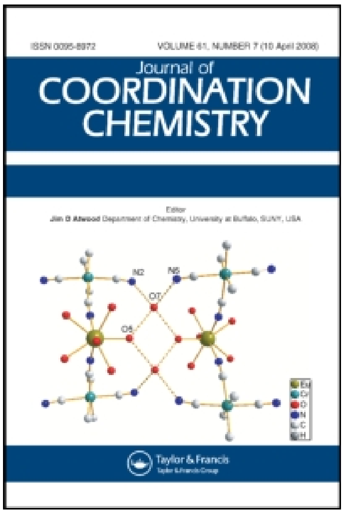

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THE EFFECT OF NON-COORDINATED CHARGED GROUPS ON THE STABILITY OF COMPLEXES IN AQUEOUS SOLUTION. THE STABILITY OF COMPLEXES OF 2,3-DIHYDROXYNAPHTHALENE-6-SULFONIC ACID

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Formation constants are determined for Ca^{2+}, Mg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, La^{3+}, Cu^{2+}, UO_2^{2+}, Al^{3+}, Th^{4+}, Fe^{3+}, with the ligand DHNSA (2,3-dihydroxynaphthalene-6-sulfonic acid). It is shown that for chelating oxygen donor ligands, plots of log K_1 for the ligand forming a complex with metal ions gives an LFER (linear free energy relationship), when plotted against log K_1 (OH^-) for the metal ions, which has an intercept of log 55.5, in agreement with previous proposals on the origin of the chelate effect. It is shown that adding sulfonic acid groups to such chelating oxygen donor ligands, as in DHNSA, gives an LFER which has an intercept much higher than log 55.5. The source of this extra stabilisation is discussed, and it is concluded that in a ligand such as DHNSA, the two phenolic oxygens are coordinated to the metal ion, while the sulfonic acid groups stabilize the complex by an outer-sphere electrostatic attraction.

INTRODUCTION

In two recent publications[1,2] it was shown that there was a linear relationship between log K_1 (L), where L was a bi-or ter-dentate oxygen donor ligand, and log K_1 (OH^-) for a wide variety of metal ions. In Figure 1 is shown such a correlation, where we reproduce the liner free energy relationship (LFER) between log K_1 (cathechol) and log K_1 (OH), and log K_1 (kojate) and log K_1 (OH^-), for all the metal ions for which the required formation constant data are available. To avoid errors due to incorrect choice of data, data used are from ref. 3. The line for the kojate LFER is a least-squares best-fit, but that for catechol has been drawn in omitting certain of the points, whose deviations are thought not to be "noise", but to have physical significance, as discussed below. What is interesting about the correlations, apart from their linearity, is the fact that the intercepts obtained on the log K_1 (chelate) axis are close to the log 55.5 expected[4] from the contribution from the asymmetry of the standard reference state to the chelate effect.[5]

LFER with intercepts close to the expected value of log 55.5, *i.e.* 1.74 log units, are found for many bidentate oxygen donor ligands, including[1,2] salicylate, acetylacetonate, tropolonate, protocatechuate, maltolate, oxalate, malonate, acethydroxamate, and a number of the above ligands with their aromatic rings containing substituents such as the chloro- or nitro- groups in various positions. It is found[2] that the slopes of all these LFER correlate well with the sums of the pK_a values of the chelating ligand. The simple behaviour of these LFER indicate that, as might be expected, the same factor, *i.e.* the strength of the bond formed by the metal ion to oxygen, governs the acidity of the metal ion, and also the strength with which it binds to the chelating oxygen-donor ligands.

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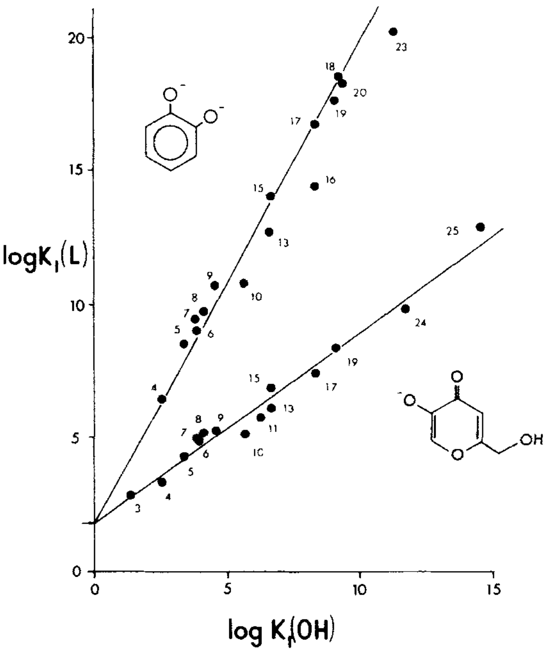

