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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$
 R factor = 0.062
 wR factor = 0.129
Data-to-parameter ratio = 12.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.On the number of uncoordinated water molecules in
the open-framework coordination compound, bis(1,2,-
4,5-benzenetetracarboxylato)dihydroxytetraqua-
pentacobalt(II) x -hydrate, and the crystal structure
of the isomorphous decahydrated zinc(II) analog

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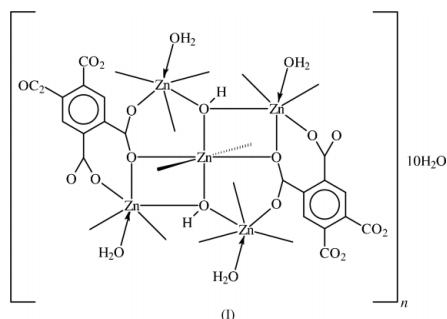
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The formula unit of bis(1,2,4,5-benzenetetracarboxylato)dihydroxytetraaquapentacobalt(II) x -hydrate includes 10 uncoordinated water molecules; the compound is isomorphous with the reported $[\text{Co}_5(\text{C}_{10}\text{H}_2\text{O}_8)_2(\text{OH})_2(\text{H}_2\text{O})_4] \cdot x\text{H}_2\text{O}$ analog [Gutschke, Price, Powell & Wood (2001). *Eur. J. Inorg. Chem.* pp. 2739–2741], for which x is most probably 10. The asymmetric unit is one-half of the formula unit, with one Zn atom lying on an inversion center.

Comment

Polymeric bis(1,2,4,5-benzenetetracarboxylato)dihydroxytetraaquapentacobalt(II) x -hydrate is a microporous compound whose coordinated and uncoordinated water molecules account for almost half the volume of the unit cell [$a = 7.452(4)$, $b = 16.462(6)$, $c = 14.586(5)\text{ \AA}$; $\beta = 95.46(4)^\circ$]; some of the water molecules can be reversibly removed by heating (Gutschke *et al.*, 2001). The value of x was assigned as 7.5 from the five independent uncoordinated water molecules that occupy general positions. However, no reason was given for the less than unity occupancy for each, although the authors had formulated the compound as $\text{C}_{20}\text{H}_{34}\text{Co}_5\text{O}_{32}$, *i.e.* a decahydrate, on the basis of C and H elemental composition. The structure determination of the present isomorphous Zn analog (Fig. 1) has confirmed the existence of 10 uncoordinated water molecules (see scheme). Most likely, the Co compound is a decahydrate; its structure has already been described in detail. According to the report, the Zn analog is isostructural, presumably on the basis of the similarity of the X-ray powder diffraction patterns. In the present crystal structure determination of the Zn compound, Zn3 lies on an inversion center, and the asymmetric unit is one-half of the formula unit.



The reason for the ready loss of water upon heating for the Co compound can be understood in terms of the small number of hydrogen-bonding interactions for the Zn analog (Table 2). In fact, one of the water molecules does not use its H atoms to interact with its neighbors.

Experimental

1,2,4,5-Benzenetetracarboxylic acid anhydride (pyromellitic anhydride, 0.22 g, 1 mmol) was dissolved in water (15 ml) containing tetramethylammonium hydroxide (0.36 g, 4 mmol). To this was added zinc nitrate hexahydrate (0.59 g, 2 mmol) dissolved in water (3 ml). The solution was placed in a 20-ml Teflon-lined stainless-steel bomb, which was then heated to 453 K for 100 h. The bomb was cooled to room temperature at a rate of 5 K h⁻¹ to yield colorless crystals. The procedure was adapted from a published synthesis, but with tetramethylammonium hydroxide in place of sodium hydroxide.

