

**CRYSTAL AND MOLECULAR STRUCTURE OF POTASSIUM
[4, A-RACEMIC-(1-PHENYLETHYLENEDIAMINE-N,N,N',N'-
-TETRAACETATO)COBALTATE(III)] SESQUIHYDRATE**

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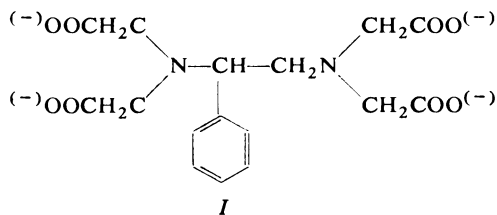
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The crystal and molecular structure of the title compound was determined by X-ray analysis. It crystallizes in the orthorhombic system, space group *Ccc2*, with cell parameters $a = 3.773(3)$, $b = 1.404(11)$, $c = 0.6962(6)$ nm, $V = 3.687$ nm³, and $Z = 8$. The main factors determining stereochemistry of the complex are intramolecular hydrophobic stacking interaction between the methylene hydrogens of the out-of-plane R₁ ring and the aromatic ring of the phenyl group, and the nonbonding van der Waals interactions between the methylene hydrogens of the central ethylenediamine (E), in-plane glycinate (G) and R rings as well as of the hydrogens of the phenyl group. The observed stereospecific coordination is due to an energy preference for the equatorially located phenyl group on the E ring.

Research on multidentate chelating agents has been stimulated by their interesting and very often unique stereochemical properties, their widespread occurrence in living matter and the many practical applications found for sequestering agents such as EDTA. One of the most exciting application of these compounds is found in medicine, where radioactive metal ions chelated to EDTA-type ligands have been used clinically for diagnosis of cancer^{1,2}. Recently² it was shown that aminophenyl-EDTA have excellent parameters for this purpose, because its aromatic amino group could be converted into a variety of useful protein-labeling reagents, so-called bifunctional chelators.

In a previous communication³ we concluded, on the basis of spectral behavior of the cobalt(III) complexes of phenyl substituted EDTA-derivatives, that E ring



conformational effects, namely hydrophobic stacking interactions⁴, contribute mainly to the overall stability of the complexes. Critical to the use of aryl-EDTA as bifunctional chelators is a detailed knowledge of the structures of its metal complexes. Therefore we describe here the crystal structure of Co(III) complex of rac-PHEDTA (I)

EXPERIMENTAL

Preparation and spectral characterization of the K[Co(rac-PHEDTA)]. 1.5 H₂O has been previously reported³.

Crystal data. The purple crystals of K[Co(rac-PHEDTA)].1.5 H₂O crystallize as needles. Crystal data: KCoC₁₆H₁₆N₂O₈·1.5 H₂O, $M_r = 489.4$, orthorhombic, $Ccc2$, $a = 3.772(3)$, $b = 1.404(11)$, $c = 0.6962(6)$ nm, $V = 3.687(2)$ nm³, $Z = 8$, $D_x = 1.763$, $D_m = 1.75(2)$ g cm⁻³, MoK α radiation, $\lambda = 0.0710$ nm, $\mu = 9.4$ cm⁻¹, $F(000) = 2008$, room temperature.

X-ray data collection. The unit cell dimensions were initially obtained from rotation and Weissenberg photographs and later adjusted by least-squares refinement of 14 accurately centered reflections ($15 < 2\theta < 40^\circ$). The space group was uniquely determined on the basis of systematically absent reflections (hkl for $h + k$ odd, $0kl$ for l odd, $h0l$ for l odd) and the number of molecules per unit cell. The intensity data were collected on a P2₁, Syntex four-circle diffractometer from a crystal of dimensions 0.10 × 0.10 × 0.50 mm. The graphite-monochromatized MoK α radiation and the $\theta - 2\theta$ scan technique were used to record the intensities for all unique reflections for which $0 < 2\theta \leq 50^\circ$, with the scanning rate in the interval 4.88 to 29.3° min⁻¹ determined on the basis of preliminary two-second measurement. The scanning range was selected and corresponded to 1° below the calculated K α_1 position to 1° above the calculated K α_2 position (in 2θ). The background was measured at both ends of the scan for a period of half of the reflection scanning time. The intensities of two standard reflections measured after each 98 recorded intensities did not exhibit significant fluctuation. The raw intensity data were corrected for Lorentz-polarization effects, but not for absorption nor extinction. A total of 1285 independent reflections were collected, of which 1068 with $I \geq 2\sigma(I)$ were considered as observed.