FIGURE 1 LFER of log K$_1$ (L), where L is either the catecholate (upper set) or kojate anion, versus log K$_1$ (OH$^-$) for each metal ion. Key to metal ions is 1, Ba^{2+}; 2, Sr^{2+}; 3, Ca^{2+}; 4, Mg^{2+}; 5, Mn^{2+}; 6, Cd^{2+}; 7, Co^{2+}; 8, Ni^{2+}; 9, Zn^{2+}; 10, La^{3+}; 11, Y^{3+}; 12, Yb^{3+}; 13, Lu^{3+}; 14, Pb^{2+}; 15, Cu^{2+}; 16, Be^{2+}; 17, UO^{2+}; 18, VO^{2+}; 19, Al^{3+}; 20, Sc^{3+}; 21, In^{3+}; 22, Th^{4+}; 23, Ga^{3+}; 24, Fe^{3+}; 25, Hf^{4+}. All constants used were selected to be at 25°C and ionic strength (I) of zero, or else were corrected to I = O using the Davies[9] form of extended Debye-Hückel equation.

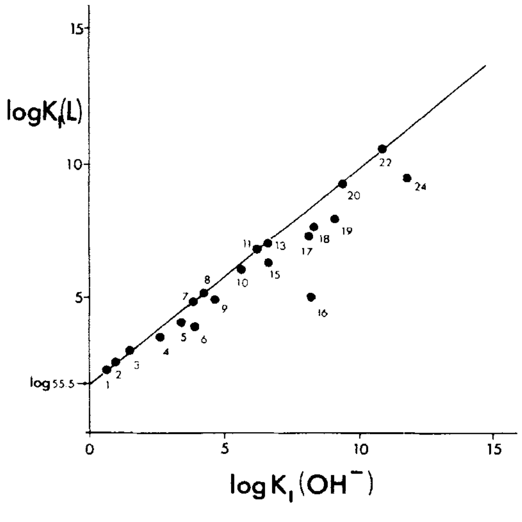

FIGURE 2 LFER of log K$_1$ (oxalate) versus log K$_1$ (OH$^-$), at 25°C and I = O. The line has been drawn in so as to pass through the points for the more ionically bound metal ions, such as Ca^{2+}, Sc^{3+}, and Th^{4+}, as discussed in the text. The points deviating downwards, such as point number 16 for Be^{2+}, are those metal ions which are thought to be less able to adapt to the steric requirements of different ligands. One should compare Figure 2 with the LFER for the more flexible malonate ligand in Figure 5(a), where there is no deviation for Be^{2+}.

LFER such as those shown in Figure 1, which have no marked deviations, appear to be fairly common. In Figure 2 we have plotted the LFER of log K_1 (oxalate) versus log K_1 (OH^-). At first sight there might appear to be no linear relation at all in Figure 2. However, one finds that for all such LFER which have an apparently large scatter of points, there is a definite pattern to the scatter. There is a group of metal ions, Sc^{III}, Y^{III}, the trivalent lanthanides, Ca^{II}, Sr^{II}, Ba^{II}, and Th^{IV}, which are at higher stability relative to the points for other metal ions of similar acidity. This group at higher stability forms a good LFER, whch passes through the expected intercept at log 55.5. If we accept that there is a linear relation for the points involving the metal ions at higher stability, we then see that there is a recurring pattern of deviation for the metal ions at lower stability. Thus Be^{II} always shows the greatest deviation, while other ions such as Mg^{II}, Cu^{II}, and Ni^{II} show moderate deviations from the LFER. The same pattern is evident for the catechol LFER in Figure 1, except that the deviations are so small that only does the Be^{II} point (number 16) depart from the LFER by much more than the background noise level.

