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Octaaquabis[dihydrogen 1,2,4,5-benzenetetracarboxylate(2–)]disodium(I)zinc(II) dihydrate

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The title compound, $[Na_2Zn(C_{10}H_4O_8)_2(H_2O)_8]\cdot 2H_2O$, consists of six-coordinated Zn^{2+} and Na^+ cations, aqua ligands, crystal water molecules and dihydrogen 1,2,4,5-benzenetetracarboxylate(2−) (H_2btc) anions. The six-coordinated zinc centers, which are situated at the inversion center, are linked into one-dimensional chains *via* six coordinated sodium ions in pairs and extended further into a three-dimensional framework *via* hydrogen bonding.

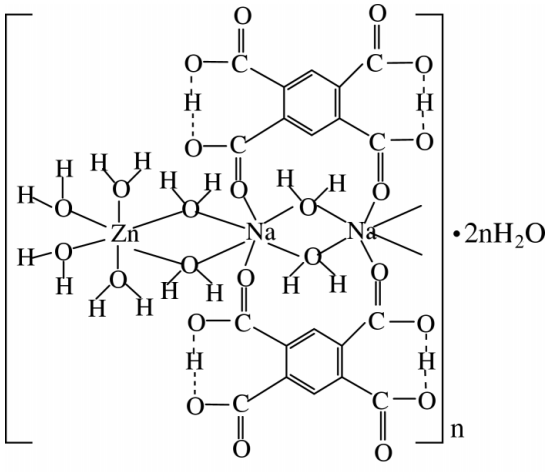
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.056
wR factor = 0.163
Data-to-parameter ratio = 9.7

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

Comment

The vast number of reported coordination polymers are normally constructed by linking transition metal centers through multidentate bridging ligands. Thus, the careful selection of bridging ligands is very important in order to build



(I)

interesting and useful architectures. The coordination chemistry of 1,2,4,5-benzenetetracarboxylic acid (H_4btc) (Takusagawa *et al.*, 1971), which has four (H_2btc) or eight (btc) potential oxygen donors and can act in a variety of ways, has been widely studied (Usubaliev *et al.*, 1982; Nectoux *et al.*, 1984; Cousson *et al.*, 1986; Xing *et al.*, 1986, 1987; Robl, 1987, 1988, 1992; Robl & Hentschel, 1991; Chaudhuri *et al.*, 1988; Poleti *et al.*, 1988; Poleti & Karanovic, 1989; Jessen & Kuppers, 1990; Wei *et al.*, 1991; Luehrs & Bowman-James, 1994; Chen *et al.*, 1996; Jaber *et al.*, 1997; Zou *et al.*, 1998; Karanovic *et al.*, 1999). As part of our interest in the H_2btc(2−) or btc(4−) bridged complexes, we tried to prepare a novel mixed-ligand bridged heterometallic polymer containing 4,4′-bipridine and

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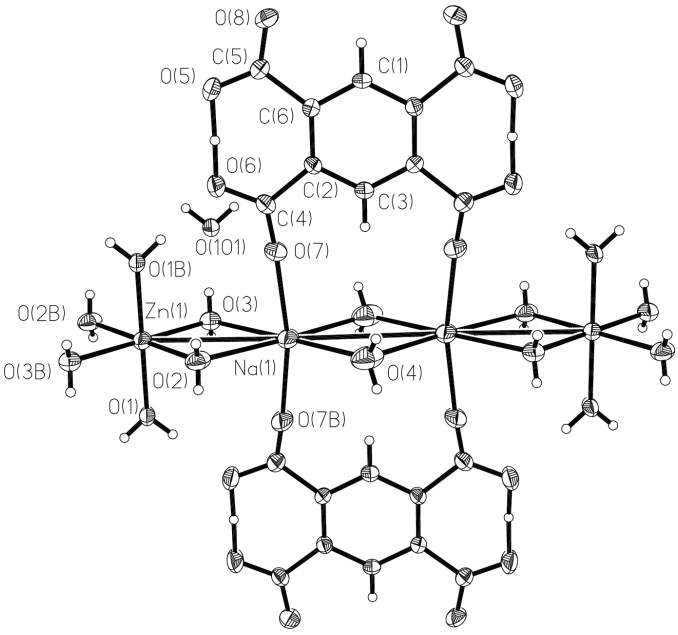

Figure 1
Part of the structure of (I) with the atom labelling (50% probability displacement ellipsoids).

