A Seven-Coordinate Structure of Iron(II)–Ethylenediamine-*N,N,N',N'*-tetraacetato Complex as Determined by X-Ray Crystal Analysis

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(Received January 11, 1993)

A single-crystal X-ray analysis has revealed that the Fe^{II}–edta complex, formulated as $Na_2[Fe(edta)(H_2O)]\cdot 2NaClO_4\cdot 6H_2O$, has a seven-coordinate structure close to a mono-capped trigonal prism (C_{2v}-CTP). The crystal data are as follows: Orthorhombic, *Pmnb*, $a=11.404(1)$, $b=23.573(2)$, $c=9.915(1)$ Å, and $Z=4$. In the complex anion, edta serves as a hexadentate ligand with its two N atoms at a unique edge and four O atoms at the corners of a quadrilateral face, which is capped with a water molecule. The presence of the labile water molecule in the first coordination sphere accounts for the kinetic lability of the Fe^{II}–edta complex, which has been frequently pointed out. A qualitative comparison of the molecular structures was made between the seven-coordinate Fe^{II}– and Fe^{III}–edta complex anions. The steric and electronic requirements for seven-coordination are also discussed concerning the transition-metal edta complexes.

Seven-coordinate metal complexes which adopt in most cases either a pentagonal-bipyramidal (PB) or mono-capped trigonal-prismatic (C_{2v}-CTP) structure, have attracted the continuing interest of coordination chemists,[1—4] because they are relatively rare and play key roles in associative substitution reactions of by-far common six-coordinate, octahedral metal complexes. It is well-known that hexadentate edta (ethylenediamine-*N,N,N',N'*-tetraacetate) sometimes forms seven-coordinate complexes with large metal ions, often with a water molecule as an additional ligand, and that they usually have spherically symmetric, or non-directional, electronic configurations, such as d^0, high-spin d^5, and d^{10}, which are in principle allowed to adopt any geometrical structure as far as crystal field stabilization is concerned.[5] However, a few exceptional seven-coordinate edta complexes have been known to date in which the central metal ion does not have such symmetric configurations: $[Os^{IV}(edta)(H_2O)]$ (low-spin d^4),[6] $[V^{III}(edta)(H_2O)]^-$ (d^2),[7] and $[Ti^{III}(edta)(H_2O)]^-$ (d^1).[8] In the present paper we describe our X-ray structure analysis of another example of such exceptional seven-coordinate edta complexes, $[Fe^{II}(edta)(H_2O)]^{2-}$, for which a structure close to a C_{2v}-CTP is established in the solid state.

Experimental

Synthesis of $Na_2[Fe^{II}(edta)(H_2O)]\cdot 2NaClO_4\cdot 6H_2O$. The Fe^{II}–edta complex was prepared by mixing freshly-prepared $FeCO_3\cdot Fe(OH)_2\cdot nH_2O$ with $Na_2H_2edta\cdot 2H_2O$ in a dilute aqueous $HClO_4$ solution which had been purged with N_2 gas in advance, followed by the addition of $NaHCO_3$ to adjust the solution so as to be almost neutral. All operations were carried out under an N_2 atmosphere, and special care had to be taken to manipulate the basic iron(II) carbonate, since it is highly sensitive to air. The addition of N_2-purged ethanol to the above-mentioned solution and standing it in a refrigerator for over two weeks led to the precipitation of faintly colored crystals, which were finally formulated as described above. The crystals are surprisingly stable against oxidation when dry, but slowly deliquesce upon prolonged exposure to air.

