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Stabilities of Metal Complexes of the Meso and *SS* Isomers of Oxydisuccinic Acid

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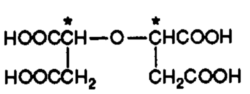
Published work with diastereomeric pairs of ligands and their interactions with metal ions is extremely limited and numbers less than 10 examples. Oxydisuccinic acid (ODS) provides a good opportunity, and its meso and *SS* forms were therefore investigated for specific activity with Ca^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Al^{3+}, Fe^{3+}, and protons. It has been shown by potentiometry that these stereoisomeric pairs of compounds possess from negligible to quite different affinities for protons, metal ions, and combinations of the two. It was found that 1:1 normal chelates are formed for all metal ions investigated with *meso*-ODS and *SS*-ODS. In addition all metals form from one to three normal protonated complexes, while the trivalent metal ions also form mono- and dihydroxo complexes. Above neutral p[H] all of these metal ions give up their ligands and undergo hydrolytic reactions.

Introduction

Oxydisuccinic acid (**1**) is a tetrabasic acid containing four carboxylate groups and an ether bridge. The carbons attached to the ether bridge are asymmetric centers forming two distinctly different ligands. For 1:1 complexation two isomers having different physical properties are formed: meso (*SR*) and racemic (*SS* and *RR*).



$$\begin{array}{lcl} \mathrm{HOOC\overset{*}{C}H} & -\mathrm{O}- & \mathrm{\overset{*}{C}HCOOH} \\ \quad | & & | \\ \mathrm{HOOCCH_2} & & \mathrm{CH_2COOH} \end{array}$$

1 (oxy-α,α′-disuccinic acid (ODS))

Since both *SS* and *RR* stereomers are expected by symmetry to behave identically toward metal ions in the formation of 1:1 complexes, an examination of Meso and either *SS* or *RR* isomers is necessary to fully describe the thermodynamic behavior of the ODS molecule toward the complexation of metal ions.

The metal ions studied possess in aqueous solution the usual coordination numbers (CN) of 4–6. The complexes of Ca(II) are sometimes found to have a CN of 8, while Fe(III) may be 7-coordinate. Nevertheless, only 1:1 metal ion:ligand complexes are expected for two reasons. The four carboxylates in most cases are sufficient to cover more than half of the CN requirements of each metal. The second reason concerns the negative charge on the carboxylates. All else being equal, the presence of negative charge in the coordination sphere greatly reduces the affinity of a coordinated metal ion for additional negatively charged ligands. For example, a 2:1 complex in the case of Ca(II)/ODS would be represented by the formula ML_2^{6-}. The mutual repulsive forces between the negative donor groups in such a complex would probably be sufficient to prevent its formation in aqueous solution.

Therefore, in this work potentiometric measurements were made on solutions containing equimolar amounts of metal ion and ligand. A few test runs on 2:1 molar ratios of ligand to metal ion showed no reaction with the second ligand anion.

Experimental Section

The potentiometric measurements were carried out with the procedures described in detail elsewhere.[1] Test solutions of *meso*-ODS were made up at 3.532×10^{-3} M, while the test solutions of the *SS* form were 4.200×10^{-3} M. Both were adjusted to 0.100 M ionic strength by the addition of KCl. The temperature was controlled at 25.00 °C by circulation of water from an external thermostat through the jacket of the experimental cell. The Corning Model 150 pH meter fitted with glass and calomel electrodes was calibrated daily with standard dilute HCl solutions so as to read hydrogen ion concentrations directly. Thus, the term p[H] in this report is defined as $-\log [H^+]$. The value of K_w ($[H^+][OH^-]$) used in the computations was $10^{-13.78}$, although its determination was not strictly necessary in this investigation and therefore $[OH^-]$ was not necessary in the mass balance equations.

All of the metal stock solutions were reagent grade nitrates made up with distilled water and standardized by either EDTA titration[2] or passage through Dowex 50W-X8 cation-exchange resin. In the latter case, the eluted acid was titrated with standard KOH solution, which was made up from CO_2-free commercial concentrate and standardized against potassium acid phthalate. In addition to the above, the stock solutions of aluminum(III) chloride were made up with a slight known excess of hydrochloric acid. Reagent grade mercury(II) chloride was employed as a primary standard for the Hg(II) stock solution.

