Crystal structure of (μ_3-ethylenedithiodiacetato-κ^6-*S*,*S*′,*O*,*O*′:*O*″:*O*‴)manganese(II), $Mn(C_6H_8O_4S_2)$

Zhong-Xiang Du* and Gui-Ying Zhang

Luoyang Normal University, College of Chemistry and Chemical Engineering, Luoyang 471022, Henan, P. R. China

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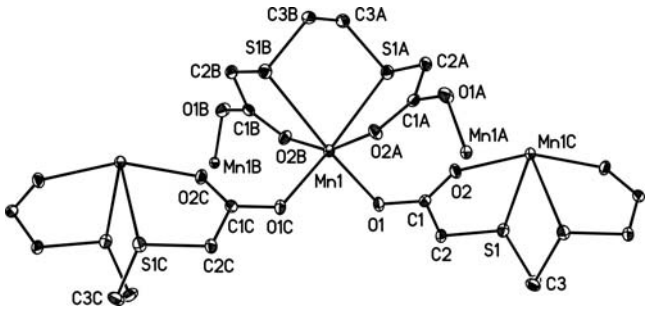

Abstract

$C_6H_8MnO_4S_2$, orthorhombic, $P2_12_12$ (no. 18), a = 9.310(2) Å, b = 5.7038(9) Å, c = 8.259(1) Å, V = 438.6 Å^3, Z = 2, $R_{gt}(F)$ = 0.016, $wR_{ref}(F^2)$ = 0.043, T = 294 K.

Source of material

$Mn(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol, 0.123 g) and ligand ethylenedithiodiacetic acid (H_2edtda, 0.5 mmol, 0.105 g) were dissolved in 20 mL H_2O and then the pH of the obtained mixture was adjusted with KOH (0.1 M) to pH = 5.0. After that, the solution was sealed in a 25 mL Teflon-lined reactor and kept under autogeneous pressure at 403 K for 5 days. After cooling to room temperature at a rate of 279 K/h, colorless block-shaped crystals of the title compound suitable for X-ray diffraction were obtained (yield 56 mg, 43 %, based on Mn). Elemental analysis — found: C, 27.41 %; H, 3.02 %; S, 24.28 %; calculated for $C_6H_8MnO_4S_2$: C, 27.36 %; H, 3.04 %; S, 24.32 %.

Experimental details

The H atoms bonded to C atoms were positioned geometrically in the riding-model approximation, with d(C—H) = 0.97 Å and U_{iso}(H) = 1.2 U_{eq}(C).

Discussion

In the development of coordination chemistry, the studies of chemical properties of transition metal complexes including coordinating carboxylate ligands is a continuously interesting subject. Polycarboxylic acids and polycarboxylate ligands are used as linking agents of solid aggregates. The existence of two or more carboxylate groups in different orientations allows the construction of one-, two- or three-dimensional frameworks, which can be further reinforced by the presence of intermolecular hydrogen bonds, π-π interactions and other weak interacting forces [1-5]. One example of an acid that contains two carboxylic groups is H_2edtda. Besides the two carboxylic, it also has two thio groups. Therefore, it is a potentially hexa-dentate ligand and a great number of metal complexes of it may be synthesized. In fact, there are several reports on the crystal structures of such coordination compounds [6-10].

The asymmetric unit of the title crystal structure contains one Mn(II) ion and one fully deprotonated edtda^{2-} ligand. The Mn(II) is six-coordinated with a significantly distorted MnO_4S_2 octahedral environment formed by S1A, S1B and O2A, O2B from one edtda^{2-} ligand and two bridging carboxylate O atoms (O1, O1C) of another two different ligands (symmetry codes A: 1.5–x,0.5+y,2–z; B: 0.5+x,2.5–y,2–z; C: 2–x,3–y,z). O2A, O2B atoms occupy the axial positions, with ∠O2A–Mn1–O2B = 157.32(7)°. The other axial angles are both less than 100°. The four atoms (S1A, S1B, O1, O1C) define the equatorial plane. The Mn(II) ion is just located in the equatorial plane.

The edtda^{2-} ligand coordinates three different Mn(II) ions through *S*,*S*′,*O*,*O*′-tetradentate chelation and mono-dentate bridging coordination modes by another two carboxylate O atoms. For the former, it forms three five-membered chelate rings and the dihedral angles of the least-squares plane between these chelate rings are 89.9° (Mn1/S1A/C2A/C1A/O2A and Mn1/S1A/C3A/C3B/S1B) and 81.9° (Mn1/S1A/C2A/C1A/O2A and Mn1/S1B/C2B/C1B/O2B), respectively. For the latter, the bridging carboxylate O atoms link two neighbouring Mn(II) centres and thus a two-dimensional (4,4) network layer structure forms in (001) plane.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.07 × 0.23 × 0.37 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	19.55 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II CCD, φ/ω
$2\theta_{max}$:	50.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3254, 802
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 778
$N(param)_{refined}$:	60
Programs:	SHELXS-97, SHELXL-97 [11]

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

Atom	Site	x	y	z	U_{iso}
H(2A)	4*c*	0.8691	0.8616	0.7424	0.026
H(2B)	4*c*	0.7891	1.0191	0.6166	0.026
H(3A)	4*c*	0.5718	0.8389	0.4706	0.034
H(3B)	4*c*	0.4323	0.7803	0.5676	0.034

