

NOTE**Synthesis and Crystal Structure of
Di(thiocyanato-κN)bis(1,10-phenanthroline-5,6-dione-κ²N,N')-
Manganese(II): [(C₁₂H₆N₂O₂)₂Mn(NCS)₂]₂**

HUA-ZE DONG*, MENG LI and BAI-ZHONG LI†
Department of Chemistry and Chemical Engineering,
Hefei Teachers College, Hefei-230061, P.R. China
E-mail: dapdong@163.com

A novel 3D supramolecular complex di(thiocyanato-κN)bis(1,10-phenanthroline-5,6-dione-κ²N,N')manganese(II) with molecular formula [(C₁₂H₆N₂O₂)₂Mn(NCS)₂]₂, was formed by the reaction of 1,10-phenanthroline-5,6-dione with Mn(NCS)₂, in which metal ion was in a six-coordinated environments with a distorted octahedral geometry. Then independent mononuclear units are linked each other and pack in 3D-supramolecular network *via* hydrogen bonds interactions. The crystal is monoclinic, space group C2/c with unit cell parameters: a = 33.371 (3) Å, b = 8.8648 (8) Å, c = 18.7352 (18) Å, α = 90°, β = 116.137 (1)°, γ = 90°, V = 4975.6 (8) Å³, Z = 4, Mr = 1182.95, Dc = 1.579 g/cm³, μ = 0.746 mm⁻¹, F(000) = 2392, R = 0.0431, wR = 0.1085 for 4363 reflections with I > 2σ(I).

Key Words: Manganese(II), 1,10-Phenanthroline-5,6-dione, Supramolecule, Hydrogen bonds.

The rational design and synthesis of coordinated complexes with physical and chemical properties derived from 1,10-phenanthroline-5,6-dione have been of increasing interest recently in materials science and chemical research¹⁻⁴. Here we report a new monomeric manganese(II) complex di(thiocyanato-κN)bis(1,10-phenanthroline-5,6-dione-κ²N,N')manganese(II) with the molecular formula [Mn(C₁₂H₆N₂O₂)₂(CNS)₂]₂.

All reagents for synthesis were commercially available and employed as received or purified by standard methods prior to use. 1,10-Phenanthroline-5,6-dione was prepared by similar procedure reported in the literature³. Analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Infrared spectra (4000-400 cm⁻¹) were recorded with a Bruker Vector 22 FT-IR spectrophotometer on KBr disks.

Synthesis: For the synthesis of present compound, a solution of ligand (0.2 mmol), MnCl₂ (0.1 mmol) and NH₄CNS (0.2 mmol) in 50 mL methanol was refluxed for 2 h and then cooled to room temperature and filtered. Single crystals suitable for X-ray analysis were grown from the methanol solution by slow evaporation at room temperature in air. Anal. calcd. for C₂₆H₁₂N₆O₄S₂Mn: C, 52.80; H, 2.04; N, 14.21. Found: C, 52.83; H, 2.08; N, 14.19.

†School of Chemistry and Chemical Engineering, Anhui University, Hefei-230039, P.R. China.

Crystal structure determination: A single crystal of compound with dimensions of 0.3 mm × 0.2 mm × 0.2 mm was selected for crystallographic data collection at 291(2)K and structure determination on a Bruker SMART CCD-4K diffractometer employing graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 12206 reflections were collected in the range of $2.4^\circ \leq \theta \leq 25.0^\circ$, of which 4363 reflections were unique with $R_{\text{int}} = 0.046$. The data were collected using SMART and reduced by the program SAINT. All the structures were solved by direct methods and refined by full-matrix least squares method on F_o^2 by using SHELXTL-PC software package. Non-hydrogen atoms were placed in geometrically calculated positions. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 371 variable parameters for 4363 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma F_o = 0.0431 \quad (1)$$

$$\text{and } wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2} = 0.1085 \quad (2)$$

where $w = 1/[\sigma^2(F_o^2) + (0.0518P)^2]$ and $P = (F_o^2 + 2F_c^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.46 and -0.40 e/\AA^3 , respectively.