The ligands *meso*-ODS and *SS*-ODS were supplied by Procter and Gamble Co. as aqueous solutions, which had been repeatedly purified by HPLC so that only very low concentrations of impurities were present. The compositions of the ligand solutions are as follows:

	anal. of ligand soln, % (mass, g)		
sample	ODS I (meso) in soln	ODS II (racemate) in soln	mass of sample, g
meso	2.20 (2.20)	0.02 (0.02)	100
SS	0.06 (0.06)	2.47 (≤5% *RR*) (2.46)	100

The potentiometric equilibrium measurements were made on 2.000-mL aliquots of ligand solutions provided by Procter and Gamble Co. Each solution was diluted to a final volume of 50.00 mL, as described above, first in the absence of metal ions and then in the presence of 1 molar equiv of each metal ion. The p[H] data were taken after additions of 0.100-mL increments of standard 0.1027 M KOH solution. This translated itself into approximately 17–21 data points (mL of KOH vs p[H]) per *a* value (mol of KOH added/mol of ligand present) for a total of approximately 68–84 useful experimental points per run. In general, duplicate titrations were not performed. This is justified by the rapid equilibria, stability of the apparatus, and the previous experience on such systems whereby measurements are quick and limited to a useful range of $2 < p[H] < 7$. The potentiometric apparatus was calibrated for each titration, with observed day-to-day changes on the order of <0.002 p[H] units. The computations were performed with the program BEST.[3] The absolute concentrations of the ligand stock solutions determined potentiometrically were found to be well within 1% of the concentrations assigned by Procter and Gamble Co.

The only assumption made in the computations was that the presence of minute amounts of the other isomer and the presence of traces of dicarboxylic acids do not affect the values of the calculated stability constants. These two assumptions are justified. Numerically, the impurities reside in trace amounts, relative to the concentrations of the components. If there is some interference from the other isomer, the stability constants of the other isomer are similar enough that at such low levels a correction would indeed be negligible. Two additional precautions were taken: a correction was made for the hydrogen ion concentrations contributed by these impurities, and the computations were done in the region terminated by *a* values somewhat less than 4.0. In either case the differences amounted to <1% variation in the constants calculated with and without corrections.

Precautions were exercised to justify the refinement of the titration data which resulted in using up to four metal species (MH_iL, where i = 0–3). For example Ca(II)–*meso*-ODS was found to be just such a system describable by the normal ML species together with three protonated complex species and a standard deviation of p[H] fit of 0.0020 over 70 titrations points. More than 80% of the calculated points were within 0.002 p[H] unit or less relative to the observed values. All the greater deviations were at the final inflection point where the p[H] rose very rapidly. When the model was restricted to i = 0, 1, and 2, the standard

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(1) Martell, A. E.; Motekaitis, R. J. *The Determination and Use of Stability Constants*; VCH Publishers: New York, 1989.

(2) Schwarzenbach, G.; Flaschka, H. *Complexametric Titrations*, 2nd ed.; Methuen: London, 1969.

(3) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 2403.

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Table I. Logarithms of Successive Protonation Constants for Meso and *SS* Isomers of ODS and for Reference Compounds Succinic Acid and Malic Acid[a]

protonation step	*meso*-ODS[b]	*SS*-ODS[b]	succinate[c]	malate[c]
1	5.97	5.97	5.24	4.68
2	4.85	4.79	4.00	3.24
3	3.98	3.40		
4	2.07	2.57		

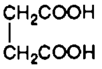
[a] Standard deviation of p[H] recalculation $\sigma_{\text{fit}} = 1/N\sum(\text{pH}_{\text{obs}} - \text{pH}_{\text{calc}})^2$ is 0.0016 (meso) and 0.009 (*SS*) before rounding. [b] This work. [c] Reference 5.

deviation of p[H] fit jumped to 0.0136 with only 60% of the points within 0.0136. Most of the new deviations were now located in the beginning region of the titration. Since the curve is quite featureless, the remaining species tried to make up for the unspecified MH_3L species, yet almost all of the calculated p[H] values were more than 1 order of magnitude outside of the confidence limit in determining p[H] (i.e. ~0.002). For these reasons MH_3L was kept. As a matter of fact, for the Ca(II)–*meso*-ODS system, MH_3L represents about 29% of the complexed metal ion at p[H] 2.6.

During determination of mercury(II) binding constants, the affinities of chloride ion to form various mercury(II) complexes were taken into account.

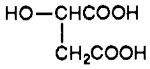
Results

The protonation constants for the meso and *SS* forms of ODS were computed from the potentiometric p[H] profiles of their solutions in the absence of metal ions. The logarithms of the successive protonation constants calculated with the aid of the program PKAS[4] are listed in Table I, together with the literature values[5] for succinic acid (**2**) and malic acid (**3**), which may be considered closely related to ODS.



