The Molecular Structure of the *trans*(O_5) Isomer of (Ethylenediamine-*N,N'*-diacetato-*N,N'*-di-3-propionato)cobaltate(III), *trans*(O_5)-$[Co(eddda)]^-$ Determined by X-ray Analysis and its Structural Comparison with some Metal(III) Complexes of Related Ligands

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Abstract

The crystal structure of $Na[Co(eddda)]\cdot 0.5NaClO_4\cdot 1.5H_2O$ (eddda = ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate) was determined by single crystal X-ray diffraction techniques. The crystal is monoclinic with the space group $P2/c$, $a = 14.213(4)$, $b = 8.247(3)$, $c = 15.251(4)$ Å, $\beta = 92.99(2)°$ and $Z = 4$. The complex anion is a *trans*(O_5) isomer in which the cobalt(III) ion is surrounded octahedrally by the two nitrogen and four oxygen atoms of eddda with the two five-membered glycine chelate rings in *trans* positions. Detailed comparison of the structural parameters among *trans*(O_5)-$[M(eddda)]^-$ (M = Co(III), Cr(III), Fe(III) and Rh(III)) and other related complexes of edta-type ligands revealed that the Co(III) and Rh(III) complexes are less distorted from a regular octahedral structure than the Cr(III) complexes and much less than the Fe(III) complexes, and that eddda encircles the M(III) ions more favorably than 1,3-pdta (1,3-propanediamine-*N,N,N',N'*-tetraacetate) and much more than edta, both of which are capable of forming five-membered glycine and five- or six-membered diamine chelate rings only.

Introduction

In the course of our structural studies on transition-metal complexes with edta-type ligands, it has been claimed that Fe(III) ion is somewhat too big in size to be surrounded octahedrally by edta alone, and that 1,3-pdta (1,3-propanediamine-*N,N,N',N'*-tetraacetate) and eddda (ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate) capable of forming longer chelate ring(s) can form more cosy and less distorted complexes with Fe(III) ion [1, 2]. That the same holds for the Co(III) ion is seen when the molecular structure is compared in $[Co(edta)]^-$ and $[Co(1,3\text{-}pdta)]^-$, both of which have been already subjected to X-ray structure analysis [3, 4]. To our surprise, structural data are not available on another Co(III) complex, $[Co(eddda)]^-$, though the molecular structures of the corresponding Cr(III) [5], Fe(III) [1] and Rh(III) [6] complexes are already known. In the present study, the molecular structure of $[Co(eddda)]^-$ is determined by X-ray crystal structure analysis, and the structural parameters are compared among $[M(edta)]^-$, $[M(1,3\text{-}pdta)]^-$ and $[M(eddda)]^-$ complexes (M = Co(III), Cr(III), Fe(III) and Rh(III)).

Experimental

Preparation of Complex

To an aqueous concentrated solution of $[Co(eddda)]^-$ prepared by the literature method [7] was added $NaClO_4$ to obtain crystals of $Na[Co(eddda)]\cdot 0.5NaClO_4\cdot 1.5H_2O$.

X-ray Measurements

Determination of cell constants and collection of intensity data of reflection were carried out on a Syntex diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Unit cell constants were determined by the least-squares refinement of 25 reflections. Intensity data were collected by an ω scan mode up to $2\theta = 55°$. No correction was made for the absorption effect ($\mu(\text{Mo K}\alpha) = 10.9$ cm^{-1}). Out of 4391 reflections measured, 3264 reflections with $|F_o| > 3\sigma(F_o)$ were included in the structural analysis.

Crystal Data

Monoclinic, space group $P2/c$, $a = 14.213(4)$, $b = 8.247(3)$, $c = 15.251(4)$ Å, $\beta = 92.99(2)°$, $D_c = 1.810$ g cm^{-3}, $V = 1785.2$ Å^3, and $Z = 4$.

