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Tris(phenanthroline-κ^2N,N')cobalt(II) fumarate fumaric acid tetrahydrate

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Key indicators

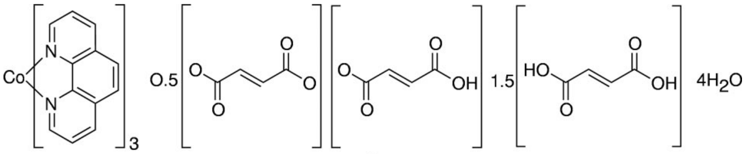
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.052
wR factor = 0.135
Data-to-parameter ratio = 15.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Co(C_{12}H_8N_2)_3](C_4H_2O_4)_{0.5}(C_4H_3O_4)\cdot 1.5C_4H_4O_4\cdot 4H_2O$, consists of the cobalt(II) complex cation with phenanthroline (phen), half a fumarate dianion, a fumarate monoanion, one and a half fumaric acid molecule and uncoordinated water molecules. The separations of 3.342 (8) and 3.493 (15) Å between the phen rings related by inversion centers indicate the existence of π–π-stacking interactions between the neighboring complex ions. These complex molecules assemble as hydrophobic layers *via* π–π stacking. Fumarate, fumaric acid and water are linked to each other to form hydrophilic layers by hydrogen bonding in the crystal structure.

Comment

Crystals of the title complex were obtained accidentally during the preparation of a Co^{II} complex bridged by fumarate. The Co^{II} complex displays an octahedral geometry (Fig. 1), formed by three chelating phenanthroline (phen) molecules. In addition to the Co^{II} complex, a fumarate dianion, fumarate monoanion and fumaric acid occur in title compound. They were recognized by comparing the differences in C—O bonds in the carboxyl groups. The smaller differences of 0.013 (6) Å in the C41-carboxyl group and 0.041 (8) Å in the C61-carboxyl group (Table 1) indicate that both the C41- and C61-carboxyls are deprotonated groups, while the larger differences of 0.055 (6) Å in the C44-carboxyl, 0.089 (8) Å in the C51-carboxyl and 0.119 (6) Å in the C53- and C55-carboxyl groups showed that these carboxyl groups are unionized. The fumarate monoanion is located in a crystallographic general position, while the fumarate dianion and neutral fumaric acid molecule are located on inversion centers. The Co^{II} complex displays an octahedral geometry, formed by three chelating phen molecules with normal bond distances and angles.



(I)

An extensive hydrogen-bonding network occurs between carboxylic/carboxylate groups and water molecules, as shown in Fig. 1 and Table 2. The separations of 3.342 (8) and 3.493 (15) Å indicate the existence of π–π-stacking interactions between neighboring phen molecules related by an inversion center, as shown in Fig. 2. An approximately parallel arrangement of the C53-fumaric acid with the N5-phen ring is observed (Fig. 3). The shorter distances to the N5-phen plane

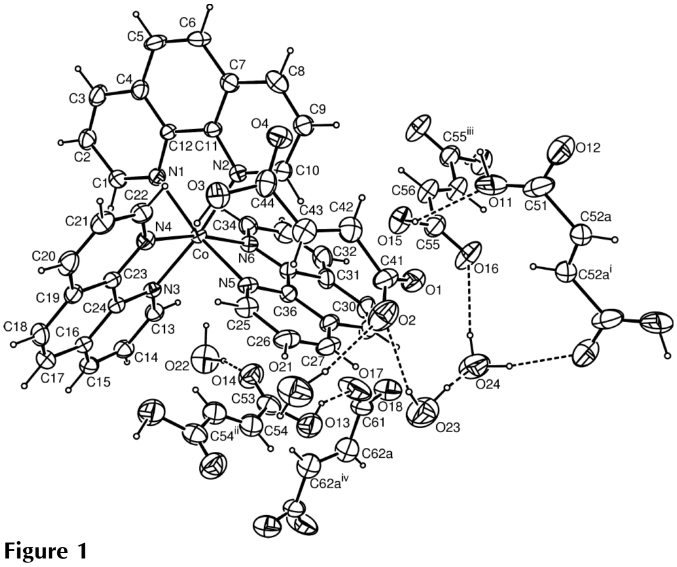


Figure 1

The molecular structure of (I) with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonding. H atoms bonded to the C atoms and disordered C atoms have been omitted for clarity. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, -z$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, -y, -z$.]

