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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.028
 wR factor = 0.075
Data-to-parameter ratio = 9.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Hexaaquazinc(II) dihydrogen-1,2,4,5-
benzenetetracarboxylate

The crystal structure of the title compound, $[\text{Zn}(\text{H}_2\text{O})_6][\text{C}_{10}\text{H}_4\text{O}_8]$, features a three-dimensional hydrogen-bonded network linking octahedral hexaaquazinc(II) dications, occupying special positions on twofold axes, and dihydrogen-1,2,4,5-benzenetetracarboxylate dianions located on crystallographic inversion centres. There are also intramolecular hydrogen bonds between adjacent carboxyl groups in the dianions.

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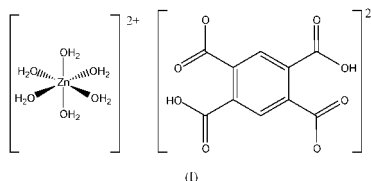
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Comment

Pyromellitic acid (also known as 1,2,4,5-benzenetetracarboxylic acid) is a versatile multi-dentate ligand capable of forming one-, two- and three-dimensional polymeric complexes (Poleti & Karanovic, 1989; Jaber *et al.*, 1997) and generating various molecular architectures. These compounds are materials with zeolite-like structures and magnetic interactions. A considerable number of reports based on pyromellitic acid complexes have appeared in recent years (Rochon & Massarweh, 2001; Wang *et al.*, 2000). At the same time, salts of pyromellitic acid have attracted interest as reagents for gravimetric analysis (Ota & Imamura, 1971), heat stabilizers (Grinblat *et al.*, 1973), and additives in dye applications (Ichikawa *et al.*, 1970). The first crystal structure determination of a salt of this acid, *viz.* $[\text{Co}(\text{H}_2\text{O})_6][\text{C}_{10}\text{H}_4\text{O}_8]$, was reported by Ward & Luehrs (1983).

As part of our study of benzenepolycarboxylate complexes, we tried to prepare a mixed-ligand Zn^{2+} complex containing 4-(2,5-dihydroxy-1,4-benzoquinonyl)-semicarbazide (Sun *et al.*, 2002) as well as a pyromellitate ligand. Instead, single crystals of the title compound were obtained (Fig. 1). Isostructural ionic compounds of the type $[\text{M}(\text{H}_2\text{O})_6][\text{C}_6\text{H}_2(\text{COO})_2(\text{COOH})_2]$, with $M = \text{Mn}^{2+}$, Co^{2+} , and Ni^{2+} , have been synthesized and characterized by X-ray diffraction (Rochon & Massarweh, 2000). However, the zinc salt of this type has not been obtained and characterized prior to the present study.



The crystalline title compound, (I), has an ionic structure built of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ dications and dianions of doubly deprotonated pyromellitic acid, which are linked to each other only through hydrogen bonds and ionic interactions. In the $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ dication, the Zn^{2+} ion is surrounded by six water

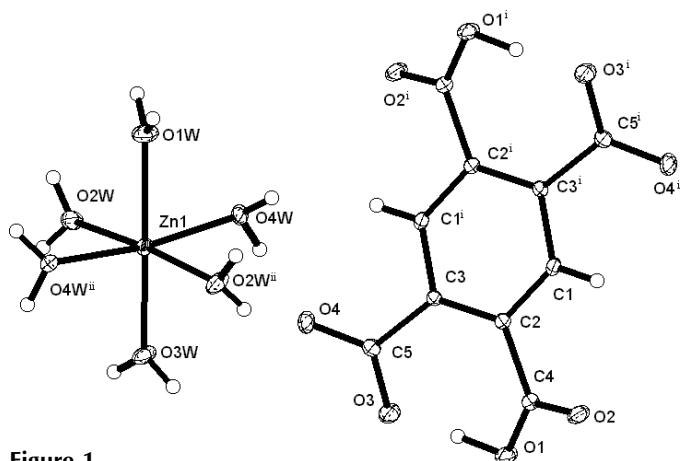


Figure 1
Structure of the cation and the anion, showing 30% probability displacement ellipsoids [symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $-x, y, \frac{3}{2} - z$].

