

## Bis(ethylenediamine)(1-phenyl-1,2-propanedione 2-oximato)cobalt(III) Diperchlorate

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**Abstract.**  $C_{13}H_{24}CoN_5O_2 \cdot 2ClO_4$ ,  $Co(C_2H_8N_2)_2(C_9H_8NO_2) \cdot 2ClO_4$ , FW = 540.2, monoclinic,  $P2_1/c$ ,  $a = 20.082$  (11),  $b = 8.942$  (4),  $c = 12.445$  (5) Å,  $\beta = 101.86$  (3)°,  $Z = 4$ ,  $D_x = 1.640$ ,  $D_m = 1.65$  Mg m<sup>-3</sup>;  $R = 0.051$  for 2567 reflections. The carbonyl-oxime anion in the mixed-ligand complex cation is coordinated to Co through the oxime N and carbonyl O atoms. There are weak hydrogen bonds between the complex cations and the perchlorate anions as well as between the different cations.

**Introduction.** This work represents a continuation of our investigation of the role of carbonyl-oxime ligands in transition-metal complexes. The structure of the title compound was solved because it involves the 1-phenyl-1,2-propanedione 2-oxime ligand already described for tris(1-phenyl-1,2-propanedione 2-oximato)cobalt(III) (Saarinen, Korvenranta & Näsäkkälä, 1978), and because, for comparative purposes, we wished to know more about its crystal and molecular structure.

Most carbonyl compounds, including carbonyl-oximes, readily react with primary amines to yield Schiff bases and, in the presence of metal ions, chelates of imine-oxime type can be isolated. In the present case preservation of the carbonyl function of the ligand was assured by preparing first the  $Co(en)_3$  complex from  $Co(ClO_4)_2$  and ethylenediamine in methanol and then replacing one of the en ligands by 1-phenyl-1,2-propanedione 2-oximate. During the process the Co ion is oxidized to the trivalent state. The brown tabular crystals of the mixed-ligand chelate perchlorate were grown in a water–acetone mixture.

Preliminary Weissenberg photographs showed the crystals to be monoclinic and the space group, from systematic absences, to be  $P2_1/c$ . Accurate unit-cell parameters were obtained by refinement of ten reflections measured with a Syntex  $P2_1$  diffractometer (Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å).

X-ray intensities were collected on the diffractometer by the  $\omega$ -scan technique ( $4 < 2\theta < 51^\circ$ ) with graphite-monochromatized Mo  $K\alpha$  radiation. The scan rate varied from 3 to 29° min<sup>-1</sup>. Of the 3590 reflections measured, the 2567 for which  $I > 3\sigma(I)$  were regarded as observed. No corrections were made for absorption [ $\mu(Mo K\alpha) = 1.12$  mm<sup>-1</sup>].

The structure was solved by direct methods (*MULTAN*; Main, Woolfson, Lessinger, Germain & Declercq, 1974) and refined by block-diagonal least-squares methods (XRAY system, 1976) first with isotropic, then with anisotropic thermal parameters. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/(40.0 + |F_o| + 0.005|F_o|^2)$ . Atomic scattering factors were those included in the program; the atomic scattering factors for Co and Cl were corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). The final  $R$  value for 2567 reflections was 0.051. Final positional parameters for the non-hydrogen and H atoms are given in Tables 1

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) for non-hydrogen atoms

	x	y	z
The complex ion			
C(1)	-1670 (3)	1288 (7)	5550 (5)
C(2)	-1958 (3)	1436 (7)	4395 (5)
C(3)	-1614 (4)	1356 (10)	3449 (6)
C(4)	-935 (3)	1370 (8)	6027 (6)
C(5)	-683 (4)	648 (10)	7021 (7)
C(6)	6 (4)	778 (11)	7507 (9)
C(7)	436 (4)	1598 (11)	7010 (9)
C(8)	194 (4)	2323 (12)	6053 (9)
C(9)	-489 (4)	2216 (10)	5542 (7)
N(1)	-2639 (2)	1518 (5)	4226 (4)
O(1)	-2076 (2)	1105 (5)	6203 (3)
O(2)	-2997 (2)	1639 (5)	3249 (3)
C(10)	-3015 (4)	-1735 (8)	6238 (7)
C(11)	-3496 (4)	-948 (8)	6817 (6)
N(2)	-3023 (3)	-945 (6)	5195 (4)
N(3)	-3311 (3)	656 (6)	6844 (4)
C(12)	-3740 (3)	3908 (7)	5616 (5)
C(13)	-4085 (3)	3198 (7)	4557 (5)
N(4)	-3025 (2)	3329 (5)	5874 (4)
N(5)	-3939 (2)	1556 (5)	4654 (4)
Co	-3015 (1)	1216 (1)	5481 (1)
The perchlorate ions			
Cl(1)	-5311 (1)	2940 (2)	1545 (1)
O(3)	-5812 (3)	3739 (6)	1987 (5)
O(4)	-5613 (4)	1998 (13)	740 (9)
O(5)	-4949 (5)	3947 (9)	1069 (11)
O(6)	-4872 (6)	2204 (14)	2324 (7)
Cl(2)	-1920 (1)	5937 (2)	4586 (1)
O(7)	-1841 (4)	7474 (7)	4529 (10)
O(8)	-2618 (4)	5543 (10)	4296 (6)
O(9)	-1718 (5)	5418 (15)	5646 (8)
O(10)	-1547 (7)	5266 (11)	3940 (13)

