Partial Molal Volumes and Volume Changes for the Complex Formation of Metal Chelate Electrolytes, $Na_2[M(edta)]$ and $K[M(hedta)(H_2O)]$

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The partial molal volumes, V^∞, of $[M(edta)]^{2-}$ and $[M(hedta)(H_2O)]^-$ (M=Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) and H_3hedta=*N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid) and two free ligands, $edta^{4-}$ and $hedta^{3-}$, have been determined from density measurements at 25 °C. From the results for V^∞, the volume changes for the complex formation of $[M(edta)]^{2-}$ and $[M(hedta)(H_2O)]^-$, ΔV^∞, were estimated. The values of ΔV^∞ for $[M(edta)]^{2-}$ (32.8 to 45.8 $cm^3 mol^{-1}$) and for $[M(hedta)(H_2O)]^-$ (25.2 to 36.5 $cm^3 mol^{-1}$) were large, positive ones, and a linear relationship between ΔV^∞ and ΔS was observed for these metal chelate ions.

The ethylenediaminetetraacetate ion, $edta^{4-}$, is well known as a chelating reagent and is capable of acting as a sexidentate ligand. The stereochemistries of various edta metal chelates have been established in the solid state by means of X-ray studies.[1] However, the structures of the edta chelates in aqueous solutions remain ambiguous, though they have been investigated by a variety of methods.[2-10] A previous study has shown that the partial molal volumes, V^∞, and volume changes for the complex formation, ΔV^∞, are useful in studying the solute-solvent interactions and complex-formation reactions of the metal chelate electrolytes.[11] The volume changes on complexation must be interpreted not only in terms of the simple electrostatic theory, but also by paying attention to the complex structural and solvation changes. Therefore, it seems of interest to compare the ΔV^∞ of $[M(edta)]^{2-}$ with that of $[M(phen)_3]^{2+}$.[11] The former has anionic and hydrophilic ligands, but the latter has neutral and hydrophobic ones.

However, the V^∞ and ΔV^∞ for the edta chelates have not been reported except for $[Ni(edta)]^{2-}$.[12] In this study, the partial molal volumes of $[M(edta)]^{2-}$ and $[M(hedta)(H_2O)]^-$ are determined, and the volume changes of complex formation are estimated.

Experimental

Materials. The edta chelates, $Na_2[Mn(edta)]\cdot 4H_2O$, $Na_2[Co(edta)]\cdot 3.5H_2O$, $Na_2[Ni(edta)]\cdot 3H_2O$, $Na_2[Cu(edta)]\cdot 3H_2O$, and $Na_2[Zn(edta)]\cdot 3.5H_2O$, were obtained from Nakarai Chemicals, Ltd., and were recrystallized twice from an water–ethanol mixture according to the literature method.[13] The hedta chelate electrolytes, $K[Mn(hedta)(H_2O)]\cdot 3H_2O$, $K[Co(hedta)(H_2O)]\cdot 1.5H_2O$, $K[Ni(hedta)(H_2O)]\cdot 1.5H_2O$, $K[Cu(hedta)(H_2O)]\cdot 1.5H_2O$, and $K[Zn(hedta)(H_2O)]\cdot 1.5H_2O$, were prepared by the following manner, similar to that used for the edta chelates.[13]

N-(2-Hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid (27.8 g, 0.1 mol) was slowly stirred into a mixture of a calculated amount of basic metal carbonate or cobalt acetate and water (50 ml). The slurry was warmed to 90 °C, after which stirring was continued for 30 min. Then, $KHCO_3$ (10 g or 30 g for the Co-chelate) was added slowly to the reaction mixture, and stirring was continued for a further 10 min at 90 °C. Absolute ethanol was vigorous stirred into the resulting solution, after which it was warmed almost to the boiling point, until the precipitate began to form. The solution was then cooled in an ice bath. The resulting precipitate was filtered and washed with ethanol and ether. The crude product was recrystallized twice from the water–ethanol mixture. The recrystallized metal chelate was placed in a desiccator over silica gel.

The purities of all the products obtained here were checked by analysis.

The metal chelate electrolytes were dried *in vacuo* for one week at 90 °C before use. The tetra sodium salt of edta and the tri sodium salt of hedta (Nakarai Chemicals, Ltd.) were used without further purification and were dehydrated *in vacuo* to a constant weight at 110 °C. All the solutions were prepared by weight with deionized and distilled water.

Apparatus. The densities were measured at 25 °C with a digital density meter (Shibayama Scientific Co., Ltd., Model SSD-200) described in a previous paper.[11] The temperature of the thermostated bath was set at ±0.03 °C and regulated to ±0.002 °C.

Results

The apparent molal volumes, ϕ_v, of the metal chelate electrolytes were calculated from the density data using this equation:

$$\phi_v = \frac{M}{d} + \frac{1000(d^\circ - d)}{m\, d\, d^\circ}, \quad (1)$$

where M is the molecular weight of the metal chelate, m is the the molality, and d° and d are the densities of the solvent and the solution respectively. The partial molal volumes at infinite dilution, V^∞, were obtained by means of the Redlich-Mayer equation:[14]

$$\phi_v - S_v C^{1/2} = V^\infty + b_v C, \quad (2)$$

where S_v is the theoretical Debye-Hückel limiting slope (1.868 and 9.706 $cm^3 dm^{3/2} mol^{-3/2}$ for 1:1 and 1:2 electrolytes respectively), C is the molar concentration, and b_v is the empirical constant. In Figs. 1 and 2, the plots of the $\phi_v - S_v C^{1/2}$ of the edta and hedta chelates against C are shown. The V^∞ and b_v values obtained by the least-squares method are shown in Table 1. The standard deviations of the fits are mostly less than 0.1 $cm^3 mol^{-1}$.

The ϕ_v of sodium salts of edta and hedta can not be directly determined from the densities of their aque-

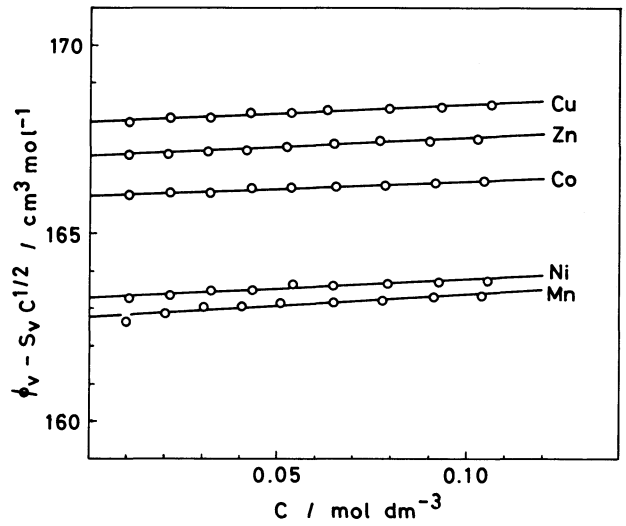

Fig. 1. Apparent Molal Volumes of $Na_2[M(edta)]$ at 25 °C.
$S_v = 1.868\,cm^3\,dm^{3/2}\,mol^{-3/2}$.

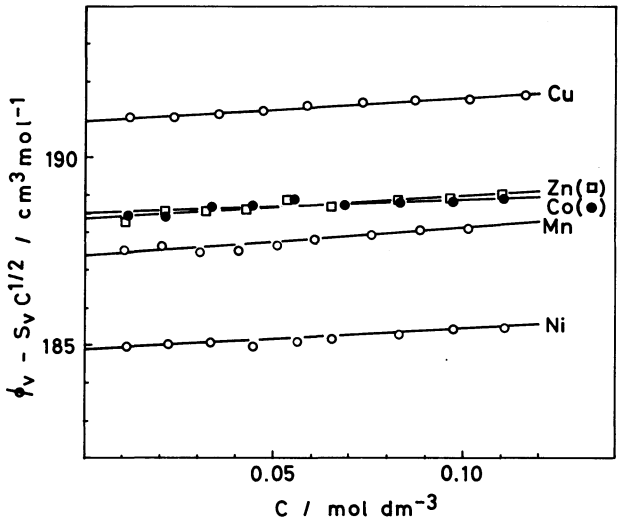

Fig. 2. Apparent Molal Volumes of $K[M(hedta)(H_2O)]$ at 25 °C.
$S_v = 9.706\,cm^3\,dm^{3/2}\,mol^{-3/2}$.

ous solutions because of the partial hydrolysis. Therefore, the stock solutions of the hypothetical solutes, $Na_4edta \cdot NaOH$ and $Na_3hedta \cdot NaOH$, were made up by mixing the anhydrous salts, stoichiometric amounts of the standard aqueous NaOH solution (0.3 mol dm^{-3}), and pure water. In this case, the pH values of the mixed solutions were around 12, and $edta^{4-}$ or $hedta^{3-}$ was assumed to be predominantly present from the pK_a values. The ϕ_v values, which were caluculated by introducing the molecular weight of the hypothetical solutes, fit the equation well over the present range of concentrations (0.01—0.1 mol dm^{-3}):

$$\phi_v = V^\infty + A_v C^{1/2} + B_v C, \quad (3)$$

where A_v and B_v are the fitting parameters. The parameters of Eq. 3, as determined by the least-squares method, are given in Table 1. The standard deviations of the fits are 0.2 $cm^3\,mol^{-1}$. The V^∞ values for Na_4 edta and Na_3 hedta are obtained by the subtraction of the V^∞ value for NaOH according to additivity rule.

The volume changes at infinite dilution, ΔV^∞, on the complex formation of:

$$[M(H_2O)_6]^{2+} + edta^{4-} \longrightarrow [M(edta)]^{2-} + 6H_2O, \quad (4)$$

$$[M(H_2O)_6]^{2+} + hedta^{3-} \longrightarrow [M(hedta)(H_2O)]^- + 5H_2O, \quad (5)$$

may be estimated from the V^∞ values of the reactants and the products according to the relationships for the edta chelates:

$$\Delta V^\infty = V^\infty([M(edta)]^{2-}) + 6V^*(H_2O) - V^\infty([M(H_2O)_6]^{2+}) - V^\infty(edta^{4-}), \quad (6)$$

and for the hedta chelates:

$$\Delta V^\infty = V^\infty([M(hedta)(H_2O)]^-) + 5V^*(H_2O) - V^\infty([M(H_2O)_6]^{2+}) - V^\infty(hedta^{3-}), \quad (7)$$

where $V^\infty([M(edta)]^{2-})$, $V^\infty([M(hedta)(H_2O)]^-)$, $V^\infty([M(H_2O)_6]^{2+})$, $V^\infty(edta^{4-})$, and $V^\infty(hedta^{3-})$ are the partial molal volumes of the species described in parentheses and $V^*(H_2O)$ is that of pure water. The V^∞ values of the hexaaqua-metal ions can be estimated by means

Table 1. Standard partial molal volumes at 25 °C

Solute	V^∞	b_v [a]	A_v [b]	B_v [b]
	$cm^3\,mol^{-1}$	$cm^3\,dm^3\,mol^{-2}$	$cm^3\,dm^{3/2}\,mol^{-3/2}$	$cm^3\,dm^3\,mol^{-2}$
$Na_2[Mn(edta)]$	162.7	6.22		
$Na_2[Co(edta)]$	166.0	3.94		
$Na_2[Ni(edta)]$	163.3	4.88		
$Na_2[Cu(edta)]$	168.0	4.56		
$Na_2[Zn(edta)]$	167.0	4.91		
$K[Mn(hedta)(H_2O)]$	187.3	7.37		
$K[Co(hedta)(H_2O)]$	188.5	2.46		
$K[Ni(hedta)(H_2O)]$	184.8	5.37		
$K[Cu(hedta)(H_2O)]$	190.9	6.46		
$K[Zn(hedta)(H_2O)]$	188.4	5.78		
$Na_4edta \cdot NaOH$	139.7		81.5	−85.0
$Na_3hedta \cdot NaOH$	143.6		87.2	−83.7

a) An adjustable parameter of Eq. 2. b) Parameters of Eq. 3.

of this relation:[11,15]

$$V^{\infty}([M(H_2O)_6]^{2+}) = V^{\infty}(M^{2+}) + 6V^{*}(H_2O), \quad (8)$$

where $V^{\infty}(M^{2+})$ is the partial molal volume of the transition metal cation, which is generally obtained in the literature. The $V^{\infty}(M^{2+})$ values were estimated from the literature values for $Mn(ClO_4)_2$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, and $Zn(ClO_4)_2$ using the additivity principle with $V^{\infty}(ClO_4^-)=49.5\,cm^3\,mol^{-1}$.[16,17] The ionic partial molal volumes of $[M(edta)]^{2-}$, $[M(hedta)(H_2O)]^-$ and the free ligands are given in Table 2; they were obtained using $V^{\infty}(Na^+)=-6.6$, $V^{\infty}(K^+)=3.6$, and $V^{\infty}(OH^-)=1.4\,cm^3\,mol^{-1}$.[17]

