

Bis(2,2'-bipyridine- κ^2N,N')(oxalato- κ^2O,O')cobalt(II) pentahydrate

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Received 29 September 2004

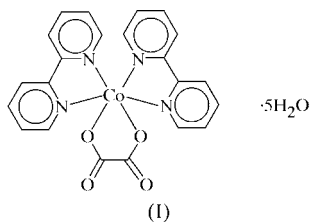
Accepted 6 October 2004

Online 31 October 2004

The synthesis and crystal structure of the mononuclear title compound, $[\text{Co}(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)_2]\cdot 5\text{H}_2\text{O}$, is reported. The Co atom is six-coordinated by two O atoms of a bidentate oxalate group and by four N atoms of two bipyridine ligands. The neutral $[\text{Co}(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ entities are connected by π - π stacking interactions of the aromatic systems into a two-dimensional layer, interconnected through a ladder-like hydrogen-bonding pattern of solvate water molecules.

Comment

Oxalate-bridged polymeric compounds of transition metal elements have attracted significant attention in the literature, mainly due to their interesting magnetic properties (Castillo, Luque & Román, 2001). Polymeric chain structures are predominant in the solid-state chemistry of cobalt(II), as represented by the compounds $\{[\text{Co}(\mu\text{-C}_2\text{O}_4)L_2]\cdot m\text{H}_2\text{O}\}_n$ [where L is H_2O (García-Couceiro *et al.*, 2004), N -amino-pyridine (Castillo, Luque, Román *et al.*, 2001), and 3-hydroxypyridine and isoquinoline (Castillo, Luque, Lloret & Román, 2001)] and $\text{Na}_2[\text{Co}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_2]$ (Price *et al.*, 2000), although two-dimensional $[\text{Co}(\mu\text{-C}_2\text{O}_4)(4,4'\text{-bpy})]_n$ (Lu *et al.*, 1999; Zheng *et al.*, 1999) and three-dimensional $[\text{Co}(2,2'\text{-bpy})_3][\text{Co}_2(\text{C}_2\text{O}_4)_3]\text{ClO}_4$ (Hernández-Molina *et al.*, 1998) have also been described (2,2'- and 4,4'-bpy are 2,2'- and 4,4'-bipyridine, respectively). Fewer data exist on the preparation



and structures of simple mononuclear cobalt(II) oxalate compounds. The reason for this is the polydentate nature of the oxalate ligand, which can be bi-, tri- or tetradentate. Recently, the compounds $[\text{Co}(\text{C}_2\text{O}_4)(2,2'\text{-bpy})]\cdot 4\text{H}_2\text{O}$ and

$[\text{Co}(\text{C}_2\text{O}_4)(4,4'\text{-bpy})_{1.5}]\cdot 2\text{H}_2\text{O}$ have been reported, but they were characterized by analytical, spectroscopic (IR and UV) and thermal techniques only (Czakis-Sulikowska *et al.*, 2000). Data on the crystal structures of simple mononuclear cobalt(II) oxalate compounds are non-existent to date. Against this background, we present here the crystal structure of the title mononuclear cobalt(II) oxalate complex, (I).

The crystal structure of (I) consists of neutral mononuclear $[\text{Co}(\text{C}_2\text{O}_4)(2,2'\text{-bpy})_2]$ units and five solvate water molecules, held together by intermolecular π - π stacking interactions and an extensive hydrogen-bonding network. A view of the mononuclear complex entity, with the atom-numbering scheme, is given in Fig. 1, and selected geometric parameters are listed in Table 1.

Two O atoms from one bidentate oxalate anion and four N atoms from two chelating bipyridine ligands form a distorted octahedron around the metal atom. Each ligand exhibits a *cis* arrangement of its two donor atoms coordinated to the Co^{II} atom. The C—O bond lengths are as expected for a bidentate oxalate ligand (Zheng *et al.*, 1999), and the C—N bond lengths are comparable with those found in $[\text{Ni}(\text{ox})(2,2'\text{-bpy})_2]\cdot 4\text{H}_2\text{O}$ (ox is oxalate; Román *et al.*, 1995). The N—Co—N and O—Co—O bite angles deviate considerably from the ideal value of 90° because of the constrained geometry of the bipyridine and oxalate ligands. The best least-squares plane of the CoN_4O_2 chromophore is defined by atoms O2, N11, N12 and N21 [greatest deviation = 0.1381 (19) Å for N11], and the Co atom is 0.0294 (2) Å out of this plane. The individual pyridine rings of the two bipyridine ligands are planar [greatest deviations from the mean planes are 0.006 (2) Å for atoms C24 and N22]. One bipyridine ligand, labelled bpy(1), is planar [dihedral angle between pyridine rings py(1) (atoms N11/C11—C15) and py(2) (atoms N12/C16—C110) is $1.38 (12)^\circ$], while the other, labelled bpy(2), is twisted, with a dihedral angle between pyridine rings py(3) (atoms N21/C21—C25) and py(4) (atoms N22/C26—C210) of $6.18 (10)^\circ$. The oxalate anion shows some deviation from planarity, with the O1—C1—C2—O2 and O11—C1—C2—O22 torsion angles