Determination and Refinement of Structure

The structure was solved by a routine application of a standard heavy-atom method, as before [1, 2],

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TABLE 1. Positional and thermal parameters for Na[Co(eddda)]·$0.5NaClO_4$·$1.5H_2O$[a]

Atom	x	y	z	B_{eq} (Å^2)[b]
Co	0.27311(4)	0.19792(7)	0.07838(3)	1.6
O1	0.4837(2)	0.2514(5)	−0.0874(2)	3.1
O2	0.3915(2)	−0.0694(4)	0.2659(2)	2.8
O3	0.3583(3)	0.5934(5)	0.1944(3)	4.5
O4	0.1213(3)	−0.1354(5)	−0.0418(3)	4.2
O5	0.3911(2)	0.2135(4)	0.0218(2)	2.4
O6	0.3330(2)	0.0213(4)	0.1394(2)	2.4
O7	0.3208(2)	0.3373(4)	0.1683(2)	2.5
O8	0.2281(2)	0.0573(4)	−0.0118(2)	2.3
N1	0.2186(3)	0.3893(5)	0.0210(2)	2.2
N2	0.1534(2)	0.1603(5)	0.1333(2)	2.1
C1	0.1137(3)	0.3704(7)	0.0257(4)	3.2
C2	0.0955(3)	0.3085(7)	0.1164(4)	3.2
C3	0.4094(3)	0.2851(6)	−0.0500(3)	2.3
C4	0.2415(4)	0.4024(7)	−0.0738(3)	3.2
C5	0.3249(3)	−0.0154(6)	0.2206(3)	2.2
C6	0.1657(3)	0.1356(7)	0.2308(3)	2.8
C7	0.3168(3)	0.4895(6)	0.1509(3)	2.6
C8	0.2522(4)	0.5364(6)	0.0720(3)	2.8
C9	0.1540(3)	−0.0276(6)	0.0049(3)	2.6
C10	0.1089(3)	0.0156(6)	0.0895(3)	2.7
Cβ	0.3465(4)	0.4155(7)	−0.0879(3)	3.6
Cγ	0.2283(3)	−0.0063(8)	0.2590(3)	3.3
Na1	0.5015(1)	0.0593(3)	0.1310(1)	2.7
Na2[c]	0.50000(0)	0.7183(3)	0.25000(0)	2.4
Cl[c]	0.00000(0)	0.6704(2)	0.25000(0)	3.5
OCl1	−0.0539(7)	0.5445(14)	0.2043(6)	6.1
OCl2	0.0971(6)	0.6420(12)	0.2377(8)	6.1
OCl3	−0.0185(9)	0.6636(13)	0.3396(6)	6.7
OCl4	−0.0260(8)	0.8239(12)	0.2143(8)	8.1
OW1	0.3818(2)	0.1676(5)	0.4549(2)	3.3
OW2[c]	0.50000(0)	0.2564(7)	0.25000(0)	3.4

[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'. [c] Atoms on special positions.

and the atomic parameters were refined anisotropically for non-hydrogen atoms by the block-diagonal least-squares methods. Since two orientations were possible for the perchlorate anion in the special position, the contribution of each orientation was treated as half. In the subsequent refinement were included the positions of hydrogen atoms assuming a bond distance of 1.09 Å for each C–H bond and tetrahedral angles around each carbon atom. The final refinement including these hydrogen atoms with isotropic temperature factors caused the R value to converge to 0.050, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. In the refinement, the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w was set equal to unity.

All the atomic scattering factors were taken from Cromer and Waber [8]. The final atomic coordinates for non-hydrogen atoms with the thermal parameters are given in Table 1, according to the numbering schemes adopted in Fig. 1. All the computations were carried out on a HITAC computer at the Hiroshima

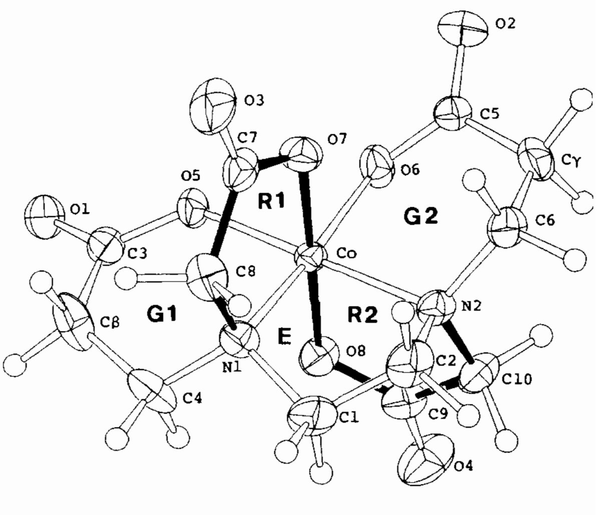

Fig. 1. Molecular structure of *trans*(O_5)-[Co(eddda)]$^-$.