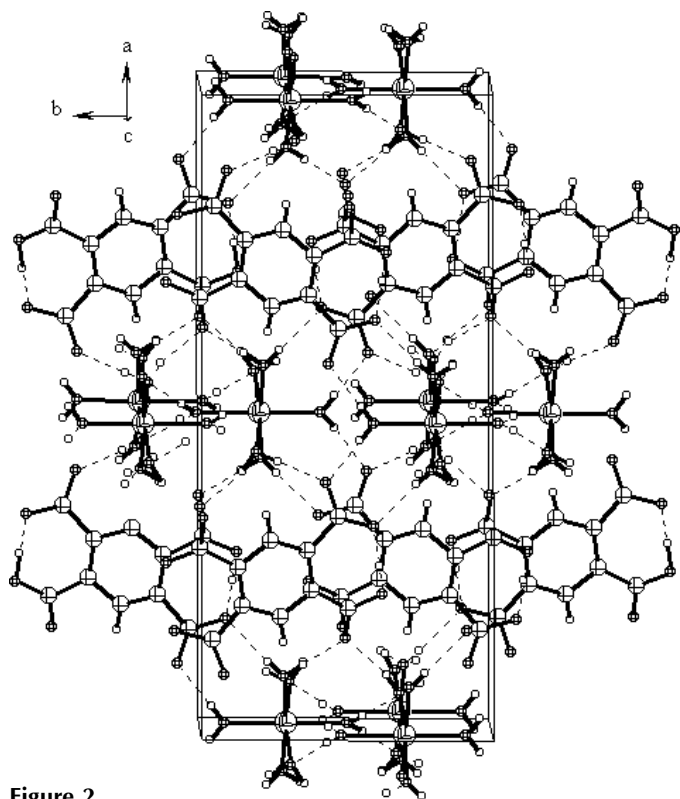


Figure 2
Packing diagram, viewed down the *c* axis.

ligands, exhibiting a slightly distorted octahedral stereochemistry. Zn^{2+} occupies a special position on a twofold axis, one pair of O atoms being on the twofold axis and the other four O atoms being related to each other in pairs by this axis. The Zn–O distances are in the range 2.042 (2)–2.125 (2) Å, and O–Zn–O angles are between 86.08 (5) and 93.92 (5)°.

The endocyclic angles in the benzene ring of the tetracarboxylate dianion are 118.5 (2)° and 117.9 (2)° for the substituted C atoms and 123.6 (2)° for the unsubstituted C atoms. The exocyclic angles C3–C2–C4 and C2–C3–C5 are significantly wider than 120° [127.4 (2)° and 127.4 (2)°, respectively], while the complementary angles C1–C2–C4

and C1ⁱ–C3–C5 [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$] are obviously narrower [114.1 (2)° and 114.6 (2)°, respectively]. This is similar to the anion in the published structures of the Co, Mn and Ni complexes (Rochon & Massarweh, 2000), but different from the parent acid, in which all the exocyclic angles are close to 120°.

All O atoms of the pyromellitic acid and all H₂O molecules are involved in the three-dimensional network of hydrogen bonds (Fig. 2). The O···O distances in the H-bonds lie between 2.413 (2) and 2.819 (2) Å.

Experimental

A mixture of pyromellitic dianhydride (0.044 g, 0.2 mmol), $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.043 g, 0.2 mmol), 4-(2,5-dihydroxy-1,4-benzoquinonyl)-semicarbazide (0.0297 g, 0.1 mmol), and H₂O (6 ml, 333.3 mmol), in a mole ratio of ca 2:2:1:3333, was sealed in a 35 ml stainless-steel reactor with a teflon liner, and was heated at 433 K for 72 h. After cooling, the mixture was filtered. Gold–yellow single crystals suitable for X-ray analysis were obtained by slow evaporation of the yellow filtrate at room temperature.

