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Crystal structure of tetraaqua-*cis*-bis(*N*-2-nitrobenzenesulfonylglycinato)manganese(II), $Mn(H_2O)_4(C_8H_7N_2O_6S)_2$

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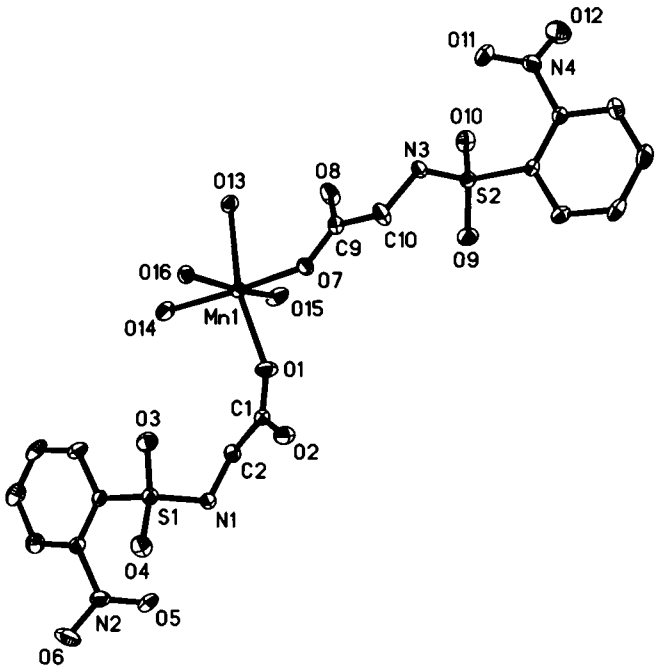

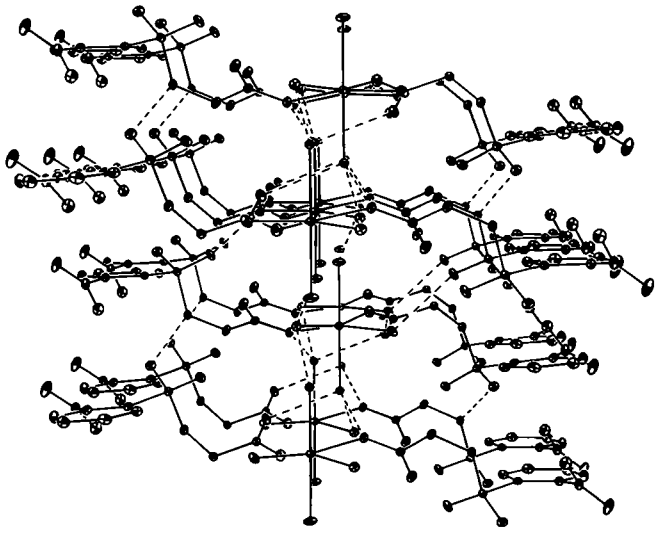

Abstract

$C_{16}H_{22}MnN_4O_{16}S_2$, monoclinic, $P12_1/n1$ (no. 14), a = 7.7703(7) Å, b = 7.7228(7) Å, c = 41.207(4) Å, β = 91.627(1)°, V = 2471.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.051, $wR_{ref}(F^2)$ = 0.128, T = 291 K.

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Source of material

A mixture of $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol) and *N*-2-nitrobenzenesulfonylglycine (1 mmol, 2-NBS-GlyH) in 10 mL H_2O was stirred about ten minutes to give a clear solution. Then the pH was adjusted to 6 with 0.1 M NaOH solution. The reaction mixture was heated on a water bath for 6 h up to 65 °C, and then filtered. Pink crystals of the title compound were separated from the mother liquor by slow evaporation at room temperature after 3 days.

Experimental details

While the hydrogen atoms attached to the carbon atoms were added geometrically, the water hydrogen atoms were found from Fourier difference maps and refined freely.

