

Diaquabis[5-(pyrazin-2-yl- κN^1)-1H-tetrazolato- κN^1]manganese(II) and diaquabis[5-(pyrazin-2-yl- κN^1)-1H-tetrazolato- κN^1]zinc(II)

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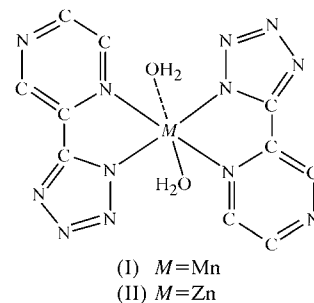
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The two new title complexes, $[\text{Mn}(\text{C}_5\text{H}_3\text{N}_6)_2(\text{H}_2\text{O})_2]$ and $[\text{Zn}(\text{C}_5\text{H}_3\text{N}_6)_2(\text{H}_2\text{O})_2]$, are isomorphous. In both compounds, the metal atom is located on an inversion center and is coordinated by four N atoms from two 5-(pyrazin-2-yl)-1H-tetrazolate anions in the basal plane and by two O atoms of water ligands in the apical positions to form a distorted octahedral geometry. Intermolecular hydrogen-bond interactions between the uncoordinated N atoms of the tetrazolate anions and the H atoms of the water molecules lead to the formation of a three-dimensional network.

Comment

Tetrazoles have attracted considerable interest because of their popular functionality and variety of applications (Butler, 1996). It is well known that tetrazoles have been used in many fields, including pharmaceuticals (Singh *et al.*, 1980), speciality explosives (Ostrovskii *et al.*, 1999), photography and information recording systems (Koldobskii & Ostrovskii, 1994), and as precursors to nitrogen-containing heterocycles (Huisgen *et al.*, 1960). Simple heating of an azide salt with a nitrile in an aqueous solution could produce the corresponding tetrazolate (Dimroth & Fester, 1910). In contrast to the previous synthetic methods, the tetrazoles are easily prepared in high yield by addition of sodium azide to a nitrile in water, with the catalysis of Lewis acids such as zinc salts (Demko & Sharpless, 2001). Although the synthetic method has been improved, the role of Lewis acids in the synthesis reaction and the exact intermediates are rarely known (Lin *et al.*, 2005; Wu *et al.*, 2005; Yu *et al.*, 2004). In order to better understand the influence of Lewis acids on the tetrazole synthesis reaction and to obtain a deeper insight into the intermediates, we report here the syntheses and structures of two isomorphous complexes, *viz.* $[\text{Mn}(5\text{-PYZTZ})_2(\text{H}_2\text{O})_2]$,

(I), and $[\text{Zn}(5\text{-PYZTZ})_2(\text{H}_2\text{O})_2]$, (II) [5-PYZTZ is 5-(pyrazin-2-yl)-1H-tetrazolate].



In (I), the Mn^{II} ion, located on an inversion center, is coordinated to two 5-PYZTZ anions and two aqua ligands to give a distorted octahedral geometry, in which the basal plane is formed by two pyrazine N atoms and two tetrazolate N atoms [atoms N1, N6, N1ⁱ and N6ⁱ; symmetry code: (i) $-x, -y, -z + 2$] of two 5-PYZTZ anions (Fig. 1). The apical positions are occupied by two O atoms (O1 and O1ⁱ) from two water molecules. Intermolecular hydrogen-bonding interactions between the uncoordinated N atoms of the tetrazolate anions and the H atoms of the water molecules result in the formation of a three-dimensional network (Fig. 2 and Table 2).

In (II), the Zn^{II} atom has the same coordination environment as the Mn atom in (I). The three-dimensional structure is also formed by intermolecular hydrogen bonds involving uncoordinated N atoms of the tetrazolate anions and the H atoms of the water molecules (Table 4).

In (I) and (II), the Mn–N and Zn–N distances (Tables 1 and 3) are comparable to the corresponding distances in related manganese (Lin *et al.*, 2005) and zinc complexes (Wang *et al.*, 2005; Zhang *et al.*, 2005), and the Mn–O and Zn–O distances are similar to the corresponding distances in water-coordinated manganese (Mautner *et al.*, 2004) and zinc complexes (Zhang *et al.*, 2005), respectively.

