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Key indicators

Single-crystal X-ray study  
T = 298 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
R factor = 0.034  
wR factor = 0.083  
Data-to-parameter ratio = 11.0

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

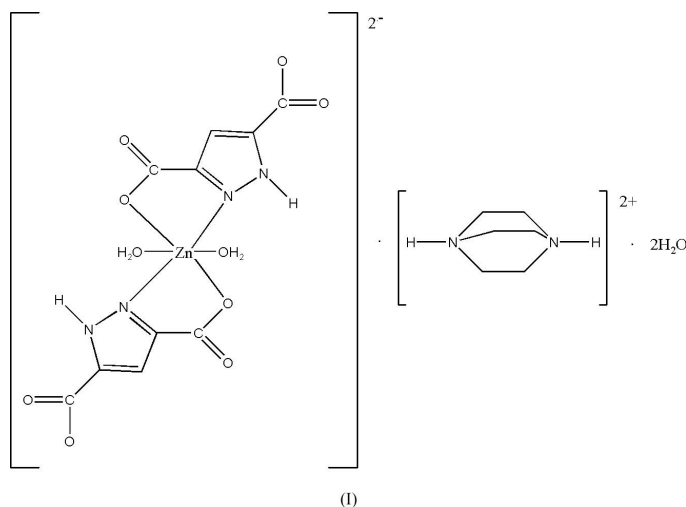
1,4-Diazoniabicyclo[2.2.2]octane diaqua-  
bis(pyrazole-3,5-dicarboxylato)zincate(II)  
dihydrate

The title compound,  $(\text{C}_6\text{H}_{14}\text{N}_2)[\text{Zn}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , consists of diaquabis(pyrazole-3,5-dicarboxylato)zincate(II) dianions, 1,4-diazoniabicyclo[2,2,2]octane dication and water molecules of crystallization, linked by  $\text{O}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds into a three-dimensional network. The geometry around the  $\text{Zn}^{2+}$  centre is octahedral.

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Comment

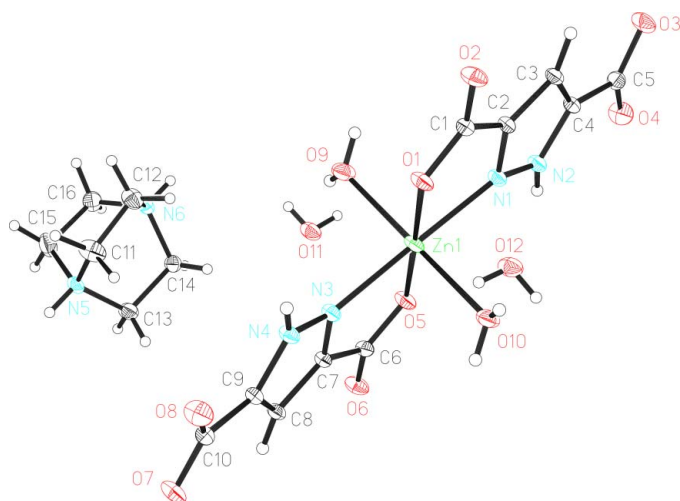
In the synthesis of crystal structures by design, the assembly of molecular units in predefined arrangements is a key goal (Desiraju, 1995, 1997; Braga *et al.*, 1998). Directional intermolecular interactions are the primary tools in achieving this goal and hydrogen bonding is currently the best among them (Zaworotko, 1997; Braga & Grepioni, 2000). In this paper, we report the structure of the title compound, (I).



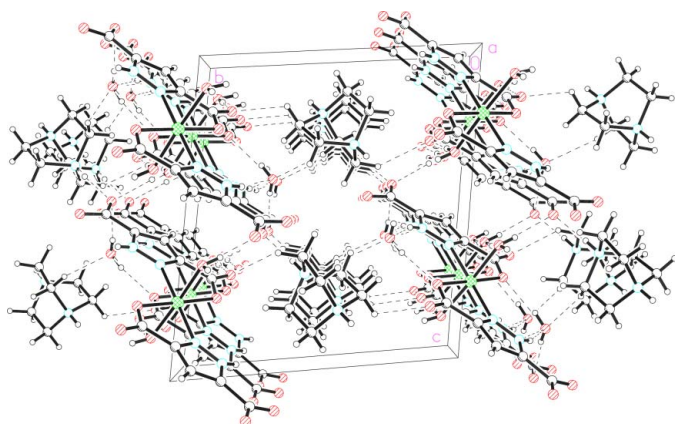
The asymmetric unit of (I) consists of a 1,4-diazoniabicyclo[2,2,2]octane dication, a diaquabis(pyrazole-3,5-dicarboxylato)zincate(II) dianion and two water molecules. The  $\text{Zn}^{2+}$  centre is six-coordinate and the geometry around it is octahedral, with bonds to two water molecules and two pyrazole-3,5-dicarboxylate anions; the pyrazole-3,5-dicarboxylate anions act in a chelating mode (Fig. 1 and Table 1). The anions, the cations and water molecules are linked by  $\text{O}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds into a three-dimensional network (Fig. 2 and Table 2).

