Crystal structure of aquabis(2,2′-bipyridyl-*N*,*N*′)(9,10-dioxo-anthracene-2,6-disulfonato)manganese(II) — water (1:1), $[Mn(H_2O)(C_{10}H_8N_2)_2][C_{14}H_6S_2O_8] \cdot H_2O$

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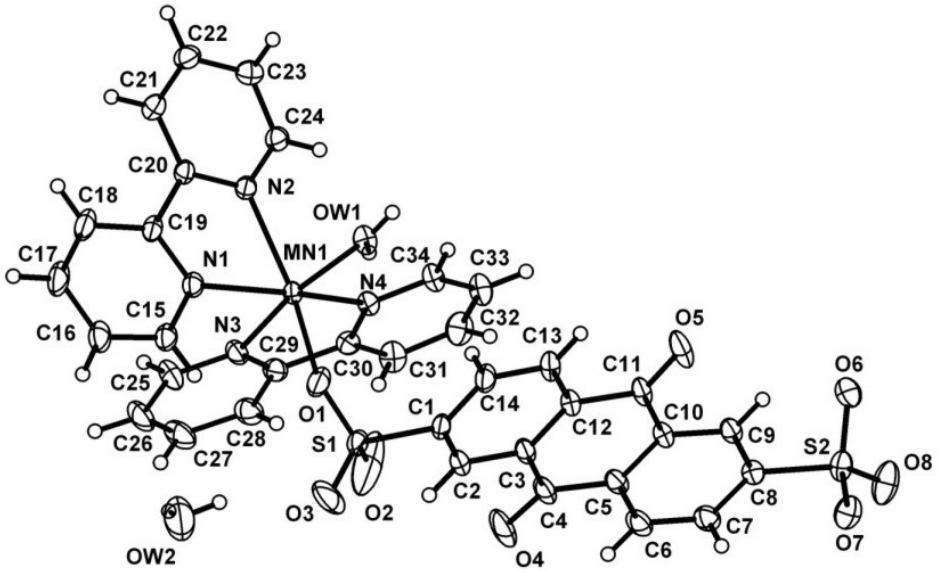
Received April 7, 2011, accepted and available on-line August 31, 2011; CCDC no. 1267/3509



Abstract

$C_{34}H_{26}MnN_4O_{10}S_2$, triclinic, $P\bar{1}$ (no. 2), a = 9.788(1) Å, b = 12.927(8) Å, c = 13.911(2) Å, α = 87.23(2)°, β = 80.60(1)°, γ = 70.19(3)°, V = 1633.7 Å^3, Z = 2, $R_{gt(F)}$ = 0.058, $wR_{ref(F^2)}$ = 0.184, T = 298 K.

Source of material

A mixture of 0.20 g of $MnCl_2 \cdot 4H_2O$ (1 mmol), 0.16 g of 2,2′-bipyridine (1 mmol), 0.31 g of 9,10-dioxoanthracene-2,6-disulfonic acid disodium salt (1 mmol), and 15 mL of deionized water was sealed into a bomb equipped with a Teflon liner (25 mL) and heated at 393 K for 2 days. Yellow rod-like crystals of the title compound were obtained when the sample was cooled to room temperature (yield 47 % based on Mn).

Elemental Analysis — found: C, 53.11 %; H, 3.45 %; N, 7.23 %; calculated for $C_{34}H_{26}MnN_4O_{10}S_2$: C, 53.06 %; H, 3.40 %; N, 7.28 %.

Experimental details

The C-bound H atoms were geometrically placed (d(C—H = 0.93 Å) and refined as riding with U_{iso}(H) = 1.2 U_{eq}(C). The O-bound H atoms were located in difference Fourier maps and refined as riding in their as-found relative positions with U_{iso}(H) = 1.2 U_{eq}(O).

Discussion

The rational design and synthesis of metal-organic coordination polymers with topological structures of different dimensionality is of great current interest because these complexes are potential candidates as new materials [1-3]. The key to successful construction of metal-organic frameworks is the judicious choice of metal ions and multifunctional bridging ligands. The approach to the supramolecular framework employed in this work is to use 2,6-ADS (9,10-dioxoanthracene-2,6-disulfonic acid disodium salt) as bisfunctional linker.