Table 2. Fractional atomic coordinates ( $\times 10^3$ ), isotropic thermal parameters and bond lengths (Å) for hydrogen atoms

	x	y	z	U (Å <sup>2</sup> )	Bond length
H1(C3)	-188 (3)	63 (8)	289 (6)	64 (22)	1.02 (7)
H2(C3)	-160 (4)	230 (9)	309 (6)	71 (24)	0.96 (8)
H3(C3)	-123 (4)	85 (8)	361 (6)	70 (23)	0.88 (7)
H(C5)	-93 (4)	11 (9)	732 (6)	69 (24)	0.84 (8)
H(C6)	17 (4)	13 (9)	819 (6)	74 (25)	1.02 (8)
H(C7)	90 (4)	179 (8)	735 (6)	65 (23)	0.96 (7)
H(C8)	47 (6)	272 (12)	551 (9)	130 (40)	1.03 (12)
H(C9)	-65 (4)	279 (10)	493 (7)	85 (28)	0.92 (8)
H1(C10)	-252 (4)	-161 (10)	681 (7)	82 (26)	1.10 (7)
H2(C10)	-313 (4)	-261 (10)	605 (7)	91 (29)	0.83 (9)
H1(C11)	-390 (5)	-105 (11)	642 (8)	117 (35)	0.86 (9)
H2(C11)	-344 (3)	-135 (8)	760 (6)	61 (21)	1.03 (7)
H1(N2)	-271 (3)	-127 (8)	492 (5)	50 (19)	0.84 (7)
H2(N2)	-337 (3)	-119 (7)	463 (5)	47 (18)	0.90 (6)
H1(N3)	303 (4)	76 (10)	736 (7)	90 (27)	0.76 (8)
H2(N3)	-363 (4)	123 (8)	701 (6)	64 (23)	0.88 (8)
H1(C12)	-377 (3)	496 (7)	560 (5)	48 (19)	0.94 (7)
H2(C12)	-399 (3)	361 (7)	622 (5)	43 (17)	1.01 (7)
H1(C13)	-459 (3)	336 (7)	442 (5)	44 (17)	1.00 (6)
H2(C13)	-388 (3)	349 (6)	401 (4)	23 (14)	0.91 (6)
H1(N4)	-279 (3)	387 (7)	551 (5)	39 (17)	0.86 (6)
H2(N4)	-289 (3)	346 (7)	656 (5)	44 (18)	0.84 (6)
H1(N5)	-398 (4)	113 (9)	392 (7)	81 (27)	0.97 (8)
H2(N5)	-424 (3)	109 (7)	496 (5)	33 (16)	0.88 (6)

and 2. The observed C—H and N—H distances are included in Table 2.\*

**Discussion.** The complex cation with the atom-numbering scheme is illustrated in Fig. 1. The central Co<sup>III</sup> ion is seen to be in a distorted-octahedral configuration, binding two bidentate ethylenediamine molecules and the carbonyl-oxime ligand, the latter through the oxime N and carbonyl O atoms. The geometry is identical to that observed earlier in the related mixed-ligand chelate of Co<sup>III</sup> formed with 7-nitroso-8-hydroxyquinoline-5-sulfonic acid and ethylenediamine (Korvenranta & Saarinen, 1978).

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34168 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

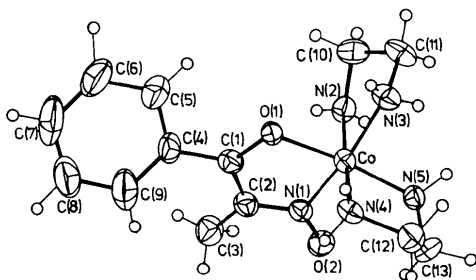


Fig. 1. A view of the complex cation and numbering of atoms. The thermal ellipsoids have been scaled to include 50% probability.

