Crystal structure of tetra(4,4'-dipyridyl sulfide-*N*)-di(*N*-isothiocyanato)manganese(II), $\text{Mn}(\text{NCS})_2(\text{C}_{10}\text{H}_8\text{N}_2\text{S})_4$

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Abstract

$\text{C}_{42}\text{H}_{32}\text{MnN}_{10}\text{S}_6$, triclinic, $P\bar{1}$ (no. 2), $a = 9.666(1)$ Å, $b = 11.077(2)$ Å, $c = 11.352(2)$ Å, $\alpha = 87.663(2)^\circ$, $\beta = 76.871(2)^\circ$, $\gamma = 67.682(2)^\circ$, $V = 1093.6$ Å³, $Z = 1$, $R_g(F) = 0.053$, $wR_{\text{ref}}(F^2) = 0.148$, $T = 296$ K.

Source of material

Manganese(II) acetate tetrahydrate (0.123 g, 0.5 mmol) and NH_4SCN (0.076 g, 1 mmol) were refluxed in anhydrous methanol (10 mL) for 50 min, then were simultaneously added 20 mL methanol solution of freshly distilled salicylaldehyde and ethylenediamine at molar ratio 2 : 1. The mixture was stirred for 5 h, 4,4'-bipyridyl sulfide (0.11 g, 0.5 mmol) was added, the pH value was adjusted to 5 with CH_3COOH solution, and the mixture was further stirred for 2 h, then filtered. The resulting clear solution was diffused with diethyl ether vapor at room temperature for three weeks, yellow crystals were collected by filtration and dried in air (yield 0.156 g, 37 %). Elemental analysis — found: C, 54.61 %; H, 3.43 %; N, 15.19 %; S, 20.74 %; calculated for $\text{C}_{42}\text{H}_{32}\text{N}_{10}\text{S}_6\text{Mn}$: C, 54.58 %; H, 3.49 %; N, 15.15 %; S, 20.82 %. IR data are available in the CIF.

Discussion

The chemistry of complexes with multi-dentate ligands such as 4,4'-bipyridyl sulfide has gained much interest because of their use as models in biological systems, organic reactions, materials [1–4]. 4,4'-Bipyridyl sulfide is an excellent rod-like bifunctional ligand and has been extensively employed as the rigid organic building block for the construction of the infinite 1D, 2D, 3D polymeric frameworks [5–7]. Manganese is an essential trace element, forming the active sites of a number of metalloproteins [8–10]. Potential importance of manganese complexes is evidenced by the realization that the active site in photosystem II (PSII) is a tetranuclear manganese complex [11]. Manganese has a vital role in many enzymatic systems such as superoxide dismutase, peroxidase, dioxygenase and catalase in which mononuclear manganese active centers are present [12].

The title crystal structure consists of manganese complex with isothiocyanato anions and 4,4'-bipyridyl sulfide molecules. The salicylaldehyde and ethylenediamine are not present in the final product. The central Mn(II) ion is coordinated by two isothiocyanato groups and two 4,4'-bipyridyl sulfide molecules in monodentate mode. The Mn(II) ion adopts a slightly distorted octahedral coordination in a MnN_6 mode, among which the two nitrogen atoms are from the coordinated isothiocyanato anions, and the other four nitrogen atoms are from two 4,4'-bipyridyl sulfide molecules, respectively. The nitrogen atoms from the two isothiocyanato groups occupy the axial positions, and four other nitrogen atoms occupy the equatorial positions. The bond distances of Mn1-N2 , Mn1-N3 , Mn1-N5 were found to be 2.363(3) Å, 2.287(3) Å, 2.158(3) Å, respectively, in which $d(\text{Mn-N}_{\text{bipyridyl}})$ are longer than $d(\text{Mn-N}_{\text{isothiocyanato}})$, and the $d(\text{Mn-N})$ are comparable with those in corresponding Mn(II) complexes involving 4,4'-bipyridine [11]. The angle $\angle \text{N5-C21-S3}$ is $178.8(3)^\circ$, which means the isothiocyanato anion is nearly linear. The torsion angles of N2-Mn1-N3-C14 , N2-Mn1-N3-C14 , N5-Mn1-N5-C21 , N3-Mn1-N5-C21 , and Mn1-N5-C21-S3 are $-55.7(3)^\circ$, $124.3(3)^\circ$, $157(100)^\circ$, $20.7(15)^\circ$, $56(17)^\circ$, respectively (symmetry code i: $-x, -y+1, -z+1$). All the atoms of the mean pyridinyl ring defined by C1/C2/C3/C4/C5/N1 are almost planar with the average deviation of 0.054 Å, and the maximum deviation are -0.096 Å for C4. As to the other ring $\text{C6/C7/C8/C9/C10/N2}$, all the atoms are almost strictly planar with the average and the maximum deviation from pyridine ring are 0.011 Å and -0.019 Å of C8, respectively. In the molecule of 4,4'-bipyridyl sulfide, the dihedral angle between two pyridine rings is 122.2° , and this is comparable with the assembly in the other complex containing 4,4'-dipyridine [13].