In (I), the N–Mn–N angles (two neighbouring atoms) are 75.15 (7) and 104.85 (7)°. The corresponding N–Zn–N angles are 78.34 (7) and 101.66 (7)°, indicating that the geometry in (I) is more distorted than that of (II).

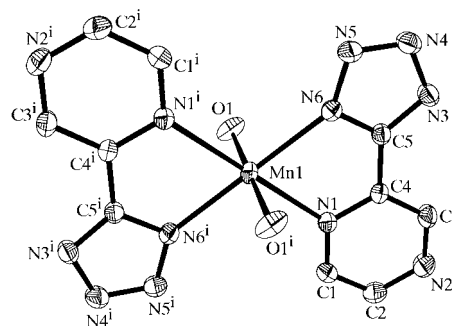
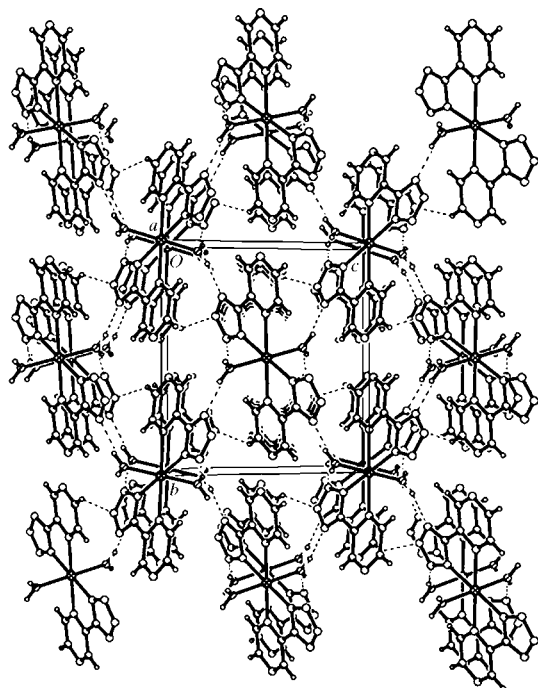


Figure 1

A view of the molecule of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity [symmetry code: (i) $-x, -y, -z + 2$]. Complex (II) is isomorphous.

**Figure 2**

The three-dimensional network in (I), formed *via* intermolecular hydrogen-bonding interactions, viewed along the *a* axis.

In both complexes, the bond distances and angles of the tetrazole ring [1.303 (3)–1.338 (3) Å and 104.6 (2)–111.6 (2)°] and the pyrazine ring [1.325 (3)–1.386 (3) Å and 116.1 (2)–122.5 (2)°] are in the normal ranges observed in pyrazine- or tetrazole-containing complexes (Mautner *et al.*, 2004; Ferigo *et al.*, 1994).

Experimental

An ethanol solution (4 ml) of pyrazine-2-carbonitrile (0.20 mmol, 21.02 mg) and an aqueous solution (4 ml) of manganese acetate (0.20 mmol, 49.02 mg) were mixed and stirred for 5 min, and an aqueous solution (2 ml) of sodium azide (0.20 mmol, 13.01 mg) was added to the mixture. After being stirred for another 5 min, the solution was filtered and the filtrate was evaporated slowly in air. After one week, colorless block-shaped crystals of (I) were isolated in 55% yield. Analysis calculated for $C_{10}H_{10}MnN_{12}O_2$: C 31.18, H 2.62, N 43.63%; found C 30.89, H 2.71, N 43.76%. Complex (II) was prepared by a similar procedure in 47% yield. Analysis calculated for $C_{10}H_{10}N_{12}O_2Zn$: C 30.36, H 2.55, N 42.48%; found C 30.09, H 2.41, N 42.65%.

