

catena-Poly[[[tetraaquacobalt(II)]- μ -pyrazine] phthalate]

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Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.011\text{ \AA}$

Disorder in main residue

R factor = 0.096

wR factor = 0.297

Data-to-parameter ratio = 10.2

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

The Co atom, the pyrazine heterocycle and the phthalate dianion are in special positions in the crystal structure of the title compound, $[\text{Co}(\text{C}_4\text{H}_4\text{N}_2)(\text{H}_2\text{O})_4](\text{C}_8\text{H}_4\text{O}_4)$; the Co atom and the N -heterocycle are located on sites of mmm symmetry, whereas the dianion is disordered over a $2mm$ site. The four water ligands constitute a square plane surrounding the Co atom, and the other two coordination sites are occupied by the N atoms of two different N -heterocycles. The cationic entity propagates as a linear μ -pyrazine-bridged chain that runs along the a axis of the orthorhombic unit cell. The dianion interacts with the Co atom through hydrogen bonds.

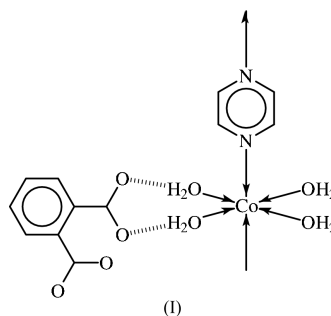
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Comment

The pyrazine N -heterocycle has been used in the preparation of coordination polymers of transition metal compounds. Among the cobalt(II) coordination polymers in particular, an unusual case in which the ligand merely binds to two adjacent Co atoms while the polymeric construction arises from bridging by the counter-ion has been reported (Yang *et al.*, 2003). The two Co atoms are separated by the ligand at a distance of 6.99 \AA in the polymeric framework.



Cobalt phthalate–pyrazine, (I), crystallizes as a tetraaqua compound. The four water ligands constitute a square plane surrounding the Co atom; the other two coordination sites are occupied by the N atoms of two different pyrazine molecules. The Co atom lies on the Wyckoff $2a$ site of mmm symmetry and the pyrazine molecule lies on another special position of mmm symmetry (Wyckoff $2b$) (Fig. 1). Arising from the symmetry, the repeat distance of the polycationic chain is the a -axial distance, *i.e.* $7.1791(5)\text{ \AA}$. The distance is exactly that found in the semiquinolate–catecholate complex, whose chain propagates along the a axis of the tetragonal unit cell (Jung & Pierpont, 1994). In the tetraaqua sulfate complexes (Fetzer *et al.*, 1994), the cobalt–pyrazine entity also lies on special positions; the corresponding distance is 7.19 \AA in the

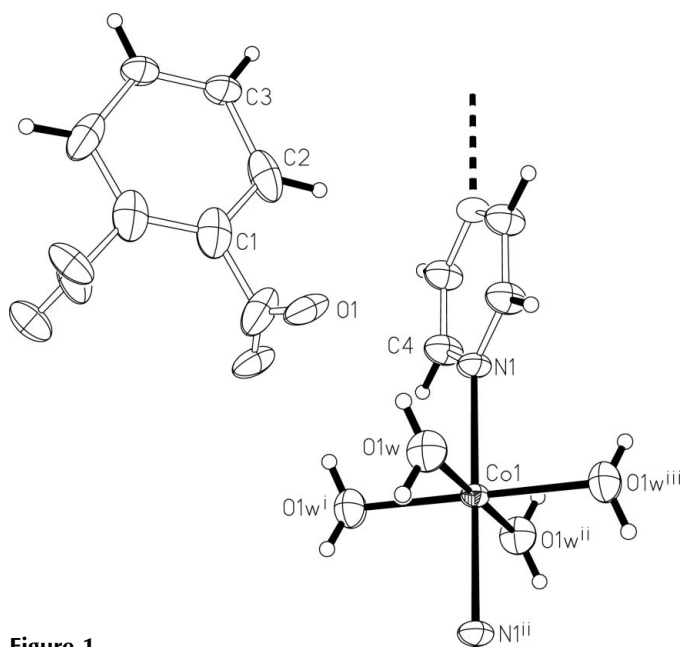


Figure 1
ORTEPII (Johnson, 1976) plot of (I); displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. The phthalate group is disordered over the Wyckoff $2f$ site. [Symmetry codes: (i) $1-x, 1-y, z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, y, 1-z$.]

compound with six water molecules and 7.12 Å in the compound with ten water molecules. In the title compound, the phthalate dianion lies on a site of $2mm$ symmetry (Wyckoff $2f$), and is disordered. It interacts with the Co atom through hydrogen bonds.