The asymmetric unit of the title crystal structure contains one Mn(II) ion, two 2,2′-bipyridine molecules, one 2,6-ADS anion and two water molecules. The six-coordinated metal centre is located on a general position, and the N_4O_2 chromophore around the Mn centre involves the four pyridine N atoms of two 2,2′-bipyridine molecules, one sulfonate O atom and one O atom of the aqua ligand. The equatorial positions are taken up by three pyridine N atoms from 2,2′-bipyridine molecule and one water molecule. The axial positions are occupied by pyridine N atom from 2,2′-bipyridine molecule and sulfonate O atom. The Mn—N distances are in agreement with values observed previously [4]. The Mn—O distances are similar to those documented elsewhere [4,5]. The angles formed by the equatorial atoms range from 72.38(1)° to 100.96(1)°. The coordinaton of Mn can be described as a distorted $Mn[O_2N_4]$ octahedron. The 2,2′-bipy ligand binds in a chelate fashion to the metal ion. The 2,6-ADS anion adopts an O-monodentate mode and coordinates the metal centre, similar to that of the Cd(II) derivative but different from that of the Yb(III)

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derivative [6,7]. In $Yb(H_2O)(OH)$(2,6-ADS), 2,6-ADS is tetradentate in μ_4-mode binding four metal centres.

In the title compound, the metal complexes are arranged in head-to-tail fashion and interact with each other via hydrogen bonds between the sulfonate groups and the coordinated water molecules, forming dimers. Additional hydrogen bonds between the remaining H atoms of the coordinated water molecules and sulfonate O atoms connect the dimeric units into infinite chains. The lattice water molecules are located between the chains and interact with the chains via hydrogen bonds formed with the sulfonate groups.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.20 × 0.40 × 0.50 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	50.61 cm^{-1}
Diffractometer, scan mode:	Xcalibur Nova, Onyx CCD, κ geometry, ω
$2\theta_{max}$:	134.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14318, 5825
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4692
$N(param)_{refined}$:	462
Programs:	SHELXS-97, SHELXL-97, SHELXTL [8]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.4479	0.9540	0.3517	0.072
H(1B)	2*i*	0.4395	0.8720	0.4239	0.072
H(2A)	2*i*	0.4524	0.8142	–0.0381	0.208
H(2B)	2*i*	0.3754	0.8824	–0.0815	0.208
H(2)	2*i*	0.8116	0.6081	0.0956	0.077
H(6)	2*i*	1.1783	0.2426	0.1416	0.078
H(7)	2*i*	1.3670	0.1315	0.2194	0.073
H(9)	2*i*	1.2907	0.3756	0.4095	0.060
H(13)	2*i*	0.9093	0.7384	0.3716	0.069
H(14)	2*i*	0.7441	0.8543	0.2800	0.072
H(15)	2*i*	0.2742	0.9902	0.0995	0.070
H(16)	2*i*	0.0779	1.1055	0.0343	0.089
H(17)	2*i*	–0.1569	1.1440	0.1247	0.108
H(18)	2*i*	–0.1848	1.0587	0.2727	0.092
H(21)	2*i*	–0.1921	1.0027	0.4211	0.066
H(22)	2*i*	–0.1921	0.9098	0.5678	0.070
H(23)	2*i*	0.0194	0.7725	0.5983	0.073
H(24)	2*i*	0.2267	0.7317	0.4813	0.063
H(25)	2*i*	0.1550	0.7940	0.1088	0.086
H(26)	2*i*	0.1365	0.6685	0.0055	0.100
H(27)	2*i*	0.2795	0.4862	0.0139	0.097
H(28)	2*i*	0.4413	0.4332	0.1283	0.085
H(31)	2*i*	0.5790	0.3954	0.2342	0.081
H(32)	2*i*	0.7238	0.3620	0.3565	0.088
H(33)	2*i*	0.7251	0.5065	0.4465	0.080
H(34)	2*i*	0.5701	0.6798	0.4196	0.067

