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КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF A NEW MANGANESE(III) COMPLEX WITH TETRADENTATE SCHIFF BASE N,N′-*O*-PHENYLENEBIS(4-METHOXYSALICYLIDENEIMINE)

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A new manganese(III) complex [Mn(L)(NCS)] (**1**) is synthesized from the Schiff base ligand N,N′-*O*-phenylenebis(4-methoxysalicylideneimine) (H_2L: derived from the condensation of 4-methoxy salicylaldehyde with *O*-phenylene-diamine) with $Mn(NO_3)_2\cdot 4H_2O$ and KSCN in a methanol/water solvent mixture. This complex is characterized by elemental analysis, FT-IR and single crystal X-ray diffraction. It crystallizes in a monoclinic system, with space group $P2_1/c$ and four molecules in the unit cell ($Z = 4$). The crystal structure shows [Mn(L)(NCS)] units joined together by the Mn···S secondary bonding interaction (SBI) to form infinite zigzag chain structures.

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In recent years extensive studies have been focused on the chemistry of manganese(III) complexes with Schiff base ligands because of growing interest in the field of molecular magnetism, metalloenzymes, and inhibitors of xanthine oxidase and in the understanding of their catalytic activities in various reactions [1—18]. Researchers have previously reported the crystal structures of Mn^{III} complexes with closely related N_2O_2 donor Schiff base ligands [5, 13, 17, 19, 20]. To our knowledge, no crystal structure of a Mn(III) complex containing a tetradentate Schiff base, N,N′-*O*-phenylenebis(4-methoxysalicylideneimine), and NCS has been reported so far.

In the present work, we report the synthesis and crystal structure of a new manganese(III) [Mn(L)(NCS)] complex.

Materials and measurements. Elemental analysis (C,H,N) was performed using a Heraeus Elemental Analyzer CHN-O-Rapid. Infrared spectra were recorded as KBr pellets using Unicam Matson 1000 FT-IR. All the chemicals and solvents used in this study were of analytical grade and used as procured without further purification. The H_2L ligand was prepared by the reported procedure [9].

Synthesis of [Mn(L)(NCS)] complex (1). The complex was synthesized by adding N,N′-*O*-phenylenebis(4-methoxysalicylideneimine) