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The 1:1 adduct of cobalt(II) terephthalate with *N,N*-dimethylformamide

Yun-Long Fu,[a] Jia-Lin Ren[a] and Seik Weng Ng[b]*

[a]School of Chemistry and Materials Science, Shanxi Normal University, Linfen 041004, People's Republic of China, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.032
wR factor = 0.093
Data-to-parameter ratio = 12.5

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

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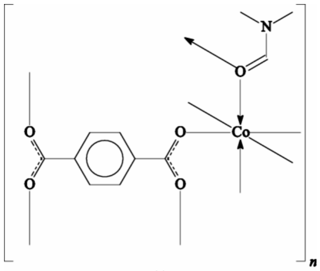
The solvothermal reaction of cobalt(II) nitrate and terephthalic acid in *N*,*N*-dimethylformamide (DMF) yields the polymeric title compound, poly[cobalt(II)-μ_2-*N*,*N*-dimethylformamide-κ^2O:O-μ_4-terephthalato-κ^4O:O':O'':O'''], $[Co(C_8H_4O_4)(C_3H_7NO)]_n$. In the crystal structure, both the Co atom and the terephthalate group occupy special positions of 2/*m* site symmetry. The DMF ligand is located on a mirror plane with the N atom on a special position of site symmetry *mm*2. The octahedral coordination polyhedron around the Co atom has two opposite sites that are occupied by the O atoms of DMF molecules; the other sites are occupied by the carboxyl O atoms of four different terephthalate groups. The compound adopts an open framework structure having channels in which the disordered DMF molecules reside.

Comment

This study is an extension to the study on the solvothermal synthesis of dicobalt(II) 1,2,4,5-benzenetetracarboxylate for which *N*,*N*-dimethylformamide was used as the solvent medium (Fu *et al.*, 2004). Water was not used in the synthesis of cobalt terephthalate to avoid the formation of dicobalt(II) dihydroxide terephthalate (Huang *et al.*, 2002). In the DMF medium, the reaction gave the desired compound as a 1:1 DMF adduct.



(I)

The adduct (Fig. 1) has the Co atom occupying a special position of 2/*m* site symmetry; it is bonded to the O atoms of four different terephthalate dianions. The planar dianion lies on another special position of 2/*m* site symmetry. The four coordinating O atoms constitute an approximate square, and the other two positions of the octahedron are occupied by the O atoms DMF. The overall motif can be regarded as an open framework, having channels into which the DMF molecules point (Fig. 2). As the DMF unit constitutes a substantial portion of the volume of the $(C_8H_4O_4)(C_3H_7NO)Co$ formula unit, its replacement by a smaller ligand should give rise to a highly porous structure.

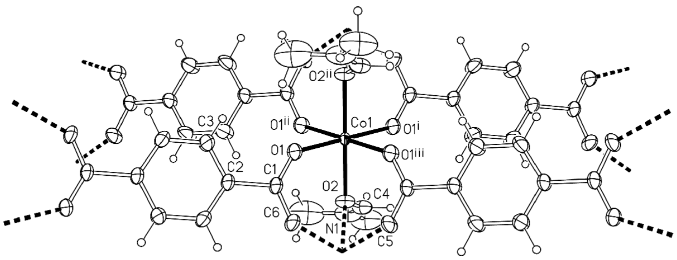


Figure 1
*ORTEP*II (Johnson, 1976) plot of a portion of the structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. The disorder in the DMF molecules is not shown. [Symmetry codes: (i) $x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, y, z$.]

