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# Octahedral and tetrahedral coordination for cobalt(II) in polymeric ($\mu_8$-benzene-1,2,4,5-tetracarboxylato)bis(*N*,*N*-dimethylformamide)dicobalt

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In the crystal structure of $[Co_2(C_{10}H_2O_8)(C_3H_7NO)_2]_n$, the tetra-anion uses seven of its eight O atoms to interact with eight $Co^{II}$ atoms, as one of these seven binds to two metal atoms simultaneously. Four of the eight Co atoms are crystallograpically equivalent and exist in a tetrahedral environment; the other four, which belong to another equivalent set, are each also coordinated by two dimethylformamide molecules in an octahedral environment.

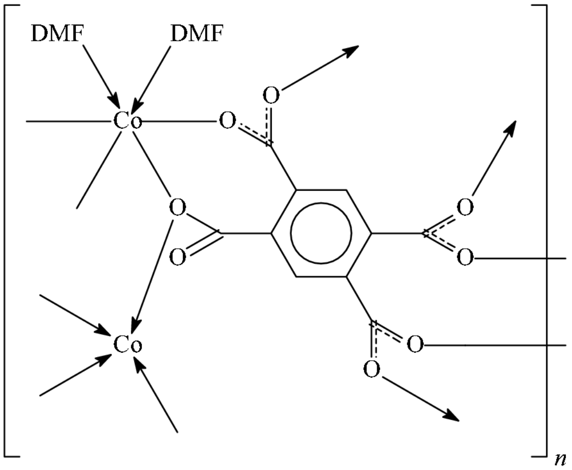
**Key indicators**

Single-crystal X-ray study
$T$ = 295 K
Mean $\sigma$(C–C) = 0.011 Å
$R$ factor = 0.055
$wR$ factor = 0.149
Data-to-parameter ratio = 11.5

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

## Comment

We have reported several molecular sieves having open-framework structures (Fu *et al.*, 2001, 2002; Liu *et al.*, 2002) that were synthesized hydrothermally. Our studies are now extended to the synthesis of a possible microporous cobalt system based on pyromellitic acid, this carboxylic acid being selected on the basis of the large number of pyromellitates that have been crystallographically authenticated in the Cambridge Structural Database (Version 5.25; Allen, 2002). Owing to the presence of four carboxyl units, the pyromellitate anion can engage in coordination in a number of bonding modes; among the pyromellitates are a number of cobalt derivatives (Cheng *et al.*, 2002*a*,*b*; Murugavel *et al.*, 2002; Poleti & Karanovic, 1989; Robl & Hentschel, 1991*a*,*b*; Rochon & Massarweh, 2001; Wang *et al.*, 2000). Pyromellitic acid reacts with cobalt salts to give products whose composition depends on the reaction conditions (Kumagai *et al.*, 2002, 2003).



(I)

The title cobalt(II) derivative, (I), unlike the previously reported cobalt derivatives, does not contain water, and (I) adopts a three-dimensional network structure. The asymmetric unit consists of two independent Co atoms, the pyro-

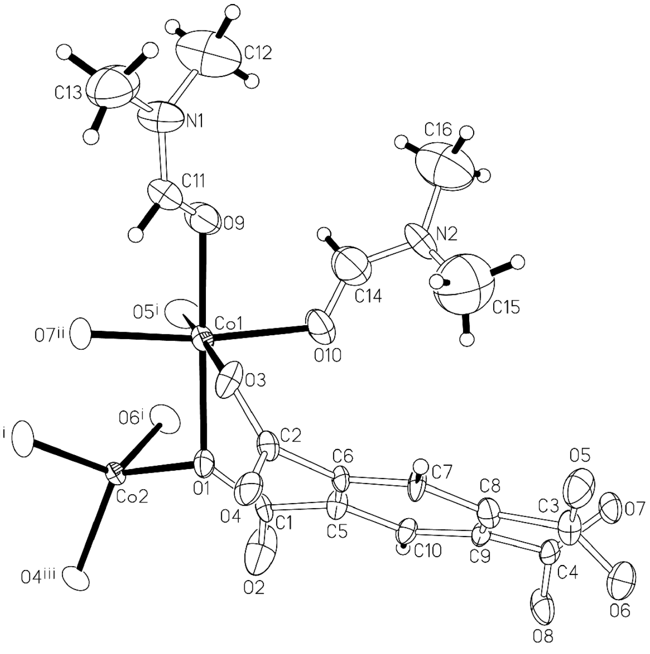


**Figure 1**

*ORTEP*II (Johnson, 1976) plot of a portion of (I). Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $x, 1 - y, z - \frac{1}{2}$.]

mellitate tetra-anion and two dimethylformamide (DMF) molecules, both of which are coordinated to the same Co atom. The tetra-anion uses seven of its eight O atoms to bind to eight Co atoms, one of the eight binding to two metal atoms. The DMF-coordinated Co atom is six-coordinate in an octahedral geometry, whereas the other Co atom is only four-coordinate. However, the tetrahedral geometry is distorted owing to a short Co2···O3 interaction of 2.443 (6) Å. A similar reaction (but not under solvothermal conditions) with DMF as solvent, but in the presence of 2,2′-bipyridine, gave bis(2,2′-bipyridine)cobalt(II) pyromellitate. The metal atom is coordinated by a water molecule in a five-coordinate geometry (Xiao *et al.*, 2004); DMF, although present in excess, does not bind to the metal.

