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

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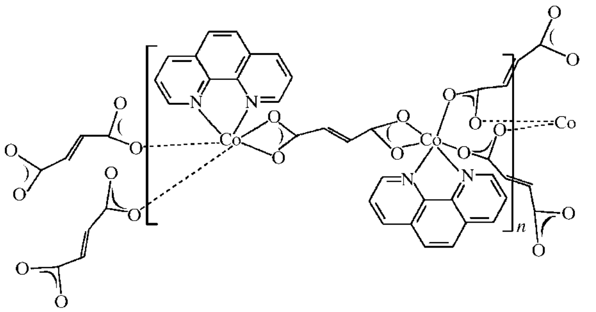
The self-assembly of three crystallographically distinct fumarate ions, two unique cobalt(II) ions and two unique *o*-phenanthroline molecules results in a two-dimensional polymeric structure with the formula $[Co_2(C_4H_2O_4)_2(C_{12}H_8N_2)_2]_n$, namely di-$\mu$-fumatato-bis(*o*-phenanthroline)dicobalt(II). 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 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 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 $[Co_2(fum)_2(phen)_2]$, (I).



(I)

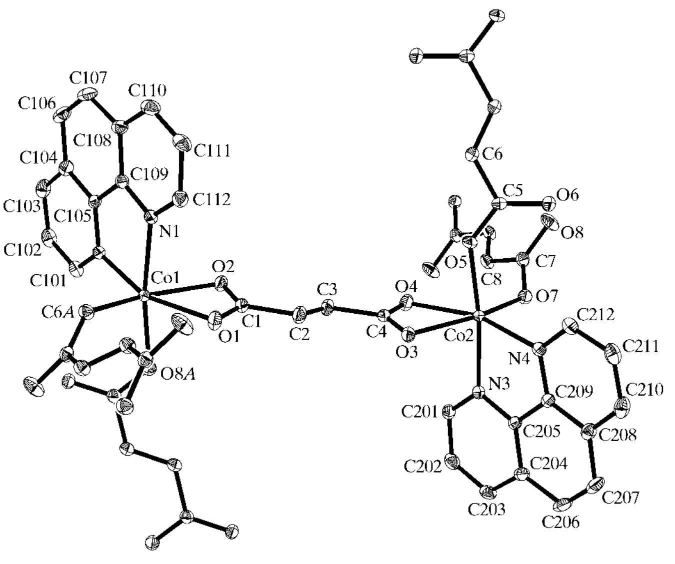


Figure 1
A view of the local coordination of the Co^{II} atoms, with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (*A*) $x, 1-y, -\frac{1}{2}+z$.]

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

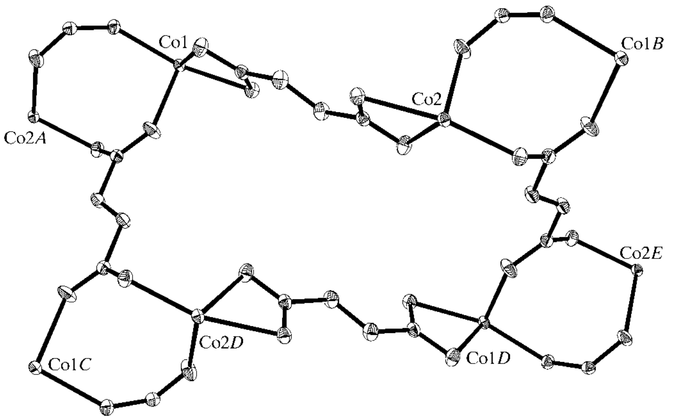


Figure 2
The large 28-membered ring and smaller eight-membered ring in (I). The *o*-phenanthroline ligands have been omitted for clarity. [Symmetry codes: (*A*) $x, 1-y, -\frac{1}{2}+z$; (*B*) $x, 1-y, \frac{1}{2}+z$; (*C*) $1-x, 1-y, 1-z$; (*D*) $1-x, y, \frac{3}{2}-z$; (*E*) $1-x, 1-y, 2-z$.]

