Jin-Feng Chu*

The crystal structure of bis(isothiocyanato- κ^1N)-(methanol- κ^1O)-[2-morpholine-4-yl-4,6-di(pyrazol-1-yl)-1,3,5-triazine- κ^3N,N',N''] manganese(II), $C_{16}H_{18}MnN_{10}O_2S_2$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.80 × 0.30 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.83 mm ⁻¹
Diffractometer, scan mode:	Xcalibur-Gemini, ω
$\theta_{\max}$, completeness:	26.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6937, 4291, 0.031
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3706
$N(\text{param})_{\text{refined}}$:	284
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	−0.1179(3)	0.3320(2)	0.37881(19)	0.0205(5)
H1	−0.1143	0.2544	0.3747	0.025*
C2	−0.2647(3)	0.4148(2)	0.4309(2)	0.0239(5)
H2A	−0.3722	0.4027	0.4661	0.029*
C3	−0.2163(3)	0.5162(2)	0.41887(19)	0.0216(5)
H3	−0.2846	0.5877	0.4443	0.026*
C4	0.0566(3)	0.56854(19)	0.32625(17)	0.0139(4)
C5	0.3093(3)	0.59727(19)	0.23619(17)	0.0148(4)
C6	0.6226(3)	0.5949(2)	0.15773(19)	0.0209(5)
H6	0.6233	0.6710	0.1668	0.025*
C7	0.7625(3)	0.5082(2)	0.1168(2)	0.0247(5)
H7	0.8782	0.5130	0.0919	0.030*
C8	0.6974(3)	0.4096(2)	0.1196(2)	0.0236(5)
H8	0.7658	0.3375	0.0959	0.028*
C9	0.0998(3)	0.74670(19)	0.31087(17)	0.0149(4)
C10	−0.1341(3)	0.90944(19)	0.39280(18)	0.0186(5)
H10A	−0.1205	0.9537	0.4527	0.022*
H10B	−0.1877	0.8483	0.4251	0.022*
C11	−0.2513(3)	0.98643(19)	0.31675(19)	0.0196(5)
H11A	−0.2694	0.9411	0.2591	0.024*
H11B	−0.3665	1.0209	0.3585	0.024*
C12	0.1249(3)	0.94790(19)	0.27484(19)	0.0187(5)
H12A	0.2350	0.9114	0.2290	0.022*
H12B	0.1527	0.9913	0.3305	0.022*
C13	−0.0002(3)	1.0289(2)	0.20327(18)	0.0194(5)
H13A	0.0519	1.0911	0.1722	0.023*
H13B	−0.0154	0.9870	0.1421	0.023*
C14	0.1349(3)	0.26710(19)	0.03082(18)	0.0165(5)
C15	0.4709(3)	0.22243(19)	0.45325(19)	0.0179(5)
C16	0.5965(3)	0.1343(2)	0.0441(2)	0.0331(6)

<https://doi.org/10.1515/ncrs-2020-0161>

Received March 26, 2020; accepted May 17, 2020; available online June 18, 2020

Abstract

$C_{16}H_{18}MnN_{10}O_2S_2$, triclinic, $P\bar{1}$ (no. 2), $a = 7.8738(7)$ Å, $b = 12.012(2)$ Å, $c = 12.182(2)$ Å, $\alpha = 85.635(16)^\circ$, $\beta = 81.077(14)^\circ$, $\gamma = 74.540(14)^\circ$, $V = 1096.3(3)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0353$, $wR_{\text{ref}}(F^2) = 0.0896$, $T = 96.5$ K.

CCDC no.: 2004283

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

2-Morpholine-4-yl-4,6-di(pyrazol-1-yl)-1,3,5-triazine (mpt) was prepared according to the literature [5]. A solution of mpt (0.1 mmol, 0.030 g) in methanol (2 mL) was added to a

*Corresponding author: Jin-Feng Chu, State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China, e-mail: chuif@mail.buct.edu.cn. <https://orcid.org/0000-0003-2818-3630>

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H16A	0.6846	0.1676	0.0008	0.050*
H16B	0.4932	0.1497	0.0070	0.050*
H16C	0.6442	0.0523	0.0527	0.050*
Mn1	0.31874(4)	0.33195(3)	0.22784(3)	0.01446(11)
N1	0.0134(2)	0.37752(15)	0.33668(15)	0.0158(4)
N2	−0.0476(2)	0.49210(15)	0.36209(14)	0.0146(4)
N3	0.2144(2)	0.52009(15)	0.26725(14)	0.0141(4)
N4	0.4804(2)	0.54796(16)	0.18301(15)	0.0162(4)
N5	0.5254(2)	0.43271(16)	0.16038(15)	0.0182(4)
N6	−0.0065(2)	0.67686(15)	0.35332(14)	0.0147(4)
N7	0.2646(2)	0.70880(15)	0.25099(14)	0.0145(4)
N8	0.0401(2)	0.85940(15)	0.32927(15)	0.0162(4)
N9	0.4094(2)	0.25665(16)	0.37471(16)	0.0199(4)
N10	0.1872(2)	0.29567(17)	0.10488(15)	0.0197(4)
O1	−0.17079(19)	1.07687(13)	0.26627(13)	0.0201(3)
O2	0.5484(2)	0.18365(14)	0.15060(13)	0.0233(4)
H2	0.632(2)	0.161(2)	0.1898(14)	0.027*
S1	0.55860(8)	0.17609(5)	0.56665(5)	0.02377(15)
S2	0.06147(8)	0.22747(6)	−0.07341(5)	0.02541(15)

solution of MnCl₂·4 H₂O (0.1 mmol, 0.020 g) in methanol (5 mL), and then an excess of a solution of potassium thiocyanate in methanol (2 mL) was added. The mixture was filtered and the filtrate was set aside to crystallize at ambient temperature. Colourless crystals of the title compound were obtained.

