Crystal structure of bis(2,4,6-tri-2-pyridyl-1,3,5-triazine)-manganese(II) bis(triiodide), $[Mn(C_{18}H_{12}N_6)_2](I_3)_2$

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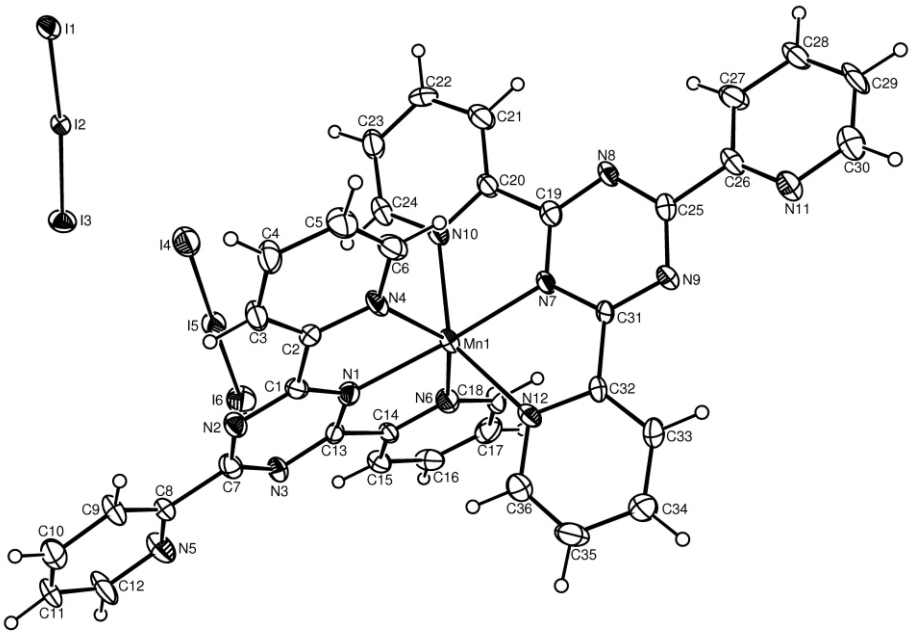

Abstract

$C_{36}H_{24}I_6MnN_{12}$, monoclinic, $P12_1/c1$ (no. 14), a = 10.929(2) Å, b = 15.328(2) Å, c = 25.553(4) Å, β = 92.541(4)°, V = 4276.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.047, $wR_{ref}(F^2)$ = 0.113, T = 200 K.

Source of material

To a solution of MnI_2 (0.3088 g, 1.000 mmol) in EtOH (30 ml) was added 2,4,6-tri-2-pyridyl-1,3,5-triazine (tptz, 0.3135 g, 1.004 mmol) and stirred for 3 h at room temperature. The formed precipitate was separated by filtration and washed with EtOH and dried at 50 °C, to give a red-brown powder (0.6093 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a 2-methoxyethanol 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 (1.14 e Å^{-3}) and the deepest hole (–1.45 e Å^{-3}) in the difference Fourier map are located 0.45 Å and 0.93 Å from the atoms I5 and I2, respectively.

Discussion

The title crystal structure consists of mononuclear cationic complexes $[Mn(tptz)_2]^{2+}$ and discrete I_3^- anions in 1:2 ratio. The structure is quite different from the previously reported Mn(II)-tptz complexes $[MnCl_2(tptz)]$ [1] and $[Mn(H_2O)Br_2(tptz)] \cdot H_2O$ [2], in which one tptz ligand and both halide ions as anionic ligands are coordinated to the Mn(II) ion, respectively.