Crystal data

$[\text{Zn}(\text{C}_{10}\text{H}_4\text{O}_8)(\text{H}_2\text{O})_6]$
 $M_r = 425.60$
Monoclinic, $C2/c$
 $a = 21.972$ (3) Å
 $b = 9.7717$ (12) Å
 $c = 7.3036$ (9) Å
 $\beta = 105.562$ (2)°
 $V = 1510.6$ (3) Å³
 $Z = 4$

$D_x = 1.872$ Mg m^{−3}
Mo $K\alpha$ radiation
Cell parameters from 48 reflections
 $\theta = 1.9$ – 25.1 °
 $\mu = 1.70$ mm^{−1}
 $T = 293$ (2) K
Column, gold–yellow
 $0.80 \times 0.46 \times 0.38$ mm

Data collection

Siemens SMART CCD diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.407$, $T_{\max} = 0.524$
2454 measured reflections

1341 independent reflections
1311 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\max} = 25.1$ °
 $h = -17 \rightarrow 26$
 $k = -9 \rightarrow 11$
 $l = -7 \rightarrow 8$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.075$
 $S = 1.08$
1341 reflections
148 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 2.3426P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.38$ e Å^{−3}
 $\Delta\rho_{\min} = -0.56$ e Å^{−3}
Extinction correction: SHELXL
Extinction coefficient: 0.0067 (7)

Table 1

Selected geometric parameters (Å, °).

Zn1–O3W	2.042 (2)	O1–C4	1.284 (3)
Zn1–O2W	2.073 (2)	O2–C4	1.229 (3)
Zn1–O1W	2.116 (2)	O3–C5	1.274 (3)
Zn1–O4W	2.125 (2)	O4–C5	1.231 (3)
O3W–Zn1–O2W	87.53 (5)	C3 ⁱⁱ –C1–C2	123.6 (2)
O2W–Zn1–O1W	92.47 (5)	C1–C2–C3	118.5 (2)
O2W–Zn1–O4W ⁱ	89.85 (7)	C1–C2–C4	114.1 (2)
O3W–Zn1–O4W	93.92 (5)	C3–C2–C4	127.4 (2)
O2W–Zn1–O4W	90.48 (7)	C1 ⁱⁱ –C3–C5	114.7 (2)
O1W–Zn1–O4W	86.08 (5)	C2–C3–C5	127.4 (2)

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

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H2...O3	1.06 (4)	1.36 (4)	2.413 (2)	171 (4)
O3W—H3...O4 ⁱ	0.76 (3)	2.00 (3)	2.755 (2)	178 (4)
O4W—H4...O4	0.81 (4)	1.92 (4)	2.733 (2)	173 (3)
O4W—H5...O2 ⁱⁱ	0.82 (3)	1.88 (3)	2.690 (2)	166 (3)
O1W—H6...O4W ⁱⁱⁱ	0.82 (3)	2.00 (3)	2.819 (2)	176 (3)
O2W—H7...O2 ^{iv}	0.81 (4)	1.99 (4)	2.794 (2)	172 (3)
O2W—H8...O3 ^v	0.75 (4)	2.01 (4)	2.758 (3)	177 (4)

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

All H atoms were located from a difference Fourier map and their positions and isotropic displacement parameters were refined. The C—H bond lengths were 0.90 (3) Å and the O—H bond lengths were in the range 0.75 (4)–1.06 (4) Å. Even though the distributions of C—O bond lengths in the C4/O1/O2 and C5/O3/O4 groups are fairly similar, the difference map yields only one position for atom H2, thus distinguishing unambiguously the protonated carboxylic acid group from the ionized carboxylated group.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999) and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick,

1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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