metal-organic papers

Polymeric cobalt(II) diformate dimethylformamide 0.33-solvate

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In the crystal structure of the title compound, poly-[[cobalt(II)-di-μ_3-formato] dimethylformamide 0.33-solvate] $[Co(CHO_2)_2] \cdot 0.33C_3H_7NO$, the units of $Co(HCO_2)_2$ are assembled into a three-dimensional framework through carboxylate bridging. The four symmetry-independent Co atoms show nearly regular octahedral coordination; two of them lie on inversion centres.

Comment

Cobalt(II) formate is an amorphous compound that is formed by dehydrating cobalt formate dihydrate (Arii & Kishi, 1999; Viertelhaus *et al.*, 2003). As a 0.33-methanol–0.33-water solvate, the compound is porous, and it has exceptional selective gas adsorption behavior (Wang *et al.*, 2005). A related study on manganese(II) formate described the isolation of manganese diformate as a 0.33-dioxane solvate; the synthesis used *N,N*-diethylformamide (DMF) as co-solvent, but this was not incorporated into the crystal structure. The manganese compound is also porous, and it similarly exhibits gas adsorption behavior (Dybtsev *et al.*, 2004). The two reports led to the present attempt to synthesize a porous cobalt formate–dioxane compound. However, the DMF that is used in the synthesis is incorporated into the resulting compound, (I) (Fig. 1). Consequently, the crystal structure has no voids. The volume of the DMF molecules accounts for about a third of the volume of the unit cell. The DMF solvent molecule is disordered, and it occupies the space within the polymeric three-dimensional cobalt formate network (Fig. 1).

(I)
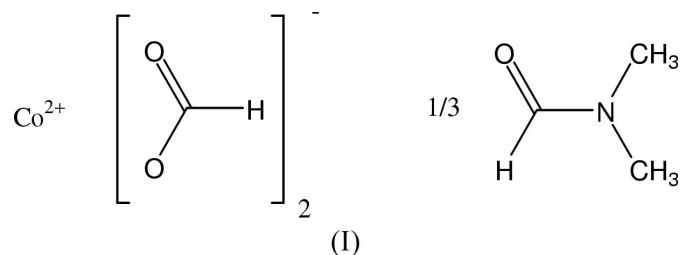
The compound has 0.33–DMF for each $Co(HCO_2)_2$ formula unit; two of the four independent Co atoms lie on special positions of site symmetry $\bar{1}$; of the 12 independent O atoms that belong to six formate anions, five form only one bond to a Co atom whereas the other seven interact with two Co atoms.

A bis-formamide complex of cobalt(II) formate is known; the formamide anion engages in bonding to the metal atom in the mononuclear adduct (Domasevitch *et al.*, 2002; Rettig *et al.*, 1999). A bis-formic acid adduct has been described in the space group *Ic* (Antsyshkina *et al.*, 1999). The structural
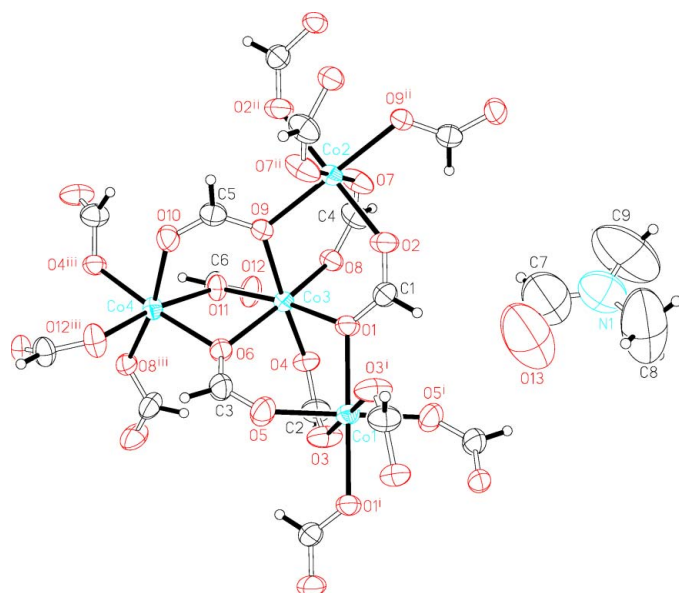
Figure 1
ORTEPII plot (Johnson, 1976) illustrating the coordination geometry of the Co atoms in polymeric (I). Displacement ellipsoids are drawn at the 70% probability level and H atoms are drawn as spheres of arbitrary radii. Symmetry codes are as given in Table 1. The major DMF component is shown.

literature on cobalt compounds having one or more formate groups has been summarized recently (Bocă *et al.*, 2004); the DMF solvate represents another addition to the literature.

Experimental

Cobalt(II) chloride hexahydrate (0.472 g, 2 mmol) and a slight excess of 88% formic acid (0.20 ml, 4.6 mmol) were mixed in 1,4-dioxane (4 ml) and DMF (8 ml). The solution was placed in a Teflon-lined stainless steel Parr bomb. The bomb was heated at 383 K for 4 d. The red crystals that were obtained from the solution were collected and washed with ethanol. The yield was about 60%. The same compound was obtained from cobalt dinitrate in place of cobalt dichloride. A reliable CH&N elemental analysis could not be secured; nitrogen was shown to be present, and the presence of DMF was corroborated by a thermogravimetric analysis (TGA) measurement.

