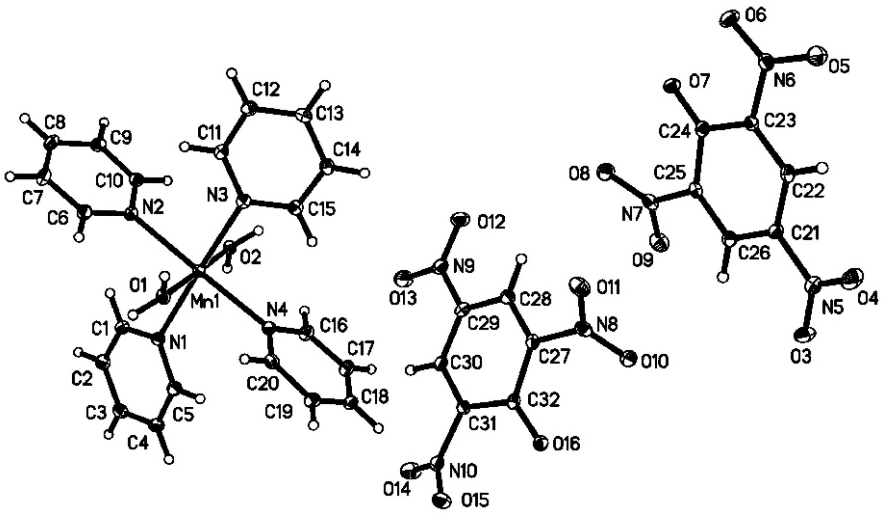
Crystal structure of diaqua-tetrapyridine-manganese(II) dipicrate, $[Mn(C_5H_5N)_4(H_2O)_4][(C_6H_2N_3O_7)]_2$

Xiao-Jing Yang, Jian-Zhong Wang, Hai-Bing Liu, Ai-Ping Yin and Cheng-Qi Liu*

Department of Chemistry, Xinzhou Teacher's University, Xinzhou 034000, Shanxi, P. R. China

Received March 21, 2011, in revised form July 10, 2011, accepted and available on-line October 8, 2011; CCDC no. 1267/3466



Abstract

$C_{32}H_{28}MnN_{10}O_{16}$, orthorhombic, $Pna2_1$ (no. 33), a = 21.729(3) Å, b = 7.402(1) Å, c = 22.677(3) Å, V = 3647.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.053, T = 113 K.

Source of material

0.2523 g manganese picrate was added into a solution containing 20 ml pyridine and 20 ml acetonitrile and the mixture was refluxed for about 1.5 hours. Red single crystals were obtained after the filtrate was allowed to stand at room temperature for about three days.

Experimental details

H atoms from water molecules were located in a difference Fourier map, and placed in idealised positions with d(O—H) = 0.854 - 0.869 Å and with U_{iso}(H) = 1.5 U_{eq}(O). Other H atoms were placed in calculated positions with d(C—H) = 0.95 Å and with U_{iso}(H) = 1.2 U_{eq}(C). All H atoms were refined as riding entities. Because the Flack parameter is 0.004(8) in the final cycles of the refinement, the absolute structure can be regarded as correct.

Discussion

In the title structure, the asymmetric unit contains one Mn(II) complex and two picrate anions. The Mn1 atom has a distorted octahdral coordination. There are hydrogen bonds between the coordinated H_2O molecules and the picrate anions. In addition to the hydrogen bonds there exists π-π stacking involving the pyridine ring and the benzene ring with the relevant distances being d(Cg1···Cg2^{i}) = 3.638(1) Å, d(Cg1···Cg2$_{perp}$) = 3.610 Å; Cg1 and Cg2 are the centroids of C2–C5N1 pyridine ring and C27–C32 benzene ring, respectively; Cg1···Cg2$^{i}_{perp}$ is the perpendicular distance from Cg1 ring to Cg2^{i} ring (symmetry code i: ½–x,½+y,–½+z). The hydrogen bonds and the π-π stacking link the complex with the uncoordinated picrate anions and stabilize the crystal.

Table 1. Data collection and handling.

Crystal:	red prism, size 0.16 × 0.18 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.52 cm^{-1}
Diffractometer, scan mode:	Bruker Smart APEX CCD, φ/ω
$2\theta_{max}$:	54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	33367, 7966
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7224
$N(param)_{refined}$:	532
Program:	SHELXTL [2]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*a*	0.3347	0.2985	0.1866	0.027
H(2)	4*a*	0.2579	0.2387	0.1185	0.031
H(3)	4*a*	0.1568	0.1935	0.1517	0.031
H(4)	4*a*	0.1360	0.2242	0.2532	0.030
H(5)	4*a*	0.2159	0.2876	0.3171	0.028
H(6)	4*a*	0.4082	0.6603	0.2481	0.028
H(7)	4*a*	0.4768	0.7564	0.1763	0.032
H(8)	4*a*	0.5443	0.5485	0.1334	0.030