Although both DMF molecules are coordinated to the Co atoms in (I), the DMF molecules can be removed by heat, as noted from a thermogravimetric analysis of the compound in the 473–873 K range (64.7% loss of weight compared with a theoretical loss of 70.8%; a residue of 35.3% compared with a theoretical residue of 32.7%); the loss is accompanied by the collapse of the framework at about 523 K.

## Experimental

The compound was synthesized solvothermally from cobalt(II) nitrate (0.30 g, 1 mmol), pyromellitic acid (0.25 g, 1 mol) and dimethylformamide (7 ml, 91 mmol). The mixture was sealed in a Teflon-lined autoclave and heated at 383 K for 96 h. The compound was isolated as purple plates. Analysis found: C 37.33, H 3.10, N 5.42%; calculated for $C_{16}H_{16}Co_2N_2O_{10}$: C 37.37, H 3.14, N 5.45%.

*Crystal data*

$[Co_2(C_{10}H_2O_8)(C_3H_7NO)_2]$
$M_r = 514.17$
Monoclinic, *Cc*
$a = 10.789 (3)$ Å
$b = 15.420 (4)$ Å
$c = 11.742 (3)$ Å
$\beta = 90.555 (4)°$
$V = 1953.4 (8)$ Å$^3$
$Z = 4$

$D_x = 1.748$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 826 reflections
$\theta = 2.3$–$19.6°$
$\mu = 1.76$ mm$^{-1}$
$T = 295 (2)$ K
Plate, purple
$0.19 \times 0.16 \times 0.07$ mm

*Data collection*

Bruker SMART APEX area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.522$, $T_{max} = 0.887$
5502 measured reflections

3163 independent reflections
2580 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 13$
$k = -18 \rightarrow 20$
$l = -15 \rightarrow 14$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.149$
$S = 1.04$
3163 reflections
275 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.063P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.63$ e Å$^{-3}$
$\Delta\rho_{min} = -0.60$ e Å$^{-3}$
Absolute structure: Flack (1983), 975 Friedel pairs
Flack parameter = 0.17 (3)

**Table 1**

Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Co1—O1 | 2.140 (6) | Co1—O10 | 2.051 (7) |
| Co1—O3 | 2.104 (6) | Co2—O1 | 2.010 (5) |
| Co1—O5$^{i}$ | 2.102 (6) | Co2—O4$^{iii}$ | 2.015 (6) |
| Co1—O7$^{ii}$ | 2.052 (5) | Co2—O6$^{i}$ | 1.961 (6) |
| Co1—O9 | 2.083 (7) | Co2—O8$^{ii}$ | 1.996 (6) |
| | | | |
| O1—Co1—O3 | 80.7 (2) | O5$^{i}$—Co1—O10 | 87.8 (3) |
| O1—Co1—O5$^{i}$ | 93.4 (2) | O7$^{ii}$—Co1—O9 | 84.7 (3) |
| O1—Co1—O7$^{ii}$ | 94.7 (2) | O7$^{ii}$—Co1—O10 | 171.9 (3) |
| O1—Co1—O9 | 171.4 (3) | O9—Co1—O10 | 87.5 (3) |
| O1—Co1—O10 | 93.3 (3) | O1—Co2—O4$^{iii}$ | 118.6 (2) |
| O3—Co1—O5$^{i}$ | 173.7 (3) | O1—Co2—O6$^{i}$ | 96.1 (2) |
| O3—Co1—O7$^{ii}$ | 92.0 (2) | O1—Co2—O8$^{ii}$ | 101.1 (2) |
| O3—Co1—O9 | 90.8 (3) | O4$^{iii}$—Co2—O6$^{i}$ | 117.1 (3) |
| O3—Co1—O10 | 90.3 (3) | O4$^{iii}$—Co2—O8$^{ii}$ | 97.1 (3) |
| O5$^{i}$—Co1—O7$^{ii}$ | 90.7 (3) | O6$^{i}$—Co2—O8$^{ii}$ | 127.4 (3) |
| O5$^{i}$—Co1—O9 | 95.1 (3) | | |

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

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 atoms) and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$ for the aromatic H atoms and $1.5U_{eq}(C)$ for the methyl H atoms. The methyl groups were allowed to rotate but not to tip. Although the $\beta$ angle of the unit cell is nearly a right angle, the diffraction pattern did not simulate that of an orthorhombic unit cell, *i.e.* the refinement did not lead to a lower *R* index when the twin matrix, $(100,0\bar{1}0,00\bar{1})$, was used.

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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