

## A novel cobalt(II) coordination polymer containing the fumarate anion and *o*-phenanthroline

Jian-Fang Ma,\* Jin Yang and Jing-Fu Liu

Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

Correspondence e-mail: jfma@public.cc.jl.cn

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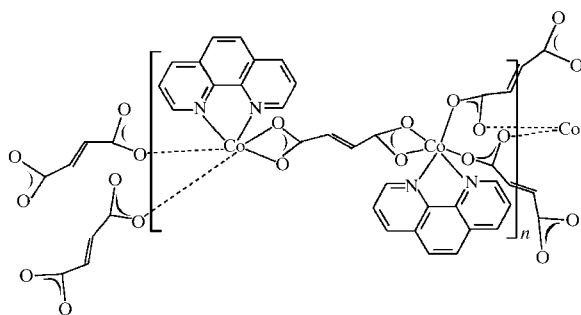
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The self-assembly of three crystallographically distinct fumarate ions, two unique cobalt(II) ions and two unique *o*-phenanthroline molecules results in a two-dimensional polymeric structure with the formula  $[\text{Co}_2(\text{C}_4\text{H}_2\text{O}_4)_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]_n$ , namely di- $\mu$ -fumatato-bis(*o*-phenanthroline)-dicobalt(II). The Co atoms are at the nodes of a two-dimensional array linked by coordinated fumarate ligands. Each Co atom is coordinated in a distorted octahedral manner to four fumarate O atoms and two N atoms from the chelating phenanthroline ligands.

### Comment

The coordination chemistry of polycarboxylic acids has been studied widely (Rochon & Massarweh, 2001). Polycarboxylic acids, such as fumaric and maleic acid, are capable of forming one-, two- or three-dimensional infinite connections between cations and anions (Ma *et al.*, 1993; Young *et al.*, 1998), thereby building chain structures, layered compounds or three-dimensional frameworks. The metal–fumarate complexes reported to date indicate that there may be a wide range of structural and chemical properties, which depend on the nature of the cations employed. To our knowledge, only a few



(I)

metal–fumarate complexes with other neutral ligands have been reported (for example, see Charpin *et al.*, 1987; Devereux *et al.*, 2000; Mukherjee *et al.*, 2001). The incorporation of a

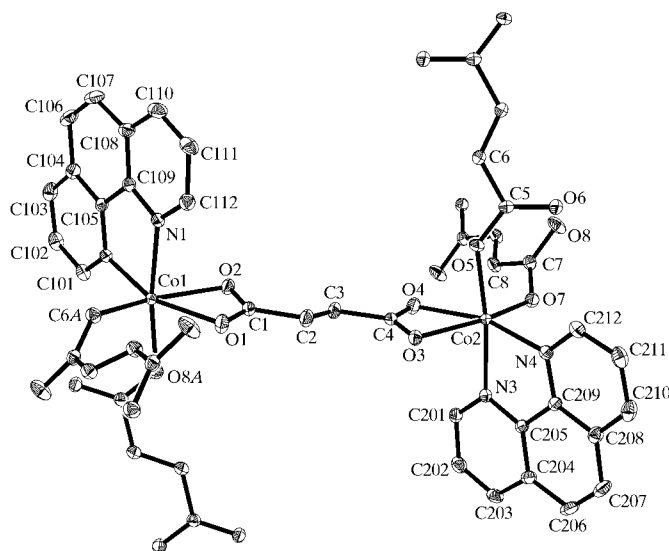


Figure 1

A view of the local coordination of the  $\text{Co}^{\text{II}}$  atoms, with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (A)  $x, 1 - y, -\frac{1}{2} + z$ .]

second organic ligand into metal–fumarate phases provides a powerful method for structural modification and synthesis of novel organic–inorganic hybrid materials. Organic components have been used as structure-directing reagents in a wide range of materials, including zeolites and mesoporous materials of the MCM-41 class (Zapf *et al.*, 1997). We report here the preparation and crystal structure of a new cobalt(II)–fumarate (fum) complex with *o*-phenanthroline (phen), namely polymeric  $[\text{Co}_2(\text{fum})_2(\text{phen})_2]_n$  (I).