TABLE 2. Intramolecular bond distances (Å) in *trans*(O_5)-[Co(eddda)]$^{-a}$

Bond		Bond		Bond	
Co–O5	1.930(3)	Co–O6	1.905(3)	Co–O7	1.888(3)
Co–O8	1.885(3)	Co–N1	1.946(4)	Co–N2	1.961(4)
O1–C3	1.258(6)	O2–C5	1.226(6)	O3–C7	1.217(7)
O4–C9	1.216(6)	O5–C3	1.283(6)	O6–C5	1.286(6)
O7–C7	1.283(6)	O8–C9	1.301(6)	N1–C1	1.504(7)
N1–C4	1.503(7)	N1–C8	1.505(6)	N2–C2	1.488(7)
N2–C6	1.501(7)	N2–C10	1.492(6)	C1–C2	1.510(8)
C3–Cβ	1.496(8)	C4–Cβ	1.522(8)	C5–Cγ	1.522(8)
C6–Cγ	1.519(8)	C7–C8	1.525(7)	C9–C10	1.512(7)

^{a}e.s.d.s given in parentheses.

TABLE 3. Intramolecular bond angles (°) in *trans*(O_5)-[Co(eddda)]$^{-a}$

Angle		Angle		Angle	
O5–Co–O6	83.9(1)	O5–Co–O7	89.8(1)	O5–Co–O8	89.1(1)
O5–Co–N1	94.6(2)	O5–Co–N2	174.6(2)	O6–Co–O7	88.7(1)
O6–Co–O8	90.7(1)	O6–Co–N1	175.6(2)	O6–Co–N2	92.6(2)
O7–Co–O8	178.8(2)	O7–Co–N1	87.3(2)	O7–Co–N2	94.2(2)
O8–Co–N1	93.4(2)	O8–Co–N2	86.9(2)	N1–Co–N2	89.2(2)
Co–O5–C3	129.2(3)	Co–O6–C5	126.2(3)	Co–O7–C7	115.8(3)
Co–O8–C9	115.8(3)	Co–N1–C1	105.5(3)	Co–N1–C4	112.9(3)
Co–N1–C8	108.3(3)	C1–N1–C4	108.6(4)	C1–N1–C8	110.4(4)
C4–N1–C8	111.1(4)	Co–N2–C2	106.3(3)	Co–N2–C6	112.7(3)
Co–N2–C10	107.0(3)	C2–N2–C6	108.5(4)	C2–N2–C10	111.2(4)
C6–N2–C10	111.1(4)	N1–C1–C2	107.2(4)	N2–C2–C1	108.5(4)
O1–C3–O5	119.9(4)	O1–C3–Cβ	118.9(5)	O5–C3–Cβ	121.1(4)
N1–C4–Cβ	113.8(4)	O2–C5–O6	121.6(4)	O2–C5–Cγ	119.1(4)
O6–C5–Cγ	119.1(4)	N2–C6–Cγ	114.9(5)	O3–C7–O7	124.1(5)
O3–C7–C8	120.4(5)	O7–C7–C8	115.4(4)	N1–C8–C7	111.4(4)
O4–C9–O8	124.5(5)	O4–C9–C10	120.4(5)	O8–C9–C10	115.1(4)
N2–C10–C9	112.4(4)	C3–Cβ–C4	117.7(5)	C5–Cγ–C6	117.1(5)

^{a}e.s.d.s given in parentheses.

University Information Precessing Center. The computer programs used were UNICS-III [9] and ORTEP [10].

Results and Discussion

Description of Molecular Structure

The molecular structure (ORTEP) of the complex anion in Na[Co(eddda)]$\cdot$0.5NaClO$_4\cdot$1.5H$_2$O is depicted in Fig. 1, where the numbering schemes adopted for respective atoms are also given. The bond distances and angles within the complex anion are given in Tables 2 and 3, respectively.

Figure 1 shows that Co(III) ion is encircled by all of the six ligand atoms (2N and 4O) of eddda to form an octahedral complex, and that the complex is a *trans*(O_5) isomer with the two glycine chelate rings in *trans* positions, which is more stable than other two possible *trans*(O_5O_6) and *trans*(O_6) isomers [7]. The complex anion as a whole is similar in structure to the corresponding Cr(III) [5] and Rh(III) [6] complexes, but to a lesser extent to the Fe(III) complex which deforms considerably from a regular octahedral structure [1].

