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Helical *catena*-poly[[tris(1*H*-benzimidazole-κN^3)cobalt(II)]-μ-maleato-$\kappa^3 O,O':O''$]

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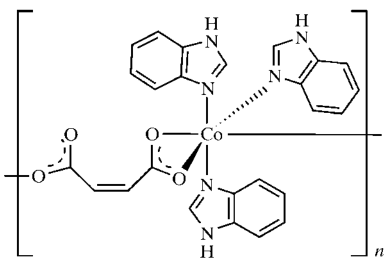
The crystal structure of the title compound, $[Co(C_4H_2O_4)(C_7H_6N_2)_3]_n$, consists of polymeric chains of the Co^{II} complex. Two maleate dianions and three benzimidazole ligands coordinate to the Co^{II} atom with a distorted octahedral geometry. The maleate dianions bridge neighbouring Co^{II} atoms *via* both terminal carboxylic acid groups, one of which is monodentate and the other bidentate, to form a helical structure of alternating maleate dianions and Co^{II} atoms, with a pitch height of 9.2667 (17) Å. The absolute structure has been determined, and the crystal contains only right-handed helices. Intrahelical N—H···O hydrogen bonds stabilize the helical structure, while interhelical N—H···O hydrogen bonds link neighbouring helices to form the supramolecular structure.

Comment

Helical metal complexes have received much attention in coordination chemistry and materials science (Munakata *et al.*, 1999), and much effort has been devoted to the preparation of helical complexes by the careful design of ligands (Erxleben, 2001; Ezuhara *et al.*, 1999). Dicarboxylates have been shown to be potential helicating ligands when their terminal carboxylic acid groups are twisted by an appropriate angle with respect to each other (Hu *et al.*, 2001). As part of a series of studies of helical metal complexes, we present here the structure of the title complex, (I), a polymeric Co^{II} complex bridged by a maleate dianion.

The coordination environment around the Co^{II} atom in (I) is illustrated in Fig. 1. Two carboxylic acid groups from two maleate dianions, related by a twofold screw axis, coordinate to the Co^{II} atom in the equatorial coordination plane. The O1/O2 carboxylic acid group coordinates in a monodentate manner, while the $O3^i/O4^i$ carboxylic acid group chelates to the Co^{II} atom in a bidentate fashion [symmetry code: (i) $x-\frac{1}{2}, \frac{1}{2}-y, -z$]. Atoms O1, $O3^i$, $O4^i$ and Co are essentially coplanar, with a maximum atomic deviation of 0.0401 (12) Å (for Co), but atom O2 is out of this mean plane by 1.120 (4) Å. Thus, the O1/O2 and O3/O4 carboxylic acid groups are twisted with respect to each other by an angle of 34.6 (4)°. Three benzimidazole molecules coordinate to the Co^{II} atom to complete the distorted octahedral coordination geometry (Table 1), with the N21-benzimidazole molecule located in the equatorial plane and the N11- and N31-benzimizadole molecules in the axial directions. The distortion of the octahedron is manifested by the larger coordinating bond angles in the equatorial plane, with O1—Co—N23 = 114.27 (11)° and N23—Co—$O3^i$ = 99.82 (10)°. This is due to weak C22—H22···O2 and C24—H24···$O3^i$ hydrogen bonding (Fig. 1 and Table 2).



(I)

With the aid of its terminal carboxylic acid groups, each maleate dianion bridges adjacent Co^{II} atoms related by a twofold screw axis. This results in a helical polymeric molecular chain of alternating maleate dianions and Co^{II} atoms, extending along the *a* axis (Fig. 2). The helix has a pitch height of 9.2667 (17) Å and the repeat unit of the helix backbone includes two Co^{II} atoms and two maleate dianions. Within the same helix, adjacent equatorial coordination planes are inclined towards each other, with a dihedral angle of 59.00 (7)°. A search of the Cambridge Structural Database

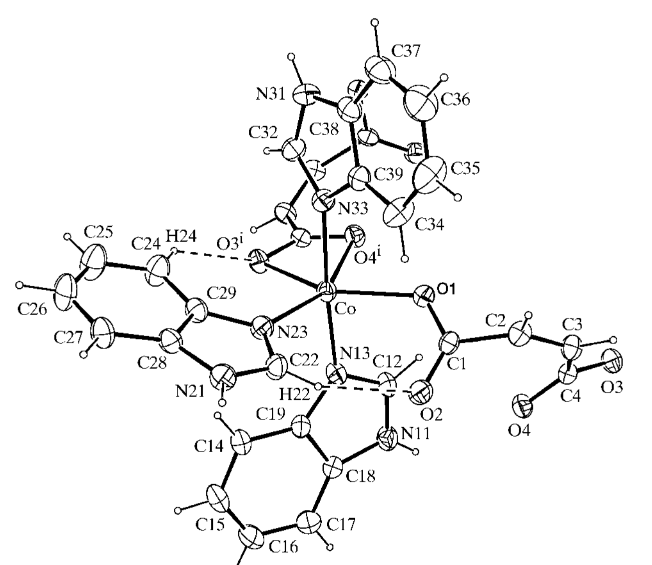


Figure 1
The coordination environment around the Co^{II} atom in (I), shown with 30% probability displacement ellipsoids [symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$].

