}	7.00	1.56		0.002	
Fe^{2+}	3.67	2.70		0.004	

[a] See Table III. [b] See Table I. [c] Refs. 3 and 4.

TABLE V
Stability Constants of Ditartronic Acid with Metal Ions at 25.0°C, $\mu = 0.100$ M.

Metal Ion	Log K_{ML}[a]	Log K_{MHL}[a]	σ fit[b]
Ca^{2+}	5.17	3.23	0.001
Mg^{2+}	3.43	3.33	0.002
Sr^{2+}	4.69	3.34	0.003
Cu^{2+}	5.54	3.56	0.002
Ni^{2+}	4.40	3.39	0.004
Co^{2+}	4.55	3.20	0.004
Zn^{2+}	5.62	2.94	0.002
Mn^{2+}	4.51	3.23	0.006
Cd^{2+}	5.44	3.10	0.003
Pb^{2+}	calculation not possible (precipitate formed)		
Sn^{2+}	7.90	2.32	0.002
Fe^{2+}	4.41	3.22	0.004

[a]See Table III. [b]See Table I.

Metal Ion Affinities

Examination of the results shown in Tables III, IV and V indicates that in general all metal-ligand interactions may be described with a very high degree of accuracy by only two metal complexes involving the following formation constants:

$$M + L \rightleftharpoons ML \qquad \beta_{ML} = \frac{[ML]}{[M][L]}$$

$$ML + H \rightleftharpoons MHL \qquad K^{H}_{MHL} = \frac{[MHL]}{[ML][H^+]}$$

It was also found that at millimolar concentrations the use of 1:2 and 2:1 molar ratios of ligand to metal ion does not alter the nature of the species formed. Therefore 2:1 or 1:2 complexes need not be invoked to account for the potentiometric data under the reaction conditions employed.

Figure 1 shows a very high degree of correlation between log K_{ML}(CMT) and log K_{ML}(DG), with R = 0.995. Similar correlations between log K_{ML} values of DT to DG and to CMT were determined to be R = 0.979 and R = 0.988, respectively. This indicates that there are no gross structural differences in the metal complexes of these ligands.

Diglycolic acid forms monoprotonated chelates at low pH, which indicates that for these metal ions there is no strong driving force for chelate formation involving both carboxyl groups as well as the bridging oxygen. Zinc(II), manganese(II), and tin(II) appear to be exceptions to this observation. Thus when the protonation equilibrium is expressed as a formation reaction and the stability constants are calculated in this way are compared

$$M + HL \rightleftharpoons MHL \qquad K_{MHL} = \frac{[MHL]}{[M][HL]}$$

to those of glycolic acid in the literature, they are found to be either a few tenths of a log unit higher or lower than the log K_{ML} of glycolic acid. The subsequent deprotonation reaction gives rise to a chelate with coordinated carboxylate groups which is probably analogous to that formed by glutaric acid. However since the log K_{ML}(DG) values are