$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

2 (succinic acid)



$$\begin{array}{l} HO-CHCOOH \\ \quad\quad | \\ \quad\quad CH_2COOH \end{array}$$

3 (malic acid)

It is instructive to note that the two stereomers meso and *SS* have slightly different protonation constants. While the first protonation reaction has the same value for both compounds, the protonation constants of the meso form are higher for the second and third steps, while the fourth protonation constant of the *SS* form is higher than that of the meso isomer. A search for similar behavior in other ligands indicates similar behavior for meso and *SS* forms of tartaric acid. The protonation constants of *meso*-tartaric acid are higher than those of (*SS*)-tartaric acid: 4.44 vs 3.95 and 2.99 vs 2.82, respectively. While this comparison of trends does not explain the results found for ODS, it does make the ODS values more credible by providing a precedent. Examination of the literature reveals only two other examples[6,7] of a meso–racemic pair of ligands which could be used for such a comparison: EHPG, *N,N'*-ethylenebis[2-(*o*-hydroxyphenyl)-glycine], and TMPHPG, *N,N'*-trimethylenebis[2-(2-hydroxy-3,5-dimethyl)glycine]. Both of the first two protonation constants of the trimethylenediamine derivative, TMPHPG, are 0.42 log units greater in the meso isomer than the racemic material, while those of the more compact EHPG are closer, with the first constant being greater for the racemic form over that of the meso. Apparently the differences in behavior arise as a result of differences in hydrogen bonding and internal charge repulsions that affect the protonation constants.

Further insight into the values of protonation constants of ODS is provided by comparing those of malate with succinate.[5] The presence of the hydroxyl substituent in malate decreases the protonation constants relative to succinate. The magnitude of the differences of the first protonation constants is smaller than that of the differences of the second protonation constants. The lower basicities of the malate carboxylate groups results from the electron-withdrawing (–I) inductive effect of the hydroxyl oxygen atom. The relevance to ODS is obvious in that the third and fourth protonation constants of ODS are lower than might at first be expected. These lower protonation constants may similarly be rationalized on the basis of the electron-withdrawing effect of the ether oxygen in ODS. Although some reasonable speculations can probably be made concerning the differences in the values of protonation constants associated with each stereomer in terms of differences in separation of the carboxyl groups, such speculations would be very tentative. The obtaining of data needed to clarify this matter is beyond the scope of this investigation.

Stability constants for ODS computed from potentiometric titration data involving a molar ratio of one metal ion to one ligand are presented in Table II. The initial computations were obtained in the form of overall stability constants or β values (eq 1).

$$m\text{M} + l\text{L} + h\text{H} \rightleftharpoons \text{M}_m\text{L}_l\text{H}_h \qquad \beta = \frac{[\text{M}_m\text{L}_l\text{H}_h]}{[\text{M}]^m[\text{L}]^l[\text{H}]^h} \tag{1}$$

$$\text{M} + \text{L} \rightleftharpoons \text{ML} \qquad K_{\text{ML}} = \frac{[\text{ML}]}{[\text{M}][\text{L}]} \tag{2}$$

$$\text{ML} + \text{H} \rightleftharpoons \text{MHL} \qquad K^{\text{H}}_{\text{MHL}} = \frac{[\text{MHL}]}{[\text{ML}][\text{H}]} \tag{3}$$

$$\text{MHL} + \text{H} \rightleftharpoons \text{MH}_2\text{L} \qquad K^{\text{H}}_{\text{MH}_2\text{L}} = \frac{[\text{MH}_2\text{L}]}{[\text{MHL}][\text{H}]} \tag{4}$$

$$\text{MH}_2\text{L} + \text{H} \rightleftharpoons \text{MH}_3\text{L} \qquad K^{\text{H}}_{\text{MH}_3\text{L}} = \frac{[\text{MH}_3\text{L}]}{[\text{MH}_2\text{L}][\text{H}]} \tag{5}$$

$$\begin{gathered} \text{ML(H}_2\text{O)} \rightleftharpoons \text{M(OH)L} + \text{H} \\ K_{\text{M(OH)L}} = \frac{[\text{M(OH)L}][\text{H}]}{[\text{ML(H}_2\text{O)}]} \end{gathered} \tag{6}$$

$$\begin{gathered} \text{ML(OH)} \rightleftharpoons \text{M(OH)}_2\text{L} + \text{H} \\ K_{\text{M(OH)}_2\text{L}} = \frac{[\text{M(OH)}_2\text{L}][\text{H}]}{[\text{ML(OH)}]} \end{gathered} \tag{7}$$

Differences between the various log β's provide the stepwise formation and protonation reactions defined by eqs 2–5. The values of the stepwise stability constants are listed in Table II. For the trivalent metal ions Al^{3+} and Fe^{3+} additional deprotonation reactions involving coordinated water molecules were found to occur. The dissociation constants for these reactions are defined by eqs 6 and 7 and are also listed in Table II.