Structure Determination. A single crystal of suitable size was mounted on a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). The reflection intensities were collected with an ω scan technique and were corrected for absorption[9] and extinction.[10] Systematic absences of the reflections suggested either $P2_1nb$ (variant of No. 33) or *Pmnb* (variant of No. 62) as the possible space group of the crystal, the former being non-centrosymmetric and the latter being centrosymmetric. In the Wilson statistics part of the computer program, Monte Carlo–Multan,[11] since the distribution of the $|E|$ values for the present data set was closer to the theoretical one for a centrosymmetric space group, *Pmnb* was chosen.[12,13] A comparison of the number of formula units in the unit cell ($Z=4$) with that of the general positions (n) of *Pmnb* ($n=8$) revealed that half of the $[Fe^{II}(edta)(H_2O)]^{2-}$ ion is crystallographically unique. The crystal structure obtained after several cycles of a least-squares refinement demonstrated that the $[Fe^{II}(edta)(H_2O)]^{2-}$ ion lies in the same crystallographic mirror plane ($x=-1/4$) in which the Fe–OH_2 bond lies, and to which the axis passing through the two nitrogen atoms of the edta ligand is exactly normal.

All of the chelate rings of the edta showed appreciable disorder, which was found to be attributable to the presence of two conformers of the complex anion correlated with the crystallographic mirror plane.[14] The three methylene carbon atoms in the asymmetric unit were then treated as three pairs of disordered atoms, whereas the nitrogen atom and the two carboxylate groups were regarded as being non-disordered, due to their relatively small disorderedness. One of the two perchlorate anions in the crystallographic mirror plane also showed the same rigid-body disorder that is often found for a perchlorate anion. The anisotropic treatment was then applied to all non-hydrogen atoms, except for the disordered methylene carbon atoms, the anisotropic treatment of which led to highly distorted thermal ellipsoids. The hydrogen atoms on the methylene groups were generated at their ideal geometries; those of the water molecules were located in a difference Fourier map. With the fixed positional and isotropic thermal parameters for these hydrogen atoms, the R value was finally reduced to 0.040 after five cycles of

a full-matrix least-squares refinement. All of the computations were carried out on a Titan-750 computer. A summary of the crystallographic data is given in Table 1. Tables of the hydrogen atom coordinates, anisotropic thermal parameters of non-hydrogen atoms, all bond distances and angles, and a list of observed and calculated structure factors are deposited as Document No. 66034 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

Results and Discussion

Structural Characteristics of the $[Fe^{II}(edta)(H_2O)]^{2-}$ Anion. The final positional and thermal parameters for non-hydrogen atoms are given in Table 2. An ORTEP drawing of the complex anion is shown in Fig. 1, where the atomic numbering is also given; selected bond distances and angles within the complex anion are listed in Table 3.

It can be seen in Fig. 1 that the Fe^{II}–edta complex anion has an approximate C_2 symmetry, and that it adopts a seven-coordinate structure close to a mono-capped trigonal prism (C_{2v}-CTP). In the complex anion, edta serves as a hexadentate ligand with its two N ligand atoms at a unique edge,[2] and the four O atoms at the corners of a quadrilateral face; a water molecule caps the face to complete the seven-coordination. These structural characteristics are common to all seven-coordinate edta complexes with approximate C_{2v}-CTP structures, such as $Na_2[Mg^{II}(edta)(H_2O)]\cdot 5H_2O$,[15] $Na[V^{III}(edta)(H_2O)]\cdot 3H_2O$,[7] $NH_4[V^{III}(edta)(H_2O)]\cdot 2.5H_2O$,[7] $Mn^{II}[Mn^{II}(Hedta)(H_2O)]_2\cdot 8H_2O$,[16] $Li_2[Mn^{II}(edta)(H_2O)]\cdot 4H_2O$,[17] $[Sn^{IV}(edta)(H_2O)]\cdot H_2O$,[18] and $[Os^{IV}(edta)(H_2O)]\cdot H_2O$.[6]