In the title complex, the Mn(II) ion is six-coordinated in a considerably distorted octahedral manner by six N atoms from two tridentate tptz ligands. The main contribution to the distortion is the tight N–Mn–N chelating angles of ∠N1–Mn1–N4 = 71.3(2)°, ∠N1–Mn1–N6 = 72.1(2)°, ∠N7–Mn1–N10 = 71.9(2)° and ∠N7–Mn1–N12 = 71.2(2)°. The apical bond angles are ∠N1–Mn1–N7 = 172.5(2)°, ∠N4–Mn1–N6 = 142.9(2)°, and ∠N10–Mn1–N12 = 142.9(2)°. The Mn—$N_{triazine}$ bonds (2.160(6) Å and 2.149(6) Å) are slightly shorter than the Mn—$N_{pyridyl}$ bonds (2.301(7) Å, 2.280(6) Å, 2.285(6) Å and 2.268(6) Å). In the crystal structure, the six pyridyl rings are located approximately parallel to their respective carrier triazine rings, making dihedral angles of 10.3(4)°, 5.9(5)°, 8.8(4)°, 6.1(5)°, 14.4(4)° and 4.1(4)°. The triazine rings are nearly planar and the dihedral angle between the least-squares planes of the two rings is 84.1(2)°. There are two types of triiodide anions, which differ from each other in the I—I bond distances and the configuration. One of them, I1–I2–I3, is slightly bent with ∠I1–I2–I3 = 174.09(3)° and reveals almost equal I—I distances with d(I1—I2) = 2.9119(8) Å and d(I2—I3) = 2.9061(8) Å, whereas the other, I4–I5–I6, is approximately linear with ∠I4–I5–I6 = 178.96(3)° and shows somewhat different I—I distances with d(I4—I5) = 2.8813(9) Å and d(I5—I6) = 2.9678(9) Å. These I—I distances are comparable to those observed in the Mn complex $[Mn(phen)_3](I_3)_2$ (2.9116(6) Å and 2.828(1) Å; where phen is 1,10-phenanthroline) [3]. The complex

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displays numerous inter- and intramolecular π–π interactions between adjacent six-membered rings. The shortest distance between Cg1 (the centroid of ring N5-C12) and Cg2^{i} (ring N11-C30, symmetry code i: $1+x,\frac{3}{2}-y,\frac{1}{2}+z$) is 3.845(5) Å, and the dihedral angle between the ring planes is 12.0(4)°. In addition, there are intramolecular hydrogen bonds with d(C9–H9···N2) = 2.76(1) Å, ∠C9–H9···N2 = 101° and d(C27–H27···N8) = 2.73(1) Å, ∠C27–H27···N8 = 100°. The complex and one of the triiodide anions are linked by intermolecular C–H···I hydrogen bonds with d(C18–H18···I1) = 3.840(8) Å and ∠C18–H18···I1 = 142°.

Table 1. Data collection and handling.

Crystal:	red-brown block, size 0.08 × 0.08 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	46.83 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	31611, 10613
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4959
$N(param)_{refined}$:	496
Programs:	SHELXS-97, SHELXL-97 [4], ORTEP-3 [5], PLATON [6]

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

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.1764	0.8821	0.3711	0.050
H(4)	4*e*	–0.0151	0.9437	0.3858	0.058
H(5)	4*e*	–0.1665	0.9406	0.3165	0.062
H(6)	4*e*	–0.1309	0.8635	0.2411	0.054
H(9)	4*e*	0.4733	0.8276	0.3962	0.048
H(10)	4*e*	0.6517	0.8337	0.4517	0.058
H(11)	4*e*	0.8158	0.7435	0.4330	0.063
H(12)	4*e*	0.8006	0.6529	0.3626	0.078
H(15)	4*e*	0.4690	0.5517	0.2054	0.042
H(16)	4*e*	0.4427	0.4723	0.1277	0.055
H(17)	4*e*	0.2783	0.5064	0.0689	0.064
H(18)	4*e*	0.1416	0.6147	0.0910	0.049
H(21)	4*e*	–0.3521	0.6322	0.1866	0.068
H(22)	4*e*	–0.3307	0.5307	0.2542	0.074
H(23)	4*e*	–0.1362	0.5046	0.2929	0.060
H(24)	4*e*	0.0292	0.5846	0.2648	0.050
H(27)	4*e*	–0.4706	0.7059	0.0713	0.062
H(28)	4*e*	–0.6486	0.7236	0.0170	0.077
H(29)	4*e*	–0.6606	0.8428	–0.0395	0.068
H(30)	4*e*	–0.4991	0.9377	–0.0428	0.068
H(33)	4*e*	0.0047	0.9397	0.0254	0.052
H(34)	4*e*	0.1953	1.0105	0.0211	0.062
H(35)	4*e*	0.3501	0.9725	0.0854	0.066
H(36)	4*e*	0.3062	0.8769	0.1501	0.056