The relative magnitudes of the normal stability constants log K_{ML} have been found to be such that the meso complex is always favored over the *SS* isomer by 0.2 (Mg^{2+}) to 1.0 (Zn^{2+}) log unit. However, a simple generalization cannot be made for the comparisons of the first, second, and third protonation reactions of the chelates (eqs 3–5) as some meso constants are higher than the racemic form, while others are lower for a given metal ion. Perhaps most surprising is the finding that triprotonated complexes MH_3L form for most of the metal ions investigated. One possible explanation lies in the aliphatic nature of the ligand in that, no matter to which carboxylate site the initial attachment of metal ion occurs, the electrostatic and electronic effects of the metal ion cannot be efficiently transmitted through the σ-bond framework to the remainder of the molecule. Thus, coordination at one site has only a minor effect on the acidity of the remaining carboxylate groups making possible the formation of triprotonated complexes. Apparently there is little tendency to actually displace protons during complexation reactions, since for most of the divalent ions (except Hg^{2+}) the magnitudes of their normal stability constants are on the order of magnitude of protonation constants for the unbound ligand.

The metal ions in Table II show three types of complex formation. Cu^{2+} and Ni^{2+} do not form the full complement of MH_iL

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(4) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 168.
(5) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1974, 1975, 1976, 1977, 1982, 1989; Vols. 1–6.
(6) Bannochie, C. J.; Martell, A. E. *J. Am. Chem. Soc.* **1989**, *111*, 4735.
(7) Bannochie, C. J.; Martell, A. E. *Inorg. Chem.* **1991**, *30*, 1385.

Table II. Logarithms of Stepwise Stability Constants[c] of *meso*- and *SS*-ODS Measured in Water at 25 °C and Ionic Strength 0.100 M

	meso				*SS*			
metal ion	ML	MHL	MH_2L	MH_3L	ML	MHL	MH_2L	MH_3L
Ca^{2+}	5.82	4.43	3.53	3.41	5.42	4.35	3.53	2.72
Mg^{2+}	5.09	4.05	3.44	3.30	4.44	4.18	4.11	2.77
Mn^{2+}	5.69	4.23	~2.4	4.25	5.40	4.02	3.72	3.13
Cu^{2+}	8.38	3.91	2.44		7.65	3.11	2.87	2.29
Ni^{2+}	7.62	3.78			6.77	3.10	2.80	3.06
Zn^{2+}	7.60	3.95	2.24	1.6	6.62	3.64	2.96	2.49
Cd^{2+}	5.38	4.32	3.41	3.49	4.94	4.28	3.74	3.05
Pb^{2+}	7.71	3.98	2.84	1.7	7.44	3.74	2.64	2.04
Hg^{2+}	14.37	5.72	4.70	3.72	13.82	5.89	4.62	3.16
Al^{3+}	9.17	3.37	-5.30[a]	-6.96[b]	8.43	3.42	-5.31[a]	-6.43[b]
Fe^{3+}	12.01	2.37	-3.96[a]	-5.49[b]	11.43	2.49	-3.87[a]	-5.37[b]

[a] Proton dissociation from ML to form M(OH)L, $K_{M(OH)L}$. [b] Proton dissociation from M(OH)L to form $M(OH)_2L$, $K_{M(OH)_2L}$. [c] The reproducibility, pH calibration, and calculations all indicate that the constants are in general known better than the second decimal place. All values were therefore rounded to two decimals. The minor species MnH_2L, ZnH_3L, and PbH_3L are three exceptions.

Table III. Logarithms of Stepwise Stability Constants of meso and *SS* Isomers Expressed as M^{n+} Combining with H_iL Directly, As Defined in Eqs 8–10.

	meso				*SS*			
metal ion	ML	MHL	MH_2L	MH_3L	ML	MHL	MH_2L	MH_3L
Ca^{2+}	5.82	4.27	2.95	2.39	5.42	3.81	2.55	1.87
Mg^{2+}	5.09	3.17	1.75	1.08	4.44	2.67	1.97	1.34
Mn^{2+}	5.69	3.95	1.4	1.74	5.40	3.46	2.38	2.12
Cu^{2+}	8.38	6.32	3.90		7.65	4.79	2.88	1.77
Ni^{2+}	7.62	5.44			6.77	3.90	1.92	1.58
Zn^{2+}	7.60	5.58	2.97	0.63	6.62	4.29	2.46	1.55
Cd^{2+}	5.38	3.73	2.28	1.80	4.94	3.25	2.20	1.85
Pb^{2+}	7.71	5.72	3.70	1.39	7.44	5.20	3.05	1.69
Hg^{2+}	14.37	14.12	13.97	13.72	13.82	13.75	13.57	13.33
Al^{3+}	9.17	6.57			8.43	5.87		
Fe^{3+}	12.01	8.41			11.43	7.95		

protonated chelates. Al^{3+} and Fe^{3+} form only a single protonated chelate and in addition induce the dissociation of two coordinated water molecules from the complexes. The third group of ions represents the remaining divalent ions with similar properties, in that they all form mono-, di-, and triprotonated complexes.