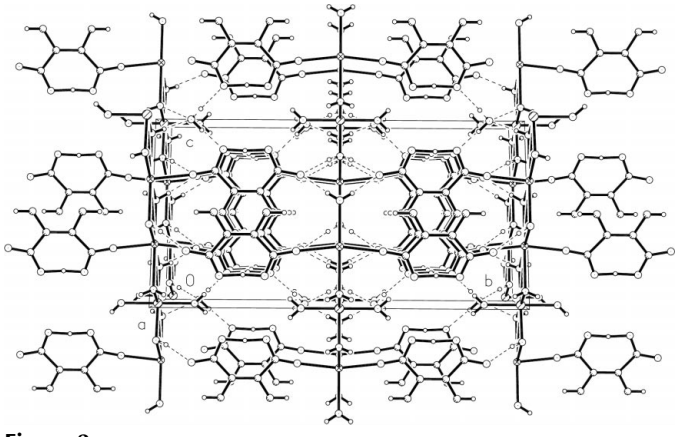

Figure 2
Cell packing of (I) viewed down the *a* axis, showing the hydrogen bonds.

H_2btc or btc ligands. Unfortunately, single crystals of the title compound, (I), were obtained.

As shown in Fig. 1, each zinc center is a six-aqua-ligand-coordinated octahedron, with Zn—O distances in the range 2.045 (4)–2.123 (4) Å and O—Zn—O angles between 84.8 (2) and 95.2 (2)°. The sodium ion displays distorted octahedral geometry and is bonded to two carboxylate O atoms of H_2btc ligands [Na—O = 2.274 (3) Å]. The four longer Na—O contacts are to bridging aqua ligands, which are coordinated to the adjacent sodium ion [Na—O = 2.450 (6)-2.558 (7) Å] and zinc center [Na—O = 2.505 (5)-2.559 (6) Å], with O—Na—O angles between 68.6 (2) and 110.1 (2)°. Each H_2btc ligand acts as bidentate ligand bridging two sodium ions, with Na...Na distances of 3.962 (5) Å. Interestingly, these H_2btc ligands bridging sodium centers link zinc centers through bridging aqua ligands into a one-dimensional polymeric chain along the *c* axis. The Zn···Zn and Zn···Na distances within a polymeric chain are 11.263 (4) and 3.653 (3) Å, respectively. It is noticeable that adjacent chains are arranged in a parallel fashion. Interchain crosslinking is achieved through complex intermolecular hydrogen bonding among aqua ligands, crystal water molecules and carboxylate groups, which connect these chains into a three-dimensional framework with O···O contacts in the range 2.722 (4)–2.853 (5) Å and O—H···O angles ranging from 170 (5) to 177 (6)° (Fig. 2).

A short intramolecular hydrogen bond also exists inside the H_2btc ligands with an O···O distance of 2.384 (5) Å and O—H distances of 1.15 (7) and 1.24 (7) Å, which might contribute to the indistinguishable COO^- and COOH groups (Karanovic *et al.*, 1999).

Experimental

A mixture of $Na_2MoO_4{\cdot}2H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$, 4,4′-bpy·$2H_2O$, 1,2,4,5-benzenetetracarboxylic anhydride, concentrated HNO_3 (63%) and water in a molar ratio of 1:1:1:1:5:2000 was sealed in a 30 ml Teflon-lined stainless steel vessel and heated at 443 K for six days under autogenous pressure. After the reaction was slowly cooled to room temperature, colorless crystals of (I) appeared.

