

Capped trigonal prism coordination geometry in a cobalt(II) chelate with a 24-membered macrocyclic ligand in which two ethylenediaminetetraacetato and two ethylenediamine groups are linked by amide bonds

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Abstract

An X-ray crystal analysis was carried out on the cobalt(II) compound of a 24-membered macrocyclic ligand with four pendant acetato groups, $\text{Co}_2(\text{C}_{24}\text{H}_{36}\text{N}_8\text{O}_{12}) \cdot 8\text{H}_2\text{O}$: the ligand molecule was prepared by a condensation reaction between ethylenediaminetetraacetic dianhydride and ethylenediamine. The cobalt(II) compound crystallized in the hexagonal space group $P6_2$ (or $P6_4$) with $a = 17.957(1)$, $c = 10.274(1)$ Å and $Z = 3$. Each ligand molecule is coordinated to two cobalt ions, which are crystallographically equivalent to each other. Each metal ion has six well-defined coordination bonds with two oxygen atoms from carboxylato groups (Co–O = 2.062 and 2.177 Å), an oxygen atom from an amide group (Co–O = 2.101 Å), two amine nitrogen atoms (Co–N = 2.229 and 2.300 Å) and an oxygen atom from a water molecule (Co–O = 2.058 Å). These six Co–X bonds form a quasi-trigonal prism around the Co atom. When an additional amide oxygen atom located at a distance of 2.720 Å from the Co atom is included in the coordination sphere, the coordination geometry is described as a capped trigonal prism. This less common coordination geometry is due to the inflexibility of the ligand molecule. A weak d–d band was observed at 515 nm in aqueous solution.

Introduction

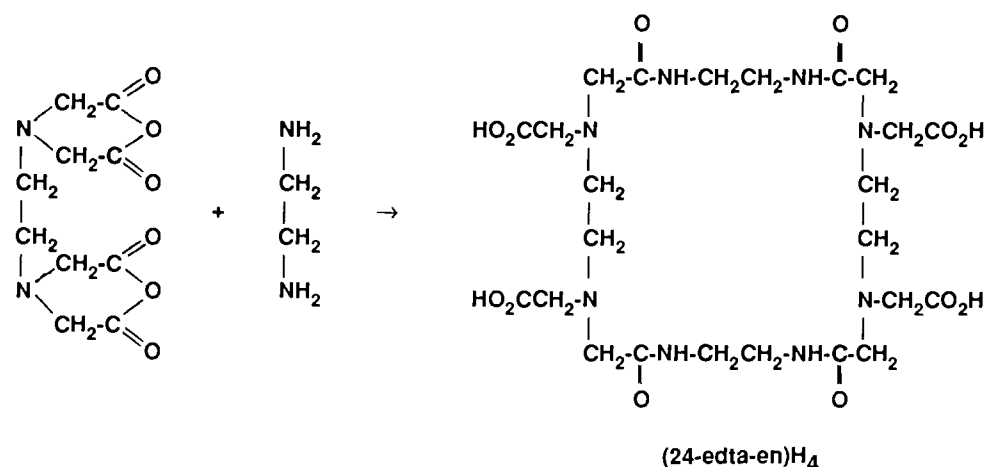
Metal chelates of macrocyclic ligands with pendant functional groups are of importance because several of their transition metal complexes are being investigated as potential magnetic resonance imaging agents or as X-ray contrast agents and, when appropriately functionalized, as radioimmunotherapeutic agents [1–9]. In our previous paper [10], we reported that a condensation reaction of ethylenediaminetetraacetic (edta) dianhydride with ethylenediamine (en) gave a new 24-membered macrocyclic ligand with four pendant acetato groups (Scheme 1); abbreviated as (24-edta-en) H_4 . The formation of the macrocyclic ring was confirmed by the X-ray crystal analysis of its manganese compound, $\text{Mn}_2(24\text{-edta-en}) \cdot 8\text{H}_2\text{O}$, in which each ligand molecule is coordinated to two manganese ions and forms the non-ionic metal chelate, $[\text{Mn}^{\text{II}}_2(24\text{-edta-en})^{4-}(\text{H}_2\text{O})_2]$. The coordination geometry around a manganese(II) ion is described as a monocapped trigonal prism resembling that reported for the $[\text{Mn}(\text{edta})\text{H}_2\text{O}]^{2-}$ com-