Discussion

Amino acid is an important biological ligand. It may coordinate to the metal ions by the carboxylate or amino groups. Research on the coordination of metal-amino acid complexes has contributed to our understanding of the function of metal ions in organisms, interactions between amino acids and DNA are of great importance in biochemistry [1-5]. Moreover *N*-sulfonyl amino acids were found to reproduce the coordination behavior of peptides and their selectivity towards metal ions [6-10]. Thus, it is of great interest in studying the coordination chemistry of *N*-sulfonylglycine acid. On the other hand, in recent years, there has been considerable interest in the design and synthesis of manganese(II) complexes. The main reason may be that these complexes can be used for investigation of the exchange coupling interactions between metal ions, as well as for a new variety of molecular-based magnetic materials [11-13]. Furthermore, manganese(II) ion plays an important role in several biological redox-active systems, for example, manganese catalase, manganese superoxide dismutase and oxygen-evolving complexes (OEC) of photosystem II in green plants [14].

X-ray analysis reveals that the title crystal structure consists of mononuclear complex molecules (figure, top). The 2-NBS-Gly ligand acts as an anion in the complex. The coordination environment around the Mn(II) ion can be described as a seriously distorted octahedron with three *trans* angles ranging from 83.61(9)° to 170.80(10)°, whereas each Mn ion is six-coordinated by two carboxylate O atoms from two different 2-NBS-Gly ligands and four water O atoms. The Mn—O(water) bond lengths are 2.128(2) Å – 2.163(2) Å, and the Mn—O(carboxylate) bond lengths are in the range of 2.156(2) Å – 2.288(2) Å, respectively, which are in the normal range of those observed in manganese(II) carboxylate complexes. The two carboxylate groups of 2-NBS-Gly ligands display the same coordination mode. The carboxyl group coordinates to the Mn(II) ion in a monodentate mode. Hydrogen bonding appears to be a key factor in defining the molecular packing, and the large network of intermolecular hydrogen

bonds helps to stabilize the crystal structure (figure, bottom). Different kinds of hydrogen bonding are observed in the structure: (a) hydrogen bonding among water molecules (O···O distances of 2.904(3) Å and 2.860(3) Å, respectively); (b) hydrogen bonding among water molecules and carboxylate oxygen atoms (O···O distances of 2.659(3) Å, 2.731(3) Å, 3.006(4) Å, 2.691(3) Å and 2.800(3) Å, respectively); (c) hydrogen bonding between water molecules and oxygen atoms of sulfonamide (O···O distance of 2.809(3) Å); (d) hydrogen bonding between nitrogen atoms of sulfonamide and oxygen atoms of sulfonamide (N···O distance of 2.781 Å). Neighboring monomeric units interact with each other via H-bonding to form a 2D network structure.

Table 1. Data collection and handling.

Crystal:	pink block, size 0.03 × 0.20 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.90 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20557, 5660
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4742
$N(param)_{refined}$:	384
Programs:	SHELXS-97 [15], SHELXL-97 [16]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.9839	1.1950	0.1270	0.040
H(3)	4e	1.0757	0.8748	0.3821	0.038
H(2A)	4e	0.9234	0.8904	0.1564	0.036
H(2B)	4e	0.8057	1.0540	0.1591	0.036
H(5)	4e	1.0839	0.7699	0.0163	0.053
H(6)	4e	1.0901	0.4868	0.0351	0.057
H(7)	4e	1.1294	0.4307	0.0891	0.054
H(8)	4e	1.1656	0.6545	0.1258	0.043
H(10A)	4e	1.2001	0.9570	0.3370	0.046
H(10B)	4e	1.0397	1.0731	0.3286	0.046
H(13)	4e	0.8920	1.2279	0.4873	0.050
H(14)	4e	0.8908	1.5139	0.4697	0.052
H(15)	4e	0.8712	1.5754	0.4153	0.048
H(16)	4e	0.8531	1.3549	0.3775	0.038
H(1W)	4e	0.998(7)	0.351(3)	0.269(1)	0.09(2)
H(2W)	4e	0.985(7)	0.477(6)	0.2942(5)	0.07(2)
H(3W)	4e	1.026(6)	0.418(3)	0.198(1)	0.09(2)
H(4W)	4e	0.915(4)	0.542(6)	0.1840(9)	0.07(2)
H(5W)	4e	0.667(5)	0.772(4)	0.238(1)	0.07(2)
H(6W)	4e	0.667(6)	0.618(6)	0.255(1)	0.10(2)
H(7W)	4e	1.323(5)	0.670(5)	0.2584(5)	0.05(1)
H(8W)	4e	1.344(5)	0.584(4)	0.2294(8)	0.05(1)