We suggest that the above pattern of deviation reflects the ability of the metal ions to adapt to the steric requirements of the ligand. Thus, the group of metal ions on the lines drawn in, such as Ca^{II} or La^{III}, show extraordinary flexibility in their coordination geometries, which relates to the very ionic nature of their bonding to donor atoms. Most show highly variable coordination numbers, and can accommodate such unusual geometries as the planar six-coordinate geometry demanded by crown ethers. For those metal ions such as Be^{II}, showing the largest deviations, there is a rigid preference for, in this case, tetrahedral coordination, and much more covalent metal to ligand bonding. A strong pattern of deviation should thus indicate rather strong steric requirements on the part of the ligand. In keeping with this, it is found that strong deviation patterns are seldom found for ligands which form six-membered chelate rings, which are likely to be more flexible than ligands forming five-membered chelate rings, which is where deviation patterns are commonly found. We can thus compare oxalate in Figure 2 with malonate in Figure 5a, where even the Be^{II} point does not deviate significantly.

A departure from the type of behaviour found in Figure 1 is found where ligands are substituted with sulphonic acid groups. This is seen in Figure 3, where log K_1 for Tiron (1,2-dihydroxybenzene-3,5-disulphonic acid) and for DHBSA (1,2-dihydroxybenzene-4-sulphonic acid) are plotted against log K_1 (OH^-) for a variety of metal ions. Reasonably linear relationships are observed, but the intercepts of the LFER are unexpectedly large. In fact, if we take the size of the intercept as diagnostic of the denticity of the ligand, the value of the intercept at about 5 log units would suggest that Tiron was coordinating to metal ions through all four possible donor atoms, *i.e.* the two phenolate and two sulphonate groups. Inspection of models shows that this is sterically impossible, and would in any case be highly unlikely in view of the weak basicity of sulphonic acid groups. The intercept of about 3.5 log units suggests similarly that the sulphonic acid group in the DHBSA complexes is coordinated, which seems equally unlikely. It should be noted that for Tiron the LFER has been drawn through those more ionic metal ions such as Ca^{II} and the lanthanides, as there is a moderately strong pattern of deviation, similar to that found for the oxalate LFER in Figure 2.

A possible explanation for the large intercept, and deviation pattern found for Tiron, is that the sulphonic acid groups are involved in an outer-sphere type of attraction for the metal ion. Using the Fuoss equation[6] to calculate log K_1 for an outer-sphere complex involving a doubly charged cation and quadruply charged anion, we arrive at a value of log K_1 equal to 5 log units for a typical[1] charge separation of 4.5 Å. We would therefore not expect log K_1 for the Ca^{2+} complex of Tiron to fall much below this value. The idea then is that for metal ions such as Ca^{II} or La^{III}, the very ionic bonding allows the ligand to twist around so as to maximise the strong outer-sphere type of interaction between the

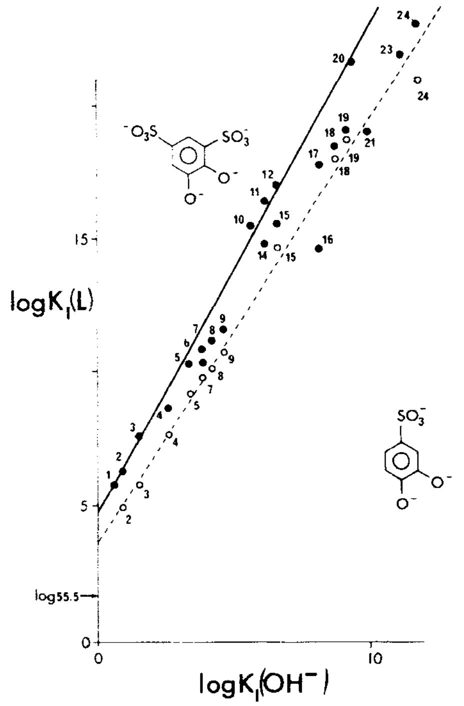

FIGURE 3 LFER of log K_1 (L), where L is either tiron (●) or 1,2-dihydroxybenzene-4-sulphonic acid, DHBSA, (○), versus log K_1 (OH^-) for each metal ion, at I = O. Key to metal ions is under Figure 1. Note the downward deviation for some of the points on the Tiron LFER, which probably reflects some degree of steric strain produced by the metal ion being attracted towards the sulphonic acid groups, and thus distorting the M-O bonds to the phenolic oxygens.