Comparison of Bond Distances

Table 4 compares the M–N and M–O bond distances among [M(edta)]$^-$ [3, 11, 12], [M(1,3-pdta)]$^-$ [4, 13, 1], *trans*(O_5)-[M(eddda)]$^-$ [5, 1, 6], and [M(Hedta)(H$_2$O)] [14–17] complexes (M = Co(III), Cr(III), Fe(III) and Rh(III)). It is seen there that the M–N and M–O bond distances in *trans*(O_5)-[Co(eddda)]$^-$ are almost similar to the corresponding distances in [Co(edta)]$^-$ and [Co(1,3-pdta)]$^-$, and that the M–O5 and M–O6 bonds lying in the equatorial plane are on average longer than the axial M–O7 and M–O8 bonds, which holds not only for

TABLE 4. Comparison of M–N and M–O bond distances (Å) in $[M(edta)]^-$, $[M(1,3\text{-}pdta)]^-$, *trans*(O_5)-$[M(eddda)]^-$ and $[M(Hedta)(H_2O)]$ [a]

Complex	M–N1	M–N2	M–O5	M–O6	M–O7	M–O8	Reference
$[Co(edta)]^-$	1.921(8)	1.929(8)	1.945(7)	1.946(7)	1.897(7)	1.887(7)	3
$[Co(1,3\text{-}pdta)]^-$	1.966(9)	1.966(9)	1.904(9)	1.904(9)	1.861(8)	1.861(8)	4
$[Co(eddda)]^-$	1.946(4)	1.961(4)	1.930(3)	1.905(3)	1.888(3)	1.885(3)	this work
$[Cr(edta)]^-$	2.044	2.059	1.969	1.999	1.952	1.965	11
$[Cr(1,3\text{-}pdta)]^-$	2.065(5)	2.065(6)	1.960(5)	1.973(5)	1.941(5)	1.949(5)	13
$[Cr(eddda)]^-$	2.097(12)	2.072(12)	1.957(10)	1.971(10)	1.962(10)	1.952(10)	5
$[Fe(edta)]^-$	2.181(4)	2.178(3)	1.973(3)	1.967(3)	1.970(3)	1.987(3)	12
$[Fe(1,3\text{-}pdta)]^-$	2.178(3)	2.209(3)	1.999(3)	1.975(3)	1.995(3)	1.987(3)	1
$[Fe(eddda)]^-$	2.205(4)	2.199(4)	1.930(4)	1.949(4)	2.003(4)	2.001(4)	1
$[Rh(1,3\text{-}pdta)]^-$	2.031(3)	2.033(3)	2.038(2)	2.050(2)	2.004(2)	2.002(2)	13
$[Rh(eddda)]^-$	2.025(2)	2.019(2)	2.044(2)	2.046(2)	2.003(2)	2.012(2)	6
$[Co(Hedta)(H_2O)]$	1.986(6)	1.937(6)	1.927(5) [b]	1.913(6)	1.881(5)	1.896(5)	14
$[Cr(Hedta)(H_2O)]$	2.141(2)	2.041(2)	2.002(2) [b]	1.932(2)	1.980(2)	1.935(2)	16
$[Fe(Hedta)(H_2O)]$	2.235	2.154	1.990 [b]	1.934	2.004	1.955	17
$[Rh(Hedta)(H_2O)]$	2.082(3)	1.988(3)	2.096(2) [b]	2.027(3)	2.030(3)	2.001(3)	15

[a] e.s.d.s given in parentheses, which are not reported for $[Cr(edta)]^-$ and $[Fe(Hedta)(H_2O)]$. [b] Bond distance of $M\text{–}OH_2$.

trans(O_5)-$[Co(eddda)]^-$, $[Co(1,3\text{-}pdta)]^-$ and $[Co(edta)]^-$, but also for the corresponding three Cr(III) complexes, *trans*(O_5)-$[Rh(eddda)]^-$ and $[Rh(1,3\text{-}pdta)]^-$ listed in Table 4, where the data on $[Rh(edta)]^-$ are unfortunately absent because its structure analysis has not yet been made. In the corresponding Fe(III) complexes, on the other hand, the equatorial M–O5 and M–O6 bonds are on average shorter than the axial M–O7 and M–O8 bonds.