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Table 1. Data collection and handling.

Crystal:	yellow block, size 0.37 × 0.42 × 0.49 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	6.32 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART CCD, ϕ/ω
2 $\theta_{\max}$:	51°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8188, 4040
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2914
$N(\text{param})_{\text{refined}}$:	268
Programs:	SHELXS-97 [14], SHELXL-97 [15], SHELXTL [16]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	2i	−0.7180	0.7548	0.1183	0.096
H(2)	2i	−0.4943	0.7772	0.1251	0.084
H(4)	2i	−0.3085	0.5889	−0.1986	0.078
H(5)	2i	−0.5403	0.5806	−0.1974	0.096
H(6)	2i	0.0858	0.6377	0.2538	0.062
H(7)	2i	0.0165	0.7128	0.0768	0.064
H(9)	2i	−0.2823	0.5353	0.1448	0.070
H(10)	2i	−0.2054	0.4678	0.3192	0.067
H(11)	2i	0.3565	0.3541	0.4811	0.066
H(12)	2i	0.5661	0.1707	0.4078	0.075
H(14)	2i	0.0933	0.2294	0.3519	0.067
H(15)	2i	0.2957	0.0437	0.2710	0.080
H(16)	2i	0.9680	0.1205	0.1059	0.160
H(17)	2i	0.7574	0.0774	0.1140	0.124
H(19)	2i	0.8344	−0.1149	0.4085	0.103
H(20)	2i	1.0475	−0.0659	0.3876	0.122

