Crystal structure of bis(2,3,5,6-tetra-2-pyridylpyrazine)-manganese(II) bis(triiodide), $[Mn(C_{24}H_{16}N_6)_2](I_3)_2$

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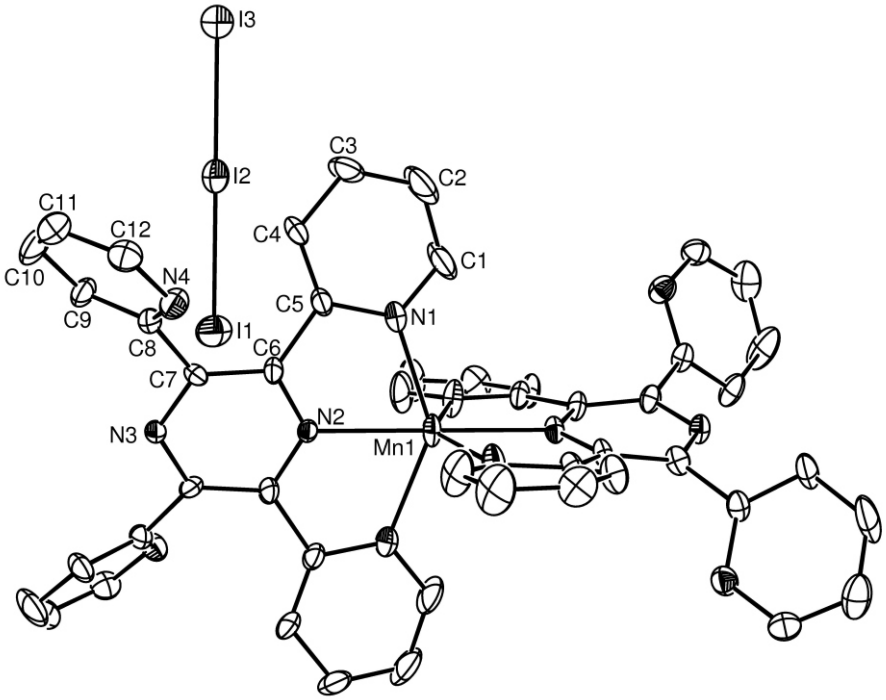

Abstract

$C_{48}H_{32}I_6MnN_{12}$, tetragonal, $I\bar{4}2d$ (no. 122), a = 13.6758(7) Å, c = 29.220(3) Å, V = 5464.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.067, $wR_{ref}(F^2)$ = 0.198, T = 200 K.

Source of material

To a solution of MnI_2 (0.3097 g, 1.003 mmol) in EtOH (30 ml) was added 2,3,5,6-tetra-2-pyridylpyrazine (tppz; 0.3898 g, 1.004 mmol) and stirred for 3 h at room temperature. The formed precipitate was separated by filtration, washed with EtOH and dried at 50 °C, to give a brown powder (0.4324 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from an acetone solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(C). The highest peak (1.70 e Å^{-3}) and the deepest hole (–1.27 e Å^{-3}) in the difference Fourier map are located 1.07 Å and 0.93 Å from the I3 atom, respectively. The Flack parameter is 0.0(2) in the final cycles of refinement. However, the parameter is meaningless, because the crystal structure was refined using TWIN and BASF instructions [1].

Discussion

The asymmetric unit of the title crystal structure consists of a quarter of a cationic Mn(II) complex $[Mn(tppz)_2]^{2+}$ and one half of an I_3^- anion. In the crystal, the complex has point group S_4. In the complex, the Mn(II) ion is located on a four-fold inversion axis and is six-coordinated in a considerably distorted octahedral manner by six N atoms from two symmetry-related tridentate tppz ligands. The main contribution to the distortion is the tight N–Mn–N chelating angle (∠N1–Mn1–N2 = 70.6(2)°), which results in non-linear *trans* arrangement of the N1–Mn1–N1^i bond (∠N1–Mn1–N1^i = 141.1(4)°; symmetry code i: $-x,1-y,z$), whereas the symmetry-related N2–Mn1–N2^{ii} (symmetry code ii: $-½+y,½-x,½-z$) bond is linear. The Mn—N distances are almost equivalent (d(Mn—$N_{pyrazine}$) = 2.242(9) Å; d(Mn—$N_{pyridyl}$) = 2.261(8) Å). The I_3^- anion is linear and disposed about a two-fold rotational molecular axis. One anion lies in the [100] direction and the other is along [010]. The two I—I distances are somewhat different with d(I1—I2) = 2.937(2) Å and d(I2—I3) = 2.876(2) Å. These distances are comparable to those observed in the complex $[Mn(phen)_3](I_3)_2$ (2.9116(6) Å and 2.828(1) Å; where phen is 1,10-phenanthroline) [2]. In the title crystal structure, the pyrazine ring is fairly distorted; the maximum deviation is 0.074(7) Å for C7 atom from the least-squares plane of the ring. The dihedral angles between the nearly planar pyridyl rings and

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the least-squares plane of their carrier pyrazine rings are 17.7(2)° for the coordinated pyridyl ring and 54.0(4)° for the uncoordinated pyridyl ring, respectively. The complex displays numerous inter- and intramolecular π–π interactions between adjacent six-membered rings. The shortest distance between Cg1 (the centroid of ring N1-C5) and Cg2^{iii} (ring N4-C12, symmetry code iii: 1–*y*,½–*x*,¼+*z*) is 4.462(7) Å, and the dihedral angle between the ring planes is 39.0(6)°. In addition, the complexes and triiodide anions are linked by intermolecular C–H···I hydrogen bonds with *d*(C1–H1···I1) = 3.77(1) Å and ∠C1–H1···I1 = 145.9°.