So-called 'acidic' edta complexes are known for some M(III) ions formulated as $[M(Hedta)(H_2O)]$ in which one acetate group of edta forming otherwise the G1 ring is protonated and is thus freed from coordination with the O5 site (defined in Fig. 1) occupied by H_2O. Structural data on these 'acidic' complexes given in Table 4 demonstrate that the equatorial M–O bonds are also longer on average than the axial M–O bonds in $[Co(Hedta)(H_2O)]$ [14], $[Rh(Hedta)(H_2O)]$ [15] and $[Cr(Hedta)(H_2O)]$ [16], whereas the reverse holds in $[Fe(Hedta)(H_2O)]$ [17], like in the 'normal' Fe(III) complexes with edta, 1,3-pdta and eddda.

It is noteworthy that, in the seven-coordinate $[Fe(edta)(H_2O)]^-$ [18] which is formed exclusively under usual conditions, the equatorial M–O bonds are by far longer than the axial ones, unlike in other Fe(III) complexes with edta-type ligands. Since $[Fe(edta)(H_2O)]^-$ has a pseudo pentagonal bipyramidal structure in which five ligand atoms occupy the equatorial plane with the other two ligand atoms in the axial-*trans* positions, the equatorial bonds should be longer.

Release of one protonated acetate group of edta from the coordination site O5 followed by occupation of the site with a water molecule leads to measurable changes in bond distances of the respective edta complexes. The remarkable changes are found in common for the M–N1 and M–O6 bonds, both of which lie on the same equatorial plane as the M–O5 bond lies on and are adjacent to the M–O5 bond directly affected by the 'dechelation'; the M–N1 bond is lengthened and the M–O6 bond *trans* to the M–N1 bond is instead shortened for all the edta complexes examined. Other M–L bonds are little or randomly affected if at all.

Another feature notable in Table 4 is that each of the M–O bond distances increases almost exactly with the increasing size of the M(III) ion (Co < Cr < Fe < Rh) for a particular edta-type ligand. In contrast, the M–N bonds are longer and shorter in the Fe(III) and Rh(III) complexes, respectively, than are expected from ionic radii; they increase in the order Co < Rh < Cr < Fe, which reflects a weaker and stronger affinity of Fe(III) and Rh(III) ions, respectively, for nitrogen ligators than for oxygen ligators. The long M–N bonds in the Fe(III) complexes may partly be responsible for the shorter equatorial M–O bonds *trans* to the M–N bonds than the axial M–O bonds. Actually, the equatorial M–O5 and M–O6 bonds are fairly short in $[Fe(edta)]^-$ and they are surprisingly short in *trans*(O_5)-$[Fe(eddda)]^-$. Moreover, the M–N bond distances change more sensitively to the size of M(III) ions than do the M–O bond distances. Exactly the same orders and trends as above are found for the M–N and M–O bonds in the 'acidic' $[M(Hedta)(H_2O)]$ complexes, except for the $M\text{–}OH_2$ bond which increases in length in the order Co < Fe < Cr < Rh [14–17].

Comparison of Bond Angles

The bond angles O–M–O, N–M–O and N–M–N were also compared. A thorough examination of

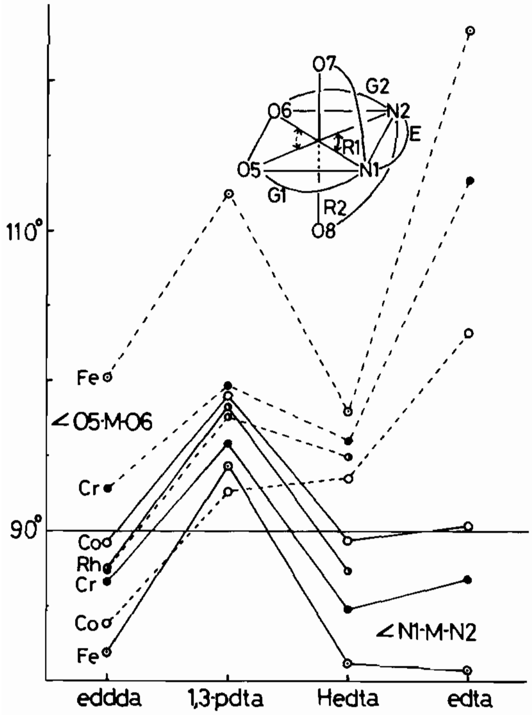

Fig. 2. Variation of bite angles L–M–L′ with edta-type ligands.