The bond lengths for non-hydrogen atoms and the important bond angles are presented in Table 3. Evidently the dimensions of the two ethylenediamine ligands are normal and the rings both form the usual *gauche* conformation with N(2)—C(10)—C(11)—N(3) and N(4)—C(12)—C(13)—N(5) torsion angles of  $-51.1$  and  $48.5^\circ$ , respectively. The Co—N(oxime) [1.889 (5) Å] and Co—O [1.918 (4) Å] bond distances are in good agreement with the respective bonds found in earlier studies on carbonyl-oxime chelates (Korvenranta & Saarinen, 1978; Saarinen, Korvenranta & Näsäkkälä, 1978; Figgis, Raston, Sharma & White, 1977). It may be noted that the present Co—N(amine) distance is significantly longer than the Co—N(oxime) distance. The average difference of 0.072 Å is nearly equal to that (average 0.079 Å) in the related mixed-ligand chelate mentioned above, and comparable to that (0.056 Å) found in dichlorobis(2-amino-2-methyl-3-butanone oximate)cobalt(III) (Schlemper, LaPlaca, Davis & Hamilton, 1978) which is a complex with typical bidentate amino oxime ligands. It is evident that the shorter Co—N(oxime) bond reflects the better donor capacities of a charged species.

The structure of the 1-phenyl-1,2-propanedione 2-oxime anion has been reported previously for the neutral cobalt(III) tris complex (Saarinen, Korvenranta & Näsäkkälä, 1978). The ligand dimensions recorded here are in relatively good agreement with those of the earlier determination. Thus, the C—N [1.342 (8) Å], C—O [1.274 (8) Å] distances and the C—N—O bond angle [120.5 (5) $^\circ$ ] found here compare well with the respective average values 1.348 (8), 1.279 (7) Å and 121.4 (2) $^\circ$  in the tris complex, while the present C(1)—C(2) [1.441 (8) Å] and N—O [1.284 (6) Å] distances are somewhat, but not very significantly,

Table 3. Bond lengths (Å) and angles ( $^\circ$ )

C(1)—C(2)	1.441 (8)	C(12)—N(4)	1.498 (8)
C(1)—C(4)	1.476 (8)	C(13)—N(5)	1.497 (8)
C(2)—C(3)	1.483 (10)	Co—O(1)	1.918 (4)
C(4)—C(5)	1.395 (10)	Co—N(1)	1.889 (5)
C(4)—C(9)	1.400 (11)	Co—N(2)	1.965 (5)
C(5)—C(6)	1.395 (11)	Co—N(3)	1.975 (5)
C(6)—C(7)	1.373 (15)	Co—N(4)	1.953 (5)
C(7)—C(8)	1.356 (15)	Co—N(5)	1.952 (4)
C(8)—C(9)	1.391 (11)	Cl(1)—O(3)	1.433 (6)
C(1)—O(1)	1.274 (8)	Cl(1)—O(4)	1.353 (11)
C(2)—N(1)	1.342 (8)	Cl(1)—O(5)	1.367 (12)
N(1)—O(2)	1.284 (6)	Cl(1)—O(6)	1.341 (10)
C(10)—C(11)	1.495 (12)	Cl(2)—O(7)	1.387 (7)
C(10)—N(2)	1.475 (10)	Cl(2)—O(8)	1.417 (7)
C(11)—N(3)	1.480 (9)	Cl(2)—O(9)	1.379 (10)
C(12)—C(13)	1.499 (9)	Cl(2)—O(10)	1.348 (16)
C(2)—C(1)—C(4)	124.0 (6)	C(3)—C(2)—N(1)	120.2 (5)
C(2)—C(1)—O(1)	118.1 (5)	C(2)—N(1)—O(2)	120.5 (5)
C(4)—C(1)—O(1)	117.9 (5)	O(1)—Co—N(1)	82.7 (2)
C(1)—C(2)—C(3)	129.1 (5)	N(2)—Co—N(3)	85.0 (2)
C(1)—C(2)—N(1)	110.3 (5)	N(4)—Co—N(5)	85.6 (2)

greater than the average values 1.421 (9) and 1.252 (7) Å reported earlier.

