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Crystal structure of *trans*-dichloridotetrakis(thiourea-κ*S*)manganese(II), $C_4H_{16}Cl_2MnN_8S_4$

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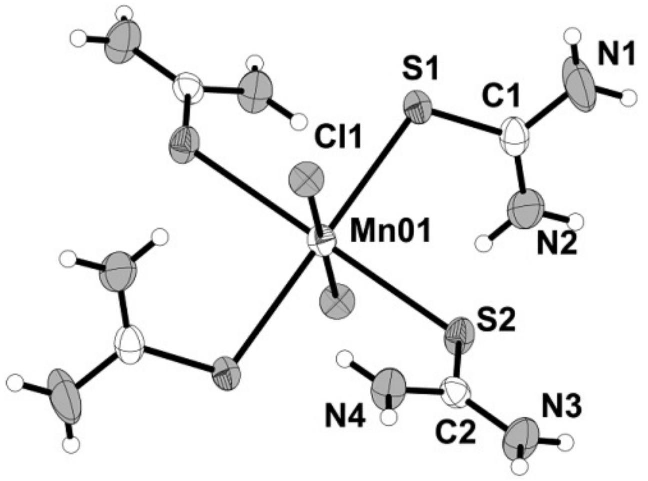

Abstract

$C_4H_{16}Cl_2MnN_8S_4$, tetragonal, $P4_2/n$ (no. 86), $a = 13.7526(9)$ Å, $c = 9.0785(9)$ Å, $V = 1717.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0294$, $wR_{ref}(F^2) = 0.0877$, $T = 290$ K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.32×0.36×0.41 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	15.65 cm^{-1}
Diffractometer, scan mode:	Gemini S Ultra, Agilent Technologies, ω
$2\theta_{max}$:	52.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4357, 1756
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1411
$N(param)_{refined}$:	89
Programs:	OLEX2 [1], SHELX [2]

Source of material

Thiourea ($SC(NH_2)_2$) and manganese chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$) with the molar ratio of 1:1 are the starting material, 5 mmol $MnCl_2{\cdot}4H_2O$ is first dissolved in 50 ml water solvent. Then, the same mole amount of $SC(NH_2)_2$ is added slowly, and the mixture is well stirred at room temperature for about 1 h until the raw materials are dissolved. The super-saturated solution is kept at elevated temperature via a water bath, and then the white, transparent and irregular crystals are formed gradually during the continuous evaporation process. The size of the grown single crystals is tightly related to the growing temperatures, and the largest single crystal with size of 5×2×1.5 mm^3 is obtained under the 50 °C water bath after two weeks.

Discussion

Recently, research on the organometallic coordination polymer has become a cutting-edge field in materials science and condensed matter physics owing to its potential applications in functional materials, such as in sorption, optics, magnetics, ferroelectrics and piezoelectricity, etc. [3-6]. As a typical organometallic compound, organometallic polymers in which the organic group and magnetic metal centers are connected through carbon chemical bond has aroused special attentions for its abundant physical properties and wide industrial applications [7-13]. $C_4H_{16}N_8S_4NiCl_2$ (*DTN*), with the tetragonal *I*4 space group, is a well-studied magnetic material in the condensed matter physics. The magnetic interaction through the super-exchange Ni-Cl-Cl-Ni path leads to the occurrence of the Bose-Einstein Condensation (*BEC*) in the *DTN* [14, 15]. Recently, a new Bose glass magnetic phase was observed after partly replace of the Cl atom by Br [16]. It thus can be expected that replacement of the Ni atom by another magnetic atoms, such as Mn, would be an effective way for the properties modulation. Furthermore, the different electron configuration of the magnetic atoms can also change the interactions between the magnetic atoms, and more novel physical behaviors might be expected. In the title structure the Mn is located at the center of symmetry, which is surrounded by two chlorido ligands and four thiourea ligands. These form a distorted octahedra, where thiourea molecules bond to Mn^{2+} cation through S. The distance of Mn and Cl is 2.5108 Å, and that of Mn–S1, Mn–S2 are 2.6363(5) Å, and 2.6859(5) Å, respectively. Furthermore, the bond angles between the atoms mentioned above are as follows: S1(S1')–Mn–S2 = 91.991° (88.009°), ∠Cl1–Mn–S2(S1) = 95.176° (87.937°).

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

Atom	Site	x	y	z	U_{iso}
H(2B)	8g	–0.0006	0.2945	–0.2272	0.067
H(2A)	8g	–0.0023	0.1866	–0.2147	0.067
H(1B)	8g	–0.0844	0.3869	–0.0687	0.092
H(1A)	8g	–0.1427	0.3412	0.0509	0.092
H(3B)	8g	0.3797	0.1266	0.1456	0.065
H(3A)	8g	0.3342	0.1911	0.0333	0.065
H(4B)	8g	0.3010	–0.0026	0.2329	0.054
H(4A)	8g	0.2013	–0.0270	0.1806	0.054