The structure contains three crystallographically distinct fumarate ions (F, F' and F''), two unique cobalt(II) ions and two unique *o*-phenanthroline molecules (Fig. 1). Ions F and F' and the two cobalt(II) ions are linked into chains with the

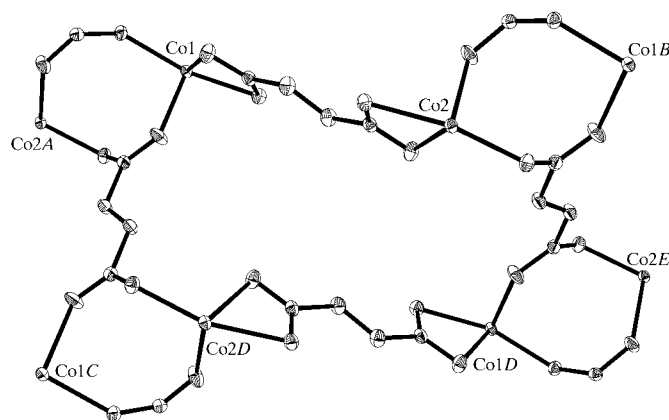
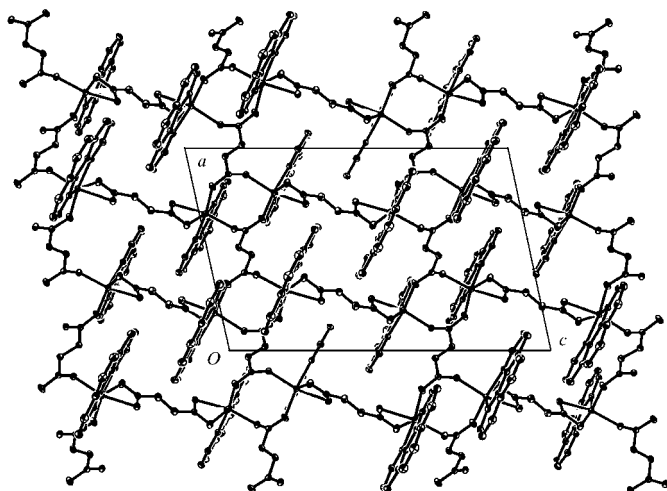


Figure 2

The large 28-membered ring and smaller eight-membered ring in (I). The *o*-phenanthroline ligands have been omitted for clarity. [Symmetry codes: (A)  $x, 1 - y, -\frac{1}{2} + z$ ; (B)  $x, 1 - y, \frac{1}{2} + z$ ; (C)  $1 - x, 1 - y, 1 - z$ ; (D)  $1 - x, \frac{3}{2} - z$ ; (E)  $1 - x, 1 - y, 2 - z$ .]



**Figure 3**  
A two-dimensional sheet in complex (I), viewed along *b*.

sequence  $\cdots\text{FCo}_2\text{F}'\text{Co}_2\cdots$  parallel to *a*. The bridging carboxylate groups give rise to eight-membered rings (Figs. 2 and 3). These chains are linked by the third fumarate ion ( $\text{F}''$ ), which forms four-membered chelate rings with a  $\text{Co}^{\text{II}}$  atom at each end of the ion, thus completing a two-dimensional polymeric arrangement containing both eight- and 28-membered rings. The trans-ring  $\text{Co}\cdots\text{Co}$  distance is 4.430 (2) Å in the eight-membered ring, while the  $\text{Co}\cdots\text{Co}$  edge lengths are 7.918 (2) and 8.728 (2) Å for the 28-membered ring. One chelating *o*-phenanthroline ligand completes a distorted octahedral coordination environment about each unique  $\text{Co}^{\text{II}}$  atom. The *o*-phenanthroline ligands fill the space formed by the 28-membered rings and contribute some additional stability to the net *via*  $\pi$ - $\pi$  interactions [the interplanar distances are 3.40 (1) and 3.59 (1) Å]. The average  $\text{Co}-\text{N}$  distance of 2.130 (1) Å is similar to that of other cobalt(II) complexes with *o*-phenanthroline (Yin & Jiang, 2001), and the  $\text{Co}-\text{O}_{\text{fum}}$  distances range from 2.0228 (13) to 2.1843 (12) Å (Table 1).

The cobalt(II) cations are thus bridged by fumarate anions to form an infinite two-dimensional polymeric structure. Many two-dimensional coordination polymers have been reported, but examples containing two kinds of rings are rarely seen (Dai *et al.*, 2002). The structure of (I) is clearly different from that of the cobalt(II)-fumarate complex reported by Gupta & Sinha (1978), in which the  $\text{Co}^{\text{II}}$  atom is six-coordinated by four water molecules and two carboxylate O atoms from the fumarate anion. It can be seen that the incorporation of an *o*-phenanthroline ligand into cobalt(II)-fumarate phases provides a powerful method for structural modification and the synthesis of novel structures. Interpenetration often occurs in compounds with two-dimensional polymeric structures (Ma *et al.*, 2000), but interpenetration does not occur in (I). We believe that the *o*-phenanthroline molecules prevent self-interpenetration by occupying the large voids in network structures.