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)	4e	1.00552(6)	0.69474(6)	0.24015(1)	0.0217(2)	0.0195(2)	0.0264(2)	−0.0006(2)	0.0008(2)	−0.0001(2)
S(1)	4e	1.1943(1)	1.0130(1)	0.12305(2)	0.0284(4)	0.0261(4)	0.0287(4)	0.0005(3)	0.0017(3)	−0.0002(3)
S(2)	4e	0.8269(1)	0.99591(9)	0.37871(2)	0.0276(4)	0.0221(3)	0.0260(4)	0.0004(3)	−0.0035(3)	−0.0029(3)
O(1)	4e	0.9570(4)	0.9320(3)	0.21528(6)	0.054(2)	0.034(1)	0.040(1)	−0.003(1)	0.000(1)	0.013(1)
O(2)	4e	1.0737(3)	1.1817(3)	0.20140(6)	0.050(2)	0.028(1)	0.034(1)	−0.006(1)	−0.009(1)	−0.0016(9)
O(3)	4e	1.2721(3)	0.9240(4)	0.15002(6)	0.037(1)	0.049(2)	0.039(1)	0.011(1)	−0.008(1)	0.003(1)
O(4)	4e	1.2873(3)	1.1439(3)	0.10618(6)	0.041(1)	0.034(1)	0.045(1)	−0.016(1)	0.007(1)	−0.004(1)
O(5)	4e	1.0010(4)	1.1561(3)	0.06153(7)	0.064(2)	0.024(1)	0.056(2)	0.008(1)	0.004(1)	0.004(1)
O(6)	4e	1.1687(5)	1.0913(4)	0.02272(7)	0.123(3)	0.055(2)	0.046(2)	−0.004(2)	0.033(2)	0.017(2)
O(7)	4e	1.0599(3)	0.8587(3)	0.28176(5)	0.039(1)	0.029(1)	0.024(1)	−0.003(1)	0.0053(9)	−0.0016(8)
O(8)	4e	0.9321(4)	0.6984(3)	0.31921(6)	0.057(2)	0.039(1)	0.036(1)	−0.021(1)	0.014(1)	−0.007(1)
O(9)	4e	0.7503(3)	1.0876(3)	0.35155(6)	0.052(2)	0.040(1)	0.038(1)	0.008(1)	−0.021(1)	−0.002(1)
O(10)	4e	0.7333(3)	0.8586(3)	0.39348(6)	0.038(1)	0.030(1)	0.049(1)	−0.013(1)	0.006(1)	−0.006(1)
O(11)	4e	0.9989(4)	0.8496(3)	0.44210(7)	0.064(2)	0.026(1)	0.056(2)	0.011(1)	0.005(1)	0.001(1)
O(12)	4e	0.8142(5)	0.9063(4)	0.47849(7)	0.111(3)	0.056(2)	0.048(2)	−0.001(2)	0.031(2)	0.020(2)
O(13)	4e	0.9957(3)	0.4616(3)	0.27429(6)	0.036(1)	0.025(1)	0.038(1)	−0.001(1)	0.003(1)	0.0001(9)
O(14)	4e	1.0025(3)	0.5275(3)	0.19724(6)	0.043(1)	0.032(1)	0.041(1)	0.006(1)	−0.014(1)	−0.007(1)
O(15)	4e	0.7287(3)	0.6782(4)	0.24136(7)	0.022(1)	0.040(2)	0.071(2)	0.005(1)	0.007(1)	0.020(1)
O(16)	4e	1.2847(3)	0.6662(3)	0.23833(5)	0.024(1)	0.032(1)	0.028(1)	0.0023(9)	−0.0001(9)	−0.0028(9)