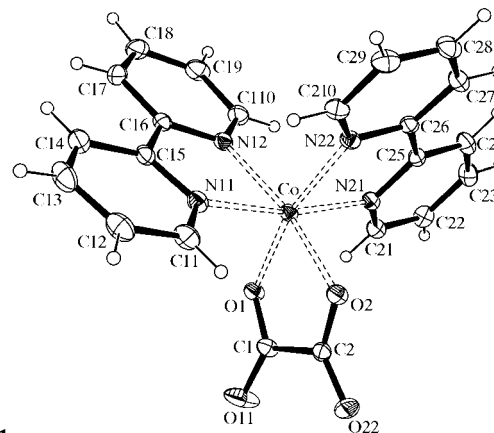


Figure 1

A view of the mononuclear $[\text{Co}(\text{ox})(\text{bpy})_2]$ entity in (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

being 13.1 (3) and 14.0 (3)°, respectively. The three ligands around the Co^{II} atom are almost perpendicular to each other. The dihedral angles between the mean oxalate plane and the mean bipyridine planes are 89.74 (7) and 89.27 (7)°, respectively, whereas that between the two mean bipyridine planes is 86.61 (6)°.

The neutral complex entities of (I) are stacked together by means of π - π intermolecular interactions between the aromatic systems of the bipyridine ligands (Fig. 2). Two different stacking interactions can be distinguished in the crystal structure. The first interaction (grey dashed lines in Fig. 2) involves ring py(3) from one entity (*A*) and ring py(4)ⁱⁱ from a neighbouring entity (*A*ⁱⁱ), mutually related through the glide-plane symmetry [symmetry code: (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$]. The distance between the centres of the py(4)ⁱⁱ and py(3) rings is 3.536 (2) Å, while the perpendicular distance from the centre of py(4)ⁱⁱ to the mean plane of py(3) is 3.388 (2) Å. The dihedral angle between the mean planes of these two pyridine rings is 1.71°. The glide-plane symmetry results in an interaction between py(4) of *A* and py(3)ⁱⁱⁱ of a neighbouring entity [*A*ⁱⁱⁱ; symmetry code (iii): $x, \frac{1}{2} - y, z - \frac{1}{2}$]. This entity is related to *A*ⁱⁱ by a translation of one repeat along the crystallographic *c* axis. In this way, one-dimensional stacking motifs are formed. The second interaction represents stacking of the bpy(1) ligands (grey dotted lines in Fig. 2). The bpy(1)ⁱⁱ ligand from one entity (*A*ⁱⁱ) interacts with the bpy(1)^{iv} ligand in a neighbouring entity [*A*^{iv}; symmetry code: (iv) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$]. These two latter entities are related through a centre of symmetry, *i*, so that the dihedral angle between the mean

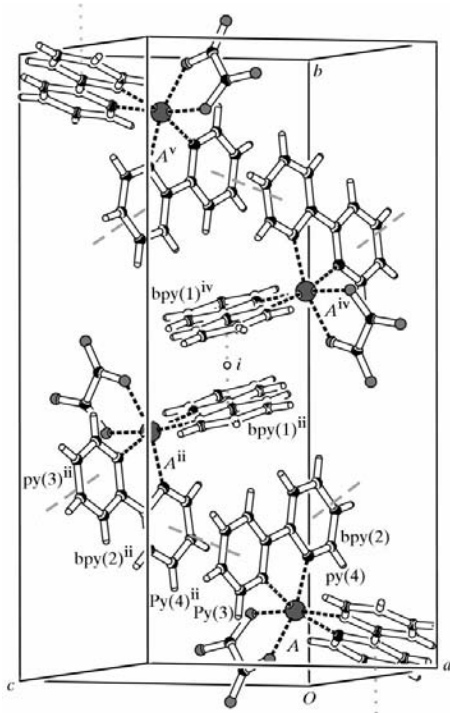


Figure 2
The crystal packing of mononuclear entities in the unit cell of (I). The two different stacking interactions of the aromatic systems in the bipyridine ligands are shown as dashed and dotted grey lines [symmetry codes: (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $1 - x, 1 - y, 1 - z$].

planes of the two stacked bipyridines is 0°. The distance between their mean planes is 3.498 (2) Å, while the distance between their centres of gravity is 3.880 (2) Å. The fact that the entire bpy(1) ligand is involved in the stacking interaction, in contrast with the bpy(2) ligands, where only individual py(3) and py(4) pyridine rings interact, could explain the greater planarity of the bpy(1) ligand. A stacking interaction between bpy(1) ligands connects one-dimensional stacking motifs, formed by interaction of the bpy(2) ligands, into two-dimensional layers parallel to the *bc* plane of the monoclinic unit cell.

