Inorganica Chimica Acta, *150* (1988) 237–244

The Crystal and Molecular Structures of Lithium Trimethylenediaminetetraacetatoferrate(III) Trihydrate Li[Fe(trdta)]·$3H_2O$ and Sodium Ethylenediamine-*N,N'*-diacetato-*N,N'*-di-3-propionatoferrate(III) Pentahydrate Na[Fe(eddda)]·$5H_2O$

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(Received March 28, 1988)

Abstract

The crystal structures of Li[Fe(trdta)]·$3H_2O$ and Na[Fe(eddda)]·$5H_2O$ (trdta = trimethylenediaminetetraacetate and eddda = ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate) have been determined by single crystal X-ray diffraction techniques. The former crystal was monoclinic with the space group $P2_1/n$, $a = 17.775(3)$, $b = 10.261(1)$, $c = 8.883(2)$ Å, $\beta = 95.86(4)°$ and $Z = 4$. The latter was also monoclinic with the space group $P2_1/n$, $a = 6.894(2)$, $b = 20.710(6)$, $c = 13.966(3)$ Å, $\beta = 101.44(2)°$ and $Z = 4$. Both complex anions were found to adopt an octahedral six-coordinate structure with all of six ligand atoms of trdta^{4-} or eddda^{4-} coordinated to the Fe(III) ion, unlike the corresponding edta^{4-} complex which is usually seven-coordinate with the seventh coordination site occupied by H_2O. Of the three geometrical isomers possible for the eddda complex, the *trans*(O_5) isomer was actually found in the latter crystal. Factors determining the structural types of metal–edta complexes are discussed in detail.

Introduction

Many structural studies have been reported on transition-metal complexes of ethylenediaminetetraacetate edta^{4-} [1], and the molecular structures they adopt in crystal have been discussed in terms of the d-electron configuration of and the size of the central metal ion M, and the difference in bond lengths between the M–N and M–O bonds involved [2, 3]. Of these complexes, the Fe(III) complex is unique in that both of the six- [4, 5] and seven-coordinate [6] structures have been established for it. This observation implies that the Fe(III) ion is slightly too big to be encircled in an octahedral environment by edta^{4-} capable of forming five-membered chelate rings only. It is therefore expected that even the Fe(III) ion forms an octahedral six-coordinate complex exclusively, if edta^{4-} is replaced with an analogous polyaminocarboxylate which can form longer chelate rings. With this expectation in mind, X-ray crystallographic analyses were made for Fe(III) complexes with trimethylenediaminetetraacetate (trdta^{4-}) and with ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate (eddda^{4-}) capable of forming one or two six-membered chelate rings upon complexation.

Experimental

Preparation of Li[Fe(trdta)]·$3H_2O$ (I) and Na[Fe(eddda)]·$5H_2O$ (II)

H_4trdta and H_4eddda were both prepared according to the procedures described in the literature [7, 8]. Since they were highly soluble in water, an appropriate amount of $Fe(NO_3)_3·9H_2O$ was added directly to the above reaction mixture after each of them was neutralized with LiOH or NaOH. Concentration with use of a rotary evaporator followed by addition of ethanol afforded crystallization of the desired complexes. Elemental analyses confirmed the above compositions for the respective complexes.

X-ray Measurements

The crystals used for the data collection had dimensions of 0.15 × 0.20 × 0.25 mm for **I** and 0.10 × 0.20 × 0.25 mm for **II**. Determination of cell constants and collection of intensity data were carried out on a Rigaku AFC-5UD diffractometer for **I** and on a Syntex diffractometer for **II** with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Unit cell constants were determined by least-squares refinement of 25 reflections for each compound. Intensity data were collected by an ω–2θ scan mode up to $2\theta = 60°$ for **I** and by an ω scan mode up to $2\theta = 55°$ for **II**. No corrections were made for absorp-

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0020-1693/88/$3.50

TABLE I. Crystallographic Data[a]

	I	II
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
Cell dimensions		
a (Å)	17.775(3)	6.894(2)
b (Å)	10.261(1)	20.710(6)
c (Å)	8.883(2)	13.966(3)
β (°)	95.86(4)	101.44(2)
V (Å^3)	1611.6(5)	1954.5(9)
Density (obs.) (g/cm^3)	1.72	1.65
Density (calc.) (g/cm^3)	1.73	1.65
No. unique reflections	5042	4626
No. reflections with $F_o > 3\sigma(F_o)$	4113	3147
Final R (%)	4.9	6.0

[a] I: $Li[Fe(trdta)]\cdot 3H_2O$; II: $Na[Fe(eddda)]\cdot 5H_2O$.