The following characteristics are noted regarding the coordination geometry of the present complex anion. The coordination sphere around the Fe^{II} ion bears a higher symmetry, close to an ideal C_{2v} symmetry, than does any other CTP edta complex, since the $[Fe^{II}(edta)(H_2O)]^{2-}$ ion lies in the crystallographic mirror plane ($x=-1/4$). The two triangular faces defined by the O3, O5, and N atoms and by the O3′, O5′, and N′ atoms almost completely overlap each other[19] when they are projected onto the mirror plane; those of other CTP edta complexes, however, are considerably twisted to

Table 1. Crystal Data, Experimental Conditions, and Refinement Details

Chemical formula	$C_{10}H_{26}Cl_2FeN_2Na_4O_{23}$
Formula weight	761.03
Crystal size/mm^3	0.38×0.42×0.20
a/Å	11.404(1)
b/Å	23.573(2)
c/Å	9.915(1)
V/Å^3	2665.5(4)
Crystal system	Orthorhombic
Space group	*Pmnb* (variant of No. 62)
Z	4
D_m and D_x/Mg m^{-3}	1.99; 2.03
λ/Å	0.71073 (Mo $K\alpha$)
T/°C	25
Monochrometer	Graphite
μ/mm^{-1}	0.854
Transmission factor	0.705—0.883
Diffractometer used	Mac Science MXC3
2θ range	$3<2\theta<55°$
Collected area	$-h, +k, +l$
No. of reflections collected	3218
Used ($\|F_o\|>3\sigma(F_o)$)	2757
Source of Scattering Factors	a)
$\Delta\rho_{max}-\Delta\rho_{min}$/e Å^{-3}	0.76— −0.48
R b)	0.040
R_w b)	0.053

a) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," ed by J. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, England (1974), Vol. IV. b) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w^{-1}=\sigma^2(F_o)$.

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors (B_{eq}) of $Na_2[Fe(edta)(H_2O)]\cdot 2NaClO_4\cdot 6H_2O$

$$B_{eq}=4/3\sum_i\sum_j \beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$$

Atom	x	y	z	B_{eq}/Å^2
Fe[a]	−2500	2528.1(2)	−1282.0(5)	1.38(2)
Cl1[b]	2500	290.9(4)	−4864.3(9)	2.08(3)
Cl2[a]	−2500	457.8(5)	1024(1)	3.11(3)
Na1	14(1)	−324.1(5)	−3091(1)	2.75(3)
Na2[a]	−2500	1023.7(7)	−2536(2)	2.69(4)
Na3[b]	2500	1160.6(6)	2134(2)	2.26(4)
O1[a]	−2500	2474(1)	−3491(3)	2.70(8)
O2	229(2)	1316.3(8)	−894(2)	2.68(5)
O3	−1288(2)	1826.9(9)	−1578(2)	3.71(6)
O4	92(2)	3810.1(8)	−741(2)	2.70(5)
O5	−1264(2)	3230.6(8)	−1599(2)	2.64(5)
O6	560(2)	−649.8(9)	2989(2)	2.55(5)
O7	1004(2)	585.7(9)	1154(2)	2.85(6)
O8[b]	2500	1617(1)	−128(3)	2.74(8)
O9[a]	−2500	1420(2)	−4809(4)	3.03(8)
O10	1485(3)	−32(1)	−4606(3)	6.4(1)
O11[b]	2500	793(1)	−4066(4)	4.5(1)
O12[b]	2500	420(2)	−6264(3)	5.2(1)
O13[a]	−2500	516(2)	−410(4)	7.6(2)
O14[c]	−3574(8)	345(6)	1310(10)	11.8(5)
O15[c]	−2008(7)	949(3)	1688(8)	8.7(3)
O16[c]	−1654(7)	20(3)	1412(8)	5.1(2)
N	−1229(2)	2531.7(8)	571(2)	1.74(5)
C1	−526(2)	1704(1)	−742(2)	1.81(6)
C21[c]	−703(5)	1940(2)	673(5)	1.76(8)
C3	−563(2)	3385(1)	−703(3)	1.87(6)
C41[c]	−235(5)	2918(2)	294(5)	2.22(9)
C51[c]	−1866(5)	2666(3)	1783(6)	2.2(1)
C22[c]	−288(5)	2148(2)	338(6)	2.18(9)
C42[c]	−763(5)	3129(2)	706(5)	1.78(8)
C52[c]	−1945(5)	2400(2)	1799(6)	2.06(9)

a) Lying in the mirror plane, $x=-1/4$. b) Lying in the mirror plane, $x=1/4$. c) Weighted as half.