* Correspondence author (e-mail: liuchengqi1919@163.com)

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(9)	4*a*	0.5401	0.2452	0.1637	0.027
H(10)	4*a*	0.4702	0.1605	0.2358	0.026
H(11)	4*a*	0.5109	0.4402	0.3384	0.026
H(12)	4*a*	0.5926	0.4372	0.4036	0.028
H(13)	4*a*	0.5787	0.3165	0.4985	0.027
H(14)	4*a*	0.4812	0.2044	0.5242	0.027
H(15)	4*a*	0.4027	0.2106	0.4557	0.025
H(16)	4*a*	0.3147	–0.0496	0.3818	0.028
H(17)	4*a*	0.2454	–0.1611	0.4499	0.030
H(18)	4*a*	0.1865	0.0414	0.5056	0.028

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(19)	4*a*	0.2006	0.3537	0.4914	0.030
H(20)	4*a*	0.2733	0.4525	0.4237	0.026
H(22)	4*a*	0.4901	0.2912	1.0579	0.024
H(26)	4*a*	0.3775	0.0985	0.9296	0.023
H(28)	4*a*	0.3907	0.1816	0.7159	0.023
H(30)	4*a*	0.2637	0.2071	0.5846	0.024
H(1A)	4*a*	0.3226	0.6473	0.3215	0.030
H(1B)	4*a*	0.3675	0.6491	0.3670	0.030
H(2A)	4*a*	0.4098	–0.0256	0.3217	0.029
H(2B)	4*a*	0.3629	–0.0156	0.2776	0.029