plex ion [11]. The coordination geometry in a metal chelate is defined by the crystal field stabilization (CFS) energy of the metal ion as well as the steric constraints imposed by the ligand [12]. In fact, edta chelates of transition metal ions have different types of coordination geometries depending on the nature of the central metal ions [11, 13]. Since manganese(II) has no CFS effect, our interest has been directed to the coordination geometry in the corresponding chelates of metal ions which have a considerable CFS energy. In this paper, we report the structure of the cobalt(II) complex, $\text{Co}_2(24\text{-edta-en}) \cdot 8\text{H}_2\text{O}$.

Experimental

The 24-membered macrocyclic ligand, (24-edta-en) H_4 , was synthesized by the method reported in our previous paper [10]. The cobalt(II) complex was prepared by a reaction between the ligand and excess cobalt(II) carbonate in water (without special precautions to exclude atmospheric oxygen). Recrystallization from an aqueous solution gave wine red crystals, which were suitable for X-ray analyses.

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Scheme 1.

The X-ray data collection was performed on a crystal of $\text{Co}_2(24\text{-edta-en}) \cdot 8\text{H}_2\text{O}$ with approximate dimensions of $0.27 \times 0.25 \times 0.17$ mm, using monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer. The space group was hexagonal $P6_2$ (No. 171) or $P6_4$ (No. 172). The cell parameters and the calculated cell volume were: $a = 17.957(1)$, $c = 10.274(1)$ Å, $V = 2869.3(6)$ Å³. For $Z = 3$ and molecular weight = 890.59 of $\text{Co}_2\text{C}_{24}\text{H}_{52}\text{N}_8\text{O}_{20}$, the calculated density was 1.55 g cm⁻³. The data were collected using the ω - 2θ scan technique in the range, $0 < 2\theta \leq 50^\circ$. A total of 5534 reflections was collected, of which 1791 were unique and not systematically absent. $\mu = 9.5$ cm⁻¹: no absorption corrections were made. The structure was solved by the Patterson heavy-atom method which revealed the position of a Co atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms of the ligand were located at their calculated positions. The structure was refined in full-matrix least-squares using 1456 reflections with intensities greater than 3 times their standard deviations. The final agreement factors were: $R = \sum |F_o - F_c| / \sum F_o = 0.043$ and $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.063$. The highest peak in the final difference Fourier had a height of $1.06(9)$ e Å⁻³ and the minimum negative peak $-0.12(9)$ e Å⁻³. All calculations were performed on a VAX computer using MolEN.

Results and discussion

The positional parameters are collected in Table 1. The Co-X distances are shown in Table 2. Figure 1 shows the molecular structure of the cobalt chelate. Two cobalt atoms that are coordinated to a ligand molecule are crystallographically equivalent to each

TABLE 1. Fractional coordinates and equivalent isotropic temperature factors for $\text{Co}_2(24\text{-edta-en}) \cdot 8\text{H}_2\text{O}$