The perchlorate ions completing the structure show some of the expected disorder and the variations in the observed Cl—O bond lengths are rather large, 1.34–1.43 Å (Table 3). The O—Cl—O angles range from 104 to 112°. Two of the O atoms in each of the perchlorate groups are apparently involved in hydrogen-bond formation to the amine N atoms. The most probable hydrogen-bonding scheme is one consisting of four relatively weak interactions [3.217 (7)–3.252 (12) Å] between the O atoms of one perchlorate and the two nearest complex cations, and three, somewhat stronger bonds [3.017 (10), 3.021 (10) and 3.263 (9) Å] between the O atoms of the other perchlorate and a total of three different cations. The hydrogen-bond contacts in the structure are not only associated with the perchlorate groups: the closest interionic contact

[2.944 (6) Å] involves the oxime O atom, which accepts a hydrogen bond from the amine N atom in an adjacent complex cation. In this way all eight amino H atoms are active in hydrogen bonding. Details of the proposed hydrogen-bond network are presented in Table 4.

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Table 4. *Hydrogen-bond distances (Å) and angles (°)*

<i>X</i> —H... <i>Y</i>	Position of <i>Y</i>	<i>X</i> ... <i>Y</i>	<i>X</i> —H... <i>Y</i>
N(2)—H1(N2)...O(7)	<i>x</i> , 1— <i>y</i> , <i>z</i>	3.021 (10)	165 (6)
N(2)—H2(N2)...O(3)	—1— <i>x</i> , — $\frac{1}{2}$ + <i>y</i> , $\frac{1}{2}$ — <i>z</i>	3.212 (7)	166 (5)
N(3)—H1(N3)...O(8)	<i>x</i> , $\frac{1}{2}$ — <i>y</i> , $\frac{1}{2}$ + <i>z</i>	3.263 (9)	138 (8)
N(3)—H2(N3)...O(5)	<i>x</i> , $\frac{1}{2}$ — <i>y</i> , $\frac{1}{2}$ + <i>z</i>	3.252 (12)	124 (6)
N(4)—H1(N4)...O(8)	<i>x</i> , <i>y</i> , <i>z</i>	3.017 (10)	157 (5)
N(4)—H2(N4)...O(2)	<i>x</i> , $\frac{1}{2}$ — <i>y</i> , $\frac{1}{2}$ + <i>z</i>	2.944 (6)	154 (6)
N(5)—H1(N5)...O(3)	—1— <i>x</i> , — $\frac{1}{2}$ + <i>y</i> , $\frac{1}{2}$ — <i>z</i>	3.217 (7)	139 (7)
N(5)—H2(N5)...O(5)	—1— <i>x</i> , — $\frac{1}{2}$ + <i>y</i> , $\frac{1}{2}$ — <i>z</i>	3.227 (10)	151 (5)

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## The Structure of the Complex Dicytosinium Tetrachlorocuprate

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**Abstract.** [C<sub>4</sub>H<sub>6</sub>N<sub>3</sub>O]<sub>2</sub>[CuCl<sub>4</sub>], triclinic, *P* $\bar{1}$ , *a* = 13.689 (2), *b* = 9.537 (1), *c* = 6.936 (1) Å,  $\alpha$  = 102.93 (2),  $\beta$  = 105.59 (2),  $\gamma$  = 112.24 (2)°, *Z* = 2, *D*<sub>m</sub> = 1.875 (3) Mg m<sup>-3</sup>. The final *R* value is 0.082 for 2711 non-zero reflections observed on a diffractometer. There is no direct coordination between the metal atoms and cytosinium cations. The base pairing related by a center of symmetry is formed by two N(1)—H...O(2) hydrogen bonds (2.85 Å). The main intermolecular interactions consist of five kinds of N—H...Cl hydrogen bonds.

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**Introduction.** Brownish crystals were prepared by slow evaporation of a 0.1 *M* HCl solution (50 ml) containing 220 mg of cytosine and 5 g of CuCl<sub>2</sub>·2H<sub>2</sub>O which had been heated at 243 K for several hours.

Three-dimensional intensity data were collected with a crystal 0.25 × 0.25 × 0.58 mm on a Rigaku computer-controlled four-circle diffractometer using monochromated Mo *K*α radiation. With the  $\omega$ —2 $\theta$  scan technique, a scan speed of 4° (2 $\theta$ ) min<sup>-1</sup> and 10 s background measurements at each end of the scan, 2711 independent non-zero reflections were obtained with  $\sin \theta/\lambda < 0.65$  Å<sup>-1</sup>.

The structure was solved by the heavy-atom method, and refined by a block-diagonal least-squares procedure