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}
C(1)	4*a*	0.29381(8)	0.2825(2)	0.20036(7)	0.020(1)	0.025(1)	0.024(1)	0.0008(7)	0.0030(8)	0.0009(7)
C(2)	4*a*	0.24831(9)	0.2463(3)	0.15929(8)	0.027(1)	0.034(1)	0.0172(9)	0.0028(9)	0.0009(8)	–0.0011(7)
C(3)	4*a*	0.18886(8)	0.2215(2)	0.17872(8)	0.024(1)	0.028(1)	0.0245(9)	0.0021(8)	–0.0042(8)	–0.0005(7)
C(4)	4*a*	0.17668(8)	0.2382(3)	0.23853(8)	0.020(1)	0.032(1)	0.024(1)	0.0023(8)	0.0006(8)	–0.0002(7)
C(5)	4*a*	0.22472(8)	0.2756(2)	0.27621(7)	0.024(1)	0.028(1)	0.0193(9)	0.0022(8)	0.0024(8)	–0.0001(7)
C(6)	4*a*	0.43534(8)	0.5748(2)	0.23086(7)	0.025(1)	0.0213(9)	0.0244(9)	0.0023(8)	0.0034(7)	–0.0005(7)
C(7)	4*a*	0.47618(8)	0.6332(2)	0.18807(8)	0.031(1)	0.024(1)	0.027(1)	–0.0037(8)	0.0064(8)	0.0032(7)
C(8)	4*a*	0.51581(8)	0.5111(2)	0.16274(8)	0.0235(9)	0.031(1)	0.0203(8)	–0.0059(8)	0.0061(7)	0.0011(7)
C(9)	4*a*	0.51341(8)	0.3325(2)	0.18068(7)	0.0198(9)	0.027(1)	0.0213(9)	–0.0004(8)	0.0023(7)	–0.0038(7)
C(10)	4*a*	0.47156(8)	0.2832(2)	0.22363(8)	0.0203(9)	0.022(1)	0.0211(9)	–0.0014(8)	–0.0008(7)	–0.0002(7)
C(11)	4*a*	0.50484(7)	0.3901(2)	0.37657(7)	0.022(1)	0.0216(9)	0.0209(8)	–0.0014(7)	0.0019(8)	–0.0005(7)
C(12)	4*a*	0.55387(8)	0.3897(2)	0.41519(7)	0.0213(9)	0.0228(9)	0.0252(9)	–0.0019(8)	0.0011(8)	–0.0030(7)
C(13)	4*a*	0.54574(8)	0.3191(2)	0.47109(8)	0.0193(9)	0.0235(9)	0.0259(9)	0.0016(8)	–0.0039(8)	–0.0021(8)
C(14)	4*a*	0.48843(8)	0.2526(2)	0.48602(7)	0.027(1)	0.0238(9)	0.0180(9)	0.0009(8)	–0.0005(8)	–0.0008(7)
C(15)	4*a*	0.44182(8)	0.2570(2)	0.44476(7)	0.0217(9)	0.0213(9)	0.0194(9)	–0.0015(8)	0.0004(8)	–0.0015(7)
C(16)	4*a*	0.29158(8)	0.0336(2)	0.40469(7)	0.0260(9)	0.020(1)	0.0229(9)	0.0004(8)	0.0060(8)	–0.0025(7)
C(17)	4*a*	0.25009(8)	–0.0344(2)	0.44491(7)	0.027(1)	0.021(1)	0.027(1)	–0.0048(8)	0.0041(8)	0.0004(7)
C(18)	4*a*	0.21564(8)	0.0846(2)	0.47771(7)	0.0195(9)	0.029(1)	0.0201(9)	–0.0011(8)	0.0028(7)	0.0020(7)
C(19)	4*a*	0.22404(9)	0.2687(2)	0.46948(7)	0.025(1)	0.029(1)	0.0209(9)	0.0051(8)	0.0053(8)	–0.0031(7)
C(20)	4*a*	0.26728(8)	0.3264(2)	0.42877(7)	0.023(1)	0.0196(9)	0.0224(9)	0.0018(8)	–0.0017(8)	–0.0002(7)
C(21)	4*a*	0.42698(7)	0.1984(2)	0.99934(7)	0.0183(9)	0.0209(9)	0.0187(8)	0.0008(7)	0.0034(7)	0.0019(7)
C(22)	4*a*	0.48445(8)	0.2509(2)	1.01847(7)	0.0237(9)	0.0207(9)	0.0153(8)	0.0003(7)	–0.0002(7)	–0.0005(6)
C(23)	4*a*	0.53357(8)	0.2447(2)	0.98018(7)	0.0161(9)	0.0179(8)	0.0170(9)	–0.0009(7)	–0.0018(7)	0.0024(6)
C(24)	4*a*	0.52844(8)	0.1843(2)	0.91964(7)	0.0204(9)	0.0137(8)	0.0182(9)	0.0017(7)	0.0017(7)	0.0030(6)
C(25)	4*a*	0.46622(7)	0.1319(2)	0.90456(7)	0.0219(9)	0.0157(8)	0.0154(8)	0.0013(7)	–0.0026(7)	0.0013(6)
C(26)	4*a*	0.41716(8)	0.1364(2)	0.94216(7)	0.0202(9)	0.0161(8)	0.0216(9)	–0.0001(7)	–0.0001(7)	0.0025(7)
C(27)	4*a*	0.30466(8)	0.2483(2)	0.74227(7)	0.0217(9)	0.0198(9)	0.0159(8)	–0.0009(7)	–0.0005(7)	0.0026(6)
C(28)	4*a*	0.34950(8)	0.2006(2)	0.70326(7)	0.0190(9)	0.0183(9)	0.0212(8)	–0.0016(7)	–0.0009(7)	0.0015(7)
C(29)	4*a*	0.33290(8)	0.1805(2)	0.64425(7)	0.0190(9)	0.0190(9)	0.0208(9)	–0.0018(7)	0.0046(7)	–0.0006(7)
C(30)	4*a*	0.27396(8)	0.2189(2)	0.62510(7)	0.0206(9)	0.0239(9)	0.0167(9)	–0.0035(7)	0.0023(7)	0.0029(7)
C(31)	4*a*	0.23028(8)	0.2740(2)	0.66485(7)	0.0166(9)	0.0192(9)	0.0202(9)	–0.0025(7)	–0.0015(7)	0.0036(7)