Experimental

Phthalic anhydride (0.15 g, 1 mmol) and sodium hydroxide (0.08 g, 2 mmol) were dissolved in water (12 ml). Cobalt(II) nitrate hexahydrate (0.29 g, 1 mmol) dissolved in water (1 ml) and pyrazine (0.08 g, 1 mmol) dissolved in water (1 ml) were added. The mixture was placed in a 20 ml Teflon-lined stainless-steel bomb, which was then heated to 413 K for 48 h. It was cooled to room temperature at a rate of 5 K h^{-1} . Orange prisms were obtained in 60% yield. Elemental CHN analysis, calculated: C 38.41, H 4.30, N 7.47%; found: C 39.14, H 4.17, 6.69%.

Crystal data

[Co(C₄H₄N₂)(H₂O)₄](C₈H₄O₄)
 $M_r = 375.20$
 Orthorhombic, $Immm$
 $a = 7.1791$ (5) Å
 $b = 9.4033$ (6) Å
 $c = 10.2886$ (7) Å
 $V = 694.55$ (8) Å³
 $Z = 2$
 $D_x = 1.794$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 2933 reflections
 $\theta = 2.9\text{--}28.4^\circ$
 $\mu = 1.28$ mm⁻¹
 $T = 298$ (2) K
 Prism, orange
 $0.45 \times 0.28 \times 0.27$ mm

Data collection

Bruker SMART APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.437$, $T_{\max} = 0.708$
 2970 measured reflections

480 independent reflections
 472 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -12 \rightarrow 11$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.096$
 $wR(F^2) = 0.297$
 $S = 1.23$
 480 reflections
 47 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1108P)^2 + 25.7589P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.67$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.59$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.05 (2)

Table 1

Selected geometric parameters (Å, °).

Co1—O1w	2.062 (9)	Co1—N1	2.20 (1)
O1w—Co1—O1w ⁱ	88.0 (6)	O1w ⁱⁱ —Co1—O1w ⁱⁱⁱ	88.0 (6)
O1w—Co1—O1w ⁱⁱ	180.0 (1)	O1w ⁱⁱ —Co1—N1	90.0 (1)
O1w—Co1—O1w ⁱⁱⁱ	92.0 (6)	O1w ⁱⁱⁱ —Co1—N1 ⁱⁱ	90.0 (1)
O1w—Co1—N1	90.0 (1)	N1—Co1—N1 ⁱⁱ	180.0 (1)
O1w—Co1—N1 ⁱⁱ	90.0 (1)		

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

A dimensionless value of 0.5 was used in the multi-scan absorption correction step. The structure was solved by difference Fourier synthesis, with the heavy atom at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ as a starting point for the refinement. The nature of the disorder in the phthalate group required the C1^{iv}—C1, C1—C2, C2—C3 and C3—C3^v bond lengths [symmetry codes: (iv) $-x, 1-y, 2-z$; (v) $x, y, 2-z$] to be restrained to 1.40 ± 0.01 Å and the 1,3-related distances to 2.80 ± 0.02 Å. The C1/C2/O1^{vi}/O1^{vii} plane [symmetry code: (vi) $-x, 1-y, z$; (vii) $-x, y, z$] was restrained to be approximately planar. The distance restraints gave a model in which the C1—C2^{vi} single bond between the ring and the carboxyl group is somewhat short; the C1—C2 bond is part of the aromatic ring, and the bond distance should not be longer than, say, 1.45 Å. On the other hand, the C2 atom could not be split into two components, as the refinement of the pair of atoms led to unacceptable anisotropic displacement parameters.

The H atoms were placed in calculated positions (C—H = 0.93 Å and O—H = 0.82 Å) and were refined using the riding-model approximation. Their displacement parameters were 1.2 times those of the displacement parameters of the parent atoms. The site occupancy of the C1 and C3 atoms is 0.25 whereas that of the atom C2 is 0.5. The site occupancy for H2 and H3 is 0.25.

The relatively high R factor is an artifact of the disorder and is not attributed to poor quality of the diffraction measurements. The crystal diffracted strongly, and almost all the reflections were beyond the $I > 2\sigma(I)$ cutoff. In the final difference map, the largest peak was 0.33 Å from C3 and the deepest hole was 0.36 Å from this atom.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: difference Fourier synthesis, with Co at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; 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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