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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
 R factor = 0.044
 wR factor = 0.074
Data-to-parameter ratio = 12.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Ethylenediammonium diaquabis(ethylene-diamine- κ^2N,N')zinc(II) bis(pyridine-2,6-dicarboxylato- κ^3,O,N,O')zincate(II) dihydrate

In the title compound, $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Zn}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]-[\text{Zn}(\text{C}_7\text{H}_3\text{NO}_4)_2]_2 \cdot 2\text{H}_2\text{O}$, the Zn atom (site symmetry $2/m$) in the $[\text{Zn}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]^{2+}$ cation is six-coordinated by four N atoms from bidentate ethylenediammonium molecules and two water O atoms. The Zn atom (site symmetry 2) in the $[\text{Zn}(\text{C}_7\text{H}_3\text{NO}_4)_2]^{2-}$ anion is six-coordinated by four O atoms and two N atoms from two tridentate pyridine-2,6-dicarboxylate ligands. An uncoordinated ethylenediammonium cation and two water molecules are also present in the structure. The crystal packing is stabilized by $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, forming a three-dimensional network.

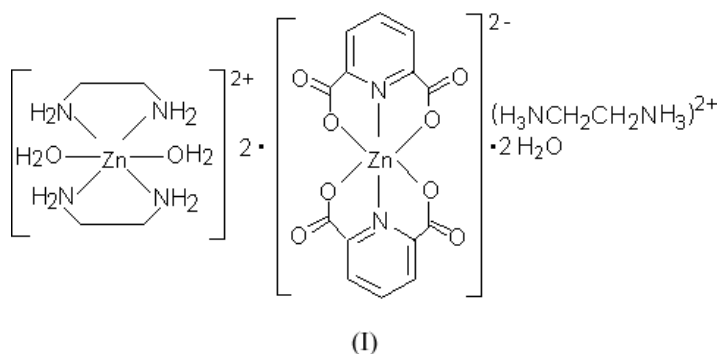
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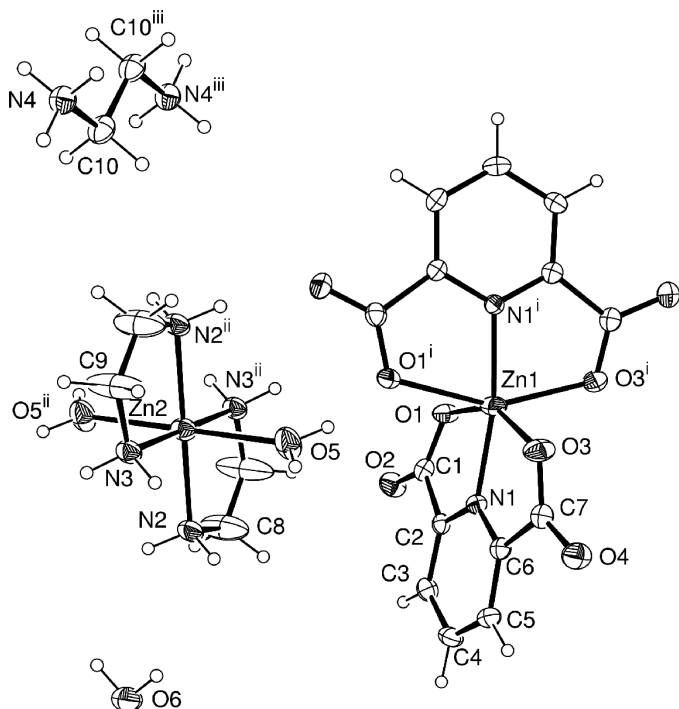
Comment

The title compound, (I), $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Zn}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]-[\text{Zn}(\text{C}_7\text{H}_3\text{NO}_4)_2]_2 \cdot 2\text{H}_2\text{O}$, (where $\text{C}_2\text{H}_8\text{N}_2$ is ethylenediamine, $L1$, $\text{C}_2\text{H}_{10}\text{N}_2$ is protonated ethylenediamine, H_2L1 , and $\text{C}_7\text{H}_3\text{NO}_4$ is pyridine-2,6-dicarboxylate, $L2$), consists of a $[\text{Zn}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]^{2+}$ cation, a $\text{C}_2\text{H}_{10}\text{N}_2^{2+}$ cation, two $[\text{Zn}(\text{C}_7\text{H}_3\text{NO}_4)_2]^{2-}$ anions and two uncoordinated water molecules (Fig. 1).



The Zn1 atom in the $[\text{Zn}(\text{C}_7\text{H}_3\text{NO}_4)_2]^{2-}$ anion is six-coordinated by four O atoms and two N atoms from two $L2$ ligands. The complete anion is generated by twofold symmetry. The *trans* angles of the ZnN_2O_4 octahedron are $169.77(18)$, $152.87(9)$ and $152.87(9)^\circ$. The *cis* angles are in the range $77.61(11)$ – $110.08(10)^\circ$, indicating a rather distorted octahedral geometry. The average Zn–O separation of $2.212(3)\text{ \AA}$ (Table 1) is in the expected range for Zn–O(carboxyl) bond lengths.

