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Bis(imidazolium) di-μ-pyrazole-3,5-dicarboxylato(3–)-bis[diaquazinc(II)]

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.027
wR factor = 0.071
Data-to-parameter ratio = 11.5

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

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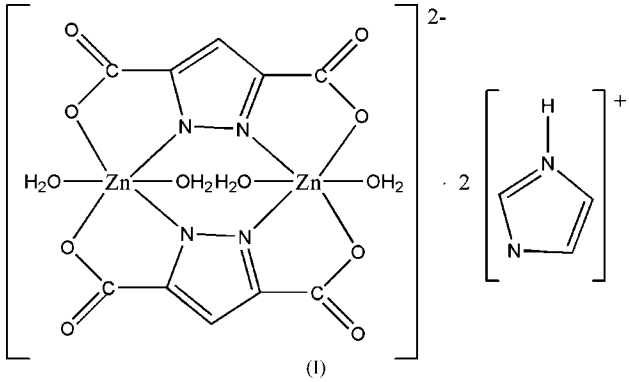
In the title compound, $(C_3H_5N_2)_2[Zn_2(C_5HN_2O_4)_2(H_2O)_4]$, two 3,5-pyrazoledicarboxylate trianions and two water molecules are coordinated to the Zn atom and the geometry is octahedral. Each pair of Zn^{II} ions is bridged by two 3,5-pyrazoledicarboxylate trianions, forming a centrosymmetric binuclear complex dianion. In the crystal structure, the cations and anions are linked by O—H···O and N—H···O hydrogen bonds to form a network structure.

Comment

The design and synthesis of supramolecular inorganic architectures exhibiting novel properties is providing exciting new opportunities in many fields of research (Swiegers & Malefetse, 2002; Johnson & Raymond, 2001; Hof *et al.*, 2002). In the synthesis of supramolecular inorganic architectures by design, the assembly of molecular units in predefined arrangements is a key goal (Desiraju, 1995, 1997; Braga *et al.*, 1998). Directional intermolecular interactions are the primary tools in achieving this goal and hydrogen bonding is currently the best tool amongst them (Zaworotko, 1997; Braga & Grepioni, 2000). We report here on the structure of the title compound, (I), which consists of two imidazolium cations and a centrosymmetric $[Zn(C_5HO_4N_2)(H_2O)_2]_2^{2-}$ dianion.



(I)

The molecular structure of compound (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The geometry around each Zn atom is octahedral, arising from coordination by two 3,5-pyrazoledicarboxylate trianions and two water molecules. A carboxylate O atom and an N atom, of one of the 3,5-pyrazoledicarboxylate trianions, are chelated to a Zn atom. Each pair of Zn^{II} ions is bridged by two 3,5-pyrazoledicarboxylate trianions, forming a centrosymmetric binuclear complex anion, as shown in Fig. 1.

In the crystal structure the cations and anions interact through O—H···O and N—H···O hydrogen bonds (Table 2) to generate a three-dimensional network structure (Fig. 2).

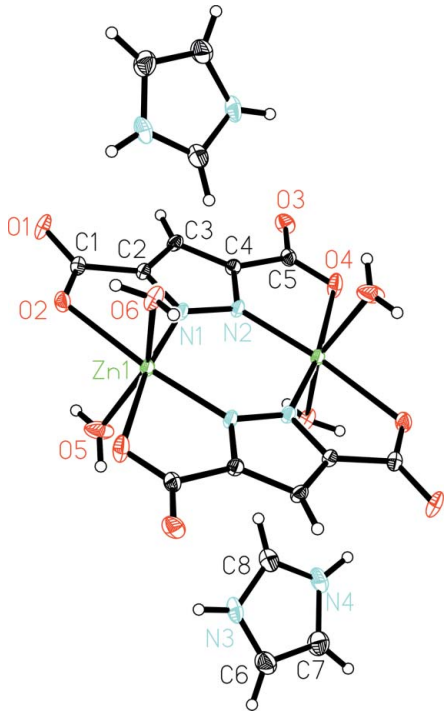


Figure 1
Twice the asymmetric unit of compound (I), showing the atom numbering and displacement ellipsoids drawn at the 50% probability level. Unlabeled atoms are related to labeled atoms by $2-x, 1-y, 1-z$.