Solution and refinement of the structure. The structure was solved by the heavy-atom method, the positions of Co and K atoms being found from three-dimensional Patterson synthesis calculated using the observed reflections. Positions of the remaining non-hydrogen atoms were found from successive Fourier syntheses of electron density. After the structure was completed, positional and isotropic thermal parameters of all non-hydrogen atoms were initially refined in three cycles by the least-squares methods using a blockdiagonal matrix and unit weights in the minimization function, $M = \sum w(\Delta F)^2$, for all the observed reflections to $R = 0.09$ ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). At this stage, a difference Fourier ($\Delta\rho$) map of the residual electron density indicated positions for all hydrogen atoms of the complex molecule and one hydrogen of the molecule of water of crystallization lying in a special position; two hydrogen atoms of the second molecule of water [0(10)] were not located due to a positional disorder of this molecule (the statistical disorder of O(10) was clearly indicated by appearance of a bundle of 4 distinct low-height maxima on $\Delta\rho$ map, separated by about 0.05–0.2 nm). The structure was finally refined by block-diagonal least-squares with respect to positional and anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for H atoms using all 1068 observed reflections and relative weights $w = |F_o|/95$ if $|F_o| < 95$ and $w = 95/|F_o|$

if $|F_o| \geq 95$ to final $R = 0.064$ and $R_w = 0.075$ ($R_w = (\sum w|\Delta F|^2 / \sum w|F_o|^2)^{1/2}$). Shifts applied to the refined parameters in the final cycle was not greater than 0.2 times its standard deviation. F_c was calculated using scattering factors for neutral atoms given in ref.⁵. Maximal residual electron density in the final difference Fourier synthesis was 570 e nm^{-3} . All crystallographic calculations were carried out on an EC 1033 computer using published programs⁶.

RESULTS AND DISCUSSION

The crystal of the title complex consists of enantiomeric pairs of Δ -[Co(R)-PHEDTA]⁻ and Λ -[Co(S)-PHEDTA]⁻, K⁺ ions and molecules of water, the pairs being joined together by carboxylic oxygens via the K⁺ ions and molecules of crystal water. One molecule of water is localized in a special position on a twofold axis, the second one is disordered among four general positions, the sum of the refined occupancy factors being close to unity. Final atomic coordinates and equivalent isotropic B 's are listed in Table I. Table II gives bond distances and angles for the complex, which is shown as the Δ -[Co(R)-PHEDTA]⁻ enantiomer in Fig. 1.

The geometry of the Co(III) coordination sphere is distorted octahedral. The Co atom is bonded to two N atoms and to four O atoms from four different carboxylic groups of the ligand. (R)-PHEDTA⁴⁻ acts as a hexadentate ligand, forming four glycine-like (R, G) and one ethylenediamine (E) chelate rings. The PHEDTA⁴⁻ coordinates stereospecifically to the metal ion due to an energy preference for equatorially located phenyl group on the central E ring.

The Co-N bond distances are 0.1971(8) and 0.2040(9) nm and they are on an average 0.007 nm longer than those commonly found in other Co(III) complexes with EDTA⁴⁻ and its diamine analogs⁷. This is due to a phenyl-induced larger puckering of the E ring which is reflected in the sum of internal angles of 511.4° in comparison with the value of 520.9° which was observed in the parent [Co(EDTA)]⁻ complex⁸. The ideal value of this parameter for the E ring of EDTA is 527.9° . The puckering of this ring can also be expressed by torsion angle N(1)—C(1)—C(2)—N(2), equal to -58.6° , which is significantly larger than that in the [Co(EDTA)]⁻ complex, where this torsion angle takes a value of 47.8° . The Co—O distances range from 0.1863 to 0.1928 nm and similar values were also found for EDTA- and EDTA-like complexes of Co(III) (ref.⁷).