metal ion and the ligand, which metal ions such as Be^{II}, Mg^{II}, or Al^{III} with more demanding steric requirements are not able to do. We might even have a gradual transition from entirely outer-sphere bonding at the lower stability end of the LFER, to bonding through the two phenolic groups only at the higher stability end.

If the sulphonic acid group on DHBSA is involved in an outer-sphere type of attraction to the metal ion, we might expect that the stability of the complex, particularly in the lower stability end of the LFER, would be sensitive to the distance of the sulphonic acid groups. We have thus undertaken a glass-electrode study of the complexing ability of the ligand DHNSA (2,3-dihydroxynaphthalene-6-sulphonic acid) with the metal ions Ca^{2+}, Mg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, La^{3+}, Al^{3+}, Th^{4+}, and as a check on accuracy, Cu^{2+}, to supplement the values already in the literature[3] for Cu^{2+}, UO_2^{2+}, and Fe^{3+}. The idea here is that the sulphonic acid group in DHNSA is further away from the metal ion than in the DHBSA complexes, assuming inner-sphere coordination to the phenolic oxygens. The outer-sphere part of the interaction might therefore be considerably reduced in the DHNSA as compared with the DHBSA complexes, and the intercept on the LFER of log K_1 (DHNSA) versus log K_1 (OH^-) for the above metal ions be closer to 1.74 log units, as expected for a bidentate ligand.

EXPERIMENTAL

Materials

Standard solutions were prepared from Merck AR grade nitrate salts of the following metal ions: Ca^{2+}, Mg^{2+}, Cd^{2+}, Ni^{2+}, La^{3+}, Cu^{2+}, Al^{3+}, and Th^{4+}. These were standardised by titration with EDTA.[7] The sodium salt of DHNSA was obtained from Koch-Light laboratories, and used without further purification. This was standardised by titration with standard acid and base solutions. From the weights of all the above reagents taken, standardisation indicated that the reagents were better than 99% pure.

Potentiometric titrations

A Radiometer PHM 84 research pH meter was used in conjunction with a Radiometer G202B glass electrode to monitor pH changes during the course of the titrations. The reference electrode was a Ag/AgCl electrode connected to the titration *via* a salt bridge to eliminate junction potentials. The titrations consisted of placing standard DHNS solution plus standard metal ion and excess standard acid solution in the cell, and titrating with standard NaOH solution. The resulting sets of potential versus volume of base added curves, three for each metal ion, were analysed using the computer program MINIQUAD.[8] The analysis indicated that only the simple DHNSA complexes were formed, with no polymeric or hydrolysed species formed under the conditions used in the study. The constants determined for each metal ion are shown in the Table, together with the log K_1 values (corrected to zero ionic strength using the Davies[9] form of extended Debye-Hückel equation) which are used in constructing Figure 4.;

TABLE I

Formation constants of complexes of the ligand 2,3-dihydroxynaphthalene-6-sulfonic acid, at 25°C in 0.1 M $NaNO_3$.[a] Figures in parentheses are log K_1 values corrected to infinite dilution using the Davies[9] form of extended Debye-Hückel equation. Error limits are those indicated by the program MINIQUAD.[8]

Metal ion	log K_1	log β_2	log β_3
Ca^{2+}	5.21 ± 0.03 (6.53)	7.92 ± 0.16	
Mg^{2+}	7.32 ± 0.02 (8.64)	11.53 ± 0.05	
Cd^{2+}	8.53 ± 0.02 (9.85)	13.79 ± 0.09	
Co^{2+}	9.44 ± 0.02 (10.76)	15.77 ± 0.06	
Ni^{2+}	9.88 ± 0.05 (11.20)	18.25 ± 0.08	
La^{3+}	9.87 ± 0.02 (11.85)	16.92 ± 0.04	
Cu^{2+}	13.88 ± 0.02 (15.20)	24.81 ± 0.04	
Al^{3+}	16.48 ± 0.02 (18.47)	29.82 ± 0.03	39.12 ± 0.07
Th^{4+}	17.39 ± 0.08 (20.03)	31.71 ± 0.18	39.12 ± 0.26

[a] The second protonation constant, pK_2, was determined to be 8.17 ± 0.01. pK_1 was taken as 12.40, from reference 12, which appears to be the most reliable value as it was determined spectroscopically.