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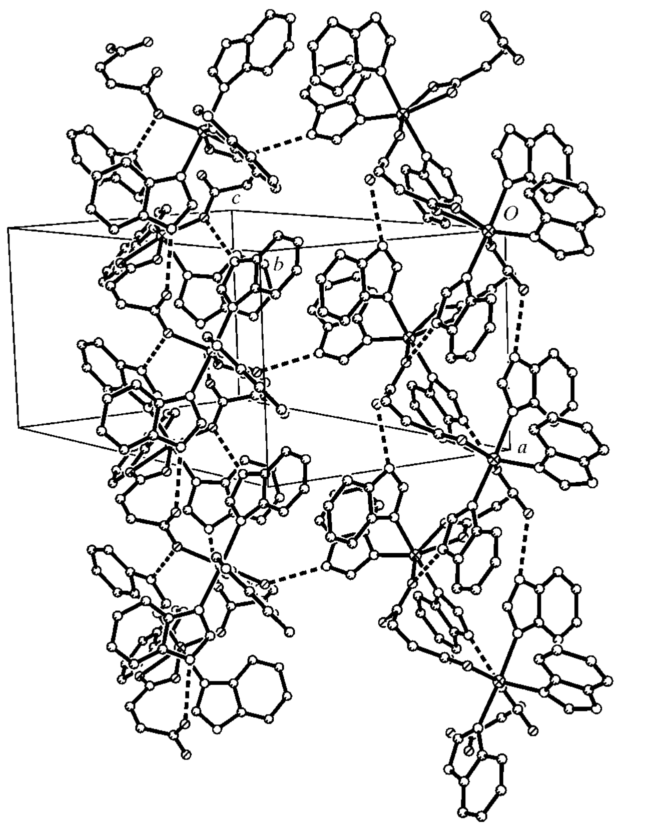

Figure 2
The molecular packing diagram for (I). Dashed lines indicate hydrogen bonds and H atoms have been omitted for clarity.

(Allen, 2002) indicates that this is the first helical metal complex with maleate as the helicating ligand.

The absolute structure of (I) was determined, and the crystal contains only right-handed helices. At present, we do not know whether the opposite enantiomer was simultaneously generated in the preparation process, with conglomerate crystallization.

Besides the weak C—H···O hydrogen bonding mentioned above, a classical hydrogen-bonding network occurs in the crystal structure of (I). Within the same helix, N—H···O hydrogen bonds between the carboxylate groups and the axial benzimidazole molecules stabilize the helical structure. Neighbouring helices link to each other *via* N—H···O hydrogen bonds between the equatorial benzimidazole ligand and the carboxylate group of an adjacent helix, forming the supramolecular structure shown in Fig. 2. The hydrogen-bonding parameters are listed in Table 2.

Experimental

An aqueous solution (5 ml) containing maleic acid (0.23 g, 2 mmol) and sodium carbonate (0.21 g, 2 mmol) was mixed with an aqueous solution (5 ml) of $CoCl_2\cdot 6H_2O$ (0.48 g, 2 mmol). After refluxing the resulting solution for 30 min, an ethanol solution (5 ml) of benzimidazole (0.47 g, 4 mmol) was added dropwise. The mixture was refluxed for a further 2 h and then filtered. The filtrate was kept at room temperature and pink single crystals of (I) were obtained after 5 d.

Crystal data

$[Co(C_4H_2O_4)(C_7H_6N_2)_3]$
$M_r = 527.40$
Orthorhombic, $P2_12_12_1$
$a = 9.2667$ (17) Å
$b = 12.1242$ (15) Å
$c = 21.099$ (19) Å
$V = 2371$ (2) Å^3
$Z = 4$
$D_x = 1.477$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21 868 reflections
$\theta = 1.7$–27.4°
$\mu = 0.77$ mm^{-1}
$T = 298$ (2) K
Prism, pink
0.29 × 0.19 × 0.11 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.788$, $T_{max} = 0.922$
22 026 measured reflections
5413 independent reflections
4569 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -25 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.114$
$S = 1.09$
5413 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 0.0433P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}
Absolute structure: Flack (1983), 2338 Friedel pairs
Flack parameter = 0.019 (16)

Table 1
Selected geometric parameters (Å, °).

Co—O1	2.100 (2)	O2—C1	1.226 (4)
Co—N13	2.104 (3)	O3—C4	1.270 (4)
Co—N23	2.122 (3)	O4—C4	1.250 (4)
Co—N33	2.145 (3)	C1—C2	1.506 (4)
Co—O3^{i}	2.230 (2)	C2—C3	1.326 (5)
Co—O4^{i}	2.277 (2)	C3—C4	1.486 (4)
O1—C1	1.274 (4)		
O1—Co—N13	89.66 (10)	N23—Co—O3^{i}	99.82 (10)
O1—Co—N23	114.27 (11)	N33—Co—O3^{i}	93.49 (9)
N13—Co—N23	97.60 (11)	O1—Co—O4^{i}	87.88 (10)
O1—Co—N33	87.16 (10)	N13—Co—O4^{i}	89.86 (10)
N13—Co—N33	175.29 (11)	N23—Co—O4^{i}	156.52 (9)
N23—Co—N33	86.88 (11)	N33—Co—O4^{i}	86.56 (10)
O1—Co—O3^{i}	145.87 (9)	O3^{i}—Co—O4^{i}	58.16 (9)
N13—Co—O3^{i}	87.21 (10)		

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11···O1^{i}	0.86	2.07	2.892 (4)	158
N21—H21···O3^{ii}	0.86	1.99	2.813 (5)	161
N31—H31···O2^{iii}	0.86	2.00	2.789 (5)	151
C22—H22···O2	0.93	2.34	3.124 (5)	141
C24—H24···O3^{iv}	0.93	2.44	3.210 (5)	141

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (ii) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$; (iii) $x - 1, y, z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, -z$.

H atoms were placed in calculated positions, with C—H = 0.93 and N—H = 0.86 Å, and were included in the final cycles of refinement in a riding model, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atom.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2002); 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) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1433). Services for accessing these data are described at the back of the journal.

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