* Correspondence author (e-mail: dzx101012@126.com)

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*a*	0	½	0.01127(4)	0.0121(2)	0.0234(2)	0.0174(2)	0.0005(2)	0	0
S(1)	4*c*	0.62853(4)	0.76616(7)	0.73767(6)	0.0187(2)	0.0218(2)	0.0244(3)	–0.0011(2)	–0.0010(2)	–0.0023(2)
O(1)	4*c*	0.9045(1)	1.2782(2)	0.8370(2)	0.0169(6)	0.0372(8)	0.0252(8)	–0.0098(6)	0.0038(5)	–0.0062(6)
O(2)	4*c*	0.6866(1)	1.2046(2)	0.9379(2)	0.0160(6)	0.0263(7)	0.0251(7)	–0.0036(5)	0.0054(5)	–0.0047(6)
C(1)	4*c*	0.7889(2)	1.1615(3)	0.8442(2)	0.0161(9)	0.0234(9)	0.018(1)	–0.0004(8)	–0.0028(8)	0.0026(7)
C(2)	4*c*	0.7839(2)	0.9564(3)	0.7257(2)	0.0140(8)	0.0282(9)	0.0222(9)	–0.0020(7)	0.0002(8)	–0.0029(9)
C(3)	4*c*	0.5203(2)	0.8715(4)	0.5702(2)	0.022(1)	0.044(1)	0.019(1)	0.0034(9)	–0.0040(9)	–0.0103(9)

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References

1. Huang, Y. G.; Wang, X. T.; Jiang, F. L.; Gao, S.; Wu, M. Y.; Gao, Q.; Wei, W.; Hong, M. C.: Cobalt-Lanthanide Coordination Polymers Constructed with Metalloligands: A Ferromagnetic Coupled Quasi-1D Dy^{3+} Chain Showing Slow Relaxation. Chem. Eur. J. **14** (2008) 10340-10347.
2. Baggio, R.; Garland, M. T.; Moreno, Y.; Peña, O.; Perec, M.; Spodine, E.: Synthesis, structure and magnetic properties of the 2,2′-oxydiacetato-bridged Cu(II)-Ln(III) complexes $[SV3Ln_2(oda)_6(H_2O)_6 \cdot 12H_2O]_n$ (Ln = Y, Gd, Eu, Nd, Pr). Dalton Trans. (2000) 2061-2066.
3. Kong, X. J.; Ren, Y. P.; Long, L. S.; Huang, R. B.; Zheng, L. S.; Kurmoo, M.: Influence of reaction conditions on the channel shape of 3*d*-4*f* heterometallic metal-organic framework. CrystEngComm **10** (2008) 1309-1314.
4. Jiang, X. Y.; Chen. W. Z.: 2D Heterometallic Complexes with Infinite Ln Chains: Synthesis, Crystal Structure and Magnetic Properties. Chin. J. Inorg. Chem. **24** (2008) 1650-1656.
5. Manna, S. C.; Konar, S.; Zangrando, E.; Ribas, J.; Chaudhuri, N. R.: 3D Heterometallic (3*d*-4*f*) coordination polymers: A ferromagnetic interaction in a Gd(III)-Cu(II) couple. Polyhedron **26** (2007) 2507-2516.
6. Podlahova, J.; Loub, J.; Nocak, C.: The Determination of the Crystal Structure of Nickel Ethylenedithiodiacetate Dihydrate (NEDDD). Acta Crystallogr. **B28** (1972) 1623-1626.
7. Yonemura, T.; Shibuya, K.; Ama, T.; Kawaguchi, H.; Okamoto, K.; Hidaka, J.; Yasui, T.: Three-Membered -$SCoCH_2$ Chelate Ring Complex Formed by Photodecarboxylation Reaction of Optically Active *trans*(O)-[Co(edtda)(en)]Cl (edtda = Ethylenedithiodiacetate). Inorg. Chem. **38** (1999) 3244-3247.
8. Pietzsch, H. J.; Gupta, A.; Reisgys, M.; Drews, A.; Seifert, S.; Syhre, R.; Spies, H.; Alberto, R.; Abram, U.; Schubiger, P. A.; Johannsen, B.: Chemical and Biological Characterization of Technetium(I) and Rhenium(I) Tricarbonyl Complexes with Dithioether Ligands Serving as Linkers for Coupling the $Tc(CO)_3$ and $Re(CO)_3$ Moieties to Biologically Active Molecules. Bioconjugate Chem. **11** (2000) 414-424.
9. Van der Meer, H.: Crystal Structure of the Copper(I) Complex of 2,5-Dithiahexane-1 ,6-dicarboxylic Acid. J. Chem. Soc., Dalton Trans. (1973) 1-2.
10. Helder, J.; Birker, P. J. M. W. L.; Verschoor, G. C.; Reedijk, J.: Strong and Symmetric Hydrogen Bonding in Coordination Compounds of Carboxylic Acid Derivatives; the Crystal Structure of (3,6-dithiaoctanedioato-*S*,*S*′-(3,6-dithiaoctanedioic acid-*S*,*S*′)copper(I) Redetermined at 173 K. Inorg. Chim. Acta **85** (1984) 169-173.
11. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.