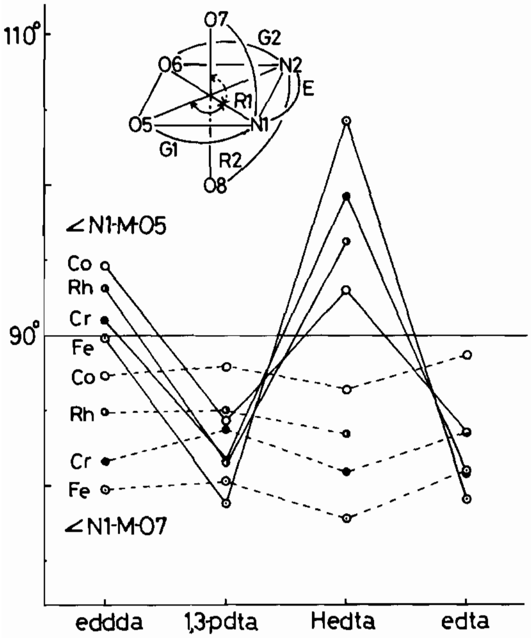

Fig. 3. Variation of bite angles L–M–L′ with edta-type ligands.

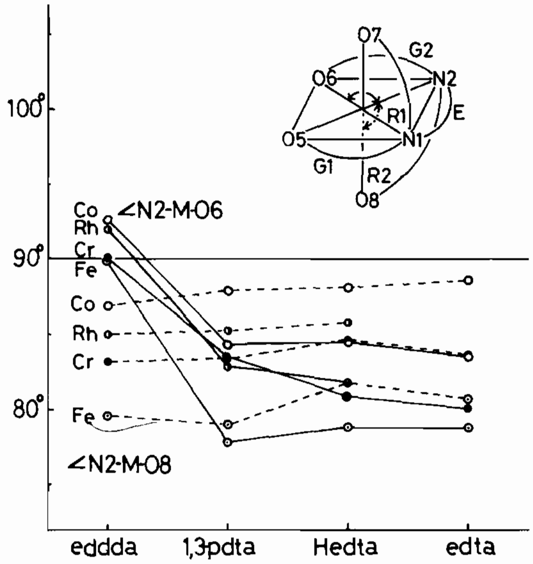

Fig. 4. Variation of bite angles L–M–L′ with edta-type ligands.

available structural data (plotted in Figs. 2–4) demonstrates that the bite angles associated with chelate rings, i.e. the N1–M–N2 (E ring), N1–M–O7 (R1 ring), N2–M–O8 (R2 ring), N1–M–O5 (G1 ring) and N2–M–O6 (G2 ring) angles, increase in the order Fe < Cr < Rh < Co, independently of the kind of edta-type ligand, though the latter two angles associated with the G rings are exceptionally wider, though slightly, in [Cr(1,3-pdta)]$^-$ than in [Rh(1,3-pdta)]$^-$. In contrast, the O5–M–O6 angle *trans* to the N1–M–N2 angle increases in the reversed order [1, 3, 11–13].

The same orders as above are found in the 'acidic' [M(Hedta)(H_2O)] complexes [14–17]; their bite angles associated with the E, R1, R2 and G2 chelate rings increase in the order Fe < Cr < Rh < Co, whereas the O6–M–OH_2 angle corresponding to the O6–M–O5 angle in the 'normal' complexes increases in the reverse order.

It is notable that the N1–M–OH_2 angle in the 'acidic' Hedta complex, which corresponds to the N1–M–O5 (G1 ring) angle in [M(edta)]$^-$, increases in the order Co < Rh < Cr < Fe, opposite to the order found in the N1–M–O5 angle of the 'normal' edta, 1,3-pdta and eddda complexes (Fig. 3). The above reversal of the angle order comes from the characteristic change in the N1–M–O5(OH_2) angle observed when [M(edta)]$^-$ rearranges to [M(Hedta)(H_2O)] upon protonation; the N1–M–O5(OH_2) angle increases more when it is smaller in [M(edta)]$^-$ (Fig. 3). Inversely, the O6–M–O5(OH_2) angle decreases more when it is greater in [M(edta)]$^-$ (Fig. 2).