The values of the valence angles given in Table II indicate that fusion of three five-membered chelate rings in the equatorial plane coupled with the presence of the bulky phenyl group in this plane yield a system with high strain which does not permit positioning of the donor atoms to the corners of an ideal square. This is reflected in a significantly different value of the intra-ring O(2)—Co—O(4) angle of 106.5° compared to the ideal value of 90° . In the present complex [Co(rac-PHEDTA)]⁻, the equatorial strain is partially compensated by intramolecular non-bonding interactions between the methylene hydrogens of the E, G, and R rings and of the phe-

TABLE I

Final atomic coordinates and equivalent isotropic thermal parameters (defined as $B_{eq} = 4/3 \sum_i \cdot \sum_j B_{ij} \sigma_i \sigma_j$) with estimated standard deviations in parentheses^a

Atom	x	y	z	B_{eq}
Co(1)	0.15978(3)	0.2232(1)	0	3.07(5)
N(1)	0.1126(2)	0.2665(6)	-0.084(1)	2.4(4)
N(2)	0.1664(2)	0.1670(5)	-0.268(1)	2.3(4)
O(1)	0.1378(2)	0.1125(5)	0.089(1)	2.7(4)
O(2)	0.1513(2)	0.2973(5)	0.217(1)	2.9(4)
O(3)	0.1822(2)	0.3339(5)	-0.110(1)	2.5(4)
O(4)	0.2046(2)	0.1648(5)	0.037(1)	3.3(3)
O(5)	0.0859(2)	0.0499(5)	0.167(1)	4.6(4)
O(6)	0.1297(2)	0.4381(5)	0.286(2)	4.4(4)
O(7)	0.2093(2)	0.3911(6)	0.367(1)	4.4(4)
O(8)	0.2355(2)	0.0356(5)	-0.050(1)	3.1(3)
C(1)	0.1130(2)	0.2604(6)	-0.304(2)	2.0(4)
C(2)	0.1298(2)	0.1650(8)	-0.358(2)	2.4(5)
C(3)	0.0765(2)	0.2791(8)	-0.397(2)	2.5(5)
C(4)	0.0540(3)	0.2084(8)	-0.463(2)	3.5(5)
C(5)	0.0226(2)	0.228(1)	-0.557(2)	4.6(6)
C(6)	0.0128(3)	0.320(1)	-0.592(2)	4.4(5)
C(7)	0.0363(2)	0.3929(9)	-0.535(2)	3.9(5)
C(8)	0.0675(2)	0.3733(8)	-0.440(2)	2.8(5)
C(9)	0.0868(2)	0.2018(7)	0.008(2)	2.3(5)
C(10)	0.1043(2)	0.1132(7)	0.095(2)	2.1(5)
C(11)	0.1096(2)	0.3641(7)	0.002(2)	2.6(5)
C(12)	0.1318(2)	0.3685(7)	0.181(2)	2.8(5)
C(13)	0.1908(3)	0.2306(7)	-0.380(2)	2.6(5)
C(14)	0.1948(3)	0.3256(7)	-0.281(2)	3.0(5)
C(15)	0.1839(3)	0.0748(7)	-0.228(2)	2.8(5)
C(16)	0.2108(3)	0.0897(8)	-0.069(2)	2.9(5)
K(1)	0.2147(1)	0.4282(2)	0.2520(5)	3.4(1)
O(9)	0.25	0.25	0.290(2)	4.7(5)
O(101)	0.004(3)	0.023(2)	0.191(8)	9(2)
O(102)	0.016(1)	-0.002(5)	0.17(1)	18(3)
O(103)	0.018(1)	0.020(5)	0.057(5)	7(2)
O(104)	0.030(1)	0.030(3)	-0.11(1)	16(3)

^a Co(1) was used to fix the origin on the two-fold axis, O(9) water oxygen lies on the two-fold axes, and O(101), O(102), O(103), O(104) represent sites of partial occupancy (c. 0.25 each) for O(10) water oxygen (see text).