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(01)	4c	0	0	0	0.0324(2)	0.0268(2)	0.0296(3)	–0.0002(2)	–0.0032(2)	–0.0006(2)
S(2)	8g	0.15624(4)	0.11656(4)	–0.01830(6)	0.0312(3)	0.0325(3)	0.0465(3)	–0.0051(2)	–0.0123(2)	0.0070(2)
Cl(1)	8g	0.00148(3)	–0.01069(4)	0.27608(6)	0.0389(3)	0.0410(3)	0.0307(3)	–0.0013(2)	–0.0037(2)	–0.0012(2)
N(2)	8g	–0.0204(1)	0.2427(1)	–0.1835(2)	0.055(1)	0.043(1)	0.069(1)	0.0046(9)	0.011(1)	0.025(1)
N(1)	8g	–0.1048(2)	0.3357(1)	–0.0239(3)	0.126(2)	0.027(1)	0.078(2)	0.004(1)	0.015(2)	0.004(1)
C(2)	8g	0.2531(1)	0.0862(1)	0.0902(2)	0.0307(9)	0.0291(9)	0.037(1)	0.0016(8)	–0.0039(9)	–0.0061(9)
N(3)	8g	0.3313(1)	0.1410(1)	0.0896(2)	0.0320(9)	0.048(1)	0.081(2)	–0.0067(9)	–0.020(1)	0.016(1)
N(4)	8g	0.2517(1)	0.0101(1)	0.1781(2)	0.0394(9)	0.041(1)	0.054(1)	–0.0030(8)	–0.0184(9)	0.0105(9)
C(1)	8g	–0.0780(2)	0.2494(1)	–0.0697(2)	0.039(1)	0.029(1)	0.047(1)	–0.0014(9)	–0.013(1)	0.005(1)
S(1)	8g	–0.11866(4)	0.14963(3)	0.02523(6)	0.0375(3)	0.0252(3)	0.0447(3)	0.0009(2)	0.0014(2)	0.0026(2)

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References

1. 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. Cryst. **42** (2009) 339-341.
2. Sheldrick G. M. :A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
3. Wu, H.; Yang, J.; Su, Z. M.; Batten, S. R.; Ma, J. F.: An Exceptional 54-Fold Interpenetrated Coordination Polymer with 10^3-srs Network Topology. J. Am. Chem. Soc. **133** (2011) 11406-11409.
4. Zeng, M. H.; Wang, Q. X.; Tan, Y. X.; Hu, S.; Zhao, H. X.; Long, L. S.; Kurmoo, M.: Rigid Pillars and Double Walls in a Porous Metal-Organic Framework: Single-Crystal to Single-Crystal, Controlled Uptake and Release of Iodine and Electrical Conductivity. J. Am. Chem. Soc. **132** (2010) 2561-2563.
5. Jiao, C. H.; He, C. H.; Geng, J. C.; Cui, G. H.: Synthesis, crystal structures and catalytic properties of two 1D cobalt(II) coordination polymers. Trans. Met. Chem. **37** (2012) 17-23.
6. Cui, G. H.; He, C. H.; Jiao, C. H.; Geng, J. C.; Blatov, V. A.: Two metal–organic frameworks with unique high-connected binodal network topologies: synthesis, structures, and catalytic properties. Cryst. Eng. Commun. **14** (2012) 4210-4216.
7. Mousa, M. A.; Ahmed, M. A.; Summan, A. M.; Badawy, A. M.: γ-Irradiation effects on the electrical conductivity of some two-dimensional complexes: $RMnCl_4$, $RCoCl_4$ and $RMn_{0.5}Co_{0.5}Cl_4$ (R = H_3N-$(CH_2)_8$-NH_3). Thermochimica Acta **146** (1989) 87-93.
8. Wang, W.; Yan, L. Q.; Cong, J. Z.; Zhao,Y. L.; Wang, F.; Shen, S. P.; Zou, T.; Zhang, D.; Wang, S. G.; Han, X. F.; Sun, Y.: Magnetoelectric coupling in the paramagnetic state of a metal-organic framework. Scientific Reports **2** (2013) 2024 m1-m5.
9. Cahiez, G.; Christophe, D.; Julien, B.: Manganese-Catalyzed Oxidative Cross-Coupling of Grignard Reagents with Oxygen as an Oxidant. Angew. Chem. **121** (2009) 6859-6862.
10. Cahiez, G.; Alexakis, A.; Normant, J. F.: Organomanganous Chlorides as a New Reagent for Ketone Synthesis via Mixed or Symmetrical Anhydrides. Synth. Commun. **9** (1979) 639-645.
11. Cahiez, G.; Figadere, B.: Highly selective addition of organomanganese halides to aldehydes in the presence of ketones. Tetrahedron Lett. **27** (1986) 4445-4448.
12. Cahiez, G.; Laboue, B.: Organomanganese (II) reagents XIX. Acylation of organomanganese chlorides by carboxylic acid chlorides in THF: A clear improvement in the field of the preparation of ketones from organomanganese compounds. Tetrahedron Lett. **30** (1989) 7369-7372.
13. Fürstner, A.; Brunner, H.: Preparation of allyl-, alkenyl- and of functionalized arylmanganese reagents by oxidative insertion of manganese-graphite into organic halides. Tetrahedron Lett. **37** (1996) 7009-7012.
14. Amparo, L. C.; Mary R. T.: The crystal and molecular structure of dichlorotetrakisthioureanickel, $[(NH_2)_2CS]_4NiCl_2$. J. Chem. Soc. (1963) 1309-1317.
15. Zapf, V. S., Correa, V. F., Batista, C. D., Murphy, T. P., Palm, E. D.,Jaime, M., Tozer, S., Laoerda, A. & Paduan-Filjo, A.: Magnetostriction in the Bose-Einstein condensate quantum magnet $NiCl_2$-$4SC(NH_2)_2$. J. Appl. Phys. **101** (2007), 09E106 m1-m5.
16. Yu, R.;Yin, L.; Sullivan, N. S.; Xia, J. S.; Huan, C.; Paduan-Filho, A.; Oliveira, N. F.; Haas, Jr, S.; Steppke, A.; Miclea, C. F.; Weickert, F.; Movshovich, R.; Mun, E. D.; Scott, B. L.; Zapf, V. S.; Roscilde, T.: Bose glass and Mott glass of quasiparticles in a doped quantum magnet. Nature **489** (2012) 379-384.