Experimental details

A suitable single crystal was mounted onto the end of a thin glass fiber using Fomblin oil. C-bound H atoms were geometrically placed (C–H = 0.93–0.97 Å) and refined as riding with *U*_{iso}(H) = 1.2–1.5 *U*_{eq}(C). The O-bound H-atom was located in a difference Fourier map but was refined with a distance restraint O–H = 0.85 ± 0.01 Å, and with *U*_{iso}(H) set to 1.5 *U*_{eq}(O).

Comment

In the past decades, the crystal materials of supramolecular complexes have attracted great interest due to their potential applications in several fields [6–8]. The structure design and synthesis of new manganese complexes are of general interest and beneficial to the research of magnetic materials [9, 10]. In the course of our efforts to explore new supramolecular architectures using mpt [11] and NCS[−] ligands, the title compound was successfully synthesized and determined by single-crystal X-ray analysis.

The molecular unit comprises one Mn(II) cation, one mpt ligand, two NCS[−] anions and one methanol ligand. Each

Mn(II) center is six-coordinated with a distorted octahedral environment by five N atoms and one O atom. The bond lengths and angles within structure are unexceptional. In details, the Mn–N bond lengths range from 2.0802(18) to 2.5015(18) Å, and the Mn–N_{mpt} bond distances are longer than the Mn–N_{NCS} distances. The Mn–O bond length is 2.3105(17) Å. The bond angles around Mn(II) range from 67.21(6)° to 148.98(6)°.

As seen from the lower view of the figure, the adjacent molecular units are linked by the intermolecular O–H···O hydrogen-bond [O2–H2···O1ⁱ: H2···O1ⁱ = 1.94 Å, O2···O1ⁱ = 2.7747(22) Å with angle at H2 = 167.6° for (i) *x* + 1, *y* − 1, *z*], and the one-dimensional chain is formed.

Acknowledgements: This work was supported by the Fundamental Research Funds for the Central Universities (XK1802-6).

References

1. Agilent Technologies: CrysAlis^{Pro}. Agilent Technologies, Version 1.171.35.11. Agilent Technologies UK Ltd, Oxford, UK (2011).
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42** (2009) 339–341.
3. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
4. Sheldrick, G. M.: SHELXL-97, Program for the Refinement of Crystal Structures. University of Göttingen, Göttingen, Germany (1997).
5. Chen, W.; Chu, J. F.; Wang, Y. Q.: Synthesis, characterization and preliminary reactivity behaviors with transitional metals of a new polydentate *N*-donor ligand. *J. Mol. Struct.* **1068** (2014) 237–244.
6. Zhang, Y.; Ali, B.; Wu, J.; Guo, M.; Yu, Y.; Tang, J.; Zhang, Y.; Liu, Z.; Tang, J.: Construction of metallosupramolecular coordination complexes: from lanthanide helicates to octahedral cages showing single-molecule magnet behavior. *Inorg. Chem.* **58** (2019) 3167–3174.
7. Freire, C.; Nunes, M.; Pereira, C.; Fernandes, D. M.; Peixoto, A. F.; Rocha, M.: Metallo(salen) complexes as versatile building blocks for the fabrication of molecular materials and devices with tuned properties. *Coord. Chem. Rev.* **394** (2019) 104–134.
8. Wang, A.; Fan, R.; Dong, Y.; Chen, W.; Song, Y.; Wang, P.; Hao, S.; Liu, Z.; Yang, Y.: (*E*)-4-Methyl-*N*-((quinolin-2-yl)ethylidene)aniline as ligand for IIB supramolecular complexes: synthesis, structure, aggregation-induced emission enhancement and application in PMMA-doped hybrid material. *Dalton Trans.* **46** (2017) 71–85.
9. Bohuslav, D.; Radovan, H.; Zdeneček, T.: Structural and magnetic properties of heptacoordinated Mn^{II} complexes containing a 15-membered pyridine-based macrocycle and halido/ pseudohalido axial coligands. *RSC Adv.* **6** (2016) 34674–34684.

10. Neumann, T.; Gallo, G.; Dinnebier, R. E.; Näther, C.: Synthesis, crystal structures, and properties of $Mn(NCS)_2$ coordination compounds with 4-picoline as coligand and crystal structure of $Mn(NCS)_2$. *Z. Anorg. Allg. Chem.* **646** (2020) 88–94.
11. Chu, J.-F.; Zhang, M.-Y.; Wang, Y.-Q.: Syntheses, crystal structures, and properties of three copper(II) complexes constructed by 4-(4,6-bis(1*H*-pyrazol-1-yl)-1,3,5-triazin-2-yl)morpholine. *Z. Anorg. Allg. Chem.* **643** (2017) 1101–1106.