In Figs. 2–4 are plotted the bite angles L–M–L′ associated with chelate rings as well as the O6–M–O5 angle, as a function of the edta-type ligands including Hedta. It is evident there that these angles change almost similarly with the change in the ligand, irrespective of the kind of M(III) ion, as mentioned

TABLE 5. Deviations of bite angles L–M–L′ and bond angle sums (°) of chelate rings in [M(Hedta)(H_2O)], [M(edta)]$^-$, [M(1,3-pdta)]$^-$ and *trans*(O_5)-[M(eddda)]$^-$

Complex	$\Sigma(\alpha_i - 90°)^2$	Chelate rings					Reference
		G1	G2	R1	R2	E	
[Co(Hedta)(H_2O)]	103.4		526.0	535.6	539.4	516.6	14
[Co(edta)]$^-$	330.3	524.6	534.0	538.6	537.0	516.5	3
[Co(1,3-pdta)]$^-$	169.2	526.5	526.5	539.5	539.5	673.8	4
[Co(eddda)]$^-$	114.9	689.3	682.6	538.2	537.2	516.7	this work
[Cr(Hedta)(H_2O)]	447.4		524.3	539.4	536.2	514.4	16
[Cr(edta)]$^-$	885.0	524.3	524.9	537.6	537.9	515.8	11
[Cr(1,3-pdta)]$^-$	359.7	525.9	530.8	538.6	539.7	672.8	13
[Cr(eddda)]$^-$	173.1	684.7	685.4	538.7	535.8	512.8	5
[Fe(Hedta)(H_2O)]	946.7		526.6	539.8	535.0	513.4	17
[Fe(edta)]$^-$	1703.1	527.5	524.9	535.8	537.1	515.0	12
[Fe(edta)(H_2O)]$^-$		525.4	525.3	538.1	531.1	517.4	18
[Fe(1,3-pdta)]$^-$	1221.9	524.0	520.0	535.3	531.6	671.1	1
[Fe(eddda)]$^-$	536.4	680.2	691.2	538.3	538.5	514.6	1
[Rh(Hedta)(H_2O)]	263.6		522.4	538.8	541.2	514.7	15
[Rh(1,3-pdta)]$^-$	356.7	524.5	529.0	539.2	539.7	673.8	13
[Rh(eddda)]$^-$	113.9	690.5	687.9	539.4	535.3	516.1	6

above, but their averaged deviations from an ideal angle of 90° increase in the order Co < Rh < Cr < Fe for each edta-type ligand. Since the crystal field stabilization is the greatest for the Co(III) and Rh(III) (low-spin d^6) complexes and is the least for the Fe(III) (high-spin d^5) complexes, it is natural that the bite angles in the former complexes heavily resist departing from 90°, while the Fe(III) complexes readily deviate from a regular octahedral structure [1]. In fact, the Fe(III) ion usually forms a pseudo pentagonal bipyramidal complex with edta, [Fe(edta)(H_2O)]$^-$ in which, for example, the N1–M–N2 angle is 73.5° much narrower than the corresponding angle of 80.7° in [Fe(edta)]$^-$ [17, 18]. Similar angle narrowing is found for the N2–M–O6 and N1–M–O5 angles as well, but only slight angle narrowing is observed for the 'axial' N1–M–O7 and N2–M–O8 angles in [Fe(edta)(H_2O)]$^-$. Other L–M–L′ angles are also more or less different between [Fe(edta)]$^-$ and [Fe(edta)(H_2O)]$^-$. Furthermore, the equatorial M–N and M–O bonds in the latter complex are considerably longer than the corresponding bonds in [Fe(edta)]$^-$. The above-mentioned structural differences are rationalized if we realize that [Fe(edta)(H_2O)]$^-$ has one additional ligand in the equatorial plane with the axial ligands almost intact, as compared with [Fe(edta)]$^-$.

How each complex deviates from a regular octahedral structure is evaluated from the value of $\Sigma(\alpha_i - 90°)^2$, where summation is carried out over all the L–M–L′ angles α_i (°) for respective complexes. The values are given in Table 5, which indicates that the Co(III) and Rh(III) complexes deviate the least and the Fe(III) complex the greatest, as expected, for each edta-type ligand, and that eddda encircles M(III) ions more favorably (if the resulting complex is a *trans*(O_5) isomer) than 1,3-pdta does and much more than edta does for all the M(III) ions examined here. As far as the edta complexes are concerned, the wider O5–M–O6 angle and narrower N1–M–O5 (G1 ring) and N2–M–O6 (G2 ring) angles than 90° are mainly responsible for their distorted structures; in short, the five-membered glycine chelate is not big enough to form a cosy G ring and the six-membered β-alanine chelate serves better for the formation of a less-strained G ring, as is evidenced by the preferential formation of the *trans*(O_5) isomers for the eddda complexes in which both of the two G rings are comprised of the six-membered β-alanine chelates. In contrast, the distortion of the 1,3-pdta complexes is attributed not only to the above wrong angles, but also to the wider N1–M–N2 (E ring) angle, as expected from the structural characteristics of 1,3-pdta forming a six-membered E ring.

