530. *The Extent of Chelate Ring Formation in EDTA Complexes of Bivalent Cations in Solution.*

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Previous views concerning the structure of EDTA complexes of bivalent cations are summarised, and it is concluded that these complexes are quinquedentate in aqueous solution.

The structures of metal–EDTA complexes in aqueous solution have been discussed by various authors [1-6] but have not been firmly established except for cobalt(III) complexes.[7] It is probable that the groups of the EDTA anion which are co-ordinated to the metal cation do not in general occupy symmetrical octahedral positions in its co-ordination sphere [1] (cf. also the structures of EDTA complexes of Co^{III}, Fe^{III}, Mn^{II}, Ni^{II} in the solid state [8]); however, the question as to how many groups are bound to the cation in a given complex appears significant and is of interest. It is the purpose of this Paper to suggest that the chelation number * in the EDTA complexes of most bivalent cations is five in aqueous solution.

Comparisons of stability constants for metal-ion complexes with EDTA and related aminopolycarboxylic acids must be regarded cautiously as a means of ascribing chelation numbers. Nevertheless, comparisons made by Martell and his co-workers [2] suggest that for bivalent transition-metal ions, Cd^{2+} and Pb^{2+}, the chelation number in the EDTA complexes exceeds four. [These authors concluded that the copper(II)–EDTA complex has a chelation number of four, but did not take into account the ability of copper(II) to form distorted octahedral complexes.] Similar comparisons can be made between stability constants obtained [9] for *N*-substituted iminodiacetic acids, including ethylenediamine-*NN*-diacetic acid, and those obtained [3] for EDTA complexes. These comparisons again suggest a chelation number higher than four for EDTA complexes of bivalent cations, including Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}.

Most EDTA complexes show basic properties in solution which can be interpreted as involving the protonation of a carboxylate group. Schwarzenbach and his co-workers [3] found that values of pK_{obs}, the negative logarithm of the acid dissociation constant for the conjugate acid of a complex, lie within 0·2 unit of 3·0 for many bivalent cations (see the Table). They concluded that in these complexes one or two carboxylate groups are not co-ordinated to the cation, but in view of Martell's comparisons [2] a chelation number as low as four appears improbable. The observation of basic properties in an EDTA

Cation	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	V^{2+}	VO^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}	Pb^{2+}	Eu^{2+}
pK_{obs}	3·9	3·2	3·9	4·6	3·5	3·0	3·1	2·8	3·0	3·2	3·0	3·0	2·9	3·1	2·8	5·2
Ref.	10	10	10	10	11	3	3	3	3	3	3	3	3	3	3	12

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* A quinquedentate complex has a chelation number of five, etc.

[1] Staveley and Randall, *Discuss. Faraday Soc.*, 1958, **26**, 157; Care and Staveley, *J.*, 1956, 4571.

[2] Chaberek and Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 6228; Courtney, Chaberek, and Martell, *J. Amer. Chem. Soc.*, 1953, **75**, 4814.

[3] Schwarzenbach, Gut, and Anderegg, *Helv. Chim. Acta*, 1954, **37**, 937.

[4] Charles, *J. Amer. Chem. Soc.*, 1954, **76**, 5854.

[5] Charles, *J. Amer. Chem. Soc.*, 1956, **78**, 3946.

[6] Martell, *Rec. Trav. chim.*, 1956, **75**, 781.

[7] Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839.

[8] Hoard, Smith, and Lind, "Advances in the Chemistry of Co-ordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 296.

[9] Schwarzenbach, Anderegg, Schneider, and Senn, *Helv. Chim. Acta*, 1955, **38**, 1147.

[10] Schwarzenbach and Ackermann, *Helv. Chim. Acta*, 1947, **30**, 1798.

[11] Schwarzenbach and Sandera, *Helv. Chim. Acta*, 1953, **36**, 1089.

[12] Eckhardt and Holleck, *Z. Elektrochem.*, 1955, **59**, 202.

complex does not in itself imply that the complex cannot be sexidentate, for the interconversion of quinque- and sexi-dentate forms is likely to be rapid for complexes of bivalent cations. Since the methods of measuring K_{obs} do not distinguish between quinque- and sexi-dentate forms, by assuming a rapid equilibrium between them we can write

$$K_{obs} = [H^+]\{[M(Y)H_2O^{2-}] + [M(Y)^{2-}]\}/[M(HY)H_2O^-],$$

where $M(Y)H_2O^{2-}$ represents a quinquedentate complex, $M(HY)H_2O^-$ its conjugate acid, and $M(Y)^{2-}$ a sexidentate complex. The true acid dissociation constant of $M(HY)H_2O^-$ is $K_H = [H^+][M(Y)H_2O^{2-}]/[M(HY)H_2O^-]$. If $K_{aq} = [M(Y)^{2-}]/[M(Y)H_2O^{2-}]$, the relation between these three equilibrium constants is