To help in understanding the coordination behavior of metal ions with this ligand, it is of interest to examine in some detail the species diagram for a 1:1 Pb^{2+}–meso-ODS solution at the 0.3-mM level. Figure 1 represents the distribution of complexes formed as a function of pH as it is varied from 2 to 7. The species PbH_3L forms only in small amounts in this system in the presence of a considerable excess of H_3L^-. The species MH_2L must be a chelate (i.e. stabilized by the chelate effect), and therefore, its concentration exceeds that of the ligand form H_2L^{2-} with which it is in direct competition. The complex MHL^- dominates at p[H] 4, in the p[H] region where the ligand is in the form H_2L^{2-}. This appears to be an indication of a rather weak tendency for the ligand to completely coordinate the metal ion with all of its donor groups, since the final proton is lost in the p[H] range as high as 3–4. The highest protonation constant of the meso ligand is 5.97, yet the diagram shows that the coordinated ligand loses its final proton just below p[H] 5. This small difference further supports the conclusion that the metal ion affinities for the fourth and possibly the third carboxylate is rather weak.

Pb^{2+} is a large ion, but it is difficult to say what role its size plays in the relative coordination tendencies, since its formation constant is relatively large. The Ca(II) ion is considerably smaller, but its formation constants are much lower than those of Pb(II) yet similar to those of Cd(II) and Mn(II). The third chelate protonation constants (eqs 3–5) of Ca(II) are larger than those for Pb^{2+}, a reflection of the stronger metal ion binding in the Pb(II) complexes.

The Hg(II) chelates have much higher stability constants than those of any other metal ions investigated. This behavior parallels that of mercury binding to citrate. The first two protonation constants of the Hg(II) chelates are much higher than those of metal ions forming much weaker complexes, but the solution structural aspects are not yet known.

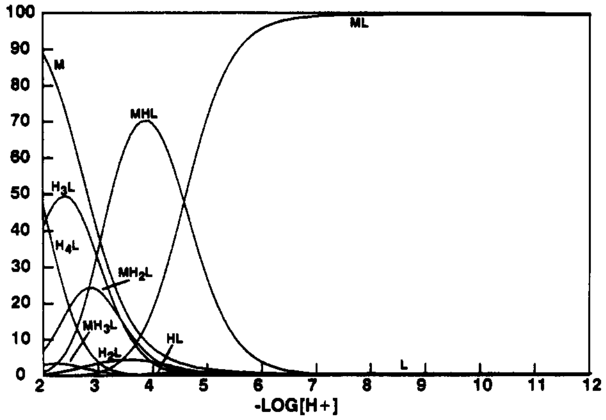


Figure 1. Distribution diagram showing species formed in a 1:1 molar ratio of *meso*-ODS to Pb(II) as a function of p[H] at 25.0 °C and 0.100 M ionic strength (KCl). $T_{Pb} = T_{ODS} = 3.5 \times 10^{-3}$ M.

The trivalent ions Al^{3+} and Fe^{3+} have high affinities for the ligand, in accordance with the fact that they do not form complexes with more than one proton. Only the MHL species is formed in each case. The two dissociation reactions which occur at *a* values above 4 (eqs 6 and 7) are characteristic of complexes of highly charged metal ions. These hydrolytic reactions are not sensitive to the stereoisomerism of the ligand, since they are very similar in magnitude for both the meso and *SS* complexes.

In eqs 8–10 the complex formation equilibria are rewritten in terms of the formation of particular protonated complex from the

$$M + HL \rightleftharpoons MHL \qquad K_{MHL} = \frac{[MHL]}{[M][HL]} \tag{8}$$

$$M + H_2L \rightleftharpoons MH_2L \qquad K_{MH_2L} = \frac{[MH_2L]}{[M][H_2L]} \tag{9}$$

$$M + H_3L \rightleftharpoons MH_3L \qquad K_{MH_3L} = \frac{[MH_3L]}{[M][H_3L]} \tag{10}$$

form of the ligand containing the same number of protons rather than in the form of proton association reactions. The advantage gained in this arrangement is the ability to compare directly the tendencies of the various protonated forms of the ligand to form the corresponding protonated complexes by direct comparison of the equilibrium constants. The values of log K_{MHL}, K_{MH_2L}, and K_{MH_3L} were obtained from the log β_{MH_iL}'s and the ligand protonation constants and are listed in Table III.

