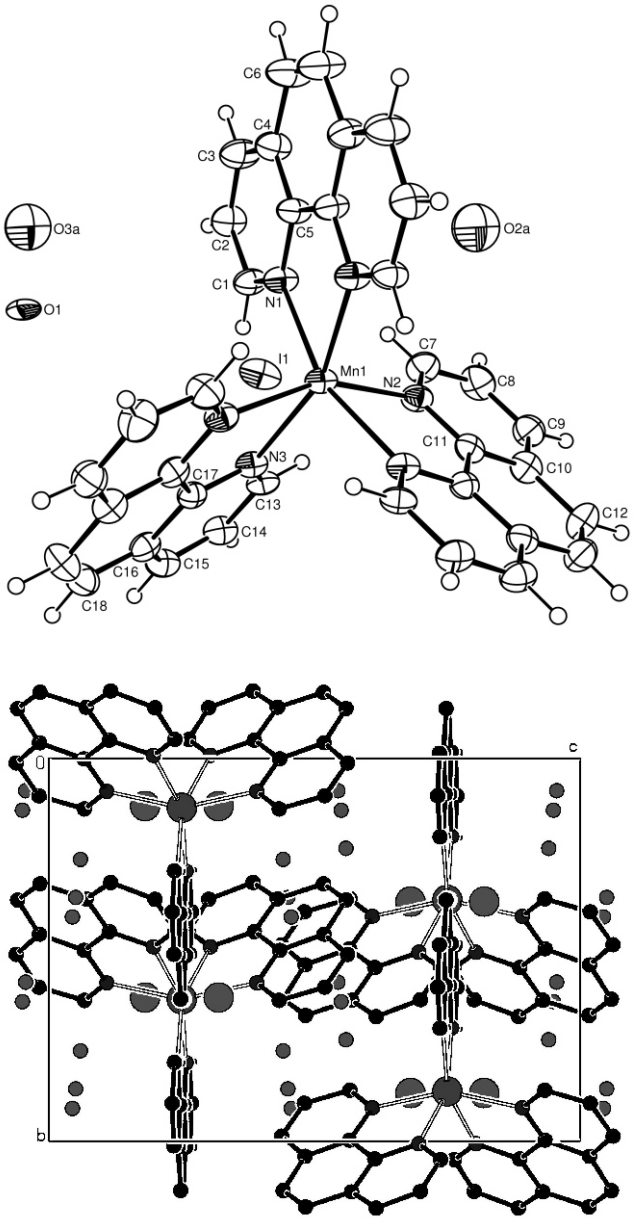
Crystal structure of tris(1,10-phenanthroline-κ^2N,N')manganese(II) diiodide — water (1:5), $[Mn(C_{12}H_8N_2)_3]I_2 \cdot 5H_2O$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received April 15, 2011, accepted and available on-line September 20, 2011; CCDC no. 1267/3530



Abstract

$C_{36}H_{34}I_2MnN_6O_5$, monoclinic, *C*12/*c*1 (no. 15), $a = 24.119(1)$ Å, $b = 10.9032(5)$ Å, $c = 18.2018(8)$ Å, $\beta = 123.901(1)°$, $V = 3973.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.063$, $wR_{ref}(F^2) = 0.198$, $T = 200$ K.

Source of material

The yellow single crystals of the title compound were unexpectedly obtained as a byproduct of an attempted preparation of a Mn(III) complex by reacting $Mn(CH_3COO)_3 \cdot 2H_2O$ (0.4015 g, 1.498 mmol), 1,10-phenanthroline (phen; 0.6496 g, 3.605 mmol) and KI (0.8302 g, 5.001 mmol) in EtOH. It seems that the Mn(III) ions were reduced to the Mn(II) ions by the I^- anions. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a CH_3NO_2 solution of the brown reaction product.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å (CH) and $U_{iso}(H) = 1.2\ U_{eq}(C)$. The H_2O solvent molecules were highly disordered, and then the O1 atom was refined anisotropically with a site occupancy factor of 0.5, and the O2 and O3 atoms were modeled isotropically as disordered over two sites using EADP instruction [1], with site occupancy factors of 0.66(1) for the O2A atom and 0.59(1) for the O3A atom. As a result it reflects on the large R values. The H atoms of the solvent molecules could neither be located from Fourier difference maps nor added geometrically. The highest peak (1.65 e Å^{-3}) and the deepest hole (–0.87 e Å^{-3}) in the difference Fourier map are located 1.27 Å and 0.85 Å from the atoms O2B and I1, respectively.