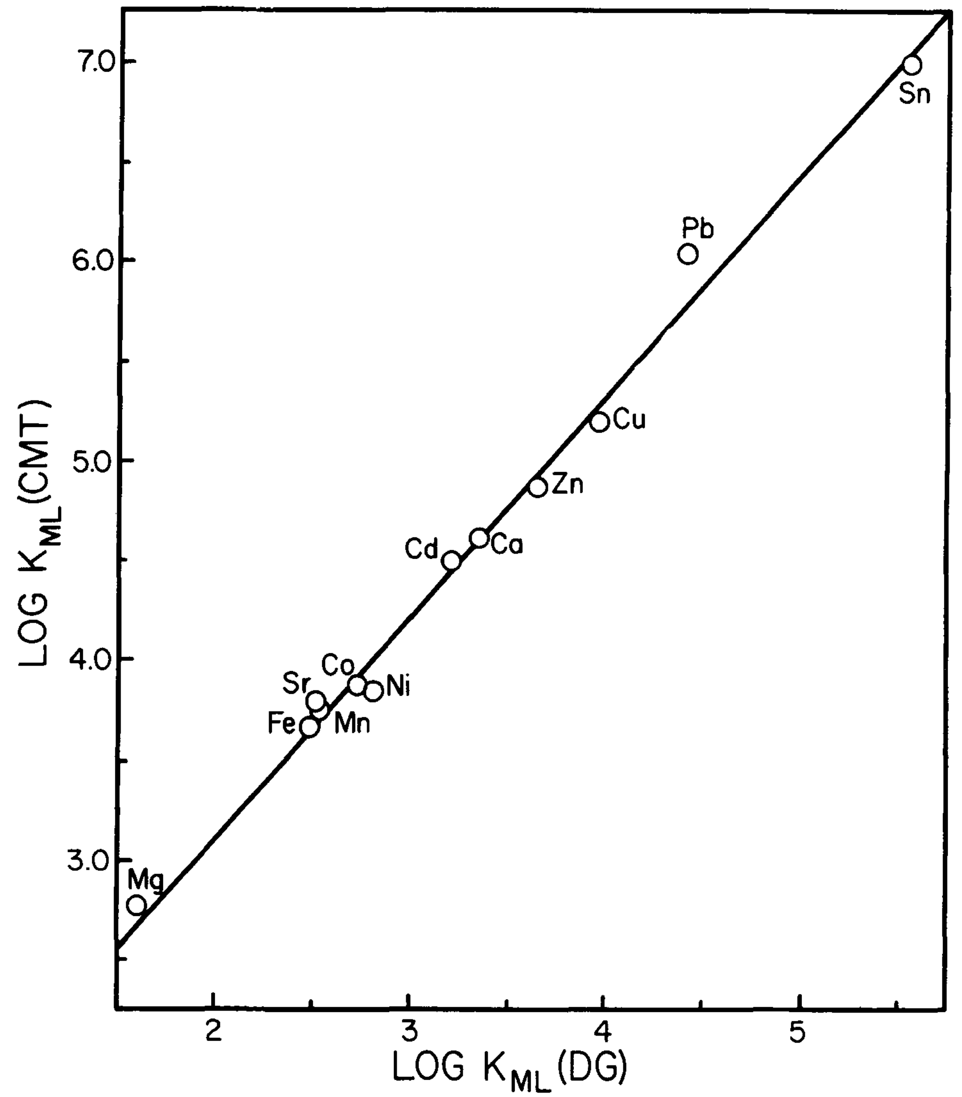

FIGURE 1 Correlation between log K_{ML} diglycolic acid and log K_{ML} carboxymethyltartronic acid (CMT) for 12 divalent metal ions. $R = 0.995$; slope = 1.10; σ (slope) = 0.03.

consistently about 1 to 1.5 log units larger than log K_{ML} (glutaric acid), there is an indication of terdentate bonding which includes the ether bridge as a weakly-coordinating partner.

The values of log K_{ML}(CMT) are all somewhat higher than log K_{ML} (tartronic). However, when expreesed as $M + HL \rightleftharpoons MHL$, the values agree among the pairs which have been previously measured, and all indicate that the initial complex (*i.e.* MHL) is entirely analogous to that of tartronic acid wherein the metal is bound to the tartronic group. For the ML complex, tetradentate coordination seems to prevail.

On the basis of considerations of this type, it is also concluded that in the case of ditartronic acid MHL consists of a metal ion coordinated to one end of the molecule, while at least four donor groups are involved in metal ion coordination in the ML species. On first inspection it appears unusual that the ordering of stability constants is such that Ca(II) ranks near Cd(II) and Zn(II) while Co(II) and Fe(II) are near Sr(II). Other anomalies are also apparent. These differences from the normal expected order are perhaps best illustrated by comparable data. Thus for the common metal ions for which data are available, the increasing order of stability constants is Mg < Fe < Sr < Co < Ni < Cd < Ca < Zn < Cu and varies from 1.61 to 3.97. For iminodiacetic acid, on the other hand, the order changes almost completely to Sr < Ca < Mg < Fe < Co < Zn < Ni < Cu with variation between the extremes of 2.23 to 10.57.

Although it is not possible to rationalize the relative magnitudes of these stability constants on the basis of current knowledge of aqueous complexes, it should be noted that these ligands do not contain basic amino groups, which were nearly always involved in stability orders reported in classical studies of metal complexes in solution. Similar variations from what would be considered the normal trends may be found in other non-nitrogen containing ligands such as tartrate, citrate, gluconate, and tripolyphosphate.