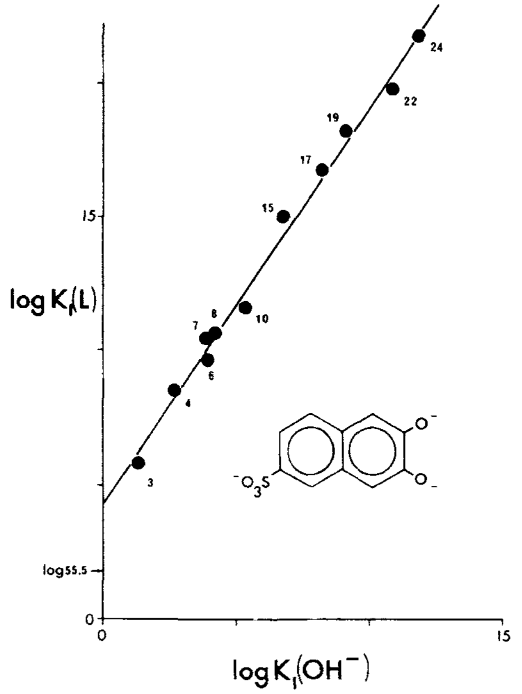

FIGURE 4 LFER of log K_1 (DHNSA), where DHNSA is 2,3-dihydroxynaphthalene-6-sulphonic acid, versus log K_1 (OH^-) for a variety of metal ions, at I = O. Key to metal ions under Figure 1. The structure shown is that of DHNSA.

DISCUSSION

In Figure 4 is shown the LFER of log K_1 (DHNSA) versus log K_1 (OH^-) for the metal ions studied in this work. It is seen that the linearity of the relation is excellent, and comparison with Figure 3 shows that it is almost superimposable on the LFER for log K_1 (DHBSA), having an equally large anomalous intercept on the log K_1 (L) axis. This shows that moving the sulfonic acid groups further away by placing them at the other end of a naphthalene group in DHNSA has had almost no effect on the coordinating properties of the ligand as compared with DHBSA, where there is only a benzene ring between the phenolic and sulfonic acid groups. The DHNSA results do not appear to support the idea that the sulfonic acid groups aid complex formation by a type of outer-sphere attraction.

In Figures 5(a) and (b) are shown two LFER which do appear[1,2] to be evidence for a switch from inner- to outer- sphere binding as we proceed to lower metal-ion acidity. This is most obvious in Figure 5(b), the LFER for log K_1 (pentanedioic acid) versus log K_1 (OH^-). The "noise" at higher metal acidity probably reflects the steric difficulty of coordinating to a ligand which forms an eight-membered chelate ring. What is of importance here is what happens when we reach the broken line in Figure 5(b). This broken line represents the stability of an outer-sphere complex formed between a divalent cation with a divalent anion, using the Fuoss[6] equation, and a charge separation of 4.5 Å. In the absence of the possibility of forming an outer-sphere complex, the LFER suggests that the stability of the complexes with pentanedioic acid would fall below the broken line as the acidity of the metal ion was decreased. However, at the point of crossover, the results

