

Structure of (Ethylenediamine)(*cis*- α -ethylenediamine-*N,N'*-diacetato)cobalt(III) Perchlorate

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Abstract. *cis*- α -[Co(C₆H₁₀N₂O₄)(C₂H₈N₂)]ClO₄, M_r = 394.5, monoclinic, *Pc*, a = 9.169 (1), b = 7.966 (1), c = 10.809 (1) Å, β = 113.64 (1)°, V = 723.21 Å³, Z = 2, D_m = 1.78 (by flotation in CCl₄/CH₃I), D_x = 1.803 Mg m⁻³, λ (Mo *K* α) = 0.7107 Å, μ = 1.47 mm⁻¹, $F(000)$ = 400, T = 295 K, final R = 0.047 for 1226 reflections. The coordination geometry around the cation is slightly distorted from an ideal octahedron, with the tetradentate chelating ligand ethylenediamine-*N,N'*-diacetic acid (EDDA) present in *cis*- α configuration. The five-membered chelate ring formed by ethylenediamine (en) has an envelope shape whereas that formed with the *E* ring of EDDA has a non-eclipsed or *gauche* (δ) configuration. The ClO₄⁻ ion has a distorted tetrahedral arrangement.

Introduction. Tetradentate chelating ligands can assume a variety of orientations in octahedral complexes depending upon the steric requirements of the ligands. Of three possible isomers (*cis*- α , *cis*- β , *trans*) a linear tetradentate ligand such as EDDA shows a high preference for the *cis*- α configuration in the complexes where the diamine ligand occupies the remaining two positions (Coleman, Legg & Steele, 1970).

Though both the primary amines have similar *trans* donor atoms, the ¹H NMR spectrum of the complex in DMSO-*d*₆ showed different peaks. It was therefore necessary to determine the geometry and isotropic form of the complex cation by single-crystal X-ray diffraction studies.

Experimental. *trans*-[Co(en)₂Cl₂]Cl + EDDA, aqueous solution, pH adjusted to 6–6.5 by addition of sodium hydroxide, concentrated on a water bath and then cooled slowly. The desired complex is precipitated by the addition of sodium perchlorate to the ice-cold

solution. The complex was recrystallized from water, washed with cold water and ethanol and finally air dried. Its purity was ascertained by UV–VIS spectral data (Kuroda & Watanabe, 1971).

Crystal dimensions 0.26 × 0.28 × 0.32 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo *K* α (λ = 0.7107 Å) radiation, lattice parameters refined from 25 reflections $5 < \theta < 10^\circ$, two standard reflections ($\bar{1}\bar{1}\bar{3}$ and $\bar{2}\bar{2}\bar{2}$) measured every 1800 s showed no significant intensity change, $\omega/2\theta$ scan, resolution d = 0.84 Å, 1457 reflections measured in the range $2 < \theta < 25^\circ$, $0 \leq h \leq 10$, $0 \leq k \leq 9$, $-12 \leq l \leq 12$, symmetry-equivalent reflections were averaged, 1309 observed reflections with $F > 3.0\sigma(F)$ used for structure determination, Lp correction, no absorption correction. The condition $h0l$, $l = 2n + 1$ absent from Weissenberg photograph implies that the space group is *Pc* or *P2/c*. The non-centrosymmetric space group was indicated by intensity statistics and confirmed by structure determination. The structure was solved by Patterson and Fourier methods. All the H atoms were located from difference maps. Structure refinement by least-squares method based on F values using anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. In the final calculation reflections with $F < 5.0\sigma(F)$ were omitted. R = 0.047, wR = 0.053, weight = $2.1846/[\sigma^2(F) + 0.0013F^2]$, $(\Delta/\sigma)_{\max}$ = 0.591, $(\Delta\rho)_{\max}$ = 0.732 e Å⁻³ near disordered ClO₄⁻ ion, $(\Delta\rho)_{\min}$ = -0.687 e Å⁻³.

The absolute configuration (λ, λ) of [Co(en)(EDDA)]⁺ has been established from the circular-dichroism (CD) spectrum (Legg, Cooke & Douglas, 1967). The final R value is 0.0525 when the structure is refined assuming that [Co(en)(EDDA)]⁺ is in the δ, λ configuration, compared to 0.047 in the λ, λ configuration.