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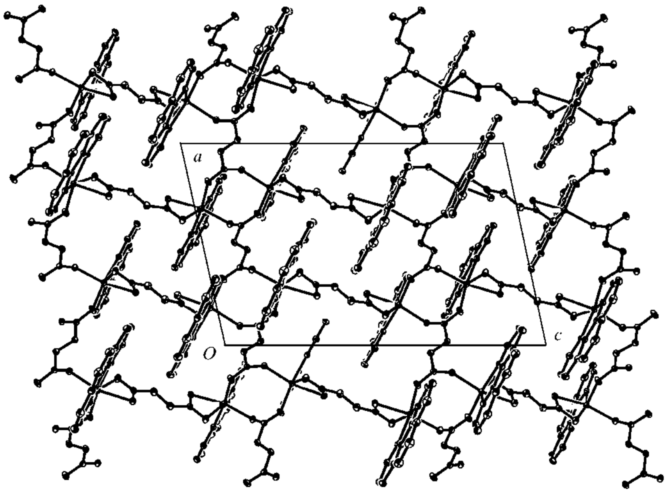

Figure 3
A two-dimensional sheet in complex (I), viewed along *b*.

sequence $\cdots FCo_2F'Co_2\cdots$ 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 (F″), which forms four-membered chelate rings with a Co^{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 Co$\cdots$Co distance is 4.430 (2) Å in the eight-membered ring, while the Co$\cdots$Co edge lengths are 7.918 (2) and 8.728 (2) Å for the 28-membered ring. One chelating *o*-phenantholine ligand completes a distorted octahedral coordination environment about each unique Co^{II} atom. The *o*-phenanthroline ligands fill the space formed by the 28-membered rings and contribute some additional stability to the net *via* π–π interactions [the interplanar distances are 3.40 (1) and 3.59 (1) Å]. The average Co—N distance of 2.130 (1) Å is similar to that of other cobalt(II) complexes with *o*-phenanthroline (Yin & Jiang, 2001), and the Co—O$_{fum}$ 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 Co^{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 $CoCl_2\cdot 6H_2O$ (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 $C_{32}H_{20}Co_2N_4O_8$: C 54.36, H 2.83, N 7.93%; found: C 54.53, H 2.68, N 8.03%. IR (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

$[Co_2(C_4H_2O_4)_2(C_{12}H_8N_2)_2]$
$M_r = 706.38$
Monoclinic, $P2/c$
$a = 12.264$ (3) Å
$b = 10.111$ (2) Å
$c = 22.650$ (5) Å
$\beta = 96.89$ (3)°
$V = 2788.2$ (11) Å^3
$Z = 4$

$D_x = 1.683$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 016 reflections
$\theta = 1.7$–27.5°
$\mu = 1.25$ mm^{-1}
$T = 193$ (2) K
Block, purple
0.44 × 0.37 × 0.24 mm

Data collection

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

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

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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}

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^{i}	2.0415 (13)
O1—Co1	2.1843 (12)	O7—Co2	2.0228 (13)
O2—Co1	2.1792 (12)	O8—Co1^{i}	2.0535 (12)
O6^{ii}—Co1—O8^{ii}	97.19 (5)	O7—Co2—O5	96.62 (5)
O6^{ii}—Co1—N2	99.27 (5)	O7—Co2—N4	94.75 (5)
O8^{ii}—Co1—N2	105.71 (5)	O5—Co2—N4	103.72 (5)
O6^{ii}—Co1—N1	88.94 (5)	O7—Co2—N3	90.43 (5)
O8^{ii}—Co1—N1	172.12 (5)	O5—Co2—N3	172.37 (5)
N2—Co1—N1	78.03 (5)	N4—Co2—N3	78.49 (5)
O6^{ii}—Co1—O2	158.43 (5)	O7—Co2—O4	100.35 (5)
O8^{ii}—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^{ii}—Co1—O1	98.19 (5)	O7—Co2—O3	161.40 (5)
O8^{ii}—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 $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

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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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