Another interesting fact to be noted in Table 5 is that [M(Hedta)(H_2O)] is much less distorted than the corresponding [M(edta)]$^-$, which is mainly due to a remarkable improvement in the O6–M–O5(OH_2) angle toward an ideal angle of 90° (Fig. 2). In other words, the protonation takes place preferentially to the most strained G ring in [M(edta)]$^-$, and the resulting substitution of the protonated acetate group with a water molecule leads to the relaxation of the strain imposed on the G ring and to the improvement in the O6–M–O5(OH_2) angle.

Finally, bond angle sums of respective chelate rings are compared in Table 5 among all the relevant complexes. For a particular edta-type ligand, the sum of each chelate ring does not appreciably depend on the kind of M(III) ions, but it is either the greatest or the smallest in most of the Fe(III) complexes. For example, the G2 and R2 rings of 1,3-pdta have the smallest angle sums and those of eddda have the greatest sums in the Fe(III) complexes. These angle sums also point to considerably distorted structures of the Fe(III) complexes. It is also confirmed in Table 5 that each glycine chelate ring always has the angle sum closer to an ideal angle sum of 538.4° [13] when it forms an R ring than when it forms a G ring for all the edta and 1,3-pdta complexes, which has been accepted as evidence that the R ring is less strained than the G ring, when both rings are comprised of the glycine part of the edta-type ligands [7]. Each of the R rings (glycine chelates) of the eddda complexes also has the angle sum close to 538.4°.

Supplementary Material

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

References

1 T. Yamamoto, K. Mikata, K. Miyoshi and H. Yoneda, *Inorg. Chim. Acta, 150* (1988) 237.

2 T. Mizuta, T. Yoshida and K. Miyoshi, *Inorg. Chim. Acta, 165* (1989) 65.

3 H. A. Wealiem and J. L. Hoard, *J. Am. Chem. Soc., 81* (1959) 549; K. Okamoto, T. Tsukihara, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn., 51* (1978) 3534.

4 R. Nagao, F. Marumo and Y. Saito, *Acta Crystallogr., Sect. B, 28* (1972) 1852.

5 F. T. Helm, W. H. Watson, D. J. Radanovic and B. E. Douglas, *Inorg. Chem., 16* (1977) 2351.

6 R. Herak, L. Manojlovic, M. I. Djuran and D. J. Radanovic, *J. Chem. Soc., Dalton Trans.,* (1985) 861.

7 W. Byers and B. E. Douglas, *Inorg. Chem., 11* (1972) 1470; D. J. Radanovic and B. E. Douglas, *Inorg. Chem., 14* (1975) 6.

8 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974.

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, TN, 1965.

11 Y. Kushi, K. Morimasa and H. Yoneda, *49th Ann. Meet. the Chemical Society of Japan, Tokyo, Japan, 1984,* Abstr. 1N31.

12 N. V. Novozhilova, T. N. Polynova, M. A. Porai-Koshits, N. I. Pechurova, L. I. Martynenko and A. Khadi, *Zh. Strukt. Khim., 14* (1973) 745; Y. Kushi, K. Morimasa, K. Yoshitsugu and H. Yoneda, *35th Symp. Coordination Chemistry, Hiroshima, Japan, 1985,* Abstr. 2B01.

13 R. Herak, G. Srdanov, M. I. Djuran, D. J. Radanovic and M. Bruvo, *Inorg. Chim. Acta, 83* (1984) 55.

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

15 G. H. Y. Lin, J. D. Leggett and R. M. Wing, *Acta Crystallogr., Sect. B, 29* (1973) 1023.

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

17 C. H. L. Kennard, *Inorg. Chim. Acta, 1* (1967) 347; T. Mizuta, T. Yamamoto, K. Miyoshi and Y. Kushi, submitted for publication.

18 X. Solans, M. Font-Altaba and J. Garcia-Oricain, *Acta Crystallogr., Sect. C, 40* (1984) 635; J. M. Lopez-Alcala, M. C. Puerta-Vizcaino, F. Gonzalez-Vilchez, E. N. Duesler and R. E. Tapscott, *Acta Crystallogr., Sect. C, 40* (1984) 939; X. Solans, M. Font-Altaba and J. Garcia-Oricain, *Acta Crystallogr., Sect. C, 41* (1985) 525.