TABLE II. Positional and Thermal Parameters for $Li[Fe(trdta)]\cdot 3H_2O$ [a]

Atom	x	y	z	B_{eq} (Å^2)[b]
Fe	0.2949(0)	0.4772(0)	0.4389(0)	1.5
O1	0.1038(1)	0.4481(2)	0.6403(3)	2.6
O2	0.4610(2)	0.3061(3)	0.2482(4)	4.4
O3	0.3955(2)	0.4374(3)	0.8588(3)	3.6
O4	0.2003(1)	0.5767(3)	0.0274(3)	3.1
O5	0.2098(1)	0.3993(2)	0.5390(3)	2.2
O6	0.3465(1)	0.3483(2)	0.3202(3)	2.5
O7	0.3741(1)	0.4371(2)	0.6081(3)	2.3
O8	0.2176(1)	0.5322(2)	0.2737(3)	2.2
N1	0.2720(1)	0.6316(2)	0.5962(3)	1.6
N2	0.3632(1)	0.6027(2)	0.3032(3)	1.6
C1	0.2930(2)	0.7662(3)	0.5526(4)	2.2
C2	0.3792(2)	0.7422(3)	0.3468(5)	2.6
C3	0.1646(2)	0.4797(3)	0.5948(4)	1.9
C4	0.1887(2)	0.6217(3)	0.5997(4)	2.2
C5	0.4137(2)	0.3816(4)	0.2879(4)	2.6
C6	0.4332(2)	0.5252(4)	0.3048(4)	2.4
C7	0.3648(2)	0.4814(4)	0.7411(4)	2.2
C8	0.3112(2)	0.5966(3)	0.7462(4)	2.3
C9	0.2406(2)	0.5701(3)	0.1472(4)	2.0
C10	0.3236(2)	0.6005(4)	0.1478(4)	2.3
Cα	0.3738(2)	0.7745(3)	0.5116(4)	2.4
Li	0.0268(3)	0.5714(7)	0.7098(8)	2.7
OW1	0.4445(1)	0.0408(3)	0.2444(4)	3.5
OW2	0.0681(2)	0.6731(3)	0.8838(3)	3.3
OW3	0.4981(2)	0.7867(3)	0.0679(4)	3.9
H(C1)1	0.288	0.832	0.674	4.0
H(C1)2	0.255	0.798	0.455	4.0
H(C2)1	0.436	0.766	0.321	4.0
H(C2)2	0.339	0.804	0.279	4.0
H(C4)1	0.160	0.673	0.502	4.0
H(C4)2	0.173	0.666	0.703	4.0
H(C6)1	0.468	0.541	0.412	4.0
H(C6)2	0.464	0.556	0.212	4.0
H(C8)1	0.270	0.570	0.823	4.0
H(C8)2	0.345	0.679	0.791	4.0
H(C10)1	0.349	0.526	0.081	4.0
H(C10)2	0.329	0.695	0.095	4.0
H(Cα)1	0.409	0.705	0.580	4.0
H(Cα)2	0.395	0.873	0.532	4.0

[a] e.s.d.s given in parentheses. [b] $B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$. See also 'Supplementary Material'.

tion effect (μ(Mo Kα) = 9.9 and 8.3 for **I** and **II**, respectively). The numbers of reflections included in structural analysis ($F_o > 3\sigma F_o$) were 4113 for **I** and 3147 for **II**.

Determination and Refinement of Crystal Structures

The crystal structure of each compound was solved by a standard heavy-atom method. The parameters for all the non-hydrogen atoms were refined anisotropically. Several cycles of the block-diagonal least-squares refinement reduced the R value ($R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$) to 0.058 and 0.068 for **I** and **II** respectively. At this stage, all the hydrogen atom positions included were calculated ones (1.09 Å for C–H bond distances and tetrahedral angles). The final refinement including these H atoms with isotropic temperature factors caused the R value to converge to 0.049 and 0.060 for **I** and **II**, respectively. In the refinement the quantity minimized was $w(|F_o| - k|F_c|)^2$. The weighting scheme used was $w = (\sigma cs^2 + a|F_o| + b|F_o|^2)^{-1}$, where σcs is the standard deviation obtained from the counting statistics for each reflection; the a and b values chosen were 0.2 and 0.0009, respectively. Crystallographic data are summarized for both **I** and **II** in Table I, and the final atomic coordinates for non-hydrogen and hydrogen atoms together with the thermal parameters are given in Tables II and III for **I** and **II**, respectively. All the computations were carried out on a HITAC computer at the Hiroshima University Information Processing Center. The computer programs used were UNICS-III [9] and ORTEP [10].

Results and Discussion

Description of Molecular Structures

In Figs. 1 and 2 are shown the molecular structures (ORTEP) of the complex anions in $Li[Fe(trdta)]\cdot 3H_2O$ (**I**) and $Na[Fe(eddda)]\cdot 5H_2O$ (**II**), respectively, where the numbering schemes for the respective atoms are also given. The bond distances and angles within the complex anion are given in Tables IV and V, respectively for **I**, and in Tables VI and VII, respectively for **II**.

Figures 1 and 2 clearly indicate that both of the trdta and eddda complexes are six-coordinate with the Fe(III) ion surrounded octahedrally by all of the six ligand atoms of trdta^{4-} or eddda^{4-}. By contrast, the corresponding edta complex adopts a seven-coordinate structure with the seventh coordination

TABLE III. Positional and Thermal Parameters for Li[Fe(eddda)]·$3H_2O$ [a]