TABLE II
Bond lengths in nm and angles in ° with their e.s.d.'s

Bond lengths			
Co–N(1)	0·1971(8)	C(4)–C(5)	0·138(2)
Co–N(2)	0·2040(9)	C(5)–C(6)	0·136(2)
Co–O(1)	0·1867(7)	C(6)–C(7)	0·142(2)
Co–O(2)	0·1863(7)	C(7)–C(8)	0·138(1)
Co–O(3)	0·1928(7)	C(9)–C(10)	0·153(1)
Co–O(4)	0·1896(7)	C(10)–O(1)	0·126(1)
N(1)–C(1)	0·153(1)	C(10)–O(5)	0·123(1)
N(1)–C(9)	0·148(1)	C(11)–C(12)	0·153(2)
N(1)–C(11)	0·149(1)	C(12)–O(2)	0·127(1)
N(2)–C(2)	0·152(1)	C(12)–O(6)	0·122(1)
N(2)–C(13)	0·150(1)	C(13)–C(14)	0·151(2)
N(2)–C(15)	0·148(1)	C(14)–O(3)	0·129(1)
C(1)–C(2)	0·153(1)	C(14)–O(7)	0·123(1)
C(1)–C(3)	0·154(1)	C(15)–C(16)	0·152(2)
C(3)–C(4)	0·139(2)	C(16)–O(4)	0·131(1)
C(3)–C(8)	0·140(2)	C(16)–O(8)	0·121(1)
Bond angles			
N(1)–Co–N(2)	87·6(3)	O(2)–Co–O(3)	87·0(3)
N(1)–Co–O(1)	87·4(3)	O(2)–Co–O(4)	106·5(3)
N(1)–Co–O(2)	85·0(3)	O(3)–Co–O(4)	90·6(3)
N(1)–Co–O(3)	91·7(3)	Co–N(1)–C(1)	105·8(6)
N(1)–Co–O(4)	168·3(3)	Co–N(1)–C(9)	105·9(6)
N(2)–Co–O(1)	92·1(3)	Co–N(1)–C(11)	103·8(6)
N(2)–Co–O(2)	168·1(3)	C(1)–N(1)–C(9)	113·9(7)

TABLE III
Intramolecular nonbonding interactions H···H < 0·25 nm with their e.s.d.'s

H(C1)···H(C8)	0·240(11)
H'(C2)···H(C4)	0·237(8)
H(C11)···H(C8)	0·249(13)
H(C1)···H(C11)	0·218(12)
H'(C9)···H'(C11)	0·207(12)
H(C2)···H(C13)	0·244(7)
H'(C2)···H(C15)	0·244(8)
H(C13)···H'(C15)	0·200(10)

TABLE IV
Hydrogen-bond distances, nm^a

A—H···B	A···B
O(9)—H(O9)···O(4)	0.273(1)
O(9)···O(4 ⁱ)	0.273(1)
O(101)···O(5)	0.313(10)
O(102)···O(5)	0.273(4)
O(103)···O(5)	0.272(4)
O(104)···O(5)	0.287(6)
O(104)···O(5 ⁱⁱ)	0.285(6)
C(8)···O(6 ⁱⁱⁱ)	0.316(1)
C(15)—H(C15)···O(1) ^b	0.286(1)

^a Symmetry code for B: i $1/2 - x, 1/2 - y, z$; ii $x, -y, z - 1/2$; iii $x, y, z - 1$. ^b Intramolecular hydrogen-bond.

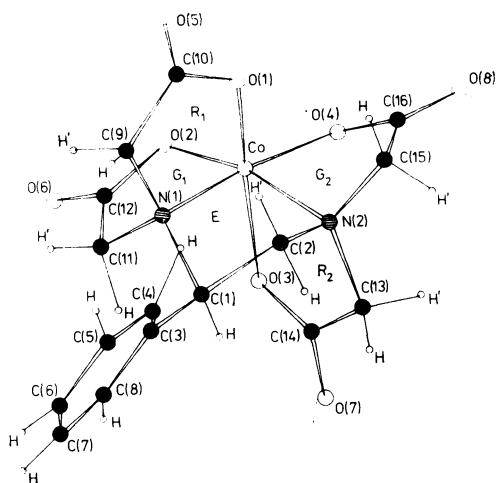


FIG. 1

Perspective view of the $[\text{Co}(\text{R})\text{-PHEDTA}]^-$ complex showing the atom-numbering scheme