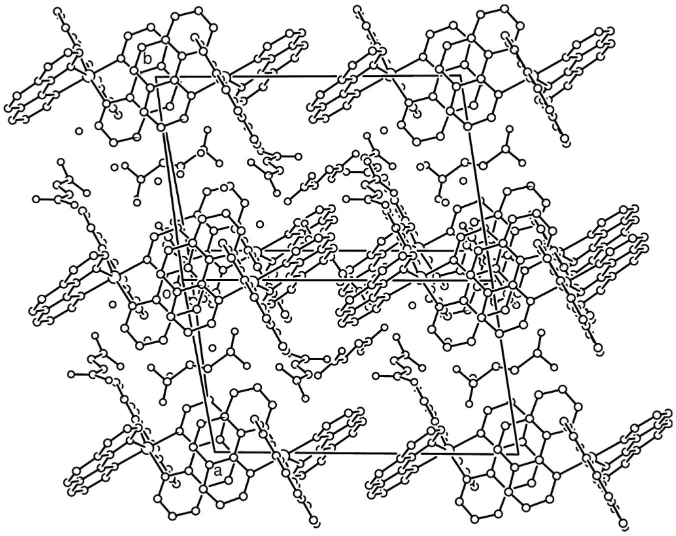


Figure 2

A molecular packing diagram; H atoms have been omitted for clarity.

of 3.341 (4) Å (C53) and 3.419 (5) Å (C54) may suggest the existence of π–π interactions between the fumaric acid and phen ring.

The carbon skeleton of the C51-fumaric acid and C61-fumarate dianion exhibit disorder, just as in a manganese complex (Liu *et al.*, 2003).

Experimental

A dimethylformamide solution (20 ml) containing $CoCl_2.6H_2O$ (0.12 g, 0.5 mmol), 1,10-phenanthroline (0.18 g, 1 mmol) and fumaric acid (0.058 g, 0.5 mmol) was refluxed in air for 2 h. Pale pink single crystals of the title compound were obtained from the filtrate after 2 weeks.

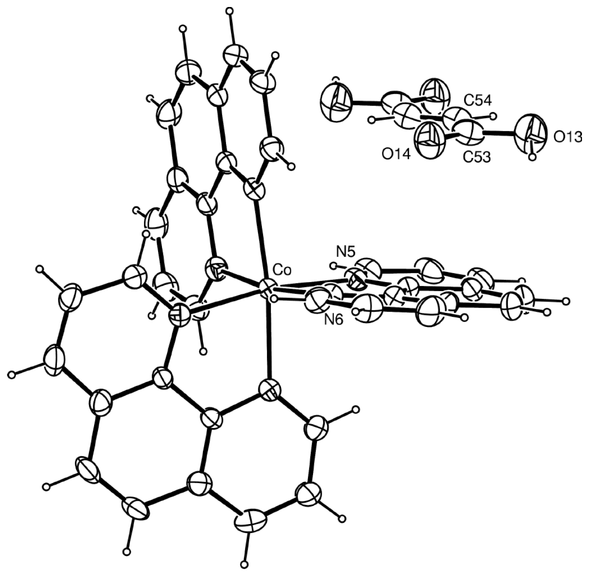


Figure 3

A diagram showing the π–π stacking between the fumaric acid and phen ring system.