Atom	x	y	z	B_{eq} (Å ²)
Co	0.41917(6)	0.16204(6)	0.000	2.28(2)
O(1)	0.3158(3)	0.1426(4)	-0.1314(6)	3.6(1)
O(2)	0.2151(3)	0.1760(3)	-0.1720(7)	3.6(1)
O(3)	0.4911(4)	0.2695(3)	-0.1133(6)	3.3(1)
O(4)	0.6137(4)	0.3933(4)	-0.1301(6)	4.4(2)
O(5)	0.3809(3)	0.0571(3)	0.1264(6)	3.1(1)
O(6)	0.5639(3)	0.1639(3)	0.0831(6)	3.1(1)
N(1)	0.3130(4)	0.1618(3)	0.1257(7)	2.5(1)
N(2)	0.4967(4)	0.2627(3)	0.1470(6)	2.2(1)
N(3)	0.3038(4)	-0.0116(4)	0.3027(7)	2.8(1)
N(4)	0.6171(4)	0.1686(4)	0.2832(7)	3.2(2)
C(1)	0.3542(5)	0.2211(5)	0.2370(8)	2.8(2)
C(2)	0.4407(4)	0.2939(4)	0.1975(8)	2.6(2)
C(3)	0.2641(5)	0.1888(5)	0.0447(8)	3.2(2)
C(4)	0.2643(5)	0.1661(5)	-0.0959(9)	2.9(2)
C(5)	0.5711(5)	0.3330(5)	0.0807(8)	3.0(2)
C(6)	0.5564(5)	0.3318(5)	-0.0648(8)	2.8(2)
C(7)	0.2601(4)	0.0714(4)	0.1708(9)	2.8(2)
C(8)	0.3194(4)	0.0374(4)	0.1998(7)	2.2(2)
C(9)	0.5278(4)	0.2295(4)	0.2537(8)	2.5(2)
C(10)	0.5719(4)	0.1844(4)	0.1987(7)	2.3(2)
C(11)	0.3568(5)	-0.0503(4)	0.3333(9)	3.0(2)
C(12)	0.6695(5)	0.1304(5)	0.252(1)	3.8(2)
O(w1)	0.4281(3)	0.0830(3)	-0.1366(6)	3.9(1)
O(w2)	0.500	0.000	-0.0157(8)	2.9(2)
O(w3)	0.1234(4)	0.8255(5)	0.2445(8)	5.4(2)
O(w4)	0.8979(5)	0.3365(5)	0.2643(8)	6.0(2)
O(w5) ^a	0.9675(8)	0.0442(7)	0.058(1)	4.0

$B_{\text{eq}} = (4/3)[a^2\beta_{1,1} + b^2\beta_{2,2} + c^2\beta_{3,3} + ab(\cos \gamma)\beta_{1,2} + ac(\cos \beta)\beta_{1,3} + bc(\cos \alpha)\beta_{2,3}]$. ^aO(w5) was disordered and refined isotropically with a fixed thermal parameter: the multiplicity was refined to be 0.46.

other. Each metal atom is coordinated to two carboxylate oxygen atoms, an amide oxygen atom, two amine nitrogen atoms and an oxygen atom from a water molecule with bond distances of 2.058–2.300 Å. Thus, a non-

TABLE 2. Selected bond distances (Å) for $M_2(24\text{-edta-en}) \cdot 8H_2O$

	Co	Mn ^a	$\Delta(\text{Co-Mn})$
M-X distances			
M-O(1) _{carboxylato}	2.177(6)	2.212(6)	-0.035
M-O(3) _{carboxylato}	2.062(5)	2.111(4)	-0.049
M-O(5) _{amide}	2.101(6)	2.184(4)	-0.083
M-O(6) _{amide}	2.720(7)	2.686(4)	+0.034
M-N(1) _{amine}	2.300(7)	2.445(5)	-0.145
M-N(2) _{amine}	2.229(5)	2.358(4)	-0.129
M-O(w1) _{water}	2.058(6)	2.137(4)	-0.079
Ionic radius ^b	0.88	0.96	-0.08
Amide groups			
C(8)-N(3)	1.31(1)	1.317(7)	
C(8)-O(5)	1.234(9)	1.226(7)	
C(10)-N(4)	1.31(1)	1.306(8)	
C(10)-O(6)	1.231(9)	1.237(7)	

^aRef. 10. ^bRef. 18.

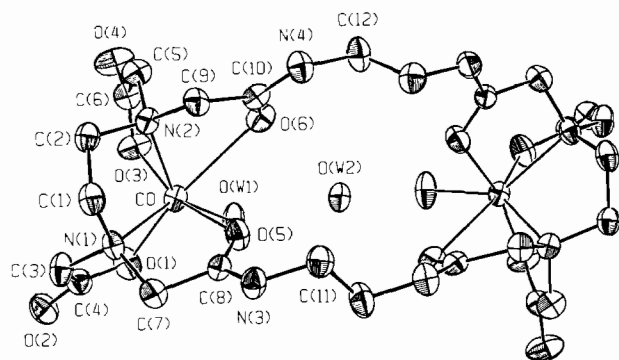


Fig. 1. Molecular structure of $[Co_2(24\text{-edta-en})(H_2O)_2]$. Atoms are shown at the 50% probability level. A C_2 axis passes through O(w2) perpendicular to the averaged molecular plane of the macrocyclic ring; half the molecule is crystallographically unique.

ionic metal chelate formulated as $[Co^{II}_2(24\text{-edta-en})^{4-}(H_2O)_2]^0$ is formed. The oxidation state of the cobalt atoms was supported by the observed magnetic moment, $\mu = 4.65$ BM per Co atom at 297 K, which fell in the range predicted for high-spin d^7 complexes [14]. The Co(II) compound is stable enough to be handled in air.