Atom	x	y	z	B_{eq} (Å^2)[b]
Fe	−0.0730(1)	0.3129(0)	0.5037(1)	1.5
O1	−0.4260(7)	0.4433(2)	0.3511(4)	4.5
O2	−0.3445(6)	0.1650(2)	0.6225(3)	2.9
O3	0.2238(7)	0.2199(2)	0.3210(3)	3.1
O4	−0.0420(7)	0.4205(2)	0.7485(3)	3.0
O5	−0.2679(6)	0.3538(2)	0.4038(3)	2.3
O6	−0.2360(6)	0.2469(2)	0.5484(3)	2.5
O7	0.0232(6)	0.2454(2)	0.4215(3)	2.2
O8	−0.1102(6)	0.3829(2)	0.5972(3)	2.4
N1	0.1633(6)	0.3671(2)	0.4533(3)	1.8
N2	0.1702(6)	0.2904(2)	0.6266(3)	1.8
C1	0.3298(8)	0.3723(3)	0.5399(4)	2.3
C2	0.3564(8)	0.3089(3)	0.5947(4)	2.5
C3	−0.2714(8)	0.4118(3)	0.3677(4)	2.4
C4	0.1010(8)	0.4332(3)	0.4187(4)	2.3
C5	−0.2085(8)	0.2017(2)	0.6131(4)	2.2
C6	0.1741(8)	0.2200(3)	0.6493(4)	2.3
C7	0.1562(8)	0.2593(3)	0.3713(4)	2.2
C8	0.2287(9)	0.3285(3)	0.3757(4)	2.3
C9	−0.0135(8)	0.3819(3)	0.6851(4)	2.1
C10	0.1439(9)	0.3309(3)	0.7119(4)	2.5
Cβ	−0.0858(9)	0.4358(3)	0.3386(5)	3.0
Cγ	−0.0095(9)	0.1944(3)	0.6806(4)	2.8
Na	−0.6108(3)	−0.0443(1)	0.5875(2)	2.6
OW1	−0.3260(7)	0.0304(2)	0.5944(3)	3.4
OW2	0.4068(7)	0.3927(2)	0.9189(3)	3.4
OW3	0.3984(7)	0.1246(2)	0.4580(3)	3.5
OW4	0.1912(8)	0.0505(2)	0.5868(4)	4.2
OW5	−0.4343(7)	0.4537(2)	0.7649(3)	3.5
H(C1)1	0.297	0.410	0.588	4.0
H(C1)2	0.466	0.384	0.515	4.0
H(C2)1	0.395	0.272	0.547	4.0
H(C2)2	0.475	0.314	0.658	4.0
H(C4)1	0.219	0.456	0.389	4.0
H(C4)2	0.071	0.462	0.480	4.0
H(C6)1	0.193	0.194	0.584	4.0
H(C6)2	0.301	0.211	0.708	4.0
H(C8)1	0.390	0.327	0.389	4.0
H(C8)2	0.172	0.350	0.305	4.0
H(C10)1	0.283	0.355	0.742	4.0
H(C10)2	0.101	0.300	0.768	4.0
H(Cβ)1	−0.110	0.486	0.315	4.0
H(Cβ)2	−0.060	0.407	0.277	4.0
H(Cγ)1	0.014	0.143	0.695	4.0
H(Cγ)2	−0.019	0.219	0.749	4.0

[a] e.s.d.s given in parentheses. [b] $B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$. See also 'Supplementary Material'.

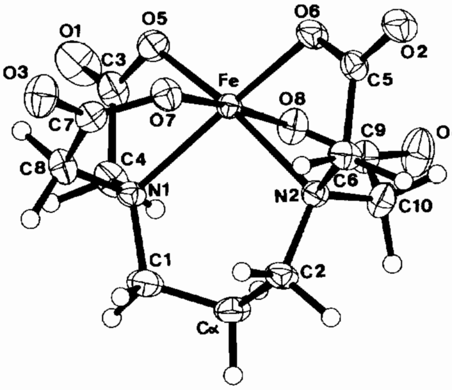

Fig. 1. Molecular structure (ORTEP) of [Fe(trdta)]$^-$ in Li[Fe(trdta)]·$3H_2O$.

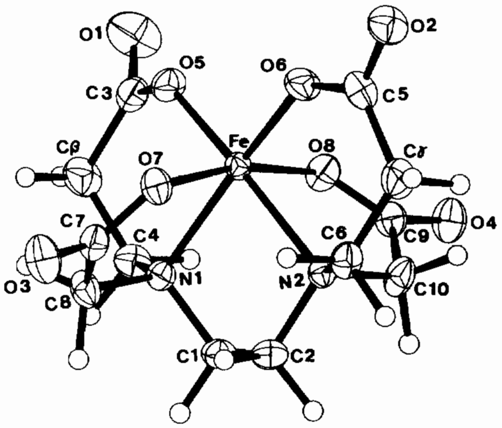

Fig. 2. Molecular structure (ORTEP) of [Fe(eddda)]$^-$ in Na[Fe(eddda)]·$5H_2O$.

