Crystal Structure of Oxalato Di(1,10-phenanthroline-*N,N'*)cobalt(III) Nitrate 3.88 Hydrate [Co(C₁₂H₈N₂)₂(C₂O₄)]NO₃·3.88H₂O

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In the title compound, the Co^{III} ion has a slightly distorted square bipyramidal environment, coordinated by one oxalate ion and two 1,10-phenanthroline ligands. Four atoms O1^a, N1, N2 and N1^a are in a square planar arrangement and two atoms O1 and N2^a are axial [average Co–N distance = 1.942(3) Å and Co–O distance = 1.899(2) Å]. The two dimensional structure is formed by parallel layers to (100) with $a = 1/4$ and $a = 3/4$ which delimits c axis tunnels. The title compound belongs to the orthorhombic space group *Ibca*, with $a = 15.492(3)$ Å, $b = 17.938(5)$ Å, $c = 19.635$ Å, $V = 5457(2)$ Å³ and $Z = 8$. Refinement gave $R = 0.049$ and $wR(F^2) = 0.1447$ for 2584 unique observed reflections ($I > 2\sigma(I)$)

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Only a limited number of crystal structures have been reported of coordination compounds containing the dianion of oxalic acid. The dianion of oxalic acid interlinked by a long C–C distance corresponding to Csp²–Csp² single bond, acts as a chelating ligand and potentially as a bridging unit. In both respects, it exhibits a striking similarity with the dianion of 2,5-dihydroxy-1,4-benzoquinone. Because of our interest in the magnetic properties of polymeric three-dimensionally linked complexes with chelating oxalate ions as bridging ligand,¹ further studies have been extended to the synthesis of transition metal compounds containing C₂O₄²⁻ and its derivatives.

Along this line, a chain compound [M(ox)phen] or [M(ox)(bpy-d8)], where (phen: 1,10-phenanthroline; ox: oxalate; bpy-d8: 4,4'-bipyridine-d8 and M: Co, Ni, Cu), exhibiting weak antiferromagnetic properties has been reported recently.² During our attempts to synthesize a polymeric cobalt(III) compound with alternating N and O coordination from 1,10-phenanthroline and C₂O₄²⁻, respectively, a mononuclear compound, M-oxalate(1,10-phenanthroline-*N,N'*)-cobalt(III) nitrate 3.88 hydrate, (I), was obtained.

The title compound was prepared by the reaction of cobalt nitrate, 1,10-phenanthroline, phosphoric acid and oxalic acid respectively (1:2:1:1 molar ratio) in ethanol/water (1:1 v/v). The resulting mixture was heated to boiling point and stirred for two hours. An orange-pink precipitate formed immediately. After two days single pink crystals were obtained by slow evaporation from aqueous solution at room temperature.

A single crystal with the dimension of (0.3 × 0.25 × 0.2) mm³ was chosen for X-ray diffraction studies. The measurements were made on a Enraf-Nonius CAD-4 diffractometer with graphite monochromated radiation (Mo K_{α}) at 293 K. The crystal and experimental data are given in Table 1. Lorentz and polarization correction were applied. The structure was solved by heavy-atom Patterson method, expanded using Fourier techniques, and refined with anisotropic temperature factors for non-hydrogen atoms, by full-matrix least-squares based on F^2 .

O3 and OW1 occupy two atomic positions each, with occupancy factors for O3 and O3' of 0.41 and 0.09, and for OW1 and OW1' of 0.35 and 0.65, respectively.

The positions of the hydrogen atoms were determined from a difference Fourier map and were refined isotropically. Details of the crystal data and a structure refinement are given in Table 1. The final positions coordinates with equivalent isotropic temperature factors for all non hydrogen atoms are given in Table 2. Selected bond lengths and bond angles are compiled in Table 3.

The complex exists on crystallographic two fold axis which passes the mid point of oxalate anion and Co atom. Nitrate and crystalline water OW2 are also on crystallographic two fold axis. The crystal structure of the title compound consists of [Co(ox)₂phen]⁺ complex cations, nitrate anions and H₂O molecules (Fig. 1). The cobalt atoms are each coordinated by

Table 1 Crystal and experimental data

Formula: C ₂₆ H _{23.76} CoN ₅ O _{10.88}	
Formula weight = 639.14	
Crystal system: orthorhombic	
Space group: <i>Ibca</i>	$Z = 8$
$a = 15.492(3)$ Å	
$b = 17.938(5)$ Å	
$c = 19.635(3)$ Å	
$V = 5457(2)$ Å ³	
$D_x = 1.556$ g cm ⁻³	$R[F^2 > 2\sigma(F^2)] = 0.0490$
$wR(F^2) = 0.1443$	
$\lambda(\text{Mo } K_{\alpha}) = 0.71073$ Å	
$\theta_{\text{max}} = 24.97^\circ$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 0.525$ e Å ⁻³	
$(\Delta\rho)_{\text{min}} = -0.817$ e Å ⁻³	
No. of reflections used = 2584	
Measurements: Enraf-Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS Software	
Structure determination: SHELXS86	
Refinement: full matrix	

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	$U_{eq}(\text{\AA}^2)$	Occupancy
Co1	0.71709(4)	0	1/4	0.0376(2)	0.5
O1	0.6279(2)	0.0548(1)	0.2065(1)	0.0438(6)	
O2	0.4844(2)	0.0602(2)	0.2031(2)	0.0675(9)	
N1	0.7193(2)	0.0740(2)	0.3220(2)	0.0451(8)	
N2	0.8037(2)	0.0628(2)	0.2070(2)	0.0442(8)	
C1	0.5511(2)	0.0333(2)	0.2241(2)	0.0439(9)	
C2	0.6757(3)	0.0763(3)	0.3797(2)	0.0564(1)	
C3	0.6810(4)	0.1389(3)	0.4237(3)	0.0749(2)	
C4	0.7327(4)	0.1973(3)	0.4073(3)	0.0740(2)	
C5	0.7806(3)	0.1961(2)	0.3471(3)	0.0602(1)	
C6	0.8171(2)	0.1267(2)	0.2435(2)	0.0474(9)	
C7	0.8457(3)	0.0530(3)	0.1489(2)	0.0570(1)	
C8	0.9009(3)	0.1084(3)	0.1221(3)	0.074(1)	
C9	0.9120(3)	0.1736(3)	0.1575(3)	0.077(2)	
C10	0.8712(3)	0.1845(2)	0.2207(3)	0.064(1)	
C11	0.8792(3)	0.2489(3)	0.2641(3)	0.074(2)	
C12	0.8377(4)	0.2541(3)	0.3227(3)	0.074(2)	
C13	0.7721(2)	0.1330(2)	0.3051(2)	0.049(1)	
N3	3/4	0.0996(4)	0	0.092(2)	0.5
O3	0.730(1)	0.0322(4)	0.0012(6)	0.071(2)	0.41(1)
O3'	0.680(3)	0.047(2)	0.013(2)	0.071(2)	0.09(1)
O4	0.6935(4)	0.1359(4)	0.0277(3)	0.166(3)	
OW1	0.5174(9)	0.1142(7)	0.0627(6)	0.101(2)	0.35(1)
OW1'	0.4490(5)	0.1168(4)	0.0722(3)	0.101(2)	0.65(1)
OW2	1	1/4	0.0077(5)	0.186(4)	0.5
OW3	0.5501(7)	0.0105(6)	0.0136(5)	0.118(5)	0.44(1)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j).$$

Table 3 Bond distances (Å) and angles (°)

Co1-O1	1.899(2)	O1-Co1-O1 ^a	86.59(15)
Co1-O1 ^a	1.899(2)	O1-Co1-N1	89.24(12)
Co1-N1	1.939(3)	O1 ^a -Co1-N1	92.21(12)
Co1-N1 ^a	1.939(3)	O1-Co1-N1 ^a	92.21(12)
Co1-N2	1.944(3)	O1 ^a -Co1-N1 ^a	89.24(12)
Co1-N2 ^a	1.944(3)	N1-Co1-N1 ^a	178.00(19)
O1-C1	1.297(4)	O1-Co1-N2	90.39(11)
O2-C1	1.213(5)	O1 ^a -Co1-N2	175.74(12)
C1-C1 ^a	1.570(8)	N1-Co1-N2	84.73(14)
		N1 ^a -Co1-N2	93.89(13)
		O1-Co1-N2 ^a	175.74(12)
		O1 ^a -Co1-N2 ^a	90.39(11)
		N1-Co1-N2 ^a	93.89(13)
		N1 ^a -Co1-N2 ^a	84.73(14)
		N2-Co1-N2 ^a	92.77(18)
		C1-O1-Co1	113.2(2)
		O2-C1-C1 ^a	121.5(2)

Code symmetry a: x, -y, 1/2 - z

four N atoms of two phen ligand and two O atoms of one oxalato group to form distorted CoN_4O_2 octahedra (Fig. 2). Four atoms O1^a, N1, N2 and N1^a constitute the equatorial plane of the Co octahedron (Fig. 2) with the mean deviation 0.036(1) Å. The three diagonal angles of the Co polyhedron are 175.73(1)°, 175.73(1)° and 177.98(1)°, respectively, indicating a slightly distorted octahedron around the cobalt.

The Co-N bond lengths (1.938(3) – 1.946(3) Å) are slightly shorter than that of the mean $\text{Co}^{\text{III}}\text{-N}(\text{amine})$ distance (2.046(4) Å). However, all the Co-N bond contacts are in normal range comparing to those in the similar compounds³

(1.935 – 1.960 Å). The Co-O bond length 1.898(2) Å is comparable to those reported for $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_3\text{O})(\text{NO}_2)_2]$ (1.889(2) – 1.880(3) Å)⁴ reflect an anionic character of the ligand atom.

The nitrate anion exhibit significant deviation from D_{3h} symmetry. In oxalato ligand the C – O bonds to the chelating O atoms are unexpectedly elongated to 1.297(5) Å, substantially larger than that (1.213(5) Å) to the non-coordinating one.

The phen ligand containing N₁ and N₂ atoms are π - π stacking. They interact with two symmetry-related phen ligand (interplanar distances: 3.761(1) and 4.023(1) Å). Obviously, such π - π stacking interactions are responsible for the supramolecular assembly of the complex cations into 2D layers parallel to (100) which delimits *c*-axis tunnels. In this layers there are weak hydrogen bonding interaction between the water oxygen OW2, OW3, OW1' and OW1 atoms ($d_{\text{OW}_2\text{-OW}_1'} = 2.56(4)$ Å and $d_{\text{OW}_3\text{-OW}_1} = 2.155(0)$ Å). A structure analysis was complicated by an extensive disorder of oxygen atoms in nitrate anion and water molecules.

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