Crystal data

[Zn₅(C₁₀H₂O₈)₂(H₂O)₄(OH)₂]_n·10H₂O
M_r = 1113.32
 Monoclinic, *P*2₁/*n*
a = 7.4087 (3) Å
b = 16.4236 (6) Å
c = 14.5347 (5) Å
 β = 94.993 (1)°
V = 1761.8 (1) Å³
Z = 2
D_x = 2.099 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 9591 reflections
 θ = 2.5–28.3°
 μ = 3.47 mm⁻¹
T = 298 (2) K
 Parallelepiped, colorless
 0.20 × 0.14 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.585, *T_{max}* = 0.708
 16789 measured reflections
 3105 independent reflections
 3079 reflections with *I* > 2σ(*I*)
R_{int} = 0.048
R_{max} = 25.0°
h = -8 → 8
k = -19 → 19
l = -17 → 17

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.062
wR(*F*²) = 0.129
S = 1.27
 3105 reflections
 259 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 13.7636P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.69 e Å⁻³
 Δρ_{min} = -0.73 e Å⁻³

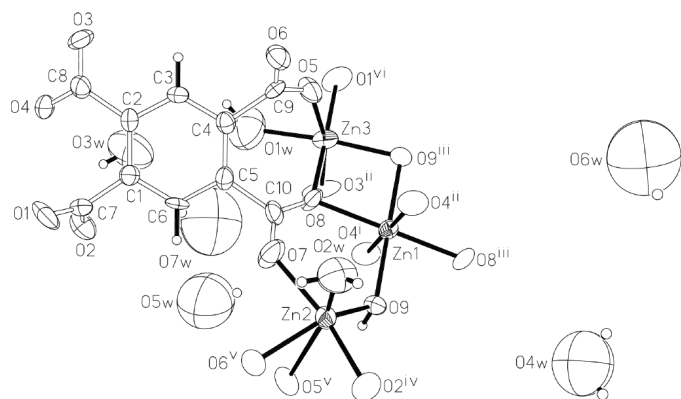


Figure 1 ORTEP (Johnson, 1976) plot of a segment of the title structure; displacement ellipsoids are drawn at the 75% probability level. H atoms are drawn as spheres of arbitrary radii. Symmetry/translational codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (v) $x - 1, y, z$; (vi) $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$.

Table 1 Selected geometric parameters (Å, °).

Zn1—O4 ⁱ	2.072 (4)	Zn2—O2 ^w	2.029 (6)
Zn1—O9	2.074 (4)	Zn3—O1 ^{iv}	2.019 (5)
Zn1—O8	2.119 (4)	Zn3—O3 ^v	1.990 (5)
Zn2—O2 ⁱⁱ	2.086 (5)	Zn3—O5	2.021 (5)
Zn2—O5 ⁱⁱⁱ	2.573 (5)	Zn3—O8	2.158 (4)
Zn2—O6 ⁱⁱⁱ	2.064 (4)	Zn3—O9 ^{vi}	2.076 (4)
Zn2—O7	2.111 (5)	Zn3—O1 ^w	2.288 (8)
Zn2—O9	1.977 (4)		
O4 ⁱ —Zn1—O4 ^v	180.0 (2)	O6 ⁱⁱⁱ —Zn2—O2 ^w	105.9 (2)
O4 ⁱ —Zn1—O8	90.5 (2)	O7—Zn2—O9	96.8 (2)
O4 ⁱ —Zn1—O8 ^{vi}	89.5 (2)	O7—Zn2—O2 ^w	85.0 (2)
O4 ⁱ —Zn1—O9	90.8 (2)	O9—Zn2—O2 ^w	119.8 (2)
O4 ⁱ —Zn1—O9 ^{vi}	89.3 (2)	O1 ^{iv} —Zn3—O3 ^v	98.8 (2)
O8—Zn1—O8 ^{vi}	180.0 (2)	O1 ^{iv} —Zn3—O5	88.2 (2)
O8—Zn1—O9	97.3 (2)	O1 ^{iv} —Zn3—O8	171.8 (2)
O8—Zn1—O9 ^{vi}	82.7 (2)	O1 ^{iv} —Zn3—O9 ^{vi}	98.2 (2)
O9—Zn1—O9 ^{vi}	180.0	O1 ^{iv} —Zn3—O1 ^w	80.5 (3)
O2 ⁱⁱ —Zn2—O5 ⁱⁱⁱ	88.4 (2)	O3 ^v —Zn3—O5	165.2 (2)
O2 ⁱⁱ —Zn2—O6 ⁱⁱⁱ	86.2 (2)	O3 ^v —Zn3—O8	89.4 (2)
O2 ⁱⁱ —Zn2—O7	164.6 (2)	O3 ^v —Zn3—O9 ^{vi}	92.7 (2)
O2 ⁱⁱ —Zn2—O9	98.6 (2)	O3 ^v —Zn3—O1 ^w	77.4 (2)
O2 ⁱⁱ —Zn2—O2 ^w	87.5 (2)	O5—Zn3—O8	83.8 (2)
O5 ⁱⁱⁱ —Zn2—O6 ⁱⁱⁱ	54.42 (16)	O5—Zn3—O9 ^{vi}	99.3 (2)
O5 ⁱⁱⁱ —Zn2—O7	94.2 (2)	O5—Zn3—O1 ^w	91.0 (2)
O5 ⁱⁱⁱ —Zn2—O9	80.0 (2)	O8—Zn3—O9 ^{vi}	81.7 (2)
O5 ⁱⁱⁱ —Zn2—O2 ^w	160.2 (2)	O8—Zn3—O1 ^w	101.1 (2)
O6 ⁱⁱⁱ —Zn2—O7	83.04 (19)	O9 ^{vi} —Zn3—O1 ^w	169.5 (2)
O6 ⁱⁱⁱ —Zn2—O9	134.1 (2)		