Ligand-Ligand-Metal Competition

The ligands studied in this investigation are not particularly strong coordinating species, and are not particularly effective in keeping metal ions in solution in

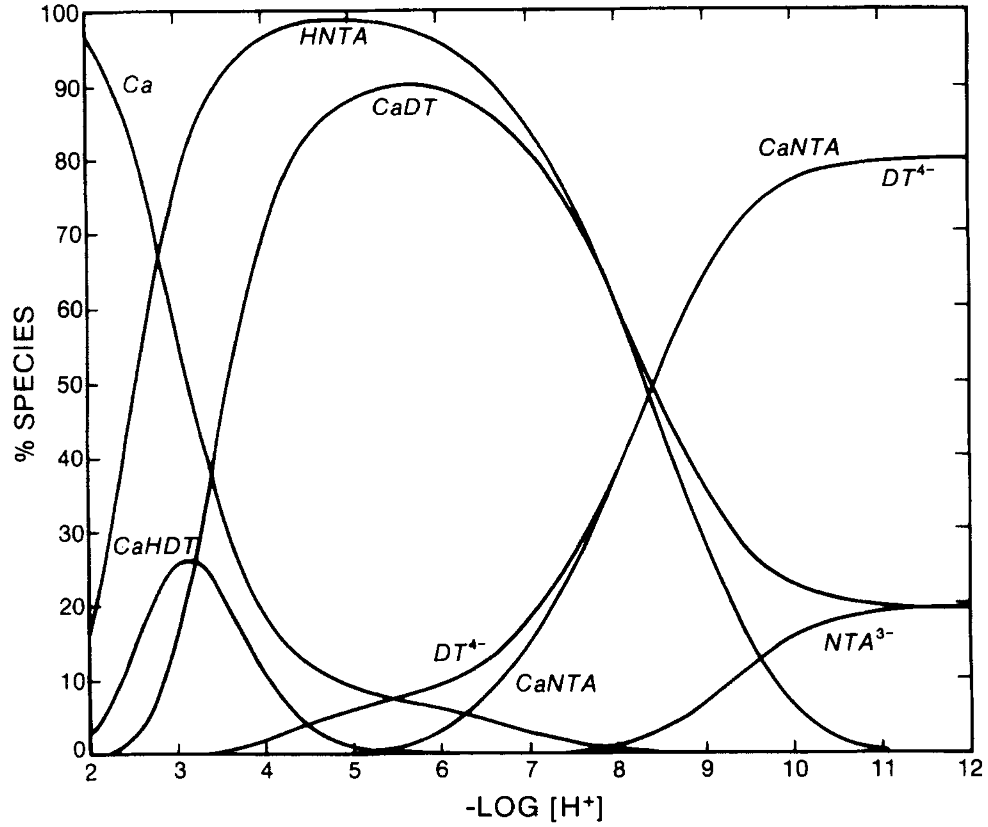

FIGURE 2 Species distribution diagram for Ca(II)/ditartronic acid/nitrilotriacetic acid 1:1:1 (1.00×10^{-3} M) at 25.0°, $\mu = 0.100$ M.

competition with their characteristic hydrolysis reactions at higher pH values. However, because of their low protonation constants, they are rather effective in coordinating metal ions at low to intermediate pH values. On the other hand, it may be recalled that because of its high protonation constant, nitrilotriacetic acid (NTA) is not very effective for many metal ions at low pH, but is quite effective at higher pH values. Figure 2 illustrates all these points with a system consisting of 1:1:1 solution containing 1×10^{-3} M Ca(II), ditartronic acid, and NTA. At pH 2, the solution consists mainly of the ligands and the metal ion. At pH 3, the $CaHDT^-$ species reaches its maximum concentration, while that of $CADT^{2-}$ steadily increases to its maximum value at pH 5.6. At higher pH CaNTA chelates start forming at the expense of $CaDT^{2-}$, and by pH 11, with all the ligands fully deprotonated, there is a constant ratio of CaNTA and CaDT species with CaNTA predominating. It is interesting that NTA does not take over completely and 20% of the Ca(II) remains bound to DT. Thus it seems that this ligand at least, is a sufficiently strong coordinator for alkaline earth ions to take over the functions of NTA, especially if it is employed in greater access than the latter sequestering agent.

ACKNOWLEDGEMENTS

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