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Disodium bis(1,2,4,5-benzenetetracarboxylato)-dihydroxytetrazincate(II) pyrazine

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The tetranuclear dianion of the title compound, $Na_2[Zn_4(C_{10}H_2O_8)_2(OH)_2]\cdot C_4H_4N_2$, forms a network framework in which the Zn atom exists in a tetrahedral environment, as it is coordinated by the carboxyl O atoms belonging to three different $(C_{10}H_2O_8)^{4-}$ anions as well as by the bridging OH group. Adjacent OH groups are linked together through the uncoordinated heterocycle, which lies on a site of $2/m$ symmetry. The octahedrally coordinated Na ion, which lies on a site of 2 symmetry, interacts with one O atom of the carboxyl group of two anions and with two O atoms of the *ortho*-carboxyl groups of two other anions.

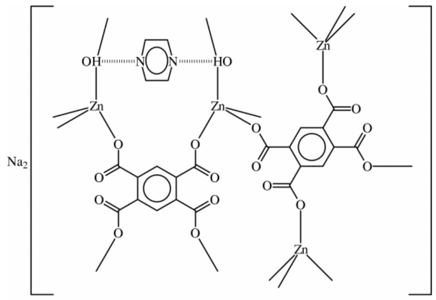
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.028
wR factor = 0.072
Data-to-parameter ratio = 12.5

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

Comment

The 4,4′-bipyridine spacer molecule has been used in the formation of a plethora of adducts with zinc carboxylates; however, the spacer was not incorporated in hydrated disodium dihydrogen 1,2,4,5-benzenetetracarboxylatozinc (Wu *et al.*, 2001) when the synthesis was performed under acidic conditions. The use of pyrazine in the metathetical reaction of the sodium salt of this acid and a zinc salt did not lead to the formation of an N-coordinated Zn complex either. The title complex, (I), is formally a hydroxide (Fig. 1), and the heterocycle merely serves as a connector that links adjacent groups together.



(I)

The compound adopts a network framework in which the Zn atom exists in a tetrahedral geometry, being covalently bonded to the carboxyl O atoms belonging to three different $(C_{10}H_2O_8)^{4-}$ anions and to the bridging OH group. Adjacent OH groups are linked together through the uncoordinated lattice heterocycle (Fig. 2). The octahedrally coordinated Na ion interacts with one O atom of the carboxyl group of two anions and with two O atoms of the *ortho*-carboxyl groups of two other anions (Fig. 3).

In the assembly of coordination polymers the use of sodium hydroxide to deprotonate carboxylic acids sometimes

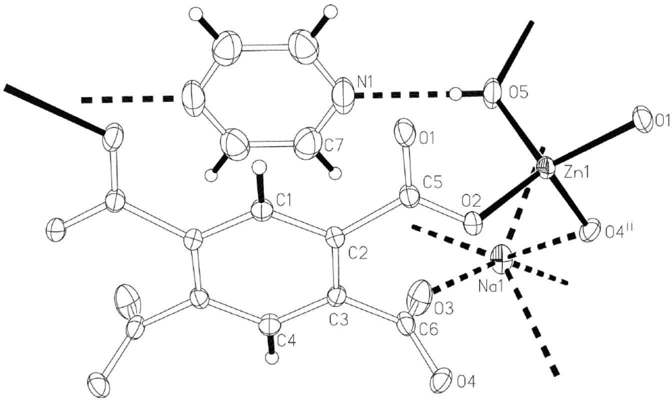


Figure 1
*ORTEP*II (Johnson, 1976) plot of a fragment of the structure of the title compound, with displacement ellipsoids drawn at the 75% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$.]

furnishes compounds having sodium ions incorporated into the crystal structure (Robl, 1992; Wu *et al.*, 2001; Yang *et al.*, 2002) because the Na^+ cation is able to form strong bonds with carboxylate groups or with water. Furthermore, it serves to compensate for the negative charge of the frameworks.

Experimental

1,2,4,5-Benzenetetracarboxylic acid anhydride (pyromellitic anhydride, 0.22 g, 1 mmol) and sodium hydroxide (0.16 g, 4 mmol) were dissolved in water (15 ml), and to the solution was added zinc dinitrate hexahydrate (0.59 g, 2 mmol) and pyrazine (0.16 g, 2 mmol) dissolved in water (5 ml). The mixture 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 5 K h^{-1}. Block-shaped colorless crystals separated from the solution.