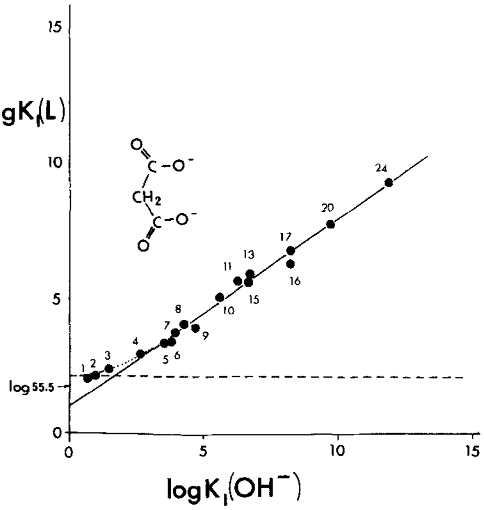

FIGURE 5(a) LFER of log K_1 (malonate) versus log K_1 (OH^-) for a variety of metal ions, at I = O and 25° C. Key to metal ions under Figure 1. The broken line is the stability calculated using the Fuoss equation[6] for a dipositive cation forming an outer-sphere complex with a divalent anion. The stability cannot fall below this value, so that as the LFER approaches the broken line, the points depart from the LFER, following the dotted line, which is log (K_{in} + K_{out}), where K_{in} is the stability expected for the inner-sphere complex, read off the LFER, and K_{out} is the stability for the outer-sphere complex predicted by the Fuoss equation. The effect is small for malonate, but is marked for pentanedioate in Figure 5(b).

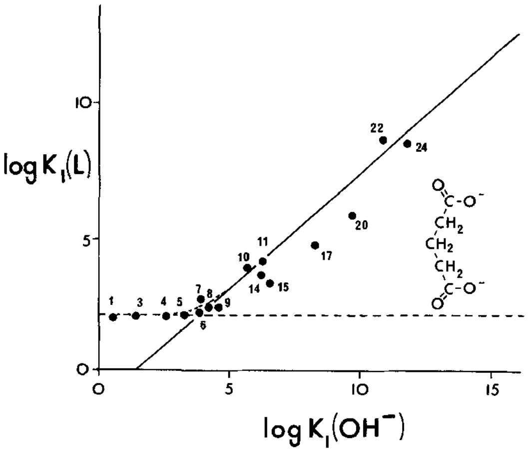

FIGURE 5(b) LFER for log K_1 (pentanedioate) versus log K_1 (OH^-). For explanation see under Figure 5(a).

of Figure 5(b) suggest that there is a change from inner- to outer- sphere bonding, and that the pentanedioic acid complexes of metal ions such as Ba^{2+}, Ca^{2+}, and Mg^{2+} are mainly outer-sphere in nature. In Figure 5(a) is shown the LFER for log K_1(malonate) versus log K_1(OH^-). We are indebted to a referee for pointing out that it is best treated in the same way as that for pentanedioic acid, with the complexes at low stability having at least a proportion of the species present as outer-sphere complexes. What is of interest in Figure 5(a) is that the intercept obtained by extrapolation is less than the expected 1.74

log units, suggesting that the longer ligand backbone is making an unfavorable entropy contribution to the chelate effect, which becomes even more marked in Figure 5(b).

We have interpreted the breaks in Figures 5(a) and (b) in terms of a change from inner- to outer- sphere bonding. By way of comparison, we see that Figures 3 and 4 do not have a break in them, showing that there is no sharp change in bonding type as we move from low to high acidity. If the complexes of Tiron, DHBSA, and DHNSA were purely outer-sphere in nature at low acidity, we wuld expect to see that, for example, the stability of the complexes of these ligands with Ba^{2+}, Sr^{2+}, and Ca^{2+} remained constant at the theoretical Fuoss value, and then a LFER containing the metal ions at higher acidity would be observed as there was a change from outer- to inner- sphere type bonding.

In Figure 6 is shown the LFER of log β_2 for catechol and 4-nitrocatechol versus log $K_1(OH^-)$. As would be expected from corelations such as those seen in Figure 1, we now have a LFER with an intercept of 2 log 55.5, or 3.4 log units, in accord with previously proposed models of the chelate effect.[4,5] What is of interest in Figure 6 is that the similar LFER of log β_2 for Tiron complexes versus log $K_1(OH^-)$ for the metal ion now also has a normal intercept of 2 log 55.5. This can be quite readily explained using the Fuoss equation.[6] We consider that for a divalent metal ion, and most of the metal ions in Figure 6 are divalent, the addition of the first Tiron, which carries four negative charges, represents the combination of such a cation with a tetravalent anion to form a divalent anion. When we add a second Tiron, we are adding a tetravalent to a divalent anion (the complex from the first step). Whatever values of a, the charge separation parameter, might be appropriate in the first step, the same must apply for the second, the only difference being that in the first step we have a charge product, $Z^+.Z^-$, of −8, and for the second step a charge product of +8. The only difference in the Fuoss equation, if we consider the two steps as the formation of outer-sphere complexes, is the charge product. We would thus expect any outer-sphere type contribution which stabilized the complex