Crystal data

$[Na_2Zn(C_{10}H_4O_8)_2(H_2O)_8]{\cdot}2H_2O$
M_r = 795.77
Monoclinic, *C*2/*m*
a = 7.2861 (15) Å
b = 20.179 (4) Å
c = 10.453 (2) Å
β = 103.47 (3)°
V = 1494.5 (5) Å^3
Z = 2
D_x = 1.768 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 13.1–14.8°
μ = 0.96 mm^{-1}
T = 293 (2) K
Prism, colorless
0.46 × 0.13 × 0.05 mm

Data collection

Enraf–Nonius CAD-4–II diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.684, T_{max} = 0.998
1633 measured reflections
1511 independent reflections
1253 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 26.0°
$h = 0 \rightarrow 8$
$k = -24 \rightarrow 0$
$l = -12 \rightarrow 12$
3 standard reflections every 300 reflections intensity decay: 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.163
S = 1.09
1511 reflections
156 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0965P)^2 + 0.7210P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −1.74 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0061 (14)

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.045 (4)	Na1—O4^{i}	2.558 (7)
Zn1—O3	2.106 (4)	Na1—O2	2.559 (6)
Zn1—O2	2.123 (4)	O5—C5	1.264 (5)
Na1—O7	2.274 (3)	O6—C4	1.281 (5)
Na1—O4	2.449 (6)	O7—C4	1.203 (5)
Na1—O3	2.505 (5)	O8—C5	1.233 (5)
O1—Zn1—O1^{ii}	180.0	O4—Na1—O3	178.7 (2)
O1—Zn1—O3	90.0	O7—Na1—O4^{i}	92.9 (1)
O3^{ii}—Zn1—O3	180.0	O4—Na1—O4^{i}	75.4 (2)
O1—Zn1—O2^{ii}	90.0	O3—Na1—O4^{i}	105.9 (2)
O3—Zn1—O2^{ii}	95.2 (2)	O7—Na1—O2	86.6 (1)
O1—Zn1—O2	90.0	O4—Na1—O2	110.1 (2)
O3—Zn1—O2	84.8 (2)	O3—Na1—O2	68.6 (2)
O2^{ii}—Zn1—O2	180.0	O4^{i}—Na1—O2	174.5 (2)
O7^{iii}—Na1—O7	167.6 (2)	Zn1—O2—Na1	102.2 (2)
O7—Na1—O4	96.1 (1)	Zn1—O3—Na1	104.4 (2)
O7—Na1—O3	83.9 (1)	Na1—O4—Na1^{i}	104.6 (2)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O6^{i}	0.83	1.94	2.765 (4)	177
O3—H3A···O101	0.78 (5)	1.95 (5)	2.722 (4)	170 (5)
O2—H2A···O8^{ii}	0.73 (5)	2.03 (5)	2.756 (4)	171 (6)
O4—H4A···O8^{iii}	0.81	2.06	2.853 (5)	171
O6—H56···O5	1.15 (7)	1.24 (7)	2.384 (5)	172 (6)
O101—H10A···O5^{iv}	0.84	1.93	2.768 (4)	176

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

H atoms were clearly visible in difference maps. The H1 and H3 atoms were refined isotropically in the subsequent least-squares refinement. The H2A, H3A and H56 atoms on O atoms were handled in the subsequent refinement with fixed isotropic displacement parameters, whereas H1A, H4A and H10A were positioned geometrically and included in the structure-factor calculations as riding atoms with fixed isotropic displacement parameters. The highest residual peak is located at (0.0391, $\frac{1}{2}$, 0.9143), 1.00 Å from Zn1 and the deepest hole is located at (0.1167, $\frac{1}{2}$, 0.0023), 0.85 Å from Zn1.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *MolEN* (Fair, 1990); data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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