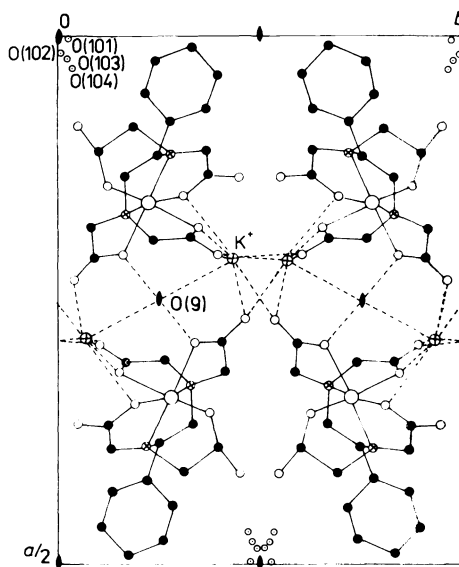


FIG. 2

The projection of the structure along the c axis. Intermolecular hydrogen bonds and ion-dipole interaction are represented by dashed lines (\circ Co, \circ O, \bullet C, \otimes N, \oplus K); O(9) water oxygen lying on the two-fold axes, O(101)–O(104): localized positions of the second water oxygen)

nyl group (Table III), which correspond to the minimum on the H···H potential curve⁹.

The overall conformation of the Δ -[Co(R)-PHEDTA]⁻ complex may be described as $\lambda - \delta\delta - \delta\delta$ following the notation suggested by Lee¹⁰. The conformations of individual chelate rings have been deduced from the torsion angles and least-squares planes. The central E ring has a gauche form of chirality λ with almost exact C_2 symmetry as expressed by asymmetry parameter¹¹, $\Delta C_2[\text{Co}] = 1.6^\circ$. Similarly, the glycine ring R_1 adopts a gauche form with low value of asymmetry parameter at atom C(10), $\Delta C_2[\text{C}(10)] = 1.2^\circ$. The second ring, R_2 , adopts an envelope conformation as reflected in the asymmetry parameter $\Delta C_5[\text{N}(2)] = 2.8^\circ$. The G-rings have envelope conformations, with the asymmetry parameters $\Delta C_5[\text{Co}] = 6.8^\circ$ for G_1 and $\Delta C_5[\text{N}(2)] = 5.3^\circ$ for G_2 ring. A degree of distortion of the chelate rings from planarity may also be measured by a mean deviation of the five atoms of the ring from its least-squares plane. For [Co(rac-PHEDTA)]⁻ complex we find the mean deviation of G_1 , G_2 , R_1 , and R_2 rings to be 0.0186, 0.0215, 0.0073 and 0.0069 nm, respectively. Apparently, planarity of the R rings is considerably higher than that of the G rings. Such a tendency is typical for Co(III) complexes with EDTA and its diamine analogs, and the mean deviations obtained for present complex compare well with data given by Lingafelter and co-workers¹².

The structure projected along the c axis is shown in Fig. 2. The enantiomeric pairs are connected via the K^+ cations and molecules of crystal water, forming infinite chains parallel to the b axis. The chains are held together by van der Waals forces only. The parameters of the hydrogen bonds formed within the chains are in Table IV.

The K^+ ion is seven coordinated to six carboxylic oxygens of five different complex ions: O(2), O(3), O(7) ($x, y, 1+x$), O(7) ($x, 1-y, z+1/2$), O(8) ($1/2-x, 1/2-y, z$), O(8) ($1/2-x, y+1/2, z+1/2$) and one water molecule O(9). The $\text{K}^+\cdots\text{O}$ distances range from 0.268(1) to 0.310(1) nm, mean 0.286(1) nm, which corresponds to the sum of the ionic radius of K^+ for coordination number seven (0.146 nm) and the van der Waals radius of O (0.140 nm) (ref.¹³).

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