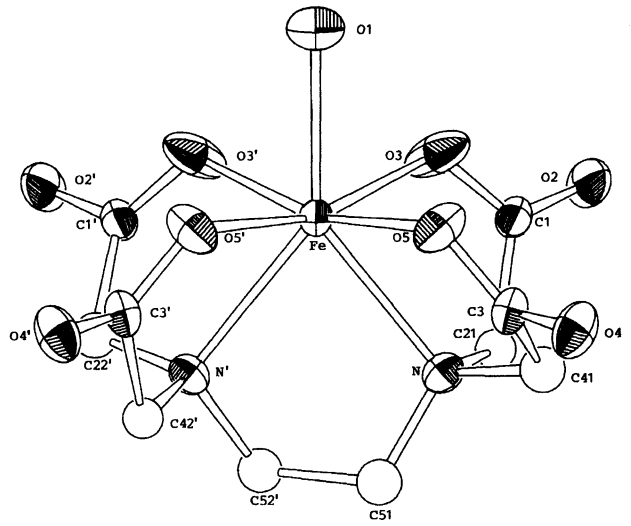

Fig. 1. ORTEP drawing of the Fe(II)–edta complex anion. Disordered carbon atoms are indicated by open circles. Hydrogen atoms are omitted for clarity.

Table 3. Bond Distances and Angles around Fe^{II}

Bond distances (Å)			
Fe–O1	2.194(3)	Fe–O5	2.198(2)
Fe–O3	2.174(2)	Fe–N	2.340(2)
Bond angles (°)			
O1–Fe–O3	79.71(8)	O5–Fe–N	73.28(7)
O1–Fe–O5	84.29(7)	O5–Fe–$O3^i$	164.00(8)
O1–Fe–N	141.63(5)	O5–Fe–$O5^i$	79.8(1)
O3–Fe–O5	98.39(8)	O5–Fe–N^i	120.46(7)
O3–Fe–N	73.45(7)	N–Fe–$O3^i$	120.16(8)
O3–Fe–$O3^i$	78.9(1)	N–Fe–$O5^i$	120.46(7)
O3–Fe–$O5^i$	164.00(8)	N–Fe–N^i	76.5(1)
O3–Fe–N^i	120.16(8)		

Symmetry code; i=$-0.5-x$, y, z.

each other in most cases.[7] The dihedral angle between these triangular faces is 3.02° in the present crystal, indicating that the two faces are almost parallel to each other, as is often the case.[7] The Fe^{II} ion deviates by 0.304 Å from the quadrilateral plane defined by the four O atoms, (O3, O5, O3′, and O5′).

The Fe^{II}–OH_2 bond distance in the present complex is 2.19 Å, somewhat greater than both the Fe^{II}–OH_2 distance (2.13 Å) in Mohr's salt, $((NH_4)_2Fe(SO_4)_2\cdot 6H_2O)$ and the Fe^{III}–OH_2 distance (2.12 Å) in $[Fe^{III}(edta)(H_2O)]^-$.[20] Thus, the presence of the labile water molecule in the coordination sphere accounts for the kinetic lability of the Fe^{II}–edta complex which has been pointed out frequently.[21—23]