Crystal data

$Na_2[Zn_4(C_{10}H_2O_8)_2(OH)_2]\cdot C_4H_4N_2$
$M_r = 921.80$
Monoclinic, $C2/m$
$a = 10.4073$ (5) Å
$b = 17.8174$ (8) Å
$c = 7.5278$ (4) Å
$\beta = 108.474$ (1)°
$V = 1324.0$ (1) Å^3
$Z = 2$
$D_x = 2.312$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5344 reflections
$\theta = 2.3$–28.3°
$\mu = 3.71$ mm^{-1}
$T = 298$ (2) K
Block, colorless
0.29 × 0.17 × 0.12 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.463$, $T_{max} = 0.641$
7636 measured reflections
1629 independent reflections
1470 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 28.3$°
$h = -13 \rightarrow 13$
$k = -23 \rightarrow 23$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.072$
$S = 1.03$
1629 reflections
130 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

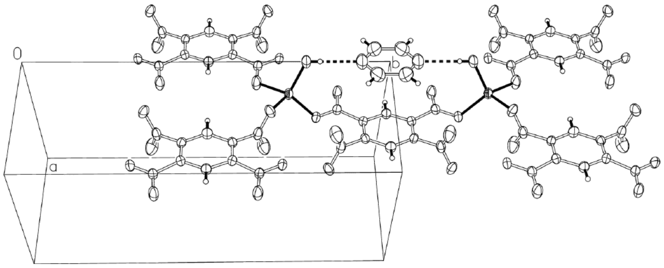


Figure 2
*ORTEP*II (Johnson, 1976) plot illustrating the hydroxyl–pyrazine–hydroxyl hydrogen bonds.

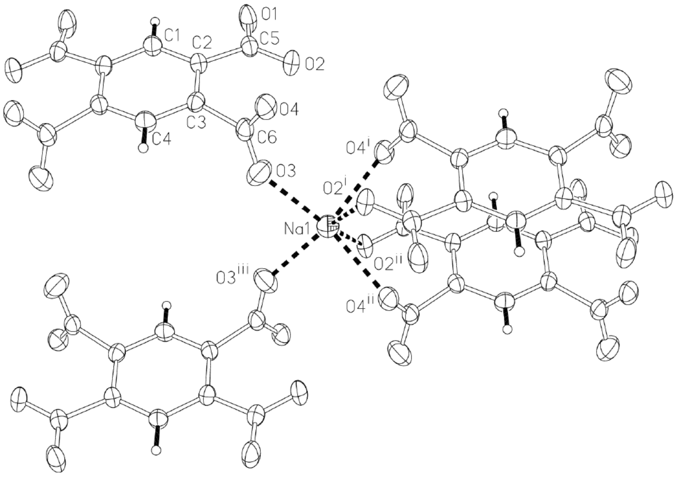


Figure 3
*ORTEP*II (Johnson, 1976) plot illustrating the coordination of the Na^+ ion. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, z$; (iii) $-x, y, 1 - z$.]

Table 1
Selected geometric parameters (Å, °).

$Zn1-O1^{i}$	1.973 (2)	$Na1-O2^{ii}$	2.542 (2)
$Zn1-O2$	1.975 (2)	$Na1-O3$	2.319 (2)
$Zn1-O4^{ii}$	1.960 (2)	$Na1-O4^{ii}$	2.406 (2)
$Zn1-O5$	1.890 (1)		
$O1^{i}-Zn1-O2$	120.3 (1)	$O2^{ii}-Na1-O3^{iv}$	136.5 (1)
$O1^{i}-Zn1-O4^{ii}$	98.5 (1)	$O2^{ii}-Na1-O4^{ii}$	73.7 (1)
$O1^{i}-Zn1-O5$	107.3 (1)	$O2^{ii}-Na1-O4^{iii}$	79.6 (1)
$O2-Zn1-O4^{ii}$	113.8 (1)	$O3-Na1-O3^{iv}$	88.1 (1)
$O2-Zn1-O5$	108.1 (1)	$O3-Na1-O4^{ii}$	91.9 (1)
$O4^{ii}-Zn1-O5$	108.2 (1)	$O3-Na1-O4^{iii}$	148.8 (1)
$O2^{ii}-Na1-O2^{iii}$	136.2 (1)	$O4^{ii}-Na1-O4^{iii}$	103.6 (1)
$O2^{ii}-Na1-O3$	79.1 (1)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O5-H5\cdots N1$	0.84 (1)	1.88 (1)	2.720 (4)	180

The diffraction measurements were of sufficiently high quality to allow for the refinement of the four H atoms, three of which lie on

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special positions, when restraints [O—H = 0.85 (1) Å and C—H 0.93 (1) Å] were applied.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); 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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References

Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

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

Robl, C. (1992). *Mater. Res. Bull.* **27**, 99–107.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Wu, C.-D., Wu, D.-M., Lu, C.-Z. & Huang, J.-S. (2001). *Acta Cryst.* E**57**, m253–m255.

Yang, S.-Y., Sun, Z.-G., Long, L.-S., Huang, R.-B. & Zheng, L.-S. (2002). *Main Group Met. Chem.* **25**, 579–580.

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