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*e*	0.0874(1)	0.74778(8)	0.18792(5)	0.0268(7)	0.0457(7)	0.0303(8)	–0.0004(6)	–0.0089(5)	0.0011(6)
N(1)	4*e*	0.2370(5)	0.7372(4)	0.2457(2)	0.035(4)	0.034(4)	0.027(4)	–0.001(3)	0.001(3)	–0.001(3)
N(2)	4*e*	0.3348(6)	0.7844(4)	0.3245(3)	0.028(4)	0.045(4)	0.032(4)	0.006(3)	–0.002(3)	–0.005(3)
N(3)	4*e*	0.4306(5)	0.6782(4)	0.2706(2)	0.035(4)	0.035(4)	0.029(4)	–0.004(3)	–0.008(3)	–0.007(3)
N(4)	4*e*	0.0412(5)	0.8295(4)	0.2600(3)	0.024(4)	0.041(4)	0.040(5)	0.005(3)	–0.012(3)	0.005(3)
N(5)	4*e*	0.6327(6)	0.6814(5)	0.3373(3)	0.037(5)	0.067(5)	0.064(6)	0.005(4)	–0.015(4)	–0.010(4)
N(6)	4*e*	0.2231(6)	0.6481(4)	0.1584(3)	0.038(4)	0.038(4)	0.039(5)	–0.003(3)	–0.004(3)	0.002(3)
N(7)	4*e*	–0.0714(5)	0.7707(4)	0.1372(2)	0.025(4)	0.036(4)	0.030(4)	–0.001(3)	–0.009(3)	0.006(3)
N(8)	4*e*	–0.2791(5)	0.7427(4)	0.1155(3)	0.025(4)	0.040(4)	0.033(4)	0.007(3)	–0.008(3)	–0.001(3)
N(9)	4*e*	–0.1674(5)	0.8444(4)	0.0652(2)	0.026(4)	0.035(4)	0.035(4)	0.000(3)	–0.008(3)	0.000(3)
N(10)	4*e*	–0.0607(5)	0.6506(4)	0.2094(3)	0.030(4)	0.041(4)	0.036(5)	0.006(3)	–0.008(3)	0.000(3)
N(11)	4*e*	–0.3894(6)	0.8813(4)	0.0111(3)	0.038(4)	0.045(5)	0.050(5)	0.000(3)	–0.014(4)	0.002(4)
N(12)	4*e*	0.1326(5)	0.8522(4)	0.1289(2)	0.022(4)	0.041(4)	0.037(4)	0.002(3)	–0.006(3)	–0.003(3)
C(1)	4*e*	0.2404(7)	0.7836(5)	0.2898(3)	0.025(4)	0.032(4)	0.034(5)	–0.001(3)	0.001(4)	0.004(4)
C(2)	4*e*	0.1289(7)	0.8329(5)	0.2992(3)	0.028(5)	0.038(5)	0.028(5)	–0.004(4)	0.000(4)	0.007(4)
C(3)	4*e*	0.1115(7)	0.8777(5)	0.3452(3)	0.038(5)	0.055(6)	0.032(5)	0.005(4)	–0.010(4)	–0.005(4)
C(4)	4*e*	0.0002(8)	0.9158(6)	0.3536(3)	0.043(6)	0.069(6)	0.033(6)	0.021(5)	–0.006(4)	–0.001(5)
C(5)	4*e*	–0.0901(8)	0.9122(6)	0.3129(4)	0.035(5)	0.069(6)	0.052(7)	0.020(5)	0.003(4)	–0.010(5)
C(6)	4*e*	–0.0677(7)	0.8676(5)	0.2677(4)	0.028(5)	0.051(6)	0.055(7)	0.002(4)	–0.002(4)	0.003(5)