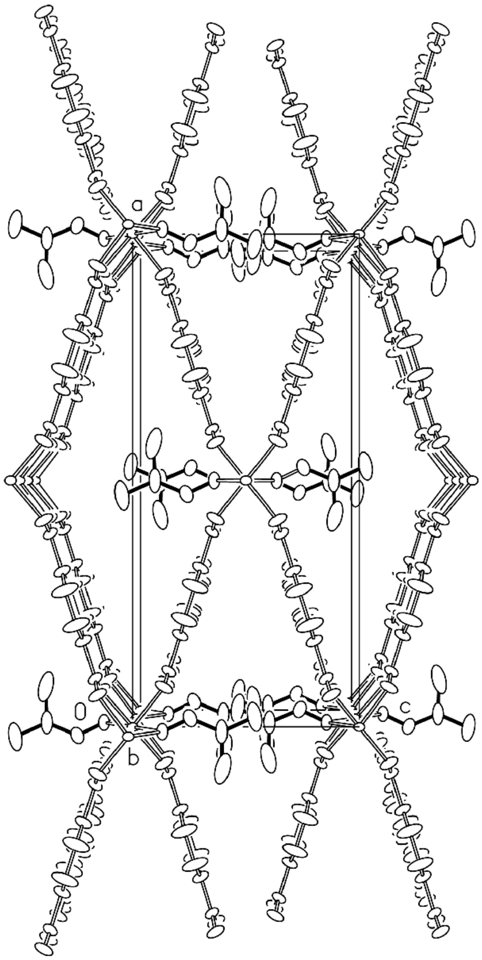


Figure 2
Projection of the unit-cell contents. H atoms not shown.

The μ_4-bridging behavior of the dianion is also found in cobalt terephthalate dihydrate; however, the dianion unit is not planar as the carboxyl unit is twisted by some 10° out of the aromatic plane (Kaduk, 2002). The title adduct represents an addition to the small number of adducts of cobalt terephthalate, most of which are adducts of nitrogen heterocycles, such as pyridine, picoline (Groeneman *et al.*, 1999), pyrazine (Groeneman *et al.*, 1998) and phenanthroline (Karanović *et al.*, 2002; Nu *et al.*, 2004; Sun *et al.*, 2001; Zhang *et al.*, 2003). An exception is the oxygen-coordinated ethyleneglycol complex (with uncoordinated DMF molecules), which is claimed to be microporous (Fang *et al.*, 2003).

Although DMF is capable of forming a plethora of adducts, it is typically monodentate to a Lewis-acidic metal, as noted from a search of the Cambridge Structural Database (Version 5.25; Allen, 2002). The carbonyl-donor bridges two Co atoms in the title compound; such bridging behavior has been previously noted in very few examples (Beauchamp *et al.*, 1987; Harrowfield *et al.*, 1991; Psomas *et al.*, 2001; Tschinkl *et al.*, 1999).

Experimental

Cobalt(II) nitrate hexahydrate (0.143 g, 0.5 mmol), terephthalic acid (0.247 g, 1.5 mmol) and *N*,*N*-dimethylformamide (7 ml) were sealed in a Teflon-lined stainless steel bomb, which was heated at 403 K for 6 d. Pink crystals were obtained when the bomb was cooled slowly to room temperature. Analysis found: C 44.92, H 3.09, N 4.76%; calculated for $C_{11}H_{11}CoNO_5$: C 44.92, H 3.09, N 4.76%.

Crystal data

$[Co(C_8H_4O_4)(C_3H_7NO)]$
$M_r = 296.14$
Orthorhombic, *Imma*
$a = 19.258$ (1) Å
$b = 7.2459$ (4) Å
$c = 8.8593$ (5) Å
$V = 1236.3$ (1) Å^3
$Z = 4$
$D_x = 1.591$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4989 reflections
$\theta = 2.5$–28.1°
$\mu = 1.40$ mm^{-1}
$T = 295$ (2) K
Prism, pink
0.39 × 0.38 × 0.33 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.536$, $T_{max} = 0.629$
6527 measured reflections
789 independent reflections
781 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 27.5°$
$h = -24 \rightarrow 24$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.093$
$S = 1.04$
789 reflections
63 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 1.9208P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.69$ e Å^{-3}
$\Delta\rho_{min} = -0.78$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.042 (1)	Co1—O2	2.185 (2)
O1—Co1—O1^{i}	85.5 (1)	O1—Co1—O1^{iii}	94.6 (1)
O1—Co1—O2	92.6 (1)	O1—Co1—O2^{ii}	87.4 (1)
O1—Co1—O1^{ii}	180	O2^{ii}—Co1—O2	180

Symmetry codes: (i) $x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, y, z$.

The DMF molecule (comprising atoms O2, N1, C4, C5 and C6) lies on the Wyckoff 4e site (of *mm*2 symmetry) and is disordered over two positions with respect to its C atoms only. As the disorder refined to give almost equal contributions, the occupancies of these C atoms constrained to be equal. The three N—C distances were restrained to within ±0.01 Å of each other; one was too short and another too long when the refinement was attempted without any restraint. H atoms were placed at calculated positions (C—H = 0.93 Å for the sp^2-hybridized parent C atoms and 0.96 Å for the methyl C atoms) and were included in the refinements in the riding-model approximation, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$ for the aromatic H atoms and $1.5U_{\rm eq}$ for the methyl H atoms. The two methyl groups were rotated so as to fit the electron density.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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