Table 1. Data collection and handling.

Crystal:	redbrown block, size 0.17 × 0.29 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	36.75 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20286, 3357
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2181
$N(param)_{refined}$:	155
Programs:	SHELXS-97, SHELXL-97 [1] ORTEP-3 [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	16*e*	0.2133	0.5128	0.2844	0.107
H(2)	16*e*	0.3767	0.5252	0.2601	0.121
H(3)	16*e*	0.4090	0.5077	0.1818	0.082
H(4)	16*e*	0.2752	0.5063	0.1312	0.069
H(9)	16*e*	0.1636	0.4597	0.0290	0.069
H(10)	16*e*	0.2718	0.5439	–0.0210	0.117
H(11)	16*e*	0.3218	0.7019	–0.0052	0.098
H(12)	16*e*	0.2753	0.7760	0.0620	0.068

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	4*a*	0	½	¼	0.071(1)	U_{11}	0.020(1)	0	0	0
N(1)	16*e*	0.1535(7)	0.5186(8)	0.2245(3)	0.059(5)	0.102(7)	0.029(3)	0.005(5)	–0.007(4)	–0.008(4)
N(2)	8*c*	0	½	0.1726(3)	0.039(5)	0.042(5)	0.024(4)	0.019(4)	0	0
N(3)	8*c*	0	½	0.0795(3)	0.029(5)	0.061(6)	0.028(4)	–0.006(4)	0	0
N(4)	16*e*	0.1879(6)	0.6666(6)	0.0844(3)	0.053(5)	0.058(5)	0.049(4)	–0.008(4)	0.009(4)	–0.009(3)
C(1)	16*e*	0.2267(9)	0.516(1)	0.2525(4)	0.077(9)	0.14(1)	0.048(6)	–0.035(8)	–0.034(6)	0.014(7)
C(2)	16*e*	0.325(1)	0.519(1)	0.2385(5)	0.09(1)	0.15(1)	0.068(8)	–0.002(9)	–0.048(8)	0.019(8)
C(3)	16*e*	0.3439(8)	0.5122(9)	0.1930(4)	0.040(5)	0.086(8)	0.079(8)	0.012(5)	–0.018(5)	0.013(6)
C(4)	16*e*	0.2642(7)	0.5120(8)	0.1632(3)	0.051(6)	0.086(7)	0.036(4)	0.011(5)	–0.020(4)	–0.006(4)
C(5)	16*e*	0.1727(7)	0.5199(7)	0.1789(3)	0.050(5)	0.055(5)	0.029(4)	0.009(4)	–0.010(4)	–0.005(4)
C(6)	16*e*	0.0829(7)	0.5186(7)	0.1502(3)	0.048(5)	0.057(5)	0.024(3)	0.009(4)	–0.002(3)	–0.009(3)
C(7)	16*e*	0.0791(6)	0.5287(7)	0.1026(3)	0.030(4)	0.054(5)	0.035(4)	0.005(3)	–0.009(3)	–0.005(3)
C(8)	16*e*	0.1548(6)	0.5752(7)	0.0733(3)	0.036(4)	0.062(6)	0.033(4)	–0.005(4)	0.000(3)	–0.008(4)
C(9)	16*e*	0.1849(7)	0.5245(9)	0.0352(3)	0.047(5)	0.086(7)	0.040(4)	–0.015(5)	0.013(4)	–0.025(5)
C(10)	16*e*	0.249(1)	0.575(1)	0.0060(4)	0.081(8)	0.15(1)	0.060(7)	–0.02(1)	0.033(7)	–0.052(8)
C(11)	16*e*	0.2803(9)	0.668(1)	0.0156(4)	0.055(7)	0.13(1)	0.060(7)	–0.010(7)	0.014(5)	0.006(7)
C(12)	16*e*	0.2514(8)	0.7126(7)	0.0548(4)	0.053(5)	0.052(5)	0.065(6)	–0.009(5)	–0.001(5)	0.001(4)
I(1)	8*d*	0.09920(9)	¼	⅛	0.0705(7)	0.0820(8)	0.1019(9)	0	0	–0.0442(7)
I(2)	8*d*	0.31395(8)	¼	⅛	0.0791(7)	0.1155(9)	0.0539(6)	0	0	–0.0268(6)
I(3)	8*d*	0.5242(1)	¼	⅛	0.0736(9)	0.422(5)	0.0763(9)	0	0	–0.034(2)

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