TABLE IV. Intramolecular Bond Distances (Å) for Li[Fe(trdta)]·$3H_2O$ [a]

Bond		Bond		Bond	
Fe–O5	1.999(3)	Fe–O6	1.975(3)	Fe–O7	1.995(3)
Fe–O8	1.987(3)	Fe–N1	2.178(3)	Fe–N2	2.209(3)
O1–C3	1.236(4)	O2–C5	1.223(5)	O3–C7	1.216(5)
O4–C9	1.223(5)	O5–C3	1.285(4)	O6–C5	1.302(5)
O7–C7	1.292(4)	O8–C9	1.294(4)	N1–C1	1.492(5)
N1–C4	1.487(5)	N1–C8	1.483(4)	N2–C2	1.503(5)
N2–C6	1.476(5)	N2–C10	1.485(5)	C1–Cα	1.521(5)
C2–Cα	1.514(6)	C3–C4	1.518(5)	C5–C6	1.518(5)
C7–C8	1.522(5)	C9–C10	1.507(5)		

[a] e.s.d.s given in parentheses.

site occupied by H_2O [6], though a six-coordinate structure has also been found under not well-established conditions [4, 5]. This suggests that edta^{4-} is slightly too small in size to encircle the Fe(III) ion in an octahedral environment, and that trdta or eddda capable of forming longer chelate rings would form an octahedral six-coordinate complex with the Fe(III) ion, as is actually the case. It should be mentioned here that the trimethylenediamine part of the trdta complex assumes a twist-boat conformation usually found in other metal–trdta complexes [11, 12] and that only the *trans*(O_5) isomer [13] is isolated for the eddda complex.

Tables VIII and IX compare the Fe–N and Fe–O bond distances, and the O–Fe–O, O–Fe–N and

TABLE V. Intramolecular Bond Angles (°) for $Li[Fe(trdta)]\cdot 3H_2O$ [a]

Angle		Angle		Angle	
O5–Fe–O6	112.5(1)	O5–Fe–O7	95.1(1)	O5–Fe–O8	86.8(1)
O5–Fe–N1	78.8(1)	O5–Fe–N2	163.5(1)	O6–Fe–O7	86.2(1)
O6–Fe–O8	96.9(1)	O6–Fe–N1	163.2(1)	O6–Fe–N2	77.8(1)
O7–Fe–O8	175.4(1)	O7–Fe–N1	80.3(1)	O7–Fe–N2	98.5(1)
O8–Fe–N1	96.1(1)	O8–Fe–N2	79.0(1)	N1–Fe–N2	94.3(1)
Fe–O5–C3	116.5(2)	Fe–O6–C5	115.3(2)	Fe–O7–C7	118.0(2)
Fe–O8–C9	118.0(2)	Fe–N1–C1	116.0(2)	Fe–N1–C4	102.5(2)
Fe–N1–C8	107.4(2)	C1–N1–C4	110.1(3)	C1–N1–C8	110.5(3)
C4–N1–C8	110.0(3)	Fe–N2–C2	121.0(2)	Fe–N2–C6	101.0(2)
Fe–N2–C10	105.3(2)	C2–N2–C6	111.9(3)	C2–N2–C10	108.3(3)
C6–N2–C10	108.7(3)	N1–C1–Cα	112.4(3)	N2–C2–Cα	115.4(3)
O1–C3–O5	124.0(3)	O1–C3–C4	119.7(3)	O5–C3–C4	116.2(3)
N1–C4–C3	110.0(3)	O2–C5–O6	124.8(4)	O2–C5–C6	119.1(4)
O6–C5–C6	116.1(3)	N2–C6–C5	109.8(3)	O3–C7–O7	124.6(4)
O3–C7–C8	119.4(3)	O7–C7–C8	116.1(3)	N1–C8–C7	113.5(3)
O4–C9–O8	124.3(3)	O4–C9–C10	118.6(3)	O8–C9–C10	117.1(3)
N2–C10–C9	112.2(3)	C1–Cα–C2	112.0(3)		

[a] e.s.d.s given in parentheses.

TABLE VI. Intramolecular Bond Distances (Å) for $Li[Fe(eddda)]\cdot 3H_2O$ [a]

Bond		Bond		Bond	
Fe–O5	1.929(4)	Fe–O6	1.949(4)	Fe–O7	2.003(4)
Fe–O8	2.001(4)	Fe–N1	2.205(4)	Fe–N2	2.199(4)
O1–C3	1.232(8)	O2–C5	1.234(7)	O3–C7	1.227(7)
O4–C9	1.237(7)	O5–C3	1.302(7)	O6–C5	1.288(7)
O7–C7	1.293(7)	O8–C9	1.276(7)	N1–C1	1.496(7)
N1–C4	1.487(7)	N1–C8	1.486(7)	N2–C2	1.490(8)
N2–C6	1.492(7)	N2–C10	1.497(7)	C1–C2	1.514(9)
C3–Cβ	1.502(9)	C4–Cβ	1.529(9)	C5–Cγ	1.510(9)
C6–Cγ	1.514(9)	C7–C8	1.516(8)	C9–C10	1.507(8)

[a] e.s.d.s given in parentheses.

N–Fe–N bond angles, respectively, among the four related Fe(III) complexes, $[Fe(trdta)]^-$, $[Fe(eddda)]^-$, six-coordinate $[Fe(edta)]^-$ [5], and seven-coordinate $[Fe(edta)(H_2O)]^-$ [14]. Though each bond distance is slightly longer in the seven-coordinate edta complex, it does not appreciably depend on the kind of the polyaminocarboxylate ligands for the six-coordinate complexes. In other words, when trdta or eddda is substituted for edta to form a six-coordinate complex, the resulting Fe–N and Fe–O bond distances remain almost intact. On the other hand, the bond angles around the Fe(III) ion are changed considerably. Briefly speaking, the structure of the $[Fe(eddda)]^-$ complex deviates the least from a regular octahedron, though all of these four complexes are more or less distorted.