Program *SHELX86* (Sheldrick, 1986) for structure solution, *SHELX76* (Sheldrick, 1976) for least-squares

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) with *e.s.d.*'s in parentheses
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Co	0†	1933 (1)	0†	18 (1)
N(1)	989 (8)	-270 (8)	464 (7)	26 (2)
N(2)	2107 (9)	2832 (9)	871 (8)	36 (3)
N(3)	-947 (8)	4171 (8)	-606 (7)	30 (2)
N(4)	-2205 (8)	1046 (8)	-756 (7)	25 (2)
O(1)	176 (8)	1786 (6)	-1680 (6)	25 (2)
O(2)	-226 (8)	2115 (7)	1666 (6)	28 (2)
O(3)	-165 (9)	3189 (7)	-3547 (7)	38 (2)
O(4)	-1849 (8)	1535 (8)	2666 (7)	37 (2)
C(1)	2628 (9)	-37 (10)	1517 (9)	48 (3)
C(2)	3267 (9)	1416 (10)	1101 (9)	51 (3)
C(3)	-627 (9)	4653 (8)	-1777 (8)	32 (2)
C(4)	-153 (9)	3106 (8)	-2387 (8)	28 (3)
C(5)	-2616 (9)	4035 (9)	-867 (8)	34 (3)
C(6)	-3224 (9)	2330 (10)	-1601 (8)	35 (3)
C(7)	-2596 (9)	506 (9)	393 (8)	34 (3)
C(8)	-1491 (8)	1444 (9)	1691 (8)	25 (2)
Cl	4078 (3)	3782 (4)	4725 (3)	42 (2)
O(5)	3573 (10)	4847 (10)	3601 (9)	91 (3)
O(6)	2792 (10)	3568 (10)	5138 (10)	94 (3)
O(7)	5158 (11)	4745 (11)	5802 (10)	119 (3)
O(8)	4621 (11)	2295 (11)	4483 (11)	142 (3)

† Fixed to define the origin.

refinements, *PLUTO78* (Motherwell & Clegg, 1978) for plotting the molecular structure and the crystal packing, computer CYBER-180. Atomic scattering factors for Co^{III} and Cl^- are taken from *International Tables for X-ray Crystallography* (1974) and those of other atoms from *SHELX76*.

Discussion. The atomic coordinates are given in Table 1, * bond lengths and bond angles in Table 2; Fig. 1 shows the stereochemical arrangement of the complex cation $[\text{Co}(\text{EDDA}(\text{en}))]^+$.

Two primary and two secondary N atoms are in a plane with Co [maximum deviation from their mean plane, N(2) -0.084 (8) \AA]. The coordinated O atoms are almost in a straight line with Co [O(1)—Co—O(2) 178.6 (3) $^\circ$] nearly perpendicular to the above plane and the coordination geometry around Co^{III} is almost octahedral (the maximum deviation from octahedral angles around Co is within 4°). The angle between the mean planes of the two glycinate (*R*) rings is 85 (1) $^\circ$. The secondary N atoms are at an average distance of 1.979 (6) \AA from Co, further than the primary N—Co distances [N(1)—Co 1.946 (6) and N(2)—Co 1.916 (7) \AA]. This difference could be due to both the electron-withdrawing carboxyl groups being bonded to *E*-ring N atoms. The average C—N bond length in the *E*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and least-squares-planes details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51467 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Distances (\AA) and principal angles ($^\circ$) with *e.s.d.*'s in parentheses

