

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

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

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The tetranuclear dianion of the title compound, $\text{Na}_2[\text{Zn}_4(\text{C}_{10}\text{H}_2\text{O}_8)_2(\text{OH})_2]\cdot\text{C}_4\text{H}_4\text{N}_2$, 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 $(\text{C}_{10}\text{H}_2\text{O}_8)^{4-}$ 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.

Received 28 July 2003

Accepted 31 July 2003

Online 15 August 2003

Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.028

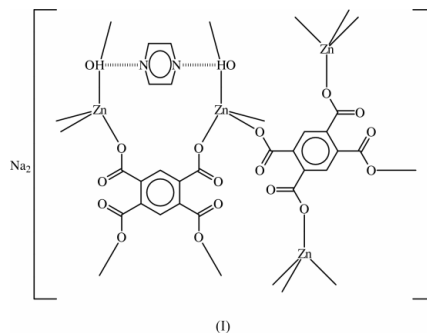
wR factor = 0.072

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.



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 $(\text{C}_{10}\text{H}_2\text{O}_8)^{4-}$ 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

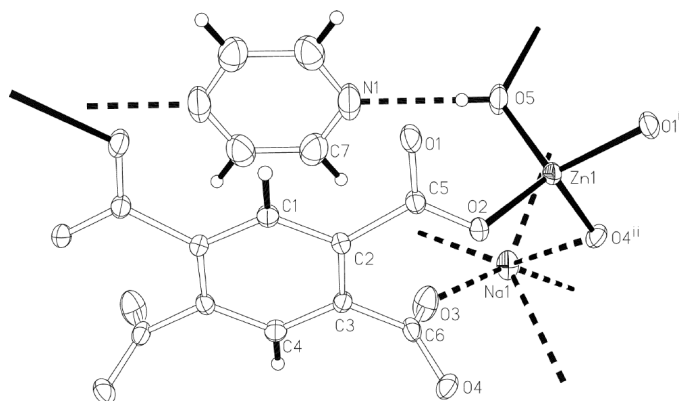


Figure 1
ORTEPII (Johnson, 1976) plot of a fragment of the structure of the title compound, with displacement ellipsoids drawn at the 75% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (ii) $\frac{1}{2} - x, \frac{1}{2}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

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 nitrate 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 ₂ O ₈) ₂ (OH) ₂]-C ₄ H ₄ N ₂	<i>D_x</i> = 2.312 Mg m ⁻³
<i>M_r</i> = 921.80	Mo <i>K</i> α radiation
Monoclinic, <i>C2/m</i>	Cell parameters from 5344 reflections
<i>a</i> = 10.4073 (5) Å	<i>θ</i> = 2.3–28.3°
<i>b</i> = 17.8174 (8) Å	<i>μ</i> = 3.71 mm ⁻¹
<i>c</i> = 7.5278 (4) Å	<i>T</i> = 298 (2) K
<i>β</i> = 108.474 (1)°	Block, colorless
<i>V</i> = 1324.0 (1) Å ³	0.29 × 0.17 × 0.12 mm
<i>Z</i> = 2	

Data collection

Bruker SMART APEX area-detector diffractometer	1629 independent reflections
<i>φ</i> and <i>ω</i> scans	1470 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.035
<i>T</i> _{min} = 0.463, <i>T</i> _{max} = 0.641	<i>θ</i> _{max} = 28.3°
7636 measured reflections	<i>h</i> = -13 → 13
	<i>k</i> = -23 → 23
	<i>l</i> = -9 → 9

Refinement

Refinement on <i>F</i> ²	All H-atom parameters refined
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.028	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0429 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.072	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 1.03	(Δ/σ) _{max} = 0.001
1629 reflections	Δρ _{max} = 0.51 e Å ⁻³
130 parameters	Δρ _{min} = -0.40 e Å ⁻³

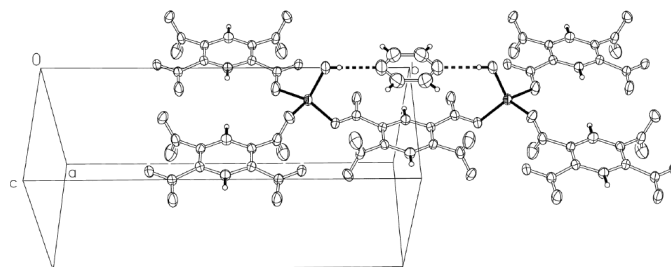


Figure 2
ORTEPII (Johnson, 1976) plot illustrating the hydroxyl-pyrazine-hydroxyl hydrogen bonds.

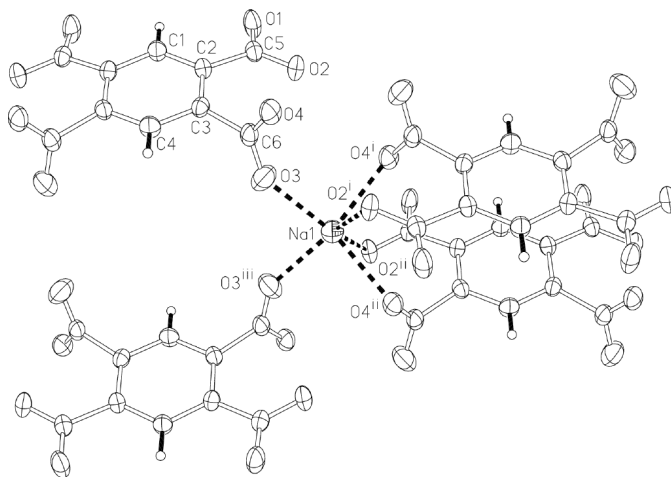


Figure 3
ORTEPII (Johnson, 1976) plot illustrating the coordination of the Na⁺ ion. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, z$; (iii) $-x, y, 1 - z$.]

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 ⁱⁱⁱ	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 ⁱⁱⁱ	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 ⁱⁱⁱ	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, °).

<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>
O5–H5...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

special positions, when restraints [$O-H = 0.85(1) \text{ \AA}$ and $C-H 0.93(1) \text{ \AA}$] were applied.

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

The authors thank the National Science Foundation of China (grant Nos. 20271044, 20273052 and 20021002), the Department of Science and Technology of China (No. 2002 CCA01600), the National Science Foundation of Fujian

Province (grant No. E0110001), and the University of Malaya for supporting this work.

References

- Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Johnson, C. K. (1976). *ORTEPII*. 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). *SHELXS97* and *SHELXL97*. 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.