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Hexaaquamanganese(II) bis[5-(4-cyanophenyl)-2*H*-tetrazolate]

Zhijie Ma,[a] Jun Tao,[a] Rong-Bin Huang[a]* and Lan-Sun Zhang[b]

[a]Department of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China, and [b]State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

Correspondence e-mail: rbhuang@xmu.edu.cn

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The reaction of terephthalonitrile and sodium azide catalyzed by manganese chloride tetrahydrate converts one nitrile group to tetrazole and leaves the other nitrile group unchanged. The Mn^{II} atom in the title compound, $[Mn(H_2O)_6](C_8H_4N_5)_2$, is coordinated by six water molecules and lies on a position of 2/*m* crystallographic symmetry. The plane of the tetrazolate anion is perpendicular to a crystallographic mirror plane.

Key indicators

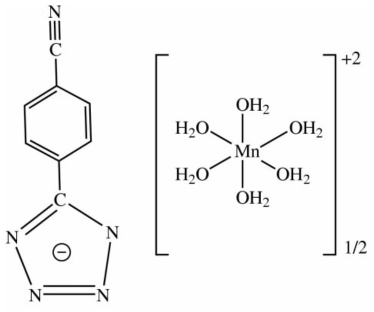
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.043
wR factor = 0.110
Data-to-parameter ratio = 11.5

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

Comment

Tetrazoles are a class of heterocycles with a wide range of applications, receiving considerable attention. Tetrazole derivatives have shown valuable properties as precursors of a variety of nitrogen-containing heterocycles (Huisgen *et al.*, 1960) and have found use in various fields (Ostrovskii *et al.*, 1999). 5-Substituted 1*H*-tetrazoles are usually obtained by the addition of azide ion to organic nitriles, and many methods are reported in the literature (Duncia *et al.*, 1991; Curran *et al.*, 1999). Unfortunately, each of those procedures suffers from some disadvantages.

Recently, Sharpless and co-workers have reported an innovative and safe procedure for the preparation of 5-substituted 1*H*-tetrazoles, starting from the corresponding nitriles, using NaN_3 and stoichiometric amounts of zinc(II) salts in water (Demko & Sharpless, 2001; Himo *et al.*, 2003). The preparation of metal–organic coordination polymers from hydrothermal reactions involving *in situ* tetrazole ligand synthesis has been carried out by Xiong *et al.* (2002). We report here the preparation and structure determination of a manganese tetrazolate involving the *in situ* synthesis of tetrazole.



(I)

The reaction converts only one nitrile group to tetrazole, leaving the other nitrile group unchanged. The X-ray analysis shows that the title compound, (I), contains two independent components, a hydrated Mn^{II} cation and a tetrazolate anion (Fig. 1). The Mn^{II} ion is octahedrally coordinated by six water molecules and lies on a position of 2/*m* crystallographic symmetry. The plane of the tetrazolate anion is perpendicular to a crystallographic mirror plane. The tetrazolate anions and counter-cations are linked by hydrogen bonds between tetrazolate N atoms and water molecules.

The cyano N atom shows positional disorder and was refined split into two positions with equal occupancy. The occupancy of both positions was fixed at 0.25.

Experimental

Manganese chloride tetrahydrate (0.049 g, 0.25 mmol), terephthalonitrile (0.032 g, 0.25 mmol) and sodium azide (0.024 g, 0.375 mmol) were added to water (5 ml) and stirred for several minutes. The solution was transferred into a Teflon-lined stainless steel autoclave and heated to 423 K, maintained at that temperature for 24 h and then cooled to room temperature. Colorless prism-shaped crystals suitable for X-ray diffraction were collected.

Crystal data

$[Mn(H_2O)_6](C_8H_4N_5)_2$
$M_r = 503.36$
Monoclinic, $C2/m$
$a = 13.5565\ (9)$ Å
$b = 10.2568\ (7)$ Å
$c = 8.1885\ (5)$ Å
$\beta = 99.5240\ (10)°$
$V = 1122.89\ (13)$ Å^3
$Z = 2$

$D_x = 1.489$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3037 reflections
$\theta = 2.5–28.1°$
$\mu = 0.64$ mm^{-1}
$T = 296\ (2)$ K
Prism, colorless
$0.40 \times 0.36 \times 0.20$ mm

Data collection

Bruker SMART APEX 2000 diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.783$, $T_{max} = 0.882$
4708 measured reflections

1284 independent reflections
1262 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.0°$
$h = -17 \rightarrow 16$
$k = -13 \rightarrow 13$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.110$
$S = 1.15$
1284 reflections
112 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.8233P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.1288 (17)	C4—C5	1.464 (3)
Mn1—O2	2.184 (3)	C5—N2	1.322 (2)
C1—C2	1.367 (4)	C6—N1	1.17 (5)
C1—C6	1.435 (4)	C6—N1′	1.18 (5)
C2—C3	1.381 (3)	N2—N3	1.336 (2)
C3—C4	1.379 (3)		
O1—Mn1—O2	88.62 (10)	N2—C5—C4	124.37 (11)
C2—C1—C6	119.69 (15)	N1—C6—C1	163 (6)
C1—C2—C3	119.7 (3)	C5—N2—N3	105.20 (17)
C4—C3—C2	120.5 (3)	N3^{iii}—N3—N2	109.18 (11)
C3—C4—C5	120.49 (14)		

Symmetry code: (iii) $x, -y, z$.

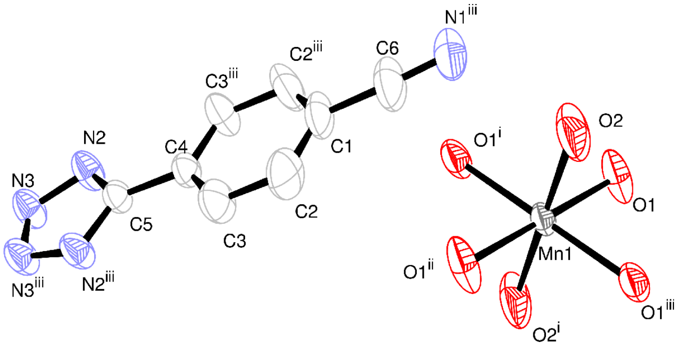


Figure 1
*ORTEP*II plot (Johnson, 1976) of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, y, -z$; (iii) $x, -y, z$.]

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2$W2$···N1	0.66 (7)	2.11 (8)	2.76 (4)	171 (4)
O1—H1$W1$···N2^{iv}	0.72 (3)	2.03 (3)	2.743 (3)	168 (3)
O1—H1$W2$···N3^{v}	0.70 (3)	2.14 (3)	2.813 (2)	164 (4)

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

Water H atoms were located in a difference Fourier map and were refined freely with isotropic displacement parameters. The benzene H atoms were constrained to an ideal geometry, with C—H distances of 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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