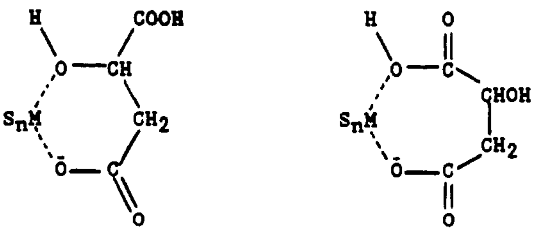
There are several characteristics of the constants in Table III which are worth pointing out. First of all, every meso log K_{MHL} is greater in magnitude than its *SS* counterpart. For Cu^{2+}, Ni^{2+}, and Zn^{2+} the meso values of K_{MHL} are greater than those of the *SS* complexes by more than 1.0 log unit, while for the other metal ions the differences are consistently about 0.5 log units. These differences in log K_{MHL} closely parallel the differences in log K_{ML}, except that, for Cu^{2+}, Ni^{2+}, and Zn^{2+}, the differences are somewhat lower than 1.0 log units for log K_{ML}. As a matter of fact each successive step serves to add roughly 1.5–2.0 stability units to the stability constant. The one exception seems to be Hg^{2+}, in accordance with the comments made above about Hg(II) complexes of these ligands.

Discussion

The MH_3L constants in Table III can be compared to the stability constants of the acetate complexes in Table IV, since H_3ODS^- coordinates with a single acetate donor group. As may be seen from the comparison in Table IV, the metal complexes of H_3ODS^- have generally higher stability constants than the corresponding acetates, with a few exceptions, indicating that the ether oxygen and perhaps even protonated carboxyl groups may assist in stabilizing the complexes as weak auxiliary donors. The exceptions to this behavior are Zn(II) and Pb(II). Hg(II) is unique because of the very high stability of the ODS complexes, as noted above.

The MH_2L constants of Table III can be compared formally to the ML values of malic acid in Table IV for each ion. The metal ions may be considered as reacting with the two deprotonated carboxylates available on each ligand. The values in these columns are quite similar for the metal ions for which malate data are available, even though the steric arrangements of the two carboxylates are quite different, and this is probably a reflection of the flexibility of these ligands.

The suggestions made above to explain the higher stabilities of the H_3ODS complexes relative to the acetates is supported by a comparison of the stabilities of the acetates with their monoprotonated malate analogues. For malic acid, the formation constants (eq 8) of the monoprotonated complexes are nearly always considerably higher than those of acetic acid. Thus, additional (weak) coordination with one of the neutral oxygen donor groups is indicated:



4 Possible coordination sites for monoprotonated metal malate complexes (S = solvent)

This type of stability enhancement is probably also responsible for the formation of several protonated complexes found for the ODS systems.

Molecular models were employed to see if there are any obvious steric differences between meso and *SS* stereomers. Indeed, the four acetate oxygens of the meso form appear to be slightly more capable of orienting around an octahedral metal. However, when partially protonated species structures are considered, such conclusions are more tenuous because of the number of possible microspecies with different protonation sites, as well as the possibility of intramolecular hydrogen bonding.

Table IV. Logarithms of Stepwise Stability Constants of Acetic Acid and Malic Acid with Selected Metal Ions Taken from the Literature[5]

metal ion	acetic acid log K_{ML}	*meso*-ODS log K_{MH_3L}	Δ	malic acid, H_2L log K_{ML}	malic acid, H_2L log K_{MHL}[b]	Δ[a]
Ca^{2+}	0.57	2.39	1.82	1.90	1.06	0.49
Mg^{2+}	0.55	1.08	0.53	1.71	0.90	0.81
Mn^{2+}	0.80	1.74	0.94	2.24		
Cu^{2+}	1.82			3.60	2.09	0.27
Ni^{2+}	0.84			3.17	1.83	0.99
Zn^{2+}	1.20	0.63	−0.57	2.93	1.66	0.46
Cd^{2+}	1.56	1.80	0.24	2.36	1.34	−0.22
Pb^{2+}	2.15	1.39	−0.76	2.45		
Hg^{2+}	3.74	13.72	9.98			
Al^{3+}	1.51			3.2[c]	1.42[c]	
Fe^{3+}	3.38			6.88[c]		

[a] log K_{MHL}(malic acid) − log K_{ML}(acetic acid). [b] M + HL = MHL. [c] Succinic acid.