$$K_{obs}/K_H = 1 + K_{aq}. \qquad (1)$$

Considering only the conjugate bases of those complexes of similar acid strength ($pK_{obs} = 3{\cdot}0 \pm 0{\cdot}2$), we should expect the free-energy change for the interconversion of quinque- and sexi-dentate forms to vary considerably, and hence the corresponding values of log K_{aq}, since the parent cations cover fairly wide ranges of electropositive character and ionic radius. Eqn. (1) then shows that two opposed interpretations are possible: either the values of K_{aq} considerably exceed unity for some complexes, but the corresponding values of K_H vary in such a way that K_{obs} remains approximately constant, or, alternatively, all values of K_{aq} are less than unity, in which case corresponding values of K_H and K_{obs} will be similar. The basicity of a free carboxylate group and the relative stability of quinque- and sexi-dentate forms do not appear to depend upon the same factors; hence a simple relationship between K_{aq} and K_H is unlikely and the second of the two extreme interpretations seems preferable. This implies that the EDTA complexes of similar basicity are more stable in the quinquedentate form and that $pK_H \approx 3{\cdot}0$. It is noteworthy that pK_H has been found[13] to be *ca.* 3·0 for quinquedentate cobalt(III)–EDTA complexes, $Co(HY)L^-$, in which the sixth co-ordination position is occupied by singly charged anion, L^-, so that the total charge is -1, as in the case of the protonated complexes of bivalent cations.

Values of pK_{obs} vary from 3·5 to 5·2 for the five remaining complexes. Although we should expect a lower value than 3·0 for the pK of the conjugate acid of a quadridentate complex, the extent of this variation suggests that factors other than a change in chelation number must be taken into account. Now, the pK of a free carboxylic acid group in an EDTA complex is likely to be affected by the extent of polarisation of the adjacent nitrogen atom by the bound cation. The polarity of bound carboxylate groups also may influence the acid strength of a protonated complex. The stronger the electropositive character of the cation, the weaker the polarisation of the co-ordinated groups and hence the weaker the acid strength of a free carboxylic acid group. The increase in pK_{obs} along the series V^{II}, Mg, Sr, Ba, Eu^{II}, accords with this view, and so the high values of pK_{obs} do not appear to be good evidence that the complexes of these metals are quadridentate. This interpretation implies that, as far as its influence upon pK_{obs} is concerned, the extent of polarisation of the co-ordinated groups by bivalent cations has almost reached a limit in the complexes of $pK_{obs} \approx 3{\cdot}0$. As a strongly electropositive metal, calcium appears anomalous in this respect.

Staveley and his co-workers[1] have plotted entropies of formation of EDTA complexes from the free anion and the corresponding aquo-cations against the reciprocals of the cationic radii. The entropy values for Mg, Ca, Sr, Ba lie on a line parallel to that passing through the values for Co^{II}, Ni, Ca, Zn, Cd, Pb, but about 12 cal. mole^{-1} deg.$^{-1}$ less positive; these authors have suggested that this may imply a difference in configuration between the EDTA complexes of these two groups of cations. However, if the more strongly

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[13] Schwarzenbach and Heller, *Helv. Chim. Acta*, **1951**, **34**, 576.

electropositive cations cause a lower polarisation of the co-ordinated groups than do the remaining cations, the carboxylate groups in the Mg, Ca, Sr, Ba complexes should interact more strongly with solvent molecules, thereby reducing the entropy of complex formation compared with complexes of less electropositive ions of similar radii. (The effect of the nitrogen atoms upon the solvent molecules is likely to be small since these atoms are partially shielded by CH_2 groups.) Consequently, the separation of the EDTA complexes into two groups in terms of their entropies of formation does not provide convincing evidence of a difference in structure.

Charles [5] has interpreted the viscosities of dilute aqueous solutions of eleven EDTA complexes of bivalent cations as indicating that their structures are similar, except for the lead complex. Values of the parameter B, which appears to be related to the apparent size of a complex in solution, are similar for transition metals, but there is a considerable increase in this parameter along the series Mg, Ca, Sr, Ba, and the value $B = 1{\cdot}07$ for the Ca complex is larger than that for Cd ($B = 0{\cdot}98$), although the two cations are of very similar ionic radius. If the apparent size of a complex includes some contribution from strongly bound solvent molecules, this is in accord with the ideas discussed above. Measured in this way, the apparent size of the lead complex is similar to that for transition metals, which would be in keeping with a relatively high degree of polarisation of the bound carboxylate groups in the lead complex and hence a correspondingly low interaction with the solvent. The high negative value of the heat content change for formation of the lead complex,[1] and the slightly low value of $pK_{obs} = 2{\cdot}8$ appear to support this view.

Summarising, the evidence discussed seems to accord best with the supposition that the EDTA complexes of most bivalent cations are quinquedentate. This conclusion is less certain for Mg, Ca, Sr, Ba, Eu^{II}, but there are no strong indications of a chelation number lower than five. In the case of manganese(II), one of the more electropositive transition metals, the value of pK_H could be as high as *ca.* 3·6, corresponding to $K_{aq} \approx 2$. Thus, the aquosexidentate form, which is known to occur in the solid state,[8] may be slightly more stable than the aquoquinquedentate form. However, there is no compelling evidence in favour of the higher chelation number in solution for this EDTA complex.

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