N(1)—Co	1.946 (6)	C(4)—O(1)	1.264 (9)
N(2)—Co	1.916 (7)	C(8)—O(2)	1.287 (11)
N(3)—Co	1.976 (6)	C(4)—O(3)	1.251 (12)
N(4)—Co	1.982 (6)	C(8)—O(4)	1.225 (12)
O(1)—Co	1.889 (8)	C(2)—C(1)	1.448 (13)
O(2)—Co	1.899 (8)	C(4)—C(3)	1.541 (11)
C(1)—N(1)	1.489 (9)	C(6)—C(5)	1.559 (10)
C(2)—N(2)	1.501 (11)	C(8)—C(7)	1.554 (10)
C(3)—N(3)	1.461 (12)	O(5)—Cl	1.399 (9)
C(5)—N(3)	1.444 (11)	O(6)—Cl	1.429 (11)
C(6)—N(4)	1.439 (9)	O(7)—Cl	1.415 (9)
C(7)—N(4)	1.487 (12)	O(8)—Cl	1.351 (10)
N(2)—Co—N(1)	86.4 (3)	C(7)—N(4)—C(6)	115.0 (7)
N(3)—Co—N(1)	175.0 (3)	C(4)—O(1)—Co	116.0 (6)
N(3)—Co—N(2)	92.7 (3)	C(8)—O(2)—Co	115.5 (5)
N(4)—Co—N(1)	94.5 (3)	C(2)—C(1)—N(1)	105.9 (6)
N(4)—Co—N(2)	175.1 (4)	C(1)—C(2)—N(2)	107.7 (8)
N(4)—Co—N(3)	86.8 (3)	C(4)—C(3)—N(3)	110.5 (6)
O(1)—Co—N(1)	88.9 (3)	O(3)—C(4)—O(1)	123.7 (7)
O(1)—Co—N(2)	92.1 (3)	C(3)—C(4)—O(1)	116.5 (8)
O(1)—Co—N(3)	86.1 (3)	C(3)—C(4)—O(3)	119.8 (6)
O(1)—Co—N(4)	92.7 (3)	C(6)—C(5)—N(3)	107.4 (7)
O(2)—Co—N(1)	92.4 (3)	C(5)—C(6)—N(4)	106.7 (5)
O(2)—Co—N(2)	88.7 (3)	C(8)—C(7)—N(4)	109.1 (6)
O(2)—Co—N(3)	92.6 (3)	O(4)—C(8)—O(2)	123.3 (7)
O(2)—Co—N(4)	86.4 (3)	C(7)—C(8)—O(2)	116.5 (8)
O(2)—Co—O(1)	178.5 (3)	C(7)—C(8)—O(4)	120.2 (7)
C(1)—N(1)—Co	107.9 (5)	O(6)—Cl—O(5)	108.5 (6)
C(2)—N(2)—Co	108.0 (5)	O(7)—Cl—O(5)	105.3 (5)
C(3)—N(3)—Co	108.1 (5)	O(7)—Cl—O(6)	101.6 (6)
C(5)—N(3)—Co	106.7 (5)	O(8)—Cl—O(5)	112.5 (7)
C(5)—N(3)—C(3)	114.5 (6)	O(8)—Cl—O(6)	111.8 (6)
C(6)—N(4)—Co	107.7 (5)	O(8)—Cl—O(7)	116.4 (5)
C(7)—N(4)—Co	107.8 (4)		

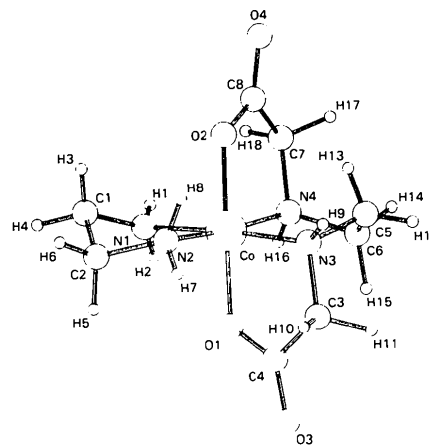


Fig. 1. A general view of the complex cation.

ring is 1.44 (1) \AA , compared to that of 1.48 (1) \AA in the rest of the molecule. The configurations of the asymmetric secondary N atoms were found to be *R,R*. The amines were in a λ,λ conformation as in the Δ isomer.

The perchlorate ion shows some distortion from the tetrahedral parameters [Cl—O(8) 1.35 (1) \AA , O(8)—Cl—O' 113.6 (6) $^\circ$ on average; O' corresponds to O(5), O(6) and O(7)]. The Cl—O' bond lengths are close to the average value of 1.44 \AA (*International Tables for X-ray Crystallography*, 1962).