It is not necessarily meaningful to compare the respective metal-ligand bond distances directly between the seven-coordinate Fe^{II}– and Fe^{III}–edta complexes, since they adopt different geometries (C_{2v}-CTP and PB,[20] respectively). However, if we confine ourselves to a qualitative comparison of the average bond distances, the Fe^{II}–O (carboxylato) bond (2.19 Å) is longer by 0.15 Å than the corresponding Fe^{III}–O bond (2.04 Å), whereas the Fe^{II}–N bond (2.34 Å) is almost comparable in length to the Fe^{III}–N bond (2.32 Å). Taking into account the radius difference of 0.14 Å between the Fe^{II} and Fe^{III} ions estimated from their oxides,[24] the Fe^{II}–N bond is shorter and/or the Fe^{III}–N bond is longer than expected, indicating that the Fe^{II} ion has a stronger affinity for the amine ligand than does the Fe^{III} ion. This is in complete agreement with our earlier assertion[25] that the greater is the ligand field stabilization that the central metal ion gains, the greater is its affinity for the amine ligand in edta-type metal complexes.

Although some seven-coordinate Fe^{II} complexes are known, most of them have a planar and/or macrocyclic pentadentate ligand in the equatorial plane, with two additional ligands in axial positions. They therefore adopt ligand-enforced PB structures.[4,26—29] The C_{2v}-CTP structure found in the present study is rather rare at present for Fe^{II} complexes.

Steric and Electronic Requirements for Seven-Coordinate edta Complexes. The coordination number (*CN*) of a particular edta complex depends primarily on the charge and size of the central metal ion.[5,15,30,31] In Fig. 2 are classified most of the metal–edta complexes, whose structures have been determined by X-ray structure analyses, as a function of the metal-ion size (r_M) and *CN*. Those which are above each line for a particular *CN*, have spherically symmetric, or non-directional, electronic configurations, and thus gain no crystal field stabilization upon complexation; those below the line have non-symmetric electronic configurations. The two lanthanoid complexes are placed above the line for $CN=8$, because their partially-filled f-orbitals are practically nonbonding.

It is evident there that, in general, the higher is the charge on the metal ion and the larger is its size, the greater is the *CN* that it takes. For divalent metal ions, *CN* changes from 6 to 7 around Zn^{II} (0.88 Å[24]) or Mg^{II} (0.86 Å[24]) ion;[31] the critical radius between

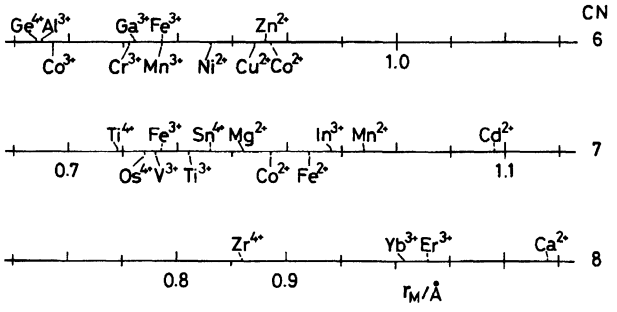

Fig. 2. Classification of some edta complexes as a function of the coordination number and metal ion size.

$CN=6$ and 7 is thus about 0.87 Å. Since the Fe^{II} ion has a radius of 0.92 Å,[24] somewhat larger than the critical radius, its edta complex may well take a CN of 7. On the other hand, the Co^{II} ion has a radius (0.885 Å[24]), which is comparable with the critical radius. Its edta complex therefore takes both six- and seven-coordinate structures,[32,33] like the edta complex of the Fe^{III} ion,[5,20,34] which has thus been proposed to have a critical radius (0.785 Å[24]) of between $CN=6$ and 7 for tervalent ions.[31] In this way, it is reasonable from a steric point of view that the Fe^{II}–edta complex has a seven-coordinate structure with a water molecule as an additional ligand.