C(32)	4*a*	0.24139(8)	0.2860(2)	0.72749(7)	0.0218(9)	0.0154(9)	0.0169(8)	–0.0022(7)	0.0015(7)	0.0011(6)
Mn(1)	4*a*	0.36642(1)	0.31307(3)	0.32316(1)	0.0174(1)	0.0177(1)	0.0151(1)	–0.0008(1)	0.0019(1)	–0.0001(1)
N(1)	4*a*	0.28347(6)	0.2963(2)	0.25854(6)	0.0188(8)	0.0213(8)	0.0173(7)	0.0005(6)	0.0009(6)	–0.0007(6)
N(2)	4*a*	0.43251(6)	0.4019(2)	0.24903(6)	0.0197(8)	0.0208(8)	0.0184(7)	–0.0020(6)	0.0016(6)	–0.0010(6)
N(3)	4*a*	0.44872(7)	0.3234(2)	0.38995(6)	0.0215(8)	0.0186(8)	0.0199(8)	0.0007(6)	0.0014(6)	–0.0021(6)
N(4)	4*a*	0.30118(6)	0.2114(2)	0.39601(6)	0.0187(7)	0.0227(8)	0.0162(7)	0.0002(6)	–0.0004(6)	–0.0008(6)
N(5)	4*a*	0.37533(7)	0.2130(2)	1.03977(6)	0.0231(9)	0.0275(9)	0.0216(8)	0.0000(7)	0.0033(7)	0.0021(6)
N(6)	4*a*	0.59251(6)	0.3061(2)	1.00356(6)	0.0211(8)	0.0235(8)	0.0185(7)	0.0009(6)	–0.0018(6)	0.0000(6)
N(7)	4*a*	0.45279(7)	0.0701(2)	0.84455(6)	0.0225(8)	0.0236(8)	0.0211(7)	0.0060(7)	–0.0047(6)	–0.0022(6)
N(8)	4*a*	0.32197(7)	0.2652(2)	0.80420(6)	0.0214(8)	0.0238(8)	0.0224(8)	0.0077(7)	–0.0023(7)	–0.0036(6)
N(9)	4*a*	0.37756(7)	0.1143(2)	0.60220(6)	0.0218(8)	0.0286(8)	0.0227(8)	–0.0020(7)	0.0037(7)	0.0011(6)
N(10)	4*a*	0.16923(6)	0.3192(2)	0.64181(6)	0.0203(8)	0.0306(8)	0.0190(7)	–0.0020(7)	0.0005(7)	0.0052(6)
O(1)	4*a*	0.34301(5)	0.5834(1)	0.34646(5)	0.0221(6)	0.0197(6)	0.0188(6)	–0.0007(5)	–0.0048(5)	0.0000(5)
O(2)	4*a*	0.38978(5)	0.0433(1)	0.29726(5)	0.0210(6)	0.0174(6)	0.0193(6)	–0.0004(5)	–0.0038(5)	0.0001(5)
O(3)	4*a*	0.32476(6)	0.1568(2)	1.02399(5)	0.0179(7)	0.0351(8)	0.0328(7)	–0.0043(6)	0.0033(6)	–0.0038(6)
O(4)	4*a*	0.38448(6)	0.2863(2)	1.08772(5)	0.0326(8)	0.065(1)	0.0213(7)	–0.0057(7)	0.0072(6)	–0.0137(6)
O(5)	4*a*	0.59654(6)	0.3311(2)	1.05698(5)	0.0272(7)	0.069(1)	0.0160(7)	–0.0052(7)	–0.0008(5)	–0.0089(6)
O(6)	4*a*	0.63493(6)	0.3347(2)	0.97015(5)	0.0230(7)	0.064(1)	0.0188(6)	–0.0162(7)	0.0041(6)	–0.0032(6)
O(7)	4*a*	0.57291(5)	0.1722(2)	0.88449(5)	0.0170(6)	0.0249(7)	0.0189(6)	–0.0013(5)	0.0026(5)	–0.0035(5)
O(8)	4*a*	0.48421(6)	0.1270(2)	0.80364(5)	0.0251(7)	0.0607(9)	0.0166(6)	0.0013(6)	0.0030(6)	–0.0007(6)
O(9)	4*a*	0.40911(5)	–0.0345(2)	0.83763(5)	0.0310(7)	0.0258(7)	0.0310(7)	–0.0039(6)	–0.0089(5)	–0.0052(5)
O(10)	4*a*	0.29098(5)	0.1858(2)	0.84116(5)	0.0238(7)	0.0482(9)	0.0196(6)	0.0052(6)	0.0032(5)	0.0038(6)
O(11)	4*a*	0.36778(5)	0.3562(2)	0.81626(6)	0.0300(7)	0.0294(7)	0.0340(8)	–0.0017(6)	–0.0115(6)	–0.0041(6)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(12)	4*a*	0.43016(5)	0.0784(2)	0.62017(5)	0.0203(7)	0.0394(8)	0.0292(7)	0.0030(6)	0.0027(6)	–0.0034(6)
O(13)	4*a*	0.36183(5)	0.0937(2)	0.55081(5)	0.0296(7)	0.0583(9)	0.0182(7)	0.0028(6)	0.0013(6)	–0.0057(6)
O(14)	4*a*	0.15400(6)	0.2499(2)	0.59439(5)	0.0255(7)	0.071(1)	0.0182(7)	0.0011(7)	–0.0034(6)	–0.0109(7)
O(15)	4*a*	0.13650(5)	0.4225(2)	0.66943(5)	0.0226(6)	0.0293(7)	0.0317(7)	0.0063(6)	–0.0010(6)	–0.0003(6)
O(16)	4*a*	0.20170(5)	0.3217(2)	0.76619(5)	0.0210(6)	0.0231(7)	0.0201(6)	0.0043(5)	0.0034(5)	0.0022(5)

Acknowledgment. The authors thank the Scientific Research Foundation of Xinzhou Teacher's University (no. 200501).

References

1. Honda, K.; Yamawaki, H.; Fujihisa, H.; Matsunaga, T.; Matsukawa, M.: Hexaaquazinc(II) dipicrate trihydrate. Acta Crystallogr. **C63** (2007) m423-m426.
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.