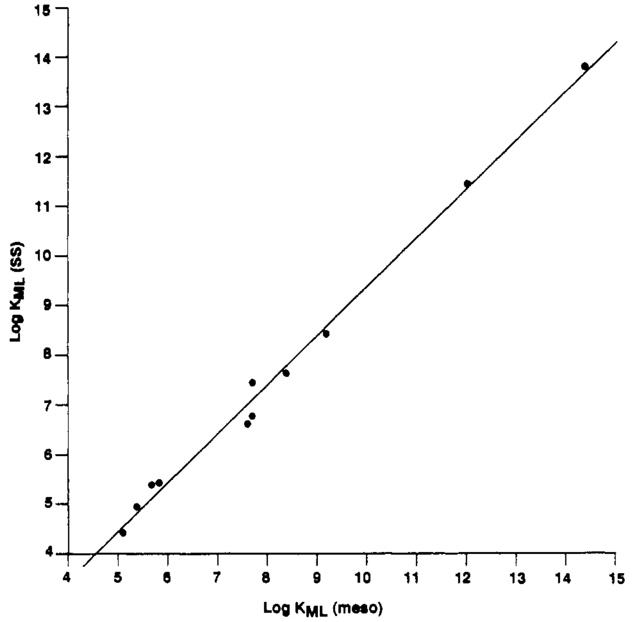


Figure 2. Correlation diagram of log K_{ML}(*SS*) with log K_{ML}(meso). $r = 0.997$.

At neutral p[H] values for all systems studied the protonated species are of no consequence, because even the highest value of log K^H_{MHL} listed in Table II is some 2 log units lower than p[H] 7. The ligand would also be ~90% deprotonated at p[H] 7. This means that unless stable hydroxo complexes are formed, the values of log K_{ML} may be taken as direct measures of metal ion affinities at neutral pH.

A comparison of log K_{ML}(*SS*) vs K_{ML}(meso) showed a very high linear correlation with none of the points greater than 2σ from the straight line of slope 0.99 (Figure 2). The largest deviations were found for Zn^{2+} (positive) and Pb^{2+} (negative), with all of the remaining metal ions falling much closer to the correlation line. Notably, Mg^{2+} and Fe^{3+} also fell on the line. The correlation coefficient r was found to be 0.997.

Two of the metal ions studied, Fe(III) and Al(III), were found to form hydroxy complexes, $ML(OH)^{2-}$ and $ML(OH)_2^{3-}$. In the pH region of the second hydrolysis, the free metal ion concentration is supersaturated relative to the metal trihydroxides, which would precipitate. Figure 3 is a distribution diagram of the species formed from a 1:1 molar ratio of *meso*-ODS and Al^{3+} as a function of pH. In this figure it can be seen that at pH near 6, the $Al(OH)_3$ precipitate is expected to form. As it forms, the complexes of Al(III) with ODS would break down and free ligand HL^{3-} would be released. Then at high pH, above 11, the $Al(OH)_3$ precipitate would be converted to soluble aluminate, $Al(OH)_4^-$. In this study, the system was supersaturated with respect to $Al(OH)_3$ and the

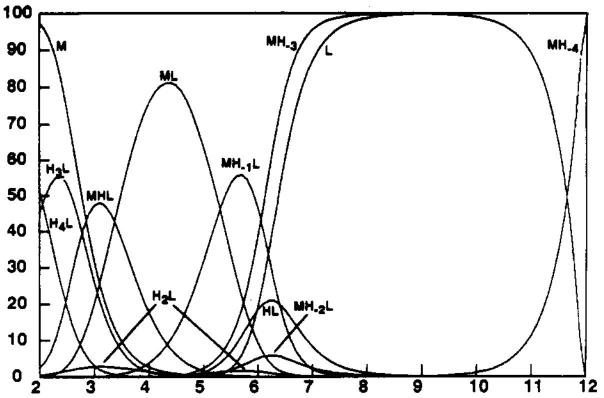


Figure 3. Distribution diagram showing species formed by a 1:1 molar ratio of Al(III) to *meso*-ODS as a function of p[H] at 25.0 °C and 0.100 M ionic strength (KCl). $T_{Al} = T_{ODS} = 1.0 \times 10^{-3}$ M.