Discussion

The values of V^{∞} found for the bivalent metal edta chelates vary from 175.9 $cm^3\,mol^{-1}$ for $[Mn(edta)]^{2-}$ to 181.2 $cm^3\,mol^{-1}$ for $[Cu(edta)]^{2-}$; therefore, they do not significantly differ from each other. The same phenomenon is found in the case of the V^{∞} values of the hedta chelate ions, which vary from 181.2 $cm^3\,mol^{-1}$ for $[Ni(hedta)(H_2O)]^-$ to 187.3 $cm^3\,mol^{-1}$ for $[Cu(hedta)(H_2O)]^-$. These V^{∞} values are almost the same as those of the free ligands. The same facts were found for $[M(phen)_3]^{2+}$, which were about 4 to 6% smaller than three times the V^{∞} values of the free 1,10-phenanthroline.[11]

The estimated ΔV^{∞} values for the complex formation of $[M(edta)]^{2-}$ are in this order:

$$[Mn(edta)]^{2-} < [Co(edta)]^{2-} < [Ni(edta)]^{2-} < [Cu(edta)]^{2-} > [Zn(edta)]^{2-}.$$

This order is the same as in the Irving-Wiliams series. The ΔV^{∞} values for $[M(hedta)(H_2O)]^-$ are in a sequence similar to that of the edta chelates. In any case, the ΔV^{∞} values for $[M(edta)]^{2-}$ and $[M(hedta)(H_2O)]^-$ are $\Delta V^{\infty}([M(edta)]^{2-}) > \Delta V^{\infty}([(M(hedta)(H_2O)]^-]$, where M^{2+} is the same central metal ion. Furthermore, the formation of Mn(II) chelate ions of edta and hedta is accompanied by a markedly small ΔV^{∞} value in comparison with those of the other metal chelate ions. This can be attributed to the larger V^{∞} value of the high-spin d^5 Mn(II) aqua ion. For the other aqua ions, the V^{∞} are not so different and the ΔV^{∞} values of these edta and hedta chelates are almost the same.

The resultant ΔV^{∞} values for the edta and hedta chelates have markedly large positive values in comparison with the ΔV^{∞} values of the other complex formation reactions and ion-pair formation reactions. These large positive ΔV^{∞} values may be due to the large amount of water molecules released from the electrostricted solvation spheres of the reactants by the partial neutralization of the charges.

The volume changes in the ion-pair formation may serve as a reference for the volume change in the neutralization of the charges. For the inner-sphere ion-pair formation of $CaSO_4$, the ΔV^{∞} value has been reported to be 25.2 $cm^3\,mol^{-1}$,[18] which is similar in magnitude to the ΔV^{∞} values of the hedta chelates. However, the ΔV^{∞} values for the transition metal sulfate ion-pairs are fairly smaller, varying from 7.4 $cm^3\,mol^{-1}$ for $MnSO_4$ to 11.4 $cm^3\,mol^{-1}$ for $CuSO_4$.[19] For these ion-pairs, the amount of the inner-sphere ion-pair is estimated to be about 20%; therefore, the electrostricted solvation spheres of the constituent ions are not completely lost upon these ion-pairing processes.[19]

A positive contribution to the ΔV^{∞} values of edta and hedta can also be expected from the delocalization of the charge on the large metal chelate ion. This contribution becomes large when the ligand is a large hydrophobic one such as 1,10-phenanthroline. Previously, the formation of $[M(phen)_3]^{2+}$ has been reported.[11] In this system, the neutralization of the charge is not included, though the ΔV^{∞} values (*ca.* 20 $cm^3\,mol^{-1}$) except for $[Fe(phen)_3]^{2+}$ are comparable to that of an inner-