It is generally accepted that the G chelate ring is more strained than the R chelate ring in the metal–edta complexes [15]. Then, if the G ring comprised of a five-membered glycine chelate is replaced with a six-membered β-alanine chelate, the strain will be relaxed to a considerable extent. Therefore, as expected the present eddda complex is the *trans*(O_5) isomer in which both of the two G rings are comprised of β-alanine parts of $eddda^{4-}$ [13, 15]. In fact, the deviation of the O_5–Fe–O_6 angle from 90°, a measure of the strain, is the least in *trans*(O_5)–$[Fe(eddda)]^-$ among the four related complexes (Table IX).

Comparison with Other Metal–trdta and –eddda Complexes

Structural data are now available on the edta, trdta and eddda complexes of Cr(III) [16, 12, 13], Co(III) [17, 11, 18], Rh(III) [19, 12, 20] and Fe(III). Here, our attention is focused on the comparison of the bond angles N–M–N and O–M–N among these complexes. They are plotted in Figs. 3 and 4, respectively, where the data for the Rh–edta complex refer to those for $[Rh(Hedta)(H_2O)]$ [19] in which the sixth coordination site is occupied by H_2O with one protonated carboxylate group of edta detached from the coordination sphere, and the data for the Fe–edta complex refer to those for six-coordinate $[Fe(edta)]^-$ [5]. It is evident in Figs. 3 and 4 that Fe(III) ion tolerates these angles deviating from an ideal angle of 90° more readily than other metal ions, when the chelate ring size is altered. In other words, Fe(III) ion does not greatly persist in adopting a regular octahedral structure, since it has a high-spin d^5 configuration for which no appreciable angular dependence of the ligand field stabilization is expected. By contrast, Cr(III) (d^3), Co(III) (low-spin d^6), and Rh(III) (low-spin d^6) complexes heavily

TABLE VII. Intramolecular Bond Angles (°) for $\mathrm{Li[Fe(eddda)]\cdot 3H_2O}$ [a]

Angle		Angle		Angle	
O5–Fe–O6	100.2(2)	O5–Fe–O7	98.9(2)	O5–Fe–O8	89.6(2)
O5–Fe–N1	89.9(2)	O5–Fe–N2	166.2(2)	O6–Fe–O7	88.4(2)
O6–Fe–O8	98.2(2)	O6–Fe–N1	165.5(2)	O6–Fe–N2	90.0(2)
O7–Fe–O8	168.2(2)	O7–Fe–N1	79.8(2)	O7–Fe–N2	90.7(2)
O8–Fe–N1	92.2(2)	O8–Fe–N2	79.6(2)	N1–Fe–N2	81.9(2)
Fe–O5–C3	129.9(4)	Fe–O6–C5	136.1(4)	Fe–O7–C7	120.5(4)
Fe–O8–C9	120.4(4)	Fe–N1–C1	106.0(3)	Fe–N1–C4	112.9(3)
Fe–N1–C8	108.0(3)	C1–N1–C4	108.8(4)	C1–N1–C8	109.4(4)
C4–N1–C8	111.5(4)	Fe–N2–C2	106.3(3)	Fe–N2–C6	110.6(3)
Fe–N2–C10	108.0(3)	C2–N2–C6	109.5(4)	C2–N2–C10	110.0(4)
C6–N2–C10	112.3(4)	N1–C1–C2	110.0(5)	N2–C2–C1	110.4(5)
O1–C3–O5	120.7(6)	O1–C3–Cβ	121.7(6)	O5–C3–Cβ	117.3(5)
N1–C4–Cβ	114.7(5)	O2–C5–O6	120.8(5)	O2–C5–Cγ	119.2(5)
O6–C5–Cγ	120.0(5)	N2–C6–Cγ	115.0(5)	O3–C7–O7	123.6(5)
O3–C7–C8	119.5(5)	O7–C7–C8	116.9(5)	N1–C8–O7	113.1(5)
O4–C9–O8	123.4(5)	O4–C9–C10	118.9(5)	O8–C9–C10	117.6(5)
N2–C10–C9	112.9(5)	C3–Cβ–C4	115.5(5)	C5–Cγ–C6	119.5(5)

[a] e.s.d.s given in parentheses.

TABLE VIII. Comparison of Fe–N and Fe–O Bond Lengths (Å)

Bond	[Fe(trdta)]$^-$	[Fe(eddda)]$^-$	[Fe(edta)]$^-$	[Fe(edta)(H$_2$O)]$^-$
Fe–N1	2.178(3)	2.205(4)	2.181(4)	2.319(2)
Fe–N2	2.209(3)	2.199(4)	2.178(3)	2.318(2)
Fe–O5	1.999(3)	1.929(4)	1.973(3)	2.096(2)
Fe–O6	1.975(3)	1.949(4)	1.967(3)	2.096(2)
Fe–O7	1.995(3)	2.003(4)	1.987(3)	1.977(2)
Fe–O8	1.987(3)	2.001(4)	1.970(3)	1.972(2)
Fe–OW				2.122(2)

TABLE IX. Comparison of O–Fe–O, O–Fe–N and N–Fe–N Bond Angles (°)