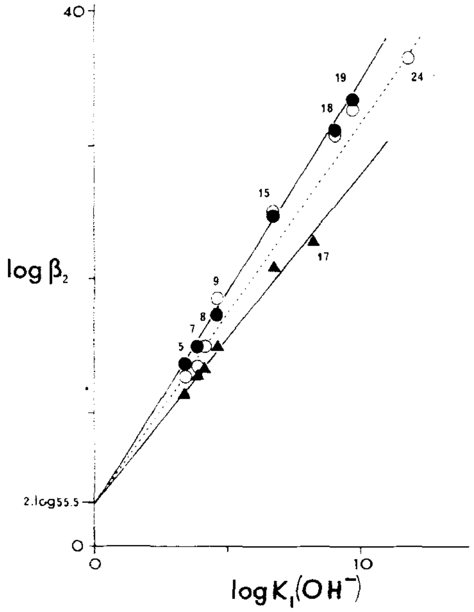

FIGURE 6 LFER of log β_2 for the catecholate (●), Tiron (○), and 4-nitrocatecholate (▲) ligands versus log $K_1(OH^-)$. The intercept is the 2 log 55.5 value expected[4] for two bidentate ligands forming a *bis* complex with a metal ion. Note that the LFER for the *bis*-Tiron complexes (-----) no longer has an anomalously high intercept. For key to metal ions see Figure 1.

formed on addition of the first Tiron ligand, to be exactly cancelled out in the second step, and this is what is observed. The extra charge on Tiron which stabilizes its *mono*-complexes of metal ions, destabilizes the *bis*-complexes by an exactly equal amount, so that, although an anomalously large intercept is found in Figures 4 and 5, in Figure 6 a normal intercept, in terms of our model[4] of the chelate effect, is found.

Other examples also exist of non-coordinated charged groups on a ligand stabilizing the complex relative to the uncharged analogue. Thus, Margerum has shown[10] that in EDTA complexes of Ni(II) in solution, one of the acetate groups is left uncoordinated. If this contributed nothing to the stability of the complex of Ni(II) with EDTA, we would expect no extra stabilisation relative to the HEDTA complex, which has a hydroxyethyl group in place of the acetate of EDTA. (HEDTA = *N*-hydroxyethylethylenediamine-*N*′, *N*″,*N*‴-triacetate). However log K_1 for Ni(II) with EDTA is[3] 18.5, while with NEDTA it is 17.1, showing that the EDTA complex is stabilized quite considerably by the presence of the non-coordinated acetate group.

We can rationalise the extra stabilisation of the complexes of ligands such as Tiron, which have non-coordinated sulfonate gorups, by an outer-sphere type of attraction, with Figure 6 obeying quite well the predictions of the Fuoss equation. One is left to ask why moving the sulfonate groups further away, as we have in comparing the stability of the DHNSA complexes with those of DHBSA, has no effect on the complex stability. The answer to this seems to be that the magnitude of log K predicted for outer-sphere complexes by the Fuoss equation is rather insensitive to charge separation. Thus, models show that the average distance to the three charged groups on DHBSA from its coordinated metal ion is about 6 Å. If we move all three charges away from the metal ion by this amount, it lowers the predicted log K by only 0.4 of a log unit. We are clearly not moving all three charges in going from DHBSA to DHNSA, and so we would, in fact, not expect much of a drop in complex stability, as seen in Figure 4.

Added sulfonic acid groups stabilize the complexes formed by catechol-type ligands by an outer-sphere type of attraction.[11] Movement of these groups further away from the metal ion does not markedly lower complex-stability, as the size of log K found for outer-sphere type complexes does not depend strongly on charge separation. The Tiron complexes and those of other similar ligands such as DHBSA or DHNSA, appear to have mixed coordination, with the phenolate oxygens bound to the metal by inner-sphere bonds, while the sulfonic acids are coordinated in an outer-sphere fashion.

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