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Mn(1)	1g	0	½	½	0.0373(4)	0.0530(4)	0.0460(4)	−0.0210(3)	−0.0109(3)	0.0064(3)
S(1)	2i	0.6081(1)	−0.0642(1)	0.2751(2)	0.0615(7)	0.0729(8)	0.185(2)	−0.0236(6)	−0.0029(8)	−0.0526(9)
S(2)	2i	−0.1969(1)	0.7012(1)	−0.04363(8)	0.0584(6)	0.0987(8)	0.0494(5)	−0.0391(5)	−0.0197(4)	0.0196(5)
S(3)	2i	0.3805(2)	0.7010(2)	0.3879(1)	0.0936(9)	0.168(1)	0.0919(9)	−0.099(1)	−0.0255(7)	0.0272(9)
N(1)	2i	−0.6527(4)	0.6654(4)	−0.0395(4)	0.076(2)	0.100(3)	0.085(3)	−0.048(2)	−0.039(2)	0.033(2)
N(2)	2i	−0.0547(3)	0.5475(3)	0.3069(2)	0.043(2)	0.055(2)	0.044(2)	−0.020(1)	−0.011(1)	0.002(1)
N(3)	2i	0.2038(3)	0.3118(3)	0.4237(2)	0.046(2)	0.061(2)	0.048(2)	−0.022(1)	−0.013(1)	0.002(1)
N(4)	2i	1.0309(5)	0.0328(5)	0.2438(6)	0.078(3)	0.136(4)	0.147(5)	−0.059(3)	−0.030(3)	0.001(4)
N(5)	2i	0.1509(3)	0.6058(3)	0.4658(3)	0.056(2)	0.073(2)	0.068(2)	−0.035(2)	−0.021(2)	0.013(2)
C(1)	2i	−0.6346(5)	0.7218(5)	0.0526(4)	0.053(2)	0.106(4)	0.078(3)	−0.028(2)	−0.014(2)	0.013(3)
C(2)	2i	−0.4999(4)	0.7353(4)	0.0580(4)	0.058(2)	0.095(3)	0.060(2)	−0.027(2)	−0.020(2)	−0.001(2)
C(3)	2i	−0.3742(4)	0.6860(4)	−0.0372(3)	0.053(2)	0.064(2)	0.049(2)	−0.024(2)	−0.020(2)	0.013(2)
C(4)	2i	−0.3909(5)	0.6255(4)	−0.1328(3)	0.070(3)	0.078(3)	0.054(2)	−0.032(2)	−0.024(2)	0.012(2)
C(5)	2i	−0.5306(6)	0.6196(5)	−0.1303(4)	0.102(4)	0.091(3)	0.075(3)	−0.055(3)	−0.045(3)	0.019(2)
C(6)	2i	0.0090(4)	0.6182(3)	0.2323(3)	0.047(2)	0.061(2)	0.054(2)	−0.025(2)	−0.018(2)	0.003(2)
C(7)	2i	−0.0321(4)	0.6642(3)	0.1255(3)	0.053(2)	0.063(2)	0.051(2)	−0.030(2)	−0.012(2)	0.009(2)
C(8)	2i	−0.1463(4)	0.6371(3)	0.0917(3)	0.044(2)	0.058(2)	0.040(2)	−0.018(2)	−0.012(1)	0.002(2)
C(9)	2i	−0.2086(4)	0.5596(4)	0.1658(3)	0.055(2)	0.077(3)	0.059(2)	−0.038(2)	−0.023(2)	0.013(2)
C(10)	2i	−0.1608(4)	0.5189(4)	0.2703(3)	0.054(2)	0.073(2)	0.053(2)	−0.036(2)	−0.016(2)	0.011(2)
C(11)	2i	0.3442(4)	0.2903(4)	0.4385(3)	0.048(2)	0.058(2)	0.060(2)	−0.018(2)	−0.017(2)	−0.006(2)
C(12)	2i	0.4707(4)	0.1807(4)	0.3950(4)	0.046(2)	0.064(2)	0.077(3)	−0.017(2)	−0.021(2)	−0.012(2)
C(13)	2i	0.4549(4)	0.0848(4)	0.3318(4)	0.052(2)	0.058(2)	0.082(3)	−0.021(2)	−0.008(2)	−0.013(2)
C(14)	2i	0.1902(4)	0.2177(4)	0.3624(3)	0.049(2)	0.068(2)	0.058(2)	−0.029(2)	−0.014(2)	−0.000(2)
C(15)	2i	0.3105(4)	0.1054(4)	0.3145(4)	0.059(2)	0.069(3)	0.079(3)	−0.032(2)	−0.011(2)	−0.017(2)
C(16)	2i	0.9415(8)	0.0712(7)	0.1688(7)	0.142(6)	0.161(6)	0.139(5)	−0.102(5)	−0.045(5)	0.064(5)
C(17)	2i	0.8140(6)	0.0469(5)	0.1728(5)	0.103(4)	0.112(4)	0.123(4)	−0.054(3)	−0.063(3)	0.054(4)
C(18)	2i	0.7698(4)	−0.0229(4)	0.2643(4)	0.051(2)	0.053(2)	0.083(3)	−0.012(2)	−0.010(2)	−0.009(2)
C(19)	2i	0.8591(6)	−0.0657(5)	0.3448(4)	0.102(4)	0.088(3)	0.070(3)	−0.040(3)	−0.015(3)	0.004(2)
C(20)	2i	0.9875(6)	−0.0357(6)	0.3311(5)	0.088(4)	0.109(4)	0.109(4)	−0.021(3)	−0.053(3)	0.000(3)
C(21)	2i	0.2466(4)	0.6455(3)	0.4346(3)	0.048(2)	0.064(2)	0.043(2)	−0.026(2)	−0.017(2)	0.005(2)

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