Compound (I)

Crystal data

$[Mn(C_5H_3N_6)_2(H_2O)_2]$	$Z = 2$
$M_r = 385.24$	$D_x = 1.745 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.9642$ (19) Å	$\mu = 0.94 \text{ mm}^{-1}$
$b = 11.715$ (4) Å	$T = 293$ (2) K
$c = 10.853$ (4) Å	Block, colorless
$\beta = 104.817$ (4)°	$0.40 \times 0.30 \times 0.25 \text{ mm}$
$V = 733.1$ (4) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	3288 measured reflections
φ and ω scans	1455 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	1235 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.705$, $T_{\max} = 0.799$	$R_{\text{int}} = 0.042$
	$\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.089P)^2]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\max} < 0.001$
1455 reflections	$\Delta\rho_{\max} = 0.62 \text{ e Å}^{-3}$
123 parameters	$\Delta\rho_{\min} = -0.62 \text{ e Å}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I).

Mn1–N1	2.313 (2)	Mn1–O1	2.138 (2)
Mn1–N6	2.217 (2)		
N6–Mn1–N1	75.15 (7)	O1–Mn1–N6	88.56 (8)
N6–Mn1–N1 ⁱ	104.85 (7)	O1–Mn1–N1 ⁱ	88.77 (7)
O1–Mn1–N1	91.23 (7)	O1–Mn1–N6 ⁱ	91.44 (8)

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

Table 2

Hydrogen-bond and short-contact geometry (Å, °) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1–H1B \cdots N4 ⁱⁱ	0.84 (1)	2.66 (2)	3.378 (3)	145 (2)
O1–H1B \cdots N3 ⁱⁱ	0.84 (1)	1.91 (1)	2.733 (3)	168 (3)
O1–H1A \cdots N4 ⁱⁱⁱ	0.84 (3)	2.70 (2)	3.408 (3)	144 (3)
O1–H1A \cdots N5 ⁱⁱⁱ	0.84 (3)	1.98 (1)	2.788 (3)	162 (3)

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

Compound (II)

Crystal data

$[Zn(C_5H_3N_6)_2(H_2O)_2]$	$Z = 2$
$M_r = 395.67$	$D_x = 1.830 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.0906$ (18) Å	$\mu = 1.75 \text{ mm}^{-1}$
$b = 11.456$ (3) Å	$T = 293$ (2) K
$c = 10.686$ (3) Å	Block, colorless
$\beta = 105.634$ (4)°	$0.40 \times 0.30 \times 0.25 \text{ mm}$
$V = 718.0$ (3) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	3206 measured reflections
φ and ω scans	1406 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	1161 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.541$, $T_{\max} = 0.669$	$R_{\text{int}} = 0.034$
	$\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.027$	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
$wR(F^2) = 0.071$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{\max} < 0.001$
1406 reflections	$\Delta\rho_{\max} = 0.43 \text{ e Å}^{-3}$
123 parameters	$\Delta\rho_{\min} = -0.37 \text{ e Å}^{-3}$

Table 3

Selected geometric parameters (Å, °) for (II).

Zn1—N1	2.194 (2)	Zn1—O1	2.099 (2)
Zn1—N6	2.115 (2)		
N6—Zn1—N1	78.34 (7)	O1—Zn1—N6	87.63 (8)
N6—Zn1—N1 ⁱ	101.66 (7)	O1—Zn1—N1 ⁱ	90.10 (7)
O1—Zn1—N1	89.90 (7)	O1—Zn1—N6 ⁱ	92.37 (8)

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

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1B \cdots N4 ⁱⁱ	0.84 (1)	2.70 (2)	3.460 (3)	153 (2)
O1—H1B \cdots N3 ⁱⁱ	0.84 (1)	1.92 (1)	2.753 (3)	173 (2)
O1—H1A \cdots N4 ⁱⁱⁱ	0.83 (1)	2.66 (2)	3.331 (3)	140 (2)
O1—H1A \cdots N5 ⁱⁱⁱ	0.83 (1)	2.03 (1)	2.834 (3)	164 (2)

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

In both complexes, the position of the water H atom was found from a difference Fourier map and refined freely along with an isotropic displacement parameter; all other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with $C-H = 0.93$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3026). Services for accessing these data are described at the back of the journal.

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