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)	2*i*	0.34667(5)	0.81486(4)	0.27323(4)	0.0358(3)	0.0481(4)	0.0412(3)	–0.0108(2)	–0.0120(2)	0.0043(2)
S(1)	2*i*	0.6358(1)	0.8308(1)	0.10808(7)	0.0387(5)	0.129(1)	0.0498(5)	–0.0068(6)	–0.0095(4)	0.0354(6)
S(2)	2*i*	1.4949(1)	0.16225(8)	0.38163(8)	0.0504(5)	0.0468(5)	0.0816(7)	–0.0123(4)	–0.0242(5)	0.0018(5)
N(1)	2*i*	0.1659(3)	0.9540(3)	0.2210(2)	0.042(2)	0.054(2)	0.052(2)	–0.015(1)	–0.013(1)	0.011(1)
N(2)	2*i*	0.1437(3)	0.8400(2)	0.3848(2)	0.039(2)	0.049(2)	0.047(2)	–0.013(1)	–0.009(1)	0.004(1)
N(3)	2*i*	0.3052(4)	0.6928(3)	0.1780(2)	0.057(2)	0.066(2)	0.044(2)	–0.026(2)	–0.018(1)	0.003(1)
N(4)	2*i*	0.4844(3)	0.6437(2)	0.3130(2)	0.049(2)	0.046(2)	0.045(2)	–0.015(1)	–0.014(1)	0.003(1)
O(1)	2*i*	0.4980(3)	0.8574(3)	0.1655(2)	0.040(1)	0.120(3)	0.077(2)	–0.014(2)	–0.010(1)	0.045(2)
O(2)	2*i*	0.6837(6)	0.9141(7)	0.0785(7)	0.088(3)	0.34(1)	0.33(1)	–0.091(5)	–0.081(5)	0.288(9)
O(3)	2*i*	0.6411(7)	0.7681(7)	0.0273(3)	0.160(5)	0.35(1)	0.072(3)	0.151(6)	–0.068(3)	–0.062(4)
O(4)	2*i*	0.9691(5)	0.4100(3)	0.1074(3)	0.128(3)	0.102(3)	0.091(2)	–0.014(2)	–0.074(2)	–0.028(2)
O(5)	2*i*	1.0987(4)	0.5637(2)	0.4179(3)	0.112(3)	0.056(2)	0.093(2)	0.004(2)	–0.074(2)	–0.018(2)
O(6)	2*i*	1.4237(4)	0.1557(3)	0.4817(2)	0.079(2)	0.104(3)	0.063(2)	–0.008(2)	–0.026(2)	0.015(2)
O(7)	2*i*	1.5530(3)	0.0571(2)	0.3336(3)	0.063(2)	0.047(2)	0.104(2)	–0.011(1)	–0.019(2)	–0.001(2)
O(8)	2*i*	1.5979(4)	0.2177(3)	0.3768(4)	0.067(2)	0.061(2)	0.175(4)	–0.026(2)	–0.044(2)	0.014(2)
OW(1)	2*i*	0.4230(3)	0.9008(2)	0.3708(2)	0.063(2)	0.060(2)	0.065(2)	–0.025(1)	–0.025(1)	0.007(1)
OW(2)	2*i*	0.3979(6)	0.8129(6)	–0.0794(4)	0.113(4)	0.302(8)	0.132(4)	–0.098(5)	–0.056(3)	0.078(5)
C(1)	2*i*	0.7635(4)	0.7414(4)	0.1793(3)	0.033(2)	0.085(3)	0.054(2)	–0.011(2)	–0.014(2)	0.018(2)
C(2)	2*i*	0.8319(4)	0.6337(4)	0.1512(3)	0.051(2)	0.100(3)	0.044(2)	–0.024(2)	–0.021(2)	0.007(2)
C(3)	2*i*	0.9322(4)	0.5619(3)	0.2059(3)	0.051(2)	0.070(2)	0.045(2)	–0.023(2)	–0.021(2)	0.007(2)
C(4)	2*i*	1.0044(5)	0.4458(4)	0.1749(3)	0.071(3)	0.073(3)	0.050(2)	–0.024(2)	–0.031(2)	–0.005(2)
C(5)	2*i*	1.1203(4)	0.3753(3)	0.2285(3)	0.062(2)	0.055(2)	0.043(2)	–0.018(2)	–0.018(2)	–0.003(2)
C(6)	2*i*	1.2008(5)	0.2694(3)	0.1956(3)	0.080(3)	0.067(3)	0.050(2)	–0.019(2)	–0.022(2)	–0.013(2)
C(7)	2*i*	1.3142(5)	0.2028(3)	0.2418(3)	0.069(3)	0.056(2)	0.054(2)	–0.012(2)	–0.013(2)	–0.010(2)
C(8)	2*i*	1.3479(4)	0.2435(3)	0.3214(3)	0.049(2)	0.048(2)	0.049(2)	–0.017(2)	–0.012(2)	0.004(2)
C(9)	2*i*	1.2677(4)	0.3492(3)	0.3554(3)	0.055(2)	0.048(2)	0.047(2)	–0.014(2)	–0.019(2)	–0.002(2)
C(10)	2*i*	1.1543(4)	0.4157(3)	0.3099(2)	0.053(2)	0.046(2)	0.045(2)	–0.019(2)	–0.022(2)	0.005(1)