The six coordinated atoms form a quasi-trigonal prism around a Co atom, as shown in Fig. 2. An amide oxygen atom, O(6), is located at a distance of $\text{Co-O} = 2.720$ Å. When this atom is included in the coordination sphere, the coordination geometry is described as a highly distorted monocapped trigonal prism (Fig. 2). Cobalt(II) complexes with six coordinated atoms usually have octahedral coordination geometry; a trigonal prism coordination geometry is much less common [15]. A seven-coordination geometry can be described by a pentagonal bipyramid, capped octahedron or capped trigonal prism. Distorted pentagonal bipyramidal geometries have been reported for more than ten Co(II)

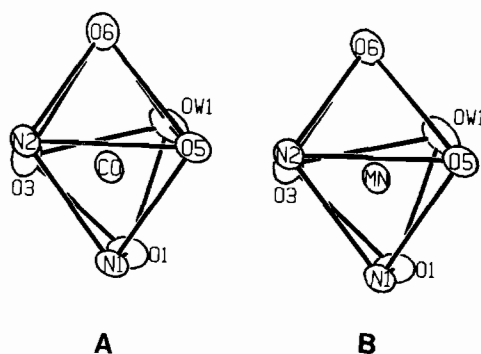


Fig. 2. Coordination geometry in $Co_2(24\text{-edta-en}) \cdot 8H_2O$ (A) and in the corresponding Mn(II) complex (B). Each polyhedron is projected perpendicular to the N(1)N(2)O(5) plane.

complexes with pyridine-based multidentate ligands or crown ethers [16]. A highly distorted capped octahedron has been reported for dinitratotris(pyridine)cobalt(II): three pyridine nitrogen atoms and two nitrate oxygen atoms form a well-defined square-based pyramid, and two additional oxygen atoms from bidentate nitrate ions are weakly bonded from the side of the basal plane [17]. No Co(II) coordination compound that has a capped trigonal prism geometry was found in our search of the literature.

The cobalt(II) complex is isostructural with the corresponding manganese(II) complex; the molecular structures of the two $[M^{II}_2(24\text{-edta-en})^{4-}(H_2O)_2]$ chelate molecules are essentially identical with each other. The distortion from the regular coordination polyhedron is, however, significantly different in the two compounds. The Mn-X distances are included in Table 2 for comparison. The Co-O(w1) distance is shorter than the Mn-O(w1) distance by 0.079 Å, which is identical to the difference, 0.08 Å, between the ionic radii of the two metal ions [18]. For other M-O distances, the differences between the corresponding interatomic distances are smaller than the difference in the ionic radii, whereas the differences in the M-N distances are larger than the ionic-radius difference. The significant difference between the two coordination geometries is due to the position of O(6): the Co-O(6) distance is longer than the Mn-O(6) distance; this is contrary to what would be expected from the difference in the ionic radii of the two metal ions. The Co-O(6) bond is much weaker than is the corresponding Mn-O bond. Table 3 shows geometrical parameters of the polyhedra of the Co(II) and the Mn(II) complexes. The dihedral angle between the two planes perpendicular to the quasi- C_3 axis, N(1)N(2)O(5) and O(3)O(1)O(w1) in Fig. 2, is smaller in the Co(II) complex than in the Mn(II) complex. The central metal ion in the Co(II) complex is located closer to the center of the trigonal prism than is the central Mn(II) ion in the Mn(II) complex.