Angle	[Fe(trdta)]$^-$	[Fe(eddda)]$^-$	[Fe(edta)]$^-$	[Fe(edta)(H$_2$O)]$^-$
O5–Fe–O6	112.5(1)	100.2(2)	123.4(1)	142.4(1)
O5–Fe–N1	78.8(1)	89.9(2)	79.1(1)	72.3(1)
O6–Fe–N2	77.8(1)	90.0(2)	78.8(1)	71.7(1)
N1–Fe–N2	94.3(1)	81.9(2)	80.7(1)	73.5(1)
O7–Fe–N1	80.3(1)	79.8(2)	81.0(1)	79.0(1)
O8–Fe–N2	79.0(1)	79.6(2)	80.7(1)	78.4(1)

resist distorting from a regular octahedral structure, in order not to lose the ligand field stabilization. Judging from these deviations in bond angles, it is safely concluded that eddda encircles these metal ions most favorably in an octahedral environment.

Structural Characteristics in Relation to d^n Configuration

A number of transition metal–edta complexes have been so far subjected to an X-ray structural analysis. Available structural data lead us to state that only metal ions with a d^0, d^5(high-spin), or d^{10} configuration may adopt a coordination number (CN) other than 6 when complexed with edta^{4-}. Since these metal ions show no appreciable angular dependence of the ligand field stabilization, they do not hesitate to abandon an octahedral six-coordinate structure, as discussed earlier.

In Table X are summarized the ionic radius *r* of M ion (for CN = 6) [21], the M–O and M–N bond distances, and their difference *D*, involved in the M–edta complexes with d^0, d^5(high-spin), and d^{10}

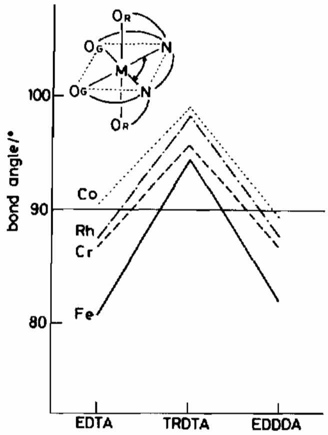

Fig. 3. Comparison of the N–M–N bond angles among M(III)–edta, –trdta, and –eddda complexes.

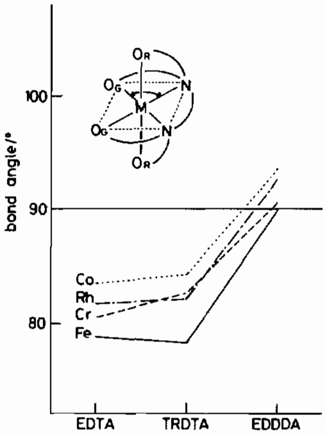

Fig. 4. Comparison of the N–M–O bond angles among M(III)–edta, –trdta, and –eddda complexes.

TABLE X. Comparison of Bond Lengths of edta^{4-} Complexes

	d^n	CN	r(M–O) (Å)	r(M–N) (Å)	D (Å)^a	r (Å)^b	Reference
Mg(II)	0	7	2.17	2.38	0.21	0.86	2
Al(III)	0	6	1.89	2.04	0.15	0.68	22
Ca(II)	0	8	2.41	2.67	0.26	1.14	23
Ti(IV)	0	7	1.95	2.30	0.35	0.75	3
Mn(II)	5	7	2.24	2.37	0.13	0.97	24
Fe(III)	5	7	2.04	2.31	0.27	0.79	14
Fe(III)	5	6	1.97	2.18	0.21	0.79	5
Zn(II)	10	6	2.08	2.15	0.07	0.88	25
Zr(IV)	0	8	2.13	2.43	0.30	0.86	26
Cd(II)	10	7	2.39	2.40	0.01	1.09	27
Sn(IV)	10	7	2.08	2.31	0.23	0.83	28
Fe(III)^c	5	7	2.05	2.29	0.24	0.79	29
Fe(III)^d	5	6	1.99	2.19	0.20	0.79	this work
Fe(III)^e	5	6	1.97	2.20	0.23	0.79	this work

$^a D = r(\text{M–N}) - r(\text{M–O})$. ^{b}Ionic radius for CN = 6; ref. 21. ^{c}cydta complex (cydta = *trans*-1,2-diaminocyclohexanetetraacetate). ^{d}trdta complex. ^{e}eddda complex.

configurations [22–29]. It is confirmed there that an increase in r and/or in the difference D favors a CN greater than 6, as Hoard *et al.* [2] have already pointed out. However, it is now possible to discuss the variation in CN for M–edta complexes in more detail. First of all, we assume here that the Fe(III) ion has a 'critical' ionic radius (0.79 Å) in determining the CN for edta complexes, since edta^{4-} encircles it both in six- and seven-coordinate structures and since both trdta and eddda, larger in size than edta, form a six-coordinate complex exclusively with the Fe(III) ion. Then, if an M ion has a greater r than 0.79 Å, its CN may exceed 6. This rule holds for most of the edta complexes listed in Table X. Ti(IV) and Zn(II) ions provide obvious exceptions; Ti(IV) ion, though smaller in size than the Fe(III) ion, takes a CN of 7, and Zn(II) ion, though larger in size than the Fe(III) ion, takes a CN of 6. These exceptions are interpreted in terms of the difference in charges on the metal ions, as follows. Since Ti(IV) ion is more highly charged than Fe(III) ion, it attracts the negatively charged oxygen atoms of edta^{4-} so favorably that the M–O bond is shortened relative to the M–N bond [3, 23]. As a result, the 'hole' created by expansion of the O–M–O bond angle *trans* to the N–M–N bond angle becomes big enough to accommodate one water molecule as an additional ligand. A similar interpretation applies to the large bond difference D in the Zr(IV) and Sn(IV) complexes which also adopt a CN greater than 6.