The central Zn2 atom in the $[\text{Zn}L1_2(\text{H}_2\text{O})_2]^{2+}$ cation has a distorted octahedral geometry, formed by four N atoms of the two bidentate $L1$ ligands and two O atoms of water ligands. Here, the complete species is generated by inversion symmetry. The chelate N–Zn1–N bite angle for the $L1$ ligand is $81.75(15)^\circ$ and the remaining *cis* angles in the Zn2


Figure 1

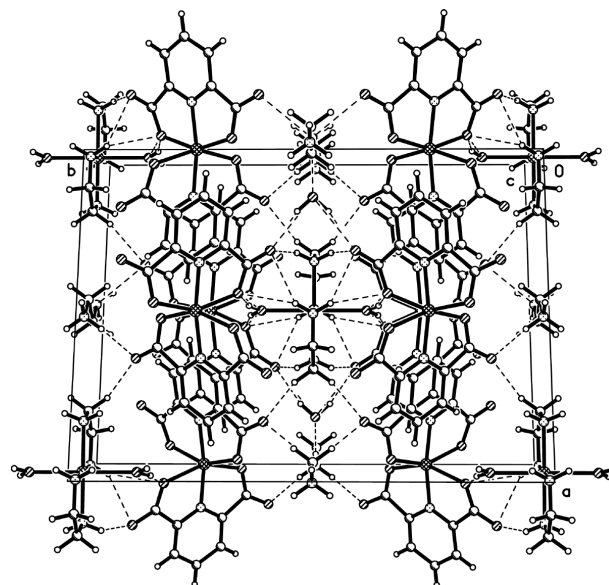
A view of the component species in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, y, -z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $-x, 1 - y, 1 - z$.]

octahedron span the range 90.0 – 98.25 (15)°. The average Zn–N bond length of 2.114 Å (Table 1) is comparable with the value of 2.181 Å observed in the $[\text{Zn}(\text{en})_3]^{2+}$ cationic complex (en is ethylenediamine) described earlier by Fu *et al.* (2004). The elongated displacement ellipsoids for atoms C8 and C9 possibly indicate unresolved positional disorder of the L1 species about the (020) mirror plane. The very short C8–C9 bond length of 1.333 (7) Å is probably an artefact of this disorder.

All the N–H groups of the L1 ligand and the H₂L1 cation, and the O–H groups of the uncoordinated water molecules, are involved in hydrogen bonds (Table 2). The O atoms of the pyridine-2,6-dicarboxylate ligands serve as acceptors, resulting in the formation of a three-dimensional hydrogen-bond network (Table 2 and Fig. 2). Atoms H3A and H3B are involved in bifurcated hydrogen bonds.

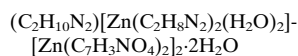
Experimental

ZnSO₄ (0.5 mmol) was dissolved in distilled water (20 ml), and an aqueous mixture (30 ml) of H₂L2 (0.75 mmol), NaOH (0.5 mmol) and ethylenediamine (0.5 mmol) was added dropwise at 333 K. The mixture was stirred for 6 h and part of the solvent was evaporated in a rotary vacuum evaporator. The resulting solution was filtered and allowed to stand in air for about 6 weeks. Large colourless block-like crystals of (I) were obtained. Analysis calculated for C₃₄H₄₆N₁₀O₂₀Zn₃: C 36.76, H 4.17, N 12.61%; found: C 36.57, H 4.09, N 12.55%.


Figure 2

The crystal packing of (I), showing the O–H...O and N–H...O hydrogen-bond interactions as dashed lines.

Crystal data



$M_r = 1110.92$

Monoclinic, $C2/m$

$a = 14.187$ (6) Å

$b = 19.218$ (8) Å

$c = 8.139$ (4) Å

$\beta = 108.061$ (7)°

$V = 2109.7$ (16) Å³

$Z = 2$

$D_x = 1.749$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 1128

reflections

$\theta = 2.6$ – 21.4 °

$\mu = 1.79$ mm⁻¹

$T = 293$ (2) K

Block, colourless

$0.42 \times 0.27 \times 0.14$ mm

Data collection

Bruker SMART CCD area detector diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 1997)

$T_{\text{min}} = 0.521$, $T_{\text{max}} = 0.788$

6170 measured reflections

2225 independent reflections

1306 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\text{max}} = 26.5$ °

$h = -17 \rightarrow 17$

$k = -24 \rightarrow 18$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.074$

$S = 1.00$

2225 reflections

173 parameters

H atoms treated by a mixture of

independent and constrained

refinement

$w = 1/[\sigma^2(F_o^2) + (0.0166P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.66$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Table 1

Selected bond lengths (Å).

Zn1–N1	1.999 (3)	Zn2–N3	2.103 (4)
Zn1–O3	2.162 (3)	Zn2–N2	2.125 (4)
Zn1–O1	2.262 (3)	Zn2–O5	2.253 (5)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A \cdots O2 ^{iv}	0.90	2.43	3.162 (4)	139
N2—H2B \cdots O2 ^v	0.90	2.43	3.162 (4)	139
N3—H3A \cdots O1 ^v	0.90	2.42	3.256 (3)	156
N3—H3A \cdots O2 ^v	0.90	2.43	3.166 (4)	139
N3—H3B \cdots O1 ^{iv}	0.90	2.42	3.256 (3)	156
N3—H3B \cdots O2 ^{iv}	0.90	2.43	3.166 (4)	139
N4—H4A \cdots O6 ^{vi}	0.89	1.98	2.839 (6)	162
N4—H4B \cdots O4 ^{vii}	0.89	1.91	2.784 (4)	169
N4—H4C \cdots O4 ^{viii}	0.89	1.91	2.784 (4)	169
O5—H11 \cdots O1 ^{iv}	0.873 (10)	2.09 (2)	2.899 (3)	155 (4)
O6—H12 \cdots O2 ^{iv}	0.876 (10)	1.979 (13)	2.838 (4)	167 (4)

Symmetry codes: (iv) $x, y, z + 1$; (v) $x, -y + 1, z + 1$; (vi) $-x + 1, -y + 1, -z + 2$; (vii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$; (viii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.

After location of the H atoms in difference maps, the water O—H distances were restrained to 0.90 (1) Å and their $U_{\text{iso}}(\text{H})$ values were allowed to refine. All other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H =

0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or with N—H = 0.90 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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