Solvate water molecules are located between the layers of neutral entities in the structure of (I). One hydrogen-bonding motif can be described as a pentagon, with the graph-set descriptor $R_3^3(10)$ (Etter *et al.*, 1990). This involves all five solvate water molecules, connected by O6—H61...O8, O6—H62...O5, O7—H71...O9, O7—H72...O5 and O9—H91...O8 hydrogen bonds (Fig. 3 and Table 2). These pentagonal rings are mutually connected by O9—H92...O6 and O8—H82...O7 hydrogen bonds (Fig. 3 and Table 2), thus forming a ladder pattern which extends along the crystallographic *c* axis. A smaller four-membered ring motif of graph set $R_4^4(8)$ can also be recognized inside the ladder pattern (Fig. 3). The remaining three hydrogen bonds include two water molecules (O8 and O5) as donors and three O atoms from oxalate ligands (O2, O11 and O22) as acceptors (Table 2). Two of them (O8—H81...O2ⁱⁱ and O5—H52...O22) connect a hydrogen-bonding ladder pattern with only one layer of neutral entities formed by stacking interactions. The hydrogen bond O5—H51...O11ⁱ connects the hydrogen-bonding ladder pattern with a second layer of neutral entities [symmetry code: (i) $-x, -y, 1 - z$]. Thus, this hydrogen bond completes the three-dimensional crystal structure of (I).

This type of crystal packing is identical to that observed in the crystal structure of [Cu(ox)(phen)₂].5H₂O, although the

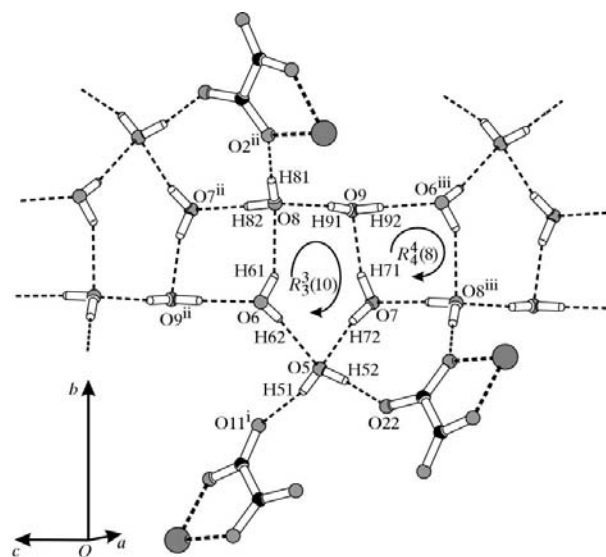


Figure 3
The hydrogen-bonding pattern formed by the solvate water molecules of (I). Ring motifs are denoted by their graph-set descriptors. Symmetry codes are as given in Table 2.

latter compound contains 1,10-phenanthroline (phen) instead of 2,2'-bipyridine (Castillo, Luque & Román, 2001). On the other hand, the compound [Ni(ox)(2,2'-bpy)₂]₂·4H₂O, with an identical set of ligands bonded to the central metal atom, has a different crystal structure (Román *et al.*, 1995). In spite of the fact that [Ni(ox)(2,2'-bpy)₂]₂·4H₂O crystallizes in the same space group as (I), it can be shown that the characteristic structural patterns formed by intermolecular π - π stacking interactions of the aromatic systems in this compound are one-dimensional chains (Román *et al.*, 1995). As shown in the present work, the characteristic structural patterns in (I) are two-dimensional layers connected by the hydrogen-bonded solvate water molecules.

Experimental

A few single crystals of (I) were formed simultaneously with crystals of [Co(bpy)₃]₂[NbO(C₂O₄)₃]Cl·12H₂O after mixing and slow evaporation of an aqueous solution of [Co(bpy)₃]Cl₂·6H₂O (0.139 g, 0.197 mmol in 8 ml) and Rb₃[NbO(C₂O₄)₃]·2H₂O (0.131 g, 0.197 mmol in 12 ml) (Šestan *et al.*, 2004).