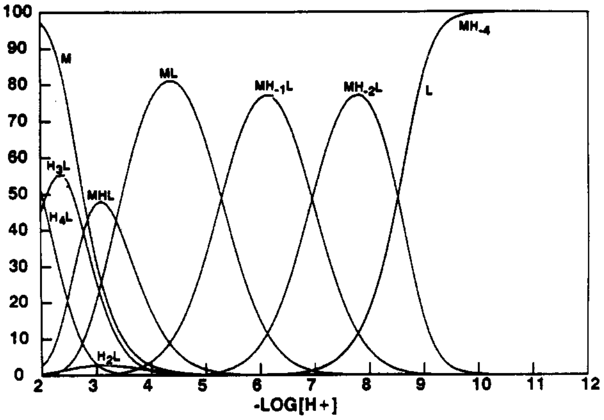


Figure 4. Distribution diagram showing species formed by a 1:1 molar ratio of Al(III) to *meso*-ODS as a function of p[H] under the assumption that no $Al(OH)_3$ precipitates (supersaturated solution) (t = 25.0 °C; 0.100 M ionic strength (KCl); $T_{Al} = T_{ODS} = 1.0 \times 10^{-3}$ M).

determination of reliable constants was possible.

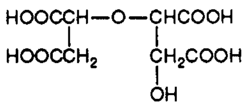
If $Al(OH)_3$ precipitate were not formed, i.e. the solution remained supersaturated throughout the pH region, the distribution curves shown in Figure 3 would be replaced by those in Figure 4. Here the successive M(OH)L and $M(OH)_2L$ species are clearly shown, and the tendency of Al(III) to hydrolyze to form the aluminate ion would start at a much lower p[H] (p[H] ~8) and would be essentially completely formed at pH 9.5.

In the potentiometric runs the p[H] increased rapidly when the *a* value of 4 was reached, and nearly all of the metal ions precipitated as hydroxide around the neutral point. The exceptions were Al(III) and Fe(III) for which precipitation was delayed because of hydroxo complex formation. Mg^{2+} and Ca^{2+} did not precipitate, but only because their hydrolytic tendencies are much lower than those of the other metal ions. In the case of Hg(II), the experimental solution could in some runs be titrated past $a = 4$ to $a = 6$, as $Hg(OH)^-$ and $Hg(OH)_2$ forms at the expense of $HgODS^{2-}$. In other cases only moderate supersaturation could be achieved depending on the speed of titration and the degree of agitation through stirring, until the colorless–clear test solution suddenly turned red and turbid as HgO separated. In either case computations were performed only up to $a = 4$, well away from the supersaturation region.

Table V. Comparison of log Stability Constants of *meso*- and *SS*-ODS with Those of Tartaric Monosuccinic Acid, TMS[6]

metal ion	K_{ML}(ODS) meso	K_{ML}(ODS) *SS*	K_{ML}(TMS) mixture of racemic and meso forms
Ca^{2+}	5.82	5.42	5.20
Mg^{2+}	5.09	4.44	3.91
Mn^{2+}	5.69	5.40	5.69
Cu^{2+}	8.38	7.65	6.63
Ni^{2+}	7.62	6.77	6.06
Zn^{2+}	7.60	6.62	6.31
Cd^{2+}	5.38	4.94	4.63
Pb^{2+}	7.71	7.44	7.01
Hg^{2+}	14.37	13.82	14.18
Al^{3+}	9.17	8.43	7.63
Fe^{3+}	12.01	11.43	10.70

Perhaps the most closely related ligand to which ODS could be compared is tartaric monosuccinic acid, TMS (**5**), which really is the same as ODS bearing a hydroxyl group and possessing three asymmetric carbon centers.[8]



$$\begin{array}{l} HOOC\underset{\displaystyle HOOCCH_2}{\underset{|}{C}}H{-}O{-}\underset{\displaystyle \underset{\displaystyle \underset{|}{OH}}{CH_2COOH}}{\underset{|}{C}}HCOOH \end{array}$$

5 (tartaric monosuccinic acid (TMS))

Optical isomerism was not considered in the previous investigation,[8] and it had been assumed that the optical isomers would possess essentially the same stability constants. Now it appears that this assumption was an approximation. Nevertheless, in order to assess the relative properties of ODS vs TMS, comparison of the stability constants listed in Table V is instructive.

In general the data in Table V show that ODS is more effective for all metal ions, regardless of which isomer is considered. This is consistent with the greater basicity of the ODS ligand relative to that of TMS. The *SS*-ODS complexes of Mn(II) and Hg(II) appear to be the only exceptions to this observation; in both cases the *SS*-ODS isomer seems to be slightly weaker than that of the TMS complexes. Very interesting is the fact that the stability constants of the ODS complexes of Cu^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, and Fe^{3+} are all over 1 log unit higher than those of the TMS complexes.

Observations made on TMS included the formation of stable monohydroxo chelates of Cu(II) and Hg(II). ODS does not have a hydroxyl group as does TMS, and quite possibly this group may responsible for the additional stabilization observed for these hydroxo TMS complexes.

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Registry No. *SS*-**1**, 137172-86-2; *meso*-**1**, 84852-72-2.

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