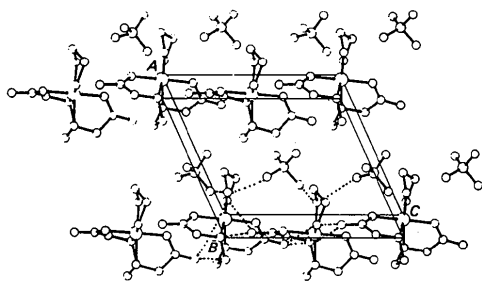


Fig. 2. Unit-cell packing diagram; dotted lines indicate hydrogen bonds.

Fig. 2 shows the crystal packing diagram. The structure is stabilized by a network of hydrogen bonds involving the N—H groups (Table 3). In ClO₄⁻, two O atoms [O(7) and O(8)] have higher thermal parameters than the other two [O(5) and O(6)], which are associated with hydrogen bonds.

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Table 3. Possible hydrogen bonds, distances (Å) and angles (°) with *e.s.d.*'s in parentheses

	N...O	∠N—H...O	Position of O
N(3)—H(9)...O(3)	2.92 (3)	153.7 (8)	<i>x</i> , 1— <i>y</i> , $\frac{1}{2}$ — <i>z</i>
N(4)—H(5)...O(4)	2.78 (3)	157.6 (8)	<i>x</i> , <i>y</i> , $\frac{1}{2}$ — <i>z</i>
N(1)—H(1)...O(3)	2.92 (4)	149.9 (9)	<i>x</i> , <i>y</i> , $\frac{1}{2}$ — <i>z</i>
N(1)—H(2)...O(4)	3.29 (5)	147.2 (10)	<i>x</i> , <i>y</i> , $\frac{1}{2}$ — <i>z</i>
N(2)—H(8)...O(5)	3.14 (4)	135.4 (10)	<i>x</i> , <i>y</i> , <i>z</i>
N(2)—H(7)...O(6)	3.08 (3)	146.5 (9)	<i>x</i> , <i>y</i> , $\frac{1}{2}$ — <i>z</i>

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Structure of Dichlorobis(triphenylphosphine)nickel(II)

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Abstract. [NiCl₂{(C₆H₅)₃P₂}]₂, *M_r* = 654.20, monoclinic, *P2₁/c* (No. 13), *a* = 11.580 (2), *b* = 8.094 (1), *c* = 17.220 (3) Å, β = 107.20 (2)°, *V* = 1541.8 (5) Å³, *Z* = 2, *D_x* = 1.409 g cm⁻³, graphite-monochromated X-radiation (λ = 0.71073 Å), μ(Mo *Kα*) = 9.29 cm⁻¹, *F*(000) = 676, *T* = 94 (5) K though held constant to within ±1 K, final *R*(*F*) = 0.038 for 8615 observed reflections [*F* > 3σ(*F*), (sinθ)/λ < 1.0 Å⁻¹]. The crystal structure requires the [NiCl₂{(C₆H₅)₃P₂}] molecule to have *C₂* symmetry. Coordination about the central Ni atom is approximately tetrahedral in accord with the observed paramagnetism of the molecule. A significant opening of the Cl—Ni—Cl angle from an ideal tetrahedral value to 127.9 (1)° is noted. In addition, a long Ni—P separation of 2.1380 (2) Å, and somewhat short

P—C(Ph) distances of 1.810–1.819 (1) Å are observed, consistent with a π back-bonding model which incorporates P—C σ* orbitals in the acceptor role.

Introduction. It was first observed by Venanzi (1962) that dichlorobis(triphenylphosphine)nickel(II) is paramagnetic. A crystal structure analysis based on visual estimates of intensities from zero-level Weissenberg photographs allowed distinction between the possible tetrahedral and *cis*-planar structures (Garton, Henn, Powell & Venanzi, 1963). However, refinement to *R* = 0.22 left structural parameters poorly defined and some ambiguity over the space group (*P2₁/c* vs *Pc*). A later crystallographic study (Bruins Slot, Van Havare, Noordik, Beurskens & Royo, 1984) based on