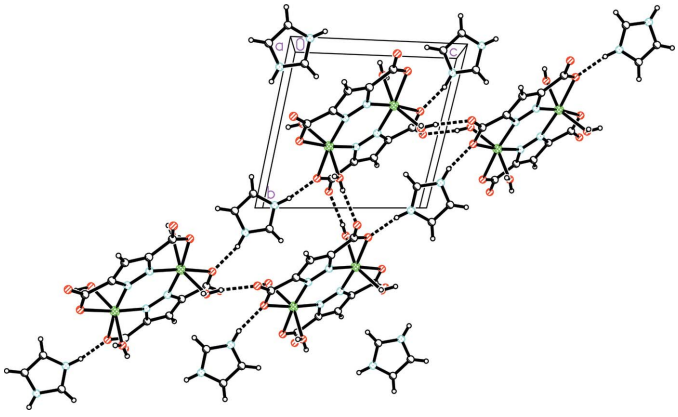


Figure 2
A perspective view along the *a* axis of the crystal packing of compound (I), with the hydrogen bonds shown as dashed lines.

Experimental

The title compound was synthesized by the hydrothermal method from a mixture of zinc nitrate hexahydrate (0.06 g, 0.2 mmol), pyrazole-3,5-dicarboxylic acid (0.08 g, 0.4 mmol), 1,1′-carbonyldiimidazole (0.03 g, 0.2 mmol) and water (8.0 ml) in a 15.0 ml Teflon-lined stainless steel reactor. The solution was heated at 423 K for two days. After reaction, the vessel was slowly cooled to room temperature to give colorless crystals. Prismatic crystals were collected, washed with distilled water and dried in air. As shown by the present crystal structure analysis, the 1,1′-carbonyldiimidazole had decomposed into two imidazoles, and a proton had been added to an imidazole, so forming an imidazolium cation to balance the charges.

Crystal data

$(C_3H_5N_2)_2[Zn_2(C_5HN_2O_4)_2(H_2O)_4]$	$Z = 1$
$M_r = 647.18$	$D_x = 1.892$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 7.3068$ (6) Å	Cell parameters from 328 reflections
$b = 9.2879$ (7) Å	$\theta = 2.3$–25.1°
$c = 9.7233$ (8) Å	$\mu = 2.19$ mm^{-1}
$\alpha = 94.621$ (1)°	$T = 298$ (2) K
$\beta = 110.496$ (1)°	Prism, colorless
$\gamma = 109.477$ (1)°	0.34 × 0.20 × 0.10 mm
$V = 568.00$ (8) Å^3	

Data collection

Bruker APEX area-detector diffractometer	2000 independent reflections
φ and ω scans	1945 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	$R_{int} = 0.012$
$T_{min} = 0.60$, $T_{max} = 0.80$	$\theta_{max} = 25.1^\circ$
3010 measured reflections	$h = -5 \rightarrow 8$
	$k = -11 \rightarrow 11$
	$l = -11 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.6561P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.071$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.36$ e Å^{-3}
2000 reflections	
174 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O5—Zn1	2.031 (2)	Zn1—N1	2.050 (2)
O6—Zn1	2.0528 (18)	Zn1—O2	2.3303 (18)
Zn1—N2^{i}	2.040 (2)	Zn1—O4^{i}	2.417 (2)
O5—Zn1—N2^{i}	100.92 (9)	O6—Zn1—O2	81.77 (7)
O5—Zn1—N1	98.09 (9)	O5—Zn1—O4^{i}	82.47 (8)
N2^{i}—Zn1—N1	98.40 (8)	N2^{i}—Zn1—O4^{i}	72.32 (7)
O5—Zn1—O6	152.74 (10)	N1—Zn1—O4^{i}	170.59 (7)
N2^{i}—Zn1—O6	98.75 (8)	O6—Zn1—O4^{i}	85.75 (7)
N1—Zn1—O6	97.50 (8)	O2—Zn1—O4^{i}	115.24 (6)
O5—Zn1—O2	81.20 (8)	N2—N1—Zn1	131.92 (15)
N2^{i}—Zn1—O2	172.42 (7)	N1—N2—Zn1^{i}	129.68 (15)
N1—Zn1—O2	74.05 (7)		

Symmetry code: (i) $-x+2, -y+1, -z+1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O3^{ii}	0.82	1.98	2.685 (3)	145
O5—H5B···O3^{iii}	0.82	1.95	2.706 (3)	153
O6—H6A···O1^{iv}	0.82	1.94	2.734 (3)	162
O6—H6B···O1^{v}	0.82	1.89	2.676 (2)	159
N4—H4···O2^{vi}	0.86	1.91	2.721 (3)	157
N3—H3B···O4^{ii}	0.86	1.89	2.709 (3)	159

Symmetry codes: (ii) $x, y-1, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $x+1, y, z$; (v) $-x+2, -y+1, -z+2$; (vi) $x, y, z-1$.

All H atoms were positioned geometrically and allowed to ride on their parent atoms with distances of O—H = 0.82 Å, C—H = 0.93 Å and N—H = 0.86 Å, with U_{iso}(H) = 1.2U_{eq}(parent C or N atom) and 1.5U_{eq}(O).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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