Crystal data

$[Co(CHO_2)_2]\cdot0.33C_3H_7NO$
$M_r = 173.33$
Monoclinic, $P2_1/n$
$a = 11.3457\ (7)$ Å
$b = 10.0117\ (7)$ Å
$c = 14.820\ (1)$ Å
$\beta = 91.372\ (1)°$
$V = 1682.9\ (2)$ Å^3
$Z = 12$

$D_x = 2.052$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3103 reflections
$\theta = 2.2–27.0°$
$\mu = 2.99$ mm^{-1}
$T = 295\ (2)$ K
Block, red
$0.12 \times 0.10 \times 0.09$ mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.537$, $T_{max} = 0.767$
9679 measured reflections

3639 independent reflections
3055 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 27.0°$
$h = -14 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.079$
$S = 0.97$
3639 reflections
270 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.142 (2)	Co3—O8	2.110 (2)
Co1—O3	2.086 (2)	Co3—O9	2.085 (2)
Co1—O5	2.066 (2)	Co3—O11	2.126 (2)
Co2—O2	2.067 (2)	Co4—O4^i	2.100 (2)
Co2—O7	2.080 (2)	Co4—O6	2.111 (2)
Co2—O9	2.126 (2)	Co4—O8^i	2.116 (2)
Co3—O1	2.062 (2)	Co4—O10	2.055 (2)
Co3—O4	2.088 (2)	Co4—O11	2.108 (2)
Co3—O6	2.109 (2)	Co4—O12^i	2.050 (2)
O1—Co1—O1^{ii}	180	O4—Co3—O8	77.27 (7)
O1—Co1—O3	94.79 (8)	O4—Co3—O9	170.46 (8)
O1—Co1—O3^{ii}	85.21 (8)	O4—Co3—O11	87.18 (7)
O1—Co1—O5	90.92 (8)	O6—Co3—O8	164.27 (7)
O1—Co1—O5^{ii}	89.08 (8)	O6—Co3—O9	93.09 (7)
O3—Co1—O3^{ii}	180	O6—Co3—O11	77.87 (7)
O3—Co1—O5	91.50 (8)	O8—Co3—O9	94.14 (8)
O3—Co1—O5^{ii}	88.50 (8)	O8—Co3—O11	88.38 (7)
O5—Co1—O5^{ii}	180	O9—Co3—O11	88.44 (7)
O2—Co2—O2^{iii}	180	O4^i—Co4—O6	172.79 (7)
O2—Co2—O7	88.55 (9)	O4^i—Co4—O8^i	76.90 (7)
O2—Co2—O7^{iii}	91.45 (9)	O4^i—Co4—O10	89.55 (8)
O4—Co3—O8	77.27 (7)	O4^i—Co4—O11	94.57 (7)
O2—Co2—O9	91.90 (8)	O4^i—Co4—O12^i	94.19 (8)
O2—Co2—O9^{iii}	88.10 (8)	O6—Co4—O8^i	102.80 (8)
O7—Co2—O7^{iii}	180	O6—Co4—O10	90.40 (8)
O7—Co2—O9	93.30 (8)	O6—Co4—O11	78.22 (7)
O7—Co2—O9^{iii}	86.70 (8)	O6—Co4—O12^i	93.02 (8)
O9—Co2—O9^{iii}	180	O8^i—Co4—O10	166.32 (8)
O1—Co3—O9	95.47 (8)	O8^i—Co4—O11	88.96 (7)
O1—Co3—O4	89.86 (8)	O8^i—Co4—O12^i	90.07 (8)
O1—Co3—O6	95.48 (7)	O10—Co4—O11	90.26 (8)
O1—Co3—O8	97.72 (8)	O10—Co4—O12^i	92.84 (9)
O1—Co3—O11	172.48 (8)	O11—Co4—O12^i	170.73 (8)
O4—Co3—O6	94.26 (7)		

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

H atoms were placed at calculated positions (C—H = 0.93 Å for the sp^2-hybridized C atoms and 0.96 Å for the methyl C atoms) and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2$ or 1.5 times $U_{eq}(C)$. The DMF molecule is disordered, and one component is rotated by 180° with respect to the other; the two components share common O and N atoms. The disorder refined to 60 (1):40(1). The two molecules were restrained to be planar and pairs of equivalent distances were restrained to be within 0.01 Å of each other.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

metal-organic papers

References

Antsyshkina, A. S., Porai-Koshits, M. A., Ostrikova, V. N., Borina, A. F., Orlova, V. T., Khoshabova, E. G. & Kharitonov, Yu. Yu. (1999). *Koord. Khim.* pp. 197–202.

Arii, T. & Kishi, A. (1999). *Thermochim. Acta*, **325**, 157–165.

Boča, M., Svoboda, I., Renz, F. & Fuess, H. (2004). *Acta Cryst.* C**60**, m631-m633.

Bruker (2002). *SADABS, SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

Domasevitch, K. V., Sieler, J., Rusanov, E. B. & Chermega, A. N. (2002). *Z. Anorg. Allg. Chem.* **628**, 51–56.

Dybtsev, D. N., Chun, H., Yoon, S. H., Kim, D. & Kim, K. (2004). *J. Am. Chem. Soc.* **126**, 32–33.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Rettig, S. J., Thompson, R. C., Trotter, J. & Xia, S. (1999). *Inorg. Chem.* **38**, 1360–1363.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Viertelhaus, M., Henke, H., Anson, C. E. & Powell, A. K. (2003). *Eur. J. Inorg. Chem.* pp. 2283–2289.

Wang, Z., Zhang, B., Kurmoo, M., Green, M. A., Fujiwara, H., Otsuka, T. & Kobayashi, H. (2005). *Inorg. Chem.* **44**, 1230–1237.