Discussion

The crystal structure of the related Mn(II) complex $[Mn(phen)_3](I_3)_2$ has previously been reported [2]. This deep brown compound was synthesized by reacting $Mn(CH_3COO)_2 \cdot 4H_2O$, 1,10-phenanthroline hydrate, I_2, KI and diluted H_2SO_4, and crystallizes in the trigonal space group $R\bar{3}$.

The crystal structure of the title compound $[Mn(phen)_3]I_2 \cdot 5H_2O$ consists of cationic Mn(II) complexes, I^- anions and solvent water molecules in ration 1:2:5 (figure, top). The complex is disposed about a twofold rotation axis running in the [010] direction passing through the Mn1 atom, and therefore the asymmetric unit contains one half of the formula unit (figure, bottom). In the complex, the Mn(II) ion is six-coordinated in a considerably distorted octahedral manner by six N atoms of the three chelate 1,10-phenanthroline ligands. The tight chelating angles ($\angle$N1–Mn1–N1^i = 73.7(2)°, $\angle$N2–Mn1–N3^i = 73.6(2)° and $\angle$N3–Mn1–N2^i = 73.6(2)°; symmetry code i: $-x,y,½-z$) contribute to the distortion of the ocatahedron. The apical N1–Mn1–N3^i and N2–Mn1–N2^i bond angles are 163.3(2)° and 156.3(3)°, respectively. The distances d(Mn—N) are almost equivalent (2.255(5) - 2.277(6) Å) and the dihedral angles between the least-squares planes of the phen ligands are 70.5(1)°

* e-mail: hakwang@chonnam.ac.kr

and 85.33(8)°. In the crystal structure, the molecules are stacked in columns along [100]. When viewed down the *c* axis, the successive complexes are stacked in the opposite manner. In the columns, numerous inter- and intramolecular π–π interactions between adjacent six-membered rings are present. For Cg1 (the centroid of ring C10-C12) and $Cg1^{ii}$ (symmetry code ii: $-x,-y,1-z$), the centroid-centroid distance is 3.769(5) Å, the rings' planes are parallel and shifted by 1.520 Å. In addition, the complex and I^- anions are linked by intermolecular C–H···I hydrogen bonds with d(C1–H1···I1) = 3.731(7) Å and ∠C1–H1···I1 = 132.6°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.16 × 0.20 × 0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	19.33 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12110, 3863
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2492
$N(param)_{refined}$:	229
Programs:	SHELXS-97, SHELXL-97 [1], ORTEP-3 [3], PLATON [4]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1)	8*f*		0.1223	0.2173	0.2344	0.047
H(2)	8*f*		0.1724	0.3968	0.2269	0.055
H(3)	8*f*		0.1295	0.5863	0.2318	0.064
H(6)	8*f*		0.0456	0.7054	0.2481	0.073
H(7)	8*f*		0.1571	0.1920	0.4040	0.053
H(8)	8*f*		0.2407	0.1344	0.5475	0.063
H(9)	8*f*		0.2184	–0.0112	0.6208	0.056
H(12)	8*f*		0.1330	–0.1573	0.6177	0.058
H(13)	8*f*		0.1344	–0.0198	0.2952	0.043
H(14)	8*f*		0.1678	–0.1579	0.2312	0.049
H(15)	8*f*		0.0906	–0.2333	0.0897	0.051
H(18)	8*f*		–0.0296	–0.2316	–0.0451	0.059
O(2A)	8*f*	0.66(1)	0.0720(7)	0.364(1)	0.4498(9)	0.097(3)
O(2B)	8*f*	0.34	0.076(1)	0.460(2)	0.476(2)	0.097(3)
O(3A)	8*f*	0.59(1)	0.2143(8)	0.415(1)	0.044(1)	0.109(4)
O(3B)	8*f*	0.41	0.137(1)	0.544(2)	–0.058(1)	0.109(4)