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

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

D—H...A	D—H	H...A	D...A	D—H...A
O9—H9...O5 ⁱ	0.98	2.44	2.96 (1)	113
O1 ^w —H1 ^w 2...O5 ^w ⁱⁱ	0.85	2.16	2.86 (2)	139
O1 ^w —H1 ^w 1...O7 ^w	0.86	2.27	2.92 (2)	133
O2 ^w —H2 ^w 1...O5 ^w ⁱⁱⁱ	0.85	2.06	2.85 (2)	153
O3 ^w —H3 ^w 1...O2	0.85	2.34	2.96 (1)	130
O3 ^w —H3 ^w 2...O6 ^w ^{iv}	0.86	1.98	2.82 (2)	169
O4 ^w —H4 ^w 1...O6 ^w ^v	0.86	2.39	2.96 (2)	125
O4 ^w —H4 ^w 2...O6 ^w ⁱ	0.86	2.13	2.87 (2)	143
O5 ^w —H5 ^w 2...O7 ^w	0.88	2.27	2.69 (2)	110
O7 ^w —H7 ^w 1...O6 ^w ^{vi}	0.89	2.57	2.97 (2)	108
O7 ^w —H7 ^w 2...O3 ^w	0.87	2.21	2.96 (2)	144

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

A value of 0.50 was used in the θ-dependent absorption correction in SADABS (Sheldrick, 1996). The atomic coordinates of the published Co compound (Gutschke *et al.*, 2001) were used as the starting point for refinement. The uncoordinated water O atoms were restrained to behave in an approximately isotropic manner. The two aromatic (C—H 0.93 Å) and one hydroxy (O—H 0.98 Å) H atoms were positioned geometrically and were allowed to ride on the carrier atoms, with *U*(H) = 1.2*U*_{eq}(C,O). The water H atoms were placed at chemically sensible positions but they were not refined; the displacement parameters were assigned an arbitrary value of 0.05 Å². The refinement converged with three intermolecular H...H contacts of about 2.1 Å, arising from interactions between uncoordinated water molecules. Attempts to place the water H atoms elsewhere led to a similar number of short contacts.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT (Bruker, 2001); program(s)

used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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