N(1)	4e	1.0203(4)	1.0991(4)	0.13532(6)	0.039(2)	0.035(2)	0.026(1)	0.013(1)	0.005(1)	0.004(1)
N(2)	4e	1.0960(4)	1.0575(4)	0.04760(7)	0.060(2)	0.027(1)	0.029(1)	−0.004(1)	0.001(1)	0.003(1)
N(3)	4e	1.0117(4)	0.9296(4)	0.36817(6)	0.035(2)	0.038(2)	0.021(1)	0.009(1)	0.002(1)	−0.002(1)
N(4)	4e	0.8969(4)	0.9447(4)	0.45506(7)	0.056(2)	0.030(2)	0.028(1)	−0.002(1)	0.000(1)	0.002(1)
C(1)	4e	0.9940(4)	1.0452(4)	0.19467(7)	0.028(2)	0.023(1)	0.027(1)	0.002(1)	0.002(1)	0.000(1)
C(2)	4e	0.9241(4)	1.0141(4)	0.16054(7)	0.028(2)	0.033(2)	0.028(2)	−0.001(1)	−0.000(1)	−0.004(1)
C(3)	4e	1.1435(4)	0.8499(4)	0.09367(7)	0.026(2)	0.020(1)	0.033(2)	0.002(1)	0.007(1)	0.000(1)
C(4)	4e	1.1154(4)	0.8810(4)	0.06054(8)	0.035(2)	0.021(1)	0.034(2)	−0.000(1)	0.006(1)	0.000(1)
C(5)	4e	1.0984(6)	0.7470(5)	0.03838(9)	0.061(2)	0.035(2)	0.037(2)	0.002(2)	0.000(2)	−0.009(2)
C(6)	4e	1.1033(5)	0.5781(5)	0.0496(1)	0.051(2)	0.027(2)	0.064(3)	−0.001(2)	−0.002(2)	−0.014(2)
C(7)	4e	1.1271(5)	0.5447(4)	0.0818(1)	0.044(2)	0.017(2)	0.073(3)	0.001(1)	−0.003(2)	0.000(2)
C(8)	4e	1.1482(4)	0.6793(4)	0.10388(9)	0.034(2)	0.025(2)	0.048(2)	0.003(1)	0.000(2)	0.009(1)
C(9)	4e	1.0138(4)	0.8272(4)	0.31069(7)	0.028(2)	0.029(2)	0.029(2)	−0.001(1)	0.003(1)	−0.004(1)
C(10)	4e	1.0753(5)	0.9586(5)	0.33582(8)	0.048(2)	0.039(2)	0.029(2)	−0.014(2)	0.013(1)	−0.009(1)
C(11)	4e	0.8631(4)	1.1562(4)	0.40922(7)	0.023(1)	0.019(1)	0.028(1)	0.003(1)	0.001(1)	−0.002(1)
C(12)	4e	0.8786(4)	1.1220(4)	0.44239(7)	0.033(2)	0.022(1)	0.028(2)	0.001(1)	0.002(1)	−0.002(1)
C(13)	4e	0.8859(5)	1.2535(5)	0.46522(9)	0.059(2)	0.037(2)	0.030(2)	0.003(2)	0.002(2)	−0.010(1)
C(14)	4e	0.8840(5)	1.4242(5)	0.45466(9)	0.053(2)	0.028(2)	0.050(2)	0.002(2)	0.000(2)	−0.014(2)
C(15)	4e	0.8721(5)	1.4608(4)	0.4222(1)	0.043(2)	0.018(1)	0.059(2)	0.004(1)	0.001(2)	−0.005(1)
C(16)	4e	0.8615(4)	1.3281(4)	0.39949(8)	0.034(2)	0.023(2)	0.038(2)	0.001(1)	−0.003(1)	0.003(1)

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