## Experimental

A mixture of fumaric acid (0.116 g, 1 mmol) and NaOH (0.080 g, 2 mmol) in water (10 ml) was added with constant stirring to a solution of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (0.237 g, 1 mmol) in water (10 ml). *o*-Phenanthroline (0.198 g, 1 mmol) was added to the solution with stirring. Purple crystals of (I) were obtained from the solution after it had been allowed to stand at room temperature for several days (68% yield based on Co). Analysis calculated for  $\text{C}_{32}\text{H}_{20}\text{Co}_2\text{N}_4\text{O}_8$ : C 54.36, H 2.83, N 7.93%; found: C 54.53, H 2.68, N 8.03%. IR ( $\text{cm}^{-1}$ , KBr): 3439 (vs), 3063 (w), 2171 (w), 1600 (vs), 1555 (s), 1515 (m), 1454 (m), 1426 (s), 1375 (m), 1199 (w), 1146 (w), 1107 (w), 985 (w), 856 (w), 801 (w), 729 (m), 696 (m), 679 (w).

## Crystal data

$[\text{Co}_2(\text{C}_4\text{H}_2\text{O}_4)_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$   
 $M_r = 706.38$   
Monoclinic,  $P2_1/c$   
 $a = 12.264$  (3) Å  
 $b = 10.111$  (2) Å  
 $c = 22.650$  (5) Å  
 $\beta = 96.89$  (3)°  
 $V = 2788.2$  (11) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.683$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 24 016 reflections  
 $\theta = 1.7$ – $27.5^\circ$   
 $\mu = 1.25$  mm<sup>-1</sup>  
 $T = 193$  (2) K  
Block, purple  
 $0.44 \times 0.37 \times 0.24$  mm

## Data collection

Rigaku R-Axis RAPID  
diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan  
(*ABSCOR*; Higashi, 1995)  
 $T_{\text{min}} = 0.549$ ,  $T_{\text{max}} = 0.744$   
24 016 measured reflections

6376 independent reflections  
5500 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.034$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = 0 \rightarrow 15$   
 $k = 0 \rightarrow 13$   
 $l = -29 \rightarrow 29$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.086$   
 $S = 1.07$   
6376 reflections  
415 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0564P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.003$   
 $\Delta\rho_{\text{max}} = 0.58$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.58$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

N1—Co1	2.1432 (15)	O3—Co2	2.1731 (13)
N2—Co1	2.1329 (14)	O4—Co2	2.1674 (12)
N3—Co2	2.1312 (14)	O5—Co2	2.0712 (12)
N4—Co2	2.1136 (14)	O6—Co1 <sup>i</sup>	2.0415 (13)
O1—Co1	2.1843 (12)	O7—Co2	2.0228 (13)
O2—Co1	2.1792 (12)	O8—Co1 <sup>i</sup>	2.0535 (12)
O6 <sup>ii</sup> —Co1—O8 <sup>ii</sup>	97.19 (5)	O7—Co2—O5	96.62 (5)
O6 <sup>ii</sup> —Co1—N2	99.27 (5)	O7—Co2—N4	94.75 (5)
O8 <sup>ii</sup> —Co1—N2	105.71 (5)	O5—Co2—N4	103.72 (5)
O6 <sup>ii</sup> —Co1—N1	88.94 (5)	O7—Co2—N3	90.43 (5)
O8 <sup>ii</sup> —Co1—N1	172.12 (5)	O5—Co2—N3	172.37 (5)
N2—Co1—N1	78.03 (5)	N4—Co2—N3	78.49 (5)
O6 <sup>ii</sup> —Co1—O2	158.43 (5)	O7—Co2—O4	100.35 (5)
O8 <sup>ii</sup> —Co1—O2	86.00 (5)	O5—Co2—O4	84.88 (5)
N2—Co1—O2	100.37 (5)	N4—Co2—O4	161.68 (5)
N1—Co1—O2	86.49 (5)	N3—Co2—O4	91.00 (5)
O6 <sup>ii</sup> —Co1—O1	98.19 (5)	O7—Co2—O3	161.40 (5)
O8 <sup>ii</sup> —Co1—O1	83.88 (5)	O5—Co2—O3	85.19 (5)
N2—Co1—O1	158.78 (5)	N4—Co2—O3	102.82 (5)
N1—Co1—O1	90.36 (5)	N3—Co2—O3	87.20 (5)
O2—Co1—O1	60.81 (4)	O4—Co2—O3	61.29 (4)

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

All H atoms attached to C atoms were positioned geometrically and refined as riding atoms, with C—H distances of 0.93 Å and  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$ .

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1410). Services for accessing these data are described at the back of the journal.

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