On the other hand, if a divalent metal ion of relatively large size carries a lower effective charge brought about by the shielding effect of d-electrons like Zn(II) ion does, its weak electrostatic interaction with the oxygen atoms of edta^{4-} renders the difference D so small that the resulting 'hole' will not be big enough to accommodate the seventh ligand. Since the Zn(II) ion forms a six-coordinate complex also with *o*-phenylenediaminetetraacetate (*o*-phdta^{4-}) [30] smaller in size than edta^{4-}, the 'critical' radius for divalent ions must be somewhat greater than 0.88 Å. The bond distance difference *D* is also small for the divalent Cd(II) ion which suffers a similar shielding effect, but its size is so large that it is forced to form a seven-coordinate complex with edta^{4-} and to form an eight-coordinate complex with *o*-phdta^{4-} [31] smaller in size than edta^{4-}.

The edta complexes of Mg(II) and Ca(II) ions (probably and Al(III) ion as well) should be treated separately from those of transition-metal ions. It is notable in Table X that Mg(II) and Ca(II) ions also have the bond distance difference *D* fairly large for divalent ions and that they thus take a CN greater than 6. The large *D* is probably due to the absence of the shielding effect of d electrons and to their inability to utilize the d orbitals efficiently in the complex formation with edta^{4-}; the covalent interaction of the Mg(II) or Ca(II) ion with the amine nitrogens is weak relative to the electrostatic interaction with the oxygen atoms. Consequently, the Mg(II) ion may well take a CN of 7, although it is smaller in size than the Zn(II) ion. The Ca(II) ion is so large that it forms an eight-coordinate complex, and the Al(III) ion is small enough to be encircled octahedrally by edta^{4-} alone.

Finally, it is worthwhile mentioning the structures of edta complexes of other first-transition-metal ions which have partially- but not half-filled d orbitals; the Cr(III) [16], Mn(III) [32], Co(III) [17], Co(II) [33], Ni(II) [34] and Cu(II) [25] complexes. Available data clearly indicate that all of them adopt in common a six-coordinate structure. Since they show more or less angular dependence of the ligand field stabilization, they resist departing from an octahedral structure. Furthermore, the former three tervalent ions are smaller in size than the 'critical' Fe(III) ion, and the latter three divalent ions are similar to or smaller in size than the almost 'critical' Zn(II) ion. Therefore, it follows that the two conditions for a six-coordinate structure are satisfied for all the above complexes. However, if a metal ion is fairly large in size and it can gain appreciable ligand field stabilization like the Ru(III) or Rh(III) ion (low-spin d^5 or d^6), it tends to take a peculiar six-coordinate structure of [M(Hedta)(H_2O)] [19, 35] in which the sixth coordination site is occupied by H_2O and one protonated acetate group of edta which otherwise forms one of the G rings is freed from coordination. This type of six-coordinate structure seems fairly stable, since such acid complexes have been isolated from acid solution for many metal ions such as Cr(III) [36], Fe(III) [37], Co(III) [38], Ni(II) [39], Cu(II) [39]*, Ga(III) [37], and Rh(III) [19], particularly when the overall charge on the complex disappears.

Supplementary Material

Observed and calculated structure factors and anisotropic thermal parameters are available from the authors on request.