The CN's of edta complexes depend on their electronic configurations as well; it is easily accepted that those metal ions which have spherically symmetric electronic configurations and, thus, gain no crystal field stabilization, form complexes with a CN greater than 6, if their ion sizes are sufficiently large to tolerate such CN's.[5] In fact, it is with these metal ions in most cases that such edta complexes are formed (Fig. 2).[15,30] Notable exceptions known to date are the seven-coordinate edta complexes with Ti^{III} (d^1),[8] V^{III} (d^2),[7] and Os^{IV} (low-spin d^4)[6] ions, which adopt a structure close to either a PB or C_{2v}-CTP with a water molecule as an additional ligand. However, they may well form such apparently exceptional seven-coordinate edta complexes as jugded from an electronic point of view, since all of the d-electrons in these complexes go into the two lower-lying d-orbitals, which are completely, or almost completely, σ-nonbonding in a PB or C_{2v}-CTP environment, respectively.[2,8] In other words, these seven-coordinate edta complexes are electronically as stable as the corresponding six-coordinate, octahedral (Oh) complexes which have three lower-lying and σ-nonbonding d-orbitals, provided that they have a d^1, d^2, low-spin d^3, or low-spin d^4 configuration. In fact, several seven-coordinate complexes are known for transition-metal ions with these configurations;[1—3] if the ligands are strong π-acceptors, such as CN^-, CNR, or CO, seven-coordination is favored over six-coordination, because the two lower-lying d-orbitals to be occupied in a PB or C_{2v}-CTP environment are now more strongly π-bonding than are the three lower-lying d-orbitals in an Oh environment.[1—3,8]

The same argument as above applies to transition-metal ions with high-spin d^6 and d^7 configurations, e.g., Fe^{II} and Co^{II} ions, since they correspond to d^1 and d^2 ions, respectively, to both of which a spherically symmetric high-spin d^5 configuration is added. As a result, their electronic configurations allow them to adopt seven-coordinate structures, if their radii are sufficiently large, as discussed above.[5,15,30,31] In fact, two seven-coordinate edta complexes have already been described for Co^{II} ion.[32] In this way, it is reasonable, based on an electronic consideration as well, that an Fe^{II} ion with a high-spin d^6 configuration forms a seven-coordinate edta complex, like the Ti^{III} ion with a d^1 configuration.

Finally, it should be noted that the critical radii between $CN=6$ and 7 are successfully used to predict the CN's of edta complexes only when the central metal ions have one of the spherically symmetric configurations (d^0, high-spin d^5, and d^{10}) and of the d^1, d^2, low-spin d^3, low-spin d^4, high-spin d^6, and high-spin d^7 configurations mentioned above. For example, the Mn^{III} ion (high-spin d^4) has a radius comparable to the critical radius of 0.785 Å for tervalent ions, but forms only a six-coordinate edta complex.[35,36] Similarly, Ru^{III} low-spin d^5), Rh^{III} (low-spin d^6), and Ir^{III} (low-spin d^6) ions all form six-coordinate edta complexes,[37—39] though their radii (0.82, 0.805, and 0.82 Å,[24] respectively) are large enough to tolerate a CN of 7.[40] In contrast, the V^{III} (d^2) ion has a radius of 0.78 Å, which is slightly smaller than the critical radius, but forms a seven-coordinate edta complex exclusively.[7] This is because the electronic requirement for $CN=7$ is fulfilled for the V^{III} ion. For the Ti^{III} ion, both the steric and electronic requirements for seven-coordination are so nicely met that its edta complex is always seven-coordinate.[8,41] These observations lead us to conclude that both the sizes and electronic configurations of the central metal ions must be taken into account in order to interpret the CN's of their edta complexes.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 03233222 from the Ministry of Education, Science and Culture.

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a similar structure and a comparable R value (0.038). However, many chemically equivalent bonds became more disparate in length for $P2_1nb$, and standard deviations of the structural parameters for $P2_1nb$ were five times as large as those for $Pmnb$. These phenomena have been discussed in detail by R. E. Marsh et al. (Ref. 13). See also the deposited Tables.

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