The selected bond lengths and bond angles in Table-1. Respecting, Fig. 1 shows the molecular structure of the present compound. Fig. 2 shows the packing diagram of the manganese(II) compound. In the compound, $[Mn(C_{12}H_6N_2O_2)_2(CNS)_2]_2$, each Mn(II) cation located on an inversion center is coordinated by four N-bonded 1,10-phenanthroline-5,6-dione ligands (L) and two N-bonded thiocyanate anions. The asymmetric unit consists of one manganese cation, two thiocyanate anions and two 1,10-phenanthroline-5,6-dione ligands. The Mn-N bond lengths in the MnN_6 core are in the range of 2.117 (3) \AA to 2.364 (2) \AA . However positional disorder happened to one anion.

TABLE-1
SELECTED BOND DISTANCES (\AA) AND ANGLES ($^\circ$)

Mn1-N1	2.364 (3)	Mn1-N2	2.271 (3)	Mn1-N3	2.301 (3)
Mn1-N4	2.281 (3)	Mn1-N5	2.148 (3)	Mn1-N6	2.116 (3)
S1-C25	1.630 (3)	S2-S2_a	1.853 (4)	S2-C26	1.628 (11)
S2'-C26'	1.608 (7)	O1-C12	1.218 (4)	O2-C11	1.209 (4)
O3-C24	1.238 (6)	O4-C23	1.233 (5)	N1-Mn1-N2	70.77 (10)
N1-Mn1-N3	79.56 (9)	N1-Mn1-N4	89.82 (10)	N1-Mn1-N5	156.72 (11)
N1-Mn1-N6	102.28 (11)	N2-Mn1-N3	100.62 (10)	N2-Mn1-N4	160.36 (9)
N2-Mn1-N5	93.33 (11)	N2-Mn1-N6	95.37 (12)	N3-Mn1-N4	71.98 (10)
N3-Mn1-N5	87.13 (10)	N3-Mn1-N6	163.53 (13)	N4-Mn1-N5	104.20 (11)
N4-Mn1-N6	91.60 (13)	N5-Mn1-N6	95.91 (12)	-	-

In crystal packing, it is observed that the C-H \cdots O intermolecular hydrogen bonds are formed between adjacent molecules resulting in a 3D supramolecular framework. All hydrogen bond patterns are given in Table-2.

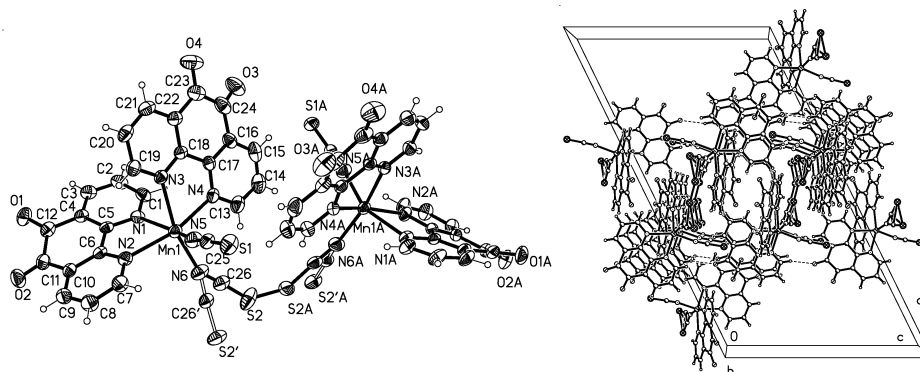


Fig. 1. Molecular structure of the manganese(II) complex
 Fig. 2. View of a 3D supramolecular framework of manganese(II) complex showing the intermolecular hydrogen bonding

TABLE-2
 HYDROGEN BOND DISTANCES (Å) AND ANGLES (°)

Type (D-H...A)	d(D-H)	d(H...A)	∠(DHA)	d(D...A)	A
C7-H7...O1	0.9300	2.3600	156.00	3.233 (4)	x, 1-y, ½ + z

Conclusion

Crystal structure of a novel 3D superamolecular manganese(II) complex has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis.

Supplementary material

Crystallographic data for the structure reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 749924.

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