Table 2. Ionic partial molal volumes at 25 °C

Ion	V^{∞}(ion) / $cm^3\,mol^{-1}$
$[Mn(edta)]^{2-}$	175.9
$[Co(edta)]^{2-}$	179.2
$[Ni(edta)]^{2-}$	176.5 (170.3)[a]
$[Cu(edta)]^{2-}$	181.2
$[Zn(edta)]^{2-}$	180.2
$[Mn(hedta)(H_2O)]^-$	183.7
$[Co(hedta)(H_2O)]^-$	184.9
$[Ni(hedta)(H_2O)]^-$	181.2
$[Cu(hedta)(H_2O)]^-$	187.3
$[Zn(hedta)(H_2O)]^-$	184.8
$edta^{4-}$	171.3 (174.4)[a]
$hedta^{3-}$	168.6

a) Ref. 12.

Table 3. Ionic partial molal volumes of M^{2+} and volume changes for the formation of $[M(edta)]^{2-}$ and $[M(hedta)(H_2O)]^-$ at 25 °C

M(II)	$V^{\infty}(M^{2+})$ / $cm^3\,mol^{-1}$	$\Delta V^{\infty}([M(edta)]^{2-})$ / $cm^3\,mol^{-1}$	$\Delta V^{\infty}([M(hedta)(H_2O)]^-)$ / $cm^3\,mol^{-1}$
Mn(II)	−28.2	32.8	25.2
Co(II)	−36.2	44.1	34.4
Ni(II)	−39.2	44.4 (25.5)[a]	33.7
Cu(II)	−35.9	45.8	36.5
Zn(II)	−35.5	44.4	33.6

a) Ref. 12.

sphere ion pairing such as $CaSO_4$.[11]

A comparison of the ΔV^∞ values of the edta and hedta chelates with those of the bivalent metal carboxylato-complex formation reactions would be more instructive. For the 1:1 complex formation of Cu^{2+} with the unidentate carboxylate anions, acetate and propionate, the volume changes in the dilute solutions, ΔV, have been reported to be 13 $cm^3 mol^{-1}$ at 30 °C.[20] Furthermore, the ΔV values for the 1:1 complex of Cu^{2+} with the bidentate dicarboxylates, malonate, tartrate and maleate, are rather larger (27, 29, and 28 $cm^3 mol^{-1}$ respectively at 30 °C); these values are twice the ΔV values produced by the formation of Cu(II)-monocarboxylato complexes.[20] Therefore, it is of interest to compare the ΔV value for the edta chelate with that of the hedta chelate of the same central metal cation. The ΔV^∞ value for the latter is about three fourths that of the former; the ΔV^∞ values of these chelates are also in proportion to the number of carboxylate groups in the ligands. This means that the great part of the large positive ΔV^∞ values for the edta and the hedta chelates is responsible for the coordination of the carboxylate groups to the metal ions, even though the contributions of the nitrogen donor atoms to the ΔV^∞ can not be estimated. However, they are assumed to be smaller than those of the carboxylate groups. For example, the ΔV for Cu(II)-glycinato and Cu(II)-alaninato complexes are reported to be 14 and 15 $cm^3 mol^{-1}$ respectively at 30 °C, and for these systems the volume changes responsible for the coordinated nitrogen donor atoms are estimated to be 1—3 $cm^3 mol^{-1}$.[20]

The complex formation reactions of edta and hedta with the bivalent transition metal cations are characterized by large positive volume and entropy changes. As is shown in Fig. 3, a linear relationship between the ΔS value at an ionic strength of 0.1 mol dm^{-3} and ΔV^∞ value for the complexation of edta and hedta is observed within the limits of experimental error. Such large values for ΔS and ΔV^∞ are related, in large part, to the electrostriction effects: *i.e.*, the neutralization effect by the coordination of the acetate groups to the metal ions and the reduction of the electrostriction by the delocalization of the residual charges on the large metal chelate ions.[12] The lower ΔS and ΔV^∞ values for the hedta chelates than for the edta chelates suggest that the 2-hydroxyethyl group is not bonded to the metal ion and that fewer molecules of water are released on the complexation of the hedta chelates.