TABLE 3. Geometrical parameters of polyhedra around a metal ion in $[M_2(24\text{-edta-en})(H_2O)_2]$

	Co	Mn
<i>Geometry of trigonal prism</i>		
Angles ($^\circ$) in the triangles		
O(5)–N(1)–N(2)	70.3(2)	71.0(2)
N(1)–N(2)–O(5)	52.4(2)	51.5(1)
O(w1)–O(1)–O(3)	64.6(2)	65.3(2)
O(1)–O(3)–O(w1)	56.0(2)	55.2(1)
Twist angle ($^\circ$) between the triangles	14.2	12.1
Dihedral angle ($^\circ$) between the triangles	2.6	4.6
Distances (\AA) of M from least-squares planes		
M–[O(5)N(1)N(2)]	1.38	1.51
M–[O(w1)O(1)O(3)]	1.30	1.26
M–[N(1)O(5)O(w1)O(1)]	0.99	1.04
M–[N(2)N(1)O(1)O(3)]	1.00	1.06
M–[O(5)N(2)O(3)O(w1)]	0.49	0.48
<i>Geometry of monocapped trigonal prism</i>		
Distance (\AA)		
O(5)–N(1)	2.70(1)	2.730(7)
N(1)–N(2)	2.869(8)	2.942(5)
N(2)–O(5)	3.212(7)	3.300(5)
O(w1)–O(1)	2.71(1)	2.858(8)
O(1)–O(3)	2.821(7)	3.000(5)
O(3)–O(w1)	2.960(8)	3.164(6)
O(5)–O(w1)	2.800(8)	2.942(6)
N(1)–O(1)	2.668(9)	2.704(6)
N(2)–O(3)	2.681(9)	2.725(6)
O(6)–O(5)	2.894(7)	2.910(5)
O(6)–N(2)	2.68(1)	2.675(7)
O(6)–O(3)	3.44(1)	3.405(7)
O(6)–O(w1)	3.100(8)	3.236(6)

Thus, the trigonal prism of the Co(II) complex is less distorted than that of the Mn(II) complex, although the twist angle between the two triangular planes in the former complex is slightly larger than that in the latter. When the coordination geometries are described as a monocapped trigonal prism, distortion from the regular polyhedron is larger in the Co(II) complex than in the Mn(II) complex. These structural differences are a result of the Co–O(6) bond being much weaker than the Mn–O(6) bond.

The unusual coordination geometry formed in $[Co_2(24\text{-edta-en})(H_2O)_2]$ is a result of the steric constraints due to the partial double bond character of amide groups in the ligand molecule: N(3)–C(8) and N(4)–C(10) distances in the amide groups are much shorter than the distance that would be expected for a single bond (Table 2). The partial double bond character of the N–C bonds of amide groups results in the planarity of the C·CO·NH·C atoms [19]. In the Co(II) chelate, the C(7)C(8)O(5)N(3)C(11) atoms which include the amide oxygen and nitrogen atoms form a plane with the maximum deviation of 0.025(6) \AA from the least-squares plane, and the C(9)C(10)O(6)N(4)C(12) plane has the maximum de-

viation of 0.033(7) \AA ; the corresponding deviations in the Mn(II) complex are 0.021(4) and 0.024(4) \AA , respectively. The dihedral angle between the two planes is 131.6(2) $^\circ$ for the Co(II) complex; 130.6(2) $^\circ$ for the Mn(II) complex. Thus, the conformation of the ligand molecule is not significantly different in the two metal chelates. The structural property of the amide group reduces the flexibility of the macrocyclic ring, and, hence, the frame of the macrocycle is sufficiently rigid to define the coordination geometry. This suggests that the ligand forms a well-defined metal chelate giving crystals only when the ligand conformation is appropriate for the metal ion. In fact, the copper(II) complex of 24-edta-en was obtained only as a vitreous solid from an aqueous solution, and crystallization has been unsuccessful.

In the electronic absorption spectra of octahedral Co(II) complexes, d–d bands are commonly observed at approximately 500 nm with a shoulder at 600 nm [20]. The present Co(II) compound in aqueous solution showed a d–d band at 515 nm ($\epsilon \sim 25 \text{ cm}^{-1} \text{ M}^{-1}$) and a dissymmetry in the peak shape on the shorter wavelength side, but no shoulder was observed in the vicinity of 600 nm. Since the Co(II) chelate is expected to retain its coordination geometry in solution, the electronic absorption band may be characteristic of Co(II) complexes with trigonal prism or distorted monocapped trigonal prism coordination.

Acknowledgements

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