Experimental

Zinc nitrate hexahydrate (0.06 g, 0.2 mmol) was dissolved in water (10 ml) and the solution was mixed with a dimethylformamide solu-



**Figure 1**  
The asymmetric unit of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.



**Figure 2**  
Perspective view of the three-dimensional network of (I), assembled via molecular interactions, which are shown as dashed lines.

tion (10 ml) of pyrazole-3,5-dicarboxylic acid (0.07 g, 0.4 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.05 g, 0.4 mmol). The reaction mixture was filtered and allowed to stand. Colourless prism-shaped crystals of (I) separated from the solution after about three months.

#### Crystal data

$(C_6H_{14}N_2)[Zn(C_5H_2N_2O_4)_2 \cdot (H_2O)_2] \cdot 2H_2O$

$M_r = 559.80$

Triclinic,  $P\bar{1}$

$a = 7.1123$  (7) Å

$b = 12.1068$  (12) Å

$c = 13.3174$  (13) Å

$\alpha = 80.602$  (2)°

$\beta = 84.430$  (2)°

$\gamma = 77.227$  (2)°

$V = 1101.12$  (19) Å<sup>3</sup>

$Z = 2$

$D_x = 1.688$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

Cell parameters from 3859

reflections

$\theta = 1.6$ – $25.1$ °

$\mu = 1.19$  mm<sup>-1</sup>

$T = 298$  (2) K

Prism, colourless

$0.39 \times 0.25 \times 0.09$  mm

#### Data collection

Bruker SMART APEX area-detector diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2002)

$T_{\min} = 0.71$ ,  $T_{\max} = 0.90$

5854 measured reflections

3859 independent reflections

3619 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\text{max}} = 25.1$ °

$h = -8 \rightarrow 8$

$k = -12 \rightarrow 14$

$l = -12 \rightarrow 15$

#### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.084$

$S = 1.09$

3859 reflections

352 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 0.6135P]$

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

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

$\Delta\rho_{\text{max}} = 0.28$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.38$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Zn1—O1	2.0750 (15)	Zn1—N1	2.1135 (17)
Zn1—O5	2.0839 (15)	Zn1—O9	2.1405 (17)
Zn1—N3	2.1026 (17)	Zn1—O10	2.1556 (17)
O1—Zn1—O5	178.94 (6)	N3—Zn1—O9	90.78 (7)
O1—Zn1—N3	101.64 (6)	N1—Zn1—O9	90.21 (7)
O5—Zn1—N3	78.03 (6)	O1—Zn1—O10	87.74 (6)
O1—Zn1—N1	78.39 (6)	O5—Zn1—O10	93.25 (7)
O5—Zn1—N1	101.96 (6)	N3—Zn1—O10	88.66 (7)
N3—Zn1—N1	179.01 (7)	N1—Zn1—O10	90.35 (7)
O1—Zn1—O9	89.28 (7)	O9—Zn1—O10	176.80 (6)
O5—Zn1—O9	89.71 (7)		

**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>
O12—H12D...O5	0.81 (2)	1.99 (2)	2.761 (2)	161 (3)
O11—H11D...O1 <sup>i</sup>	0.82 (2)	1.93 (2)	2.720 (2)	162 (3)
O11—H11C...O7 <sup>ii</sup>	0.80 (2)	2.14 (2)	2.935 (3)	173 (3)
N6—H6N...O7 <sup>ii</sup>	0.86 (3)	1.78 (3)	2.620 (2)	165 (3)
N5—H5N...O3 <sup>iii</sup>	0.87 (3)	1.74 (3)	2.599 (2)	167 (3)
N4—H4N...O11 <sup>iv</sup>	0.81 (3)	2.02 (3)	2.800 (3)	160 (2)
N2—H2N...O12	0.81 (3)	2.05 (3)	2.810 (3)	158 (3)
O10—H10D...O3 <sup>v</sup>	0.79 (2)	2.11 (2)	2.898 (2)	174 (3)
O10—H10C...O2 <sup>vi</sup>	0.81 (2)	1.88 (2)	2.686 (2)	177 (3)
O9—H9D...O6 <sup>vii</sup>	0.80 (2)	1.90 (2)	2.708 (2)	180 (3)
O9—H9C...O7 <sup>viii</sup>	0.81 (2)	1.96 (2)	2.765 (2)	172 (3)

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

Water and amine H atoms were located in a difference Fourier map and refined isotropically, with O—H distance restraints of 0.82 (3) Å. The N—H distances are in the range 0.81 (3)–0.87 (3) Å. All other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.97 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$ .

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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