C(7)	4*e*	0.4288(7)	0.7316(5)	0.3119(3)	0.038(5)	0.030(5)	0.040(6)	–0.008(4)	–0.008(4)	0.001(4)
C(8)	4*e*	0.5393(7)	0.7339(5)	0.3492(3)	0.025(5)	0.041(5)	0.032(5)	–0.001(4)	–0.006(4)	0.002(4)
C(9)	4*e*	0.5417(7)	0.7913(5)	0.3901(3)	0.034(5)	0.043(5)	0.043(6)	0.007(4)	–0.016(4)	–0.015(4)
C(10)	4*e*	0.6467(8)	0.7952(6)	0.4226(4)	0.047(6)	0.050(6)	0.048(6)	–0.002(5)	–0.013(5)	0.002(5)
C(11)	4*e*	0.7426(8)	0.7424(6)	0.4116(3)	0.037(6)	0.077(7)	0.042(6)	–0.010(5)	–0.022(4)	–0.001(5)
C(12)	4*e*	0.7321(8)	0.6885(7)	0.3696(4)	0.029(5)	0.103(8)	0.060(7)	0.013(5)	–0.022(5)	–0.029(6)
C(13)	4*e*	0.3320(7)	0.6837(5)	0.2387(3)	0.031(5)	0.028(4)	0.021(5)	–0.003(3)	0.000(3)	0.003(3)
C(14)	4*e*	0.3207(6)	0.6298(5)	0.1913(3)	0.021(4)	0.036(4)	0.024(5)	0.000(3)	–0.001(3)	–0.007(4)
C(15)	4*e*	0.4028(7)	0.5643(5)	0.1812(3)	0.029(5)	0.037(5)	0.039(6)	0.002(4)	0.000(4)	–0.006(4)
C(16)	4*e*	0.3871(8)	0.5176(5)	0.1356(4)	0.036(5)	0.046(5)	0.055(7)	–0.008(4)	0.012(5)	–0.013(5)
C(17)	4*e*	0.2896(9)	0.5372(6)	0.1010(4)	0.067(7)	0.058(6)	0.036(6)	–0.015(5)	0.013(5)	–0.009(5)
C(18)	4*e*	0.2094(8)	0.6022(5)	0.1143(3)	0.048(5)	0.049(5)	0.025(5)	–0.017(4)	–0.012(4)	–0.010(4)
C(19)	4*e*	–0.1774(7)	0.7290(5)	0.1444(3)	0.034(5)	0.034(5)	0.027(5)	0.006(4)	–0.002(4)	–0.009(4)
C(20)	4*e*	–0.1722(7)	0.6637(5)	0.1869(3)	0.028(5)	0.039(5)	0.036(5)	–0.005(4)	–0.009(4)	0.004(4)
C(21)	4*e*	–0.2739(8)	0.6208(6)	0.2029(4)	0.031(5)	0.074(7)	0.064(7)	–0.004(5)	–0.010(5)	0.025(6)
C(22)	4*e*	–0.2613(8)	0.5613(7)	0.2426(4)	0.033(6)	0.095(8)	0.057(7)	–0.021(5)	0.009(5)	0.025(6)
C(23)	4*e*	–0.1474(8)	0.5464(6)	0.2656(3)	0.051(6)	0.056(6)	0.040(6)	–0.001(5)	–0.013(5)	0.008(5)
C(24)	4*e*	–0.0494(7)	0.5935(5)	0.2483(3)	0.037(5)	0.048(5)	0.039(6)	0.006(4)	–0.015(4)	–0.005(5)
C(25)	4*e*	–0.2702(7)	0.8015(5)	0.0766(3)	0.036(5)	0.023(4)	0.027(5)	0.010(3)	–0.005(4)	–0.004(3)