Smaller ΔS values for the edta and hedta chelates of Mn(II) than those of the analogous chelates are also found in the same manner as with ΔV^∞. The edta chelate of Mn(II) has been shown to have a seven-coordinated structure, with one water molecule.[6,9] This may be one of the reasons why the formation of the Mn(II)-edta chelate ion is accompanied by smaller ΔS and ΔV^∞ values, for at least one water molecule remains in the electronic field of the central metal cation. Therefore, it may be considered that the smaller ΔS and

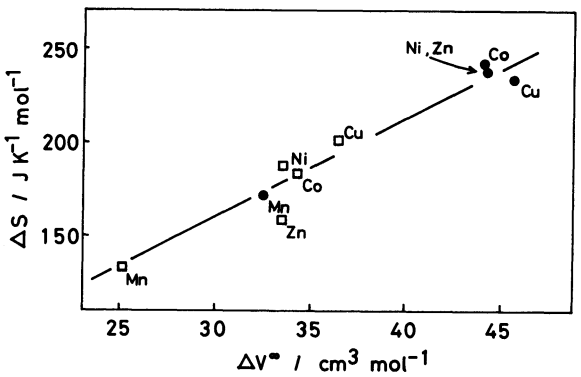

Fig. 3. Relationship between ΔV^∞ and ΔS at 25 °C.
●: $[M(edta)]^{2-}$, □: $[M(hedta)(H_2O)]^-$.

ΔV^∞ values of the Mn(II)-edta chelate than those of the other edta chelates are due to the different coordination geometry and the larger ionic size of the Mn(II) aqua ion. In the case of Mn(II)-hedta, its structure is not known; however, the present result may be supposed to indicate that the Mn(II)-hedta chelate has the same seven-coordinated structure as the Mn(II)-edta chelate, except for the two coordinated water molecules.

Many authors have concluded, on the basis of various methods of studies, that the edta chelates of Co(II), Ni(II), Cu(II), and Zn(II) in aqueous solutions are dynamic equilibrium mixtures between the dominant sexidentate form and the quinquedentate form, which contains one water molecule and a free carboxylate group.[2-10] If that is the case, the V^∞ values of the edta chelates may be written as:

$$V^\infty = \alpha V^\infty_{\mathrm{I}} + (1-\alpha)V^\infty_{\mathrm{II}} - (1-\alpha)V^*(H_2O), \quad (9)$$

where the V^∞_{I} and α are the partial molal volume and the fraction of the edta chelate in the sexidentate form and where V^∞_{II} is the partial molal volume in the quinquedentate form or the seven-coordinated form for the Mn(II)-edta chelate respectively. Therefore, the ΔV^∞ values for the edta chelates are expressed as:

$$\Delta V^\infty = V^\infty_{\mathrm{I}} + (1-\alpha)V^\infty_{\mathrm{II}} + (5+\alpha)V^*(H_2O) - V^\infty([M(H_2O)_6]^{2+}) - V^\infty(edta^{4-}). \quad (10)$$

The substitution of Eq. 9 into Eq. 10 leads to the same result as Eq. 6. The α's were estimated in the range from 60 to 80% for the edta complexes of Co(II), Ni(II), Cu(II), and Zn(II),[3,9,10] and the volume change between the quinquedentate form and the sexidentate form ($\Delta V^\infty_{\mathrm{II}\to\mathrm{I}} = V^\infty_{\mathrm{I}} + V^*(H_2O) - V^\infty_{\mathrm{II}}$) is calculated to be 4.9 $cm^3 mol^{-1}$ for the Co(II)-edta chelate.[10] When one substitutes these values into Eq. 10, the V^∞_{I} and V^∞_{II} values can be estimated separately. Such a treatment indicates that the dynamic equilibrium between the sexidentate form and the quinquedentate form of the edta chelate should have only a small effect on ΔV^∞, which is estimated to be 1—2 $cm^3 mol^{-1}$. The ΔV^∞ values for the edta chelates, except for Mn(II)-edta, are, unfortunately, not so effective in determining the structures of the edta chelates in aqueous solutions.

However, the large differences between the ΔV^{∞} values for the edta and the hedta chelate and the rather small volume change between the quinquedentate form and the sexidentate form of the edta chelate may be ascribed to the fact that the uncoordinated carboxylate group of the edta chelate in the quinquedentate form has already been situated in the second coordination sphere of the central metal cation and weakly interacts with it. This figure, except for the case of the Mn(II)–edta chelate, does not conflict with the results of the recent work on the structures of the edta chelates in aqueous solutions.

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