References

1 R. H. Nuttall and D. M. Stalker, *Talanta, 24,* 355 (1977).
2 J. J. Stezowski, R. Countryman and J. L. Hoard, *Inorg. Chem., 12,* 1749 (1973).
3 J. P. Fackler, Jr., F. J. Kristine, A. M. Mazany, T. J. Moyer and R. E. Shepherd, *Inorg. Chem., 24,* 1857 (1985).
4 N. V. Novozhilova, T. N. Polynova, M. A. Porai-Koshits, N. I. Pechurova, L. I. Martynenko and A. Khadi, *Zh. Strukt. Khim., 14,* 745 (1973).
5 Y. Kushi, K. Morimasa, K. Yoshitsugu and H. Yoneda, *35th Symposium on Coordination Chemistry,* Hiroshima, Japan, 1985, Abstr. 2B01.
6 M. D. Lind, J. L. Hoard, M. J. Hamor and T. A. Mamor, *Inorg. Chem., 3,* 34 (1964).
7 J. A. Weyh and R. E. Hamm, *Inorg. Chem., 7,* 2431 (1968).
8 W. Byers and B. E. Douglas, *Inorg. Chem., 11,* 1470 (1972).
9 T. Ashida, in T. Sakurai (ed.), 'The Universal Crystallographic Computation Program System', The Crystallographic Society of Japan, Tokyo, 1979.
10 C. K. Johnson, *Report ORNL-3794,* Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
11 R. Nagao, F. Marumo and Y. Saito, *Acta Crystallogr., Sect. B, 28,* 1852 (1972).
12 R. Herak, G. Srdanov, M. I. Djuran, D. J. Radanovic and M. Bruvo, *Inorg. Chim. Acta, 83,* 55 (1984).
13 F. T. Helm, W. H. Watson, D. J. Radanovic and B. E. Douglas, *Inorg. Chem., 16,* 2351 (1977).
14 J. M. Lopez-Alcala, M. C. Puerta-Vizcaino, F. Gonzalez-Vilchez, E. N. Duesler and R. E. Tapscott, *Acta Crystallogr., Sect. C, 40,* 939 (1984).
15 D. J. Radanovic and B. E. Douglas, *Inorg. Chem., 14,* 6 (1975).
16 Y. Kushi, K. Morimasa and H. Yoneda, *49th Annual Meeting of the Chemical Society of Japan,* Tokyo, Japan, 1984, Abstract 1N31.
17 H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc., 81,* 549 (1959).
18 K. Miyoshi *et al.*, unpublished work.
19 G. H. Y. Lin, J. D. Leggett and R. M. Wing, *Acta Crystallogr., Sect. B, 29,* 1023 (1973).
20 R. Herak, L. Manojlovic-Muir, M. I. Djuran and D. J. Radanovic, *J. Chem. Soc., Dalton Trans.*, 861 (1985).
21 R. D. Shannon, *Acta Crystallogr., Sect. A, 32,* 751 (1976).
22 T. N. Polynova, N. P. Belskaya, D. Tyurk de Garcia Banus, M. A. Porai-Koshits and L. I. Martynenko, *Zh. Strukt. Khim., 11,* 164 (1970).
23 B. L. Barnett and V. A. Uchtman, *Inorg. Chem., 18,* 2674 (1979).
24 S. Richards, B. Pedersen, J. V. Silverton and J. L. Hoard, *Inorg. Chem., 3,* 27 (1964); T. N. Polynova, N. N. Ananeva, M. A. Porai-Koshits, L. I. Martynenko and N. I. Pechurova, *Zh. Strukt. Khim., 12,* 335 (1971).

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*The structure of six-coordinate [M(II)(H_2edta)(H_2O)] type complexes has been discussed in this ref.

25 X. Solans, M. Font-Altaba, J. Oliva and J. Herrera, *Acta Crystallogr., Sect. C, 39,* 435 (1983).

26 A. I. Pozhidaev, M. A. Porai-Koshits and T. N. Polynova, *Zh. Strukt. Khim., 15,* 644 (1974).

27 X. Solans, S. Gali, M. Font-Altaba, J. Oliva and J. Herrera, *Acta Crystallogr., Sect. C, 39,* 438 (1983)

28 F. P. Remoortere, J. J. Flynn and F. P. Boer, *Inorg. Chem., 10,* 2313 (1971).

29 G. H. Cohen and J. L. Hoard, *J. Am. Chem. Soc., 88,* 3228 (1966).

30 S. Azuma, N. Nakasuka and M. Tanaka, *Acta Crystallogr., Sect. C, 42,* 1736 (1986).

31 N. Nakasuka, S. Azuma and M. Tanaka, *Acta Crystallogr., Sect. C, 42,* 673 (1986).

32 T. Lis, *Acta Crystallogr., Sect. B, 34,* 1342 (1978); J. Stein, J. P. Fackler, Jr., G. J. McClune, L. A. Fee and L. T. Chan, *Inorg. Chem., 18,* 3511 (1979).

33 E. F. K. McCandlish, T. K. Michael, J. A. Neal, E. C. Lingafelter and N. J. Rose, *Inorg. Chem., 17,* 1383 (1978).

34 E. Coronado, M. Drillon, A. Fuertes, D. Beltran, A. Mosset and J. Galy, *J. Am. Chem. Soc., 108,* 900 (1986).

35 T. Matsubara and C. Creutz, *Inorg. Chem., 18,* 1956 (1979).

36 L. E. Gerdon, N. A. Baenziger and H. M. Goff, *Inorg. Chem., 20,* 1606 (1981).

37 J. L. Hoard, C. H. L. Kennard and G. S. Smith, *Inorg. Chem., 2,* 1316 (1963); C. H. L. Kennard, *Inorg. Chim. Acta, 1,* 347 (1967).

38 H. Okazaki, K. Tomioka and H. Yoneda, *Inorg. Chim. Acta, 74,* 169 (1983).

39 G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc., 81,* 556 (1959); F. S. Stephens, *J. Chem. Soc. A,* 1723 (1969).

40 Y. Saito, M. Shimoi and H. Ogino, *56th Annual Meeting of Chemical Society of Japan,* Tokyo, Japan, 1988, Abstr. 2IVA01.

Note Added in Proof

It has been reported very recently that V(III) ion forms a seven-coordinate edta complex with $r(\text{M}-\text{O}) = 2.05$ Å and $r(\text{M}-\text{N}) = 2.22$ Å [40]. This unexpected result is attributed to the much bigger size of the V(III) ion than the 'critical' Fe(III) ion; Pauling's ionic radius is 0.74 Å for the V(III) ion and 0.64 Å for the Fe(III) ion. Anyway, the V(III) complex is, to our knowledge, the only one metal–edta complex with partially-filled d orbitals that adopts a CN greater than 6.