C(26)	4*e*	–0.3838(7)	0.8133(5)	0.0433(3)	0.027(5)	0.045(5)	0.040(6)	0.008(4)	–0.011(4)	–0.007(4)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(27)	4*e*	–0.4779(7)	0.7532(6)	0.0473(4)	0.027(5)	0.054(6)	0.073(8)	–0.003(4)	–0.007(5)	0.017(5)
C(28)	4*e*	–0.5827(8)	0.7639(7)	0.0156(4)	0.027(5)	0.088(8)	0.077(8)	–0.007(5)	–0.018(5)	0.028(6)
C(29)	4*e*	–0.5893(8)	0.8335(6)	–0.0176(4)	0.027(5)	0.077(7)	0.064(7)	0.019(5)	–0.021(4)	0.000(6)
C(30)	4*e*	–0.4929(8)	0.8899(6)	–0.0191(4)	0.051(6)	0.060(6)	0.057(7)	0.012(5)	–0.012(5)	0.004(5)
C(31)	4*e*	–0.0713(6)	0.8263(5)	0.0973(3)	0.029(4)	0.033(4)	0.014(4)	–0.002(3)	–0.003(3)	–0.008(3)
C(32)	4*e*	0.0450(6)	0.8729(5)	0.0911(3)	0.032(5)	0.030(4)	0.019(4)	0.004(3)	–0.006(3)	–0.003(3)
C(33)	4*e*	0.0675(8)	0.9285(5)	0.0515(3)	0.044(6)	0.050(6)	0.034(6)	0.006(4)	–0.007(4)	0.012(4)
C(34)	4*e*	0.1803(8)	0.9697(6)	0.0480(4)	0.045(6)	0.055(6)	0.055(7)	–0.006(5)	–0.001(5)	0.016(5)
C(35)	4*e*	0.2706(8)	0.9477(6)	0.0863(4)	0.031(5)	0.064(7)	0.072(8)	–0.011(5)	0.003(5)	0.002(6)
C(36)	4*e*	0.2434(8)	0.8907(6)	0.1246(3)	0.042(6)	0.058(6)	0.040(6)	–0.008(5)	–0.005(4)	–0.005(5)
I(1)	4*e*	–0.07338(5)	0.20129(4)	0.51348(2)	0.0342(3)	0.0555(4)	0.0451(4)	0.0055(3)	–0.0023(3)	–0.0024(3)
I(2)	4*e*	0.12558(5)	0.09586(3)	0.47532(2)	0.0313(3)	0.0437(3)	0.0338(3)	–0.0028(2)	–0.0037(2)	0.0010(3)
I(3)	4*e*	0.34121(5)	0.00187(4)	0.44380(3)	0.0403(4)	0.0649(4)	0.0650(5)	0.0049(3)	0.0081(3)	–0.0111(4)
I(4)	4*e*	0.11231(5)	0.61423(4)	0.38579(2)	0.0485(4)	0.0595(4)	0.0483(4)	0.0020(3)	–0.0041(3)	–0.0061(3)
I(5)	4*e*	0.27733(5)	0.49856(4)	0.33480(2)	0.0425(3)	0.0452(3)	0.0415(4)	–0.0078(3)	–0.0028(3)	0.0031(3)
I(6)	4*e*	0.44344(6)	0.37760(4)	0.28149(3)	0.0521(4)	0.0658(4)	0.0645(5)	0.0106(3)	0.0047(3)	–0.0014(4)

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