C(11)	2*i*	1.0736(4)	0.5296(3)	0.3453(3)	0.060(2)	0.048(2)	0.056(2)	–0.013(2)	–0.033(2)	–0.000(2)
C(12)	2*i*	0.9620(4)	0.6029(3)	0.2882(3)	0.047(2)	0.051(2)	0.052(2)	–0.017(2)	–0.022(2)	0.006(2)
C(13)	2*i*	0.8905(4)	0.7118(3)	0.3160(3)	0.050(2)	0.053(2)	0.072(2)	–0.012(2)	–0.030(2)	0.003(2)
C(14)	2*i*	0.7916(4)	0.7811(4)	0.2614(3)	0.043(2)	0.064(2)	0.069(2)	–0.010(2)	–0.021(2)	0.012(2)
C(15)	2*i*	0.1802(4)	1.0040(3)	0.1343(3)	0.046(2)	0.069(3)	0.061(2)	–0.019(2)	–0.016(2)	0.021(2)
C(16)	2*i*	0.0640(5)	1.0738(4)	0.0950(4)	0.056(2)	0.095(3)	0.075(3)	–0.027(2)	–0.028(2)	0.039(3)
C(17)	2*i*	–0.0753(5)	1.0958(5)	0.1485(4)	0.048(2)	0.115(4)	0.098(4)	–0.013(3)	–0.029(2)	0.050(3)
C(18)	2*i*	–0.0916(4)	1.0459(4)	0.2369(4)	0.036(2)	0.096(3)	0.090(3)	–0.013(2)	–0.017(2)	0.034(3)
C(19)	2*i*	0.0300(4)	0.9769(3)	0.2722(3)	0.035(2)	0.052(2)	0.060(2)	–0.013(2)	–0.013(2)	0.010(2)
C(20)	2*i*	0.0198(4)	0.9199(3)	0.3673(3)	0.038(2)	0.050(2)	0.052(2)	–0.016(2)	–0.011(1)	–0.001(2)
C(21)	2*i*	–0.1075(4)	0.9476(3)	0.4344(3)	0.042(2)	0.058(2)	0.065(2)	–0.016(2)	–0.006(2)	–0.003(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(22)	2*i*	–0.1074(4)	0.8920(3)	0.5216(3)	0.051(2)	0.068(3)	0.057(2)	–0.024(2)	0.002(2)	–0.006(2)
C(23)	2*i*	0.0177(5)	0.8107(4)	0.5399(3)	0.064(2)	0.066(3)	0.052(2)	–0.024(2)	–0.003(2)	0.003(2)
C(24)	2*i*	0.1415(4)	0.7870(3)	0.4693(3)	0.048(2)	0.055(2)	0.051(2)	–0.014(2)	–0.008(2)	0.007(2)
C(25)	2*i*	0.2134(6)	0.7207(4)	0.1125(3)	0.083(3)	0.088(3)	0.056(2)	–0.035(3)	–0.035(2)	0.006(2)
C(26)	2*i*	0.2014(6)	0.6459(5)	0.0504(3)	0.096(4)	0.124(5)	0.056(2)	–0.060(4)	–0.034(2)	0.002(3)
C(27)	2*i*	0.2861(6)	0.5380(5)	0.0554(3)	0.108(4)	0.101(4)	0.057(2)	–0.059(4)	–0.021(2)	–0.016(3)
C(28)	2*i*	0.3825(5)	0.5062(4)	0.1234(3)	0.079(3)	0.085(3)	0.060(2)	–0.040(3)	–0.011(2)	–0.013(2)
C(29)	2*i*	0.3881(4)	0.5871(3)	0.1837(3)	0.053(2)	0.063(2)	0.044(2)	–0.028(2)	–0.006(2)	–0.002(2)
C(30)	2*i*	0.4876(4)	0.5595(3)	0.2584(3)	0.049(2)	0.047(2)	0.048(2)	–0.023(2)	–0.006(2)	0.003(2)
C(31)	2*i*	0.5774(5)	0.4528(3)	0.2726(4)	0.073(3)	0.050(2)	0.084(3)	–0.020(2)	–0.022(2)	0.001(2)
C(32)	2*i*	0.6648(5)	0.4334(4)	0.3449(4)	0.072(3)	0.050(2)	0.095(3)	–0.014(2)	–0.024(2)	0.014(2)
C(33)	2*i*	0.6645(5)	0.5182(4)	0.3991(3)	0.069(3)	0.065(3)	0.074(3)	–0.024(2)	–0.035(2)	0.017(2)
C(34)	2*i*	0.5721(4)	0.6218(3)	0.3818(3)	0.061(2)	0.054(2)	0.057(2)	–0.017(2)	–0.027(2)	0.006(2)

Acknowledgment. The work was financially supported by the Natural Science Foundation of Henan Insititute of Science and Technology (grants no.7031 and no. 06038).

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