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	0.1297(1)	¼	0.0291(7)	0.0254(7)	0.0448(8)	0	0.0232(7)	0
N(1)	8*f*		0.0524(3)	0.2952(5)	0.2418(4)	0.035(3)	0.029(3)	0.059(4)	0.001(2)	0.035(3)	0.000(3)
N(2)	8*f*		0.0862(3)	0.0868(5)	0.3912(4)	0.035(3)	0.032(3)	0.047(3)	–0.006(2)	0.026(3)	–0.004(3)
N(3)	8*f*		0.0397(3)	–0.0072(4)	0.1962(4)	0.026(3)	0.028(3)	0.045(3)	0.000(2)	0.022(3)	0.001(2)
C(1)	8*f*		0.1045(3)	0.2943(6)	0.2359(5)	0.042(4)	0.030(3)	0.058(5)	0.000(3)	0.036(4)	0.002(3)
C(2)	8*f*		0.1352(4)	0.4014(7)	0.2318(5)	0.040(4)	0.045(4)	0.062(5)	–0.004(3)	0.035(4)	–0.001(4)
C(3)	8*f*		0.1101(4)	0.5123(7)	0.2349(6)	0.054(5)	0.037(4)	0.081(6)	–0.011(3)	0.045(5)	–0.001(4)
C(4)	8*f*		0.0555(4)	0.5159(6)	0.2427(5)	0.048(4)	0.035(4)	0.066(5)	–0.006(3)	0.042(4)	–0.004(3)
C(5)	8*f*		0.0275(3)	0.4059(6)	0.2459(5)	0.041(4)	0.026(3)	0.057(4)	–0.002(3)	0.034(4)	–0.004(3)
C(6)	8*f*		0.0263(5)	0.6294(6)	0.2479(7)	0.071(6)	0.032(4)	0.109(7)	–0.004(4)	0.069(6)	–0.005(4)
C(7)	8*f*		0.1472(4)	0.1329(6)	0.4334(5)	0.036(4)	0.044(4)	0.048(4)	–0.010(3)	0.021(3)	–0.001(3)
C(8)	8*f*		0.1977(4)	0.0984(7)	0.5192(5)	0.040(4)	0.060(5)	0.051(5)	–0.013(4)	0.021(4)	–0.011(4)
C(9)	8*f*		0.1847(4)	0.0126(7)	0.5621(5)	0.044(4)	0.048(4)	0.042(4)	–0.005(3)	0.020(4)	–0.004(3)
C(10)	8*f*		0.1208(3)	–0.0399(6)	0.5180(5)	0.033(4)	0.045(4)	0.047(4)	0.002(3)	0.024(3)	–0.002(3)
C(11)	8*f*		0.0734(3)	0.0019(6)	0.4342(4)	0.030(3)	0.036(3)	0.042(4)	0.001(3)	0.025(3)	–0.005(3)
C(12)	8*f*		0.1010(4)	–0.1296(6)	0.5593(5)	0.044(4)	0.055(5)	0.047(4)	0.004(4)	0.026(4)	0.015(4)
C(13)	8*f*		0.1023(3)	–0.0487(5)	0.2371(5)	0.032(4)	0.025(3)	0.048(4)	–0.003(3)	0.022(3)	0.002(3)
C(14)	8*f*		0.1226(4)	–0.1314(6)	0.1994(5)	0.036(4)	0.037(4)	0.059(5)	0.004(3)	0.032(4)	0.001(3)
C(15)	8*f*		0.0774(4)	–0.1752(6)	0.1160(5)	0.043(4)	0.035(3)	0.059(5)	–0.001(3)	0.035(4)	–0.003(3)
C(16)	8*f*		0.0110(3)	–0.1325(5)	0.0699(5)	0.038(4)	0.035(3)	0.047(4)	0.004(3)	0.030(3)	0.007(3)
C(17)	8*f*		–0.0045(3)	–0.0470(5)	0.1134(4)	0.034(3)	0.029(3)	0.040(4)	–0.002(3)	0.025(3)	0.001(3)
C(18)	8*f*		–0.0403(4)	–0.1718(7)	–0.0169(5)	0.060(5)	0.043(4)	0.053(5)	–0.002(4)	0.037(4)	–0.008(4)
I(1)	8*f*		0.26359(2)	0.12519(5)	0.31937(4)	0.0395(4)	0.0509(4)	0.0905(5)	–0.0062(2)	0.0418(3)	–0.0167(3)
O(1)	8*f*	0.50	0.2821(7)	0.2644(8)	0.0591(8)	0.11(1)	0.024(5)	0.078(8)	–0.016(6)	0.063(8)	–0.003(5)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2010-0029626).

References

1. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
2. Ramalakshmi, D.; Rajender Reddy, K.; Padmavathy, D.; Rajasekharan, M. V.; Arulsamy, N.; Hodgson, D. J.: Polyiodides of transition metal trischelate cations: syntheses, structures, and spectral and electrical conductivity studies of $[Mn(phen)_3](I_3)_2$ and $[Mn(bpy)_3](I_3)_{1.5}(I_8)_{0.25}$. Inorg. Chim. Acta **284** (1999) 158-166.
3. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
4. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.