Crystal data

$[Co(C_{12}H_8N_2)_3](C_4H_2O_4)_{0.5}(C_4H_3O_4)\cdot1.5C_4H_4O_4\cdot4H_2O$
$M_r = 1017.81$
Triclinic, $P\overline{1}$
$a = 12.167$ (2) Å
$b = 12.487$ (2) Å
$c = 17.040$ (2) Å
$\alpha = 102.85$ (2)°
$\beta = 90.28$ (1)°
$\gamma = 116.39$ (2)°
$V = 2245.0$ (8) Å^3
$Z = 2$
$D_x = 1.506$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13658 reflections
$\theta = 1.5$–27.0°
$\mu = 0.47$ mm^{-1}
$T = 298$ (2) K
Plate, pink
0.42 × 0.22 × 0.08 mm

Data collection

Bruker SMART CCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\rm min} = 0.82$, $T_{\rm max} = 0.96$
14499 measured reflections
9991 independent reflections
5138 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\rm max} = 27.6°$
$h = -15 \rightarrow 15$
$k = -10 \rightarrow 16$
$l = -22 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.135$
$S = 0.86$
9991 reflections
658 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.76$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.46$ e Å^{-3}

Table 1

Selected geometric parameters (Å).

Co—N5	2.078 (2)	O4—C44	1.217 (4)
Co—N3	2.084 (2)	O11—C51	1.277 (6)
Co—N6	2.086 (3)	O12—C51	1.188 (6)
Co—N4	2.097 (3)	O13—C53	1.295 (5)
Co—N1	2.101 (2)	O14—C53	1.176 (4)
Co—N2	2.111 (2)	O15—C55	1.307 (4)
O1—C41	1.242 (4)	O16—C55	1.188 (4)
O2—C41	1.255 (4)	O17—C61	1.207 (6)
O3—C44	1.272 (4)	O18—C61	1.248 (5)

m298 Liu *et al.* • $[Co(C_{12}H_8N_2)_3](C_4H_2O_4)_{0.5}(C_4H_3O_4)\cdot1.5C_4H_4O_4$ *Acta Cryst.* (2003). E**59**, m297–m299

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H03···O18^{v}	0.86	1.69	2.457 (4)	147
O13—H013···O17	0.94	1.67	2.537 (5)	152
O15—H015···O1	0.87	1.89	2.488 (4)	124
O11—H011···O4^{vi}	0.88	1.87	2.642 (5)	146
O21—H211···O2	1.00	2.01	2.962 (5)	158
O21—H212···O22^{vii}	0.95	1.98	2.847 (5)	151
O22—H221···O14	0.99	1.89	2.863 (6)	167
O22—H222···O23^{viii}	0.99	1.92	2.822 (5)	151
O23—H231···O24	0.94	2.09	2.860 (5)	138
O23—H232···O2	0.90	2.07	2.874 (5)	149
O24—H241···O12^{ix}	0.93	2.07	2.990 (5)	171
O24—H242···O16	0.84	2.34	3.168 (5)	167

Symmetry codes: (v) $x, 1+y, z$; (vi) $1-x, 2-y, 1-z$; (vii) $1-x, 1-y, -z$; (viii) $1+x, y, z$; (ix) $-x, 1-y, 1-z$.

The H atoms on C atoms, except those on disordered C atoms, were placed in calculated positions with C—H = 0.93 Å and included in the final cycles of refinement in a riding model, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$ of the carrier atom. Other H atoms were located with a combination of difference Fourier maps and theoretical calculation (Nardelli, 1993), and were included in the final cycles of refinement with fixed coordinates and isotropic displacement parameters of 0.08 Å^2. An unreasonably short distance C54═C54($1-x, 1-y, -z$) of 1.135 (7) Å and a longer C53—C54 distance of 1.539 (6) Å were observed in the structure. These may be due to disorder. The larger displacement parameters implied possible disorder of atom C54 , but it was not successfully resolved.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Acta Cryst. (2003). E**59**, m297–m299 Liu *et al.* • $[Co(C_{12}H_8N_2)_3](C_4H_2O_4)_{0.5}(C_4H_3O_4)\cdot 1.5C_4H_4O_4$ **m299**