Crystal data

| | |
|--|---|
| [Co(C ₂ O ₄)(C ₁₀ H ₈ N ₂) ₂] ₂ ·5H ₂ O | $D_x = 1.514 \text{ Mg m}^{-3}$ |
| $M_r = 549.40$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 13 313 reflections |
| $a = 10.001 (2) \text{ \AA}$ | $\theta = 2.1\text{--}30.0^\circ$ |
| $b = 22.861 (5) \text{ \AA}$ | $\mu = 0.77 \text{ mm}^{-1}$ |
| $c = 10.844 (2) \text{ \AA}$ | $T = 200 (3) \text{ K}$ |
| $\beta = 103.57 (3)^\circ$ | Needle, yellow |
| $V = 2410.1 (9) \text{ \AA}^3$ | $0.20 \times 0.10 \times 0.05 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|---|--|
| Nonius KappaCCD area-detector diffractometer | 6777 independent reflections |
| ω scans | 4778 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (DENZO and SCALEPACK; Otwinowski & Minor, 1997) | $R_{\text{int}} = 0.033$ |
| $T_{\text{min}} = 0.85$, $T_{\text{max}} = 0.96$ | $\theta_{\text{max}} = 30.0^\circ$ |
| 13 313 measured reflections | $h = -14 \rightarrow 14$ |
| | $k = -32 \rightarrow 32$ |
| | $l = -14 \rightarrow 14$ |

Refinement

| | |
|---------------------|--|
| Refinement on F^2 | H atoms treated by a mixture of independent and constrained refinement |
| $R(F) = 0.040$ | $w = 1/[\sigma^2(F_o^2) + (0.0794P)^2]$ |
| $wR(F^2) = 0.137$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.07$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 6777 reflections | $\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$ |
| 365 parameters | $\Delta\rho_{\text{min}} = -1.02 \text{ e \AA}^{-3}$ |

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|-----------|-------------|------------|-------------|
| Co—O1 | 2.0939 (15) | Co—N12 | 2.091 (2) |
| Co—O2 | 2.0213 (17) | Co—N21 | 2.1872 (19) |
| Co—N11 | 2.262 (2) | Co—N22 | 2.1367 (19) |
| O1—Co—O2 | 76.27 (7) | O2—Co—N22 | 93.33 (7) |
| O1—Co—N11 | 97.94 (7) | N11—Co—N12 | 68.75 (8) |
| O1—Co—N12 | 98.45 (7) | N11—Co—N21 | 168.08 (7) |
| O1—Co—N21 | 91.63 (7) | N11—Co—N22 | 93.04 (8) |
| O1—Co—N22 | 166.06 (7) | N12—Co—N21 | 102.91 (8) |
| O2—Co—N11 | 100.54 (7) | N12—Co—N22 | 93.51 (8) |
| O2—Co—N12 | 167.58 (7) | N21—Co—N22 | 78.68 (8) |
| O2—Co—N21 | 88.59 (7) | | |

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

| $D\text{---}H\cdots A$ | $D\text{---}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{---}H\cdots A$ |
|----------------------------|----------------|-------------|-------------|------------------------|
| O5—H51···O11 ⁱ | 0.82 (2) | 1.89 (3) | 2.678 (3) | 159 (3) |
| O5—H52···O22 | 0.83 (3) | 1.90 (3) | 2.681 (3) | 156 (3) |
| O6—H61···O8 | 0.83 (3) | 2.19 (2) | 2.946 (3) | 153 (3) |
| O6—H62···O5 | 0.85 (3) | 2.10 (3) | 2.932 (3) | 168 (3) |
| O7—H71···O9 | 0.85 (2) | 1.95 (2) | 2.768 (3) | 164 (3) |
| O7—H72···O5 | 0.86 (3) | 1.99 (3) | 2.843 (3) | 169 (3) |
| O8—H81···O2 ⁱⁱ | 0.83 (3) | 1.89 (3) | 2.709 (2) | 170 (3) |
| O8—H82···O7 ⁱⁱ | 0.86 (4) | 1.84 (4) | 2.698 (3) | 178 (4) |
| O9—H91···O8 | 0.83 (2) | 2.145 (19) | 2.970 (3) | 174 (3) |
| O9—H92···O6 ⁱⁱⁱ | 0.85 (3) | 1.91 (3) | 2.763 (3) | 177 (4) |

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

H atoms were located from a difference Fourier synthesis. In the final refinements, O—H bonds were restrained to a target value of 0.84 \AA and H—O—H angles were restrained to a target value of 104°. All other H atoms were treated as riding, with C—H distances of 0.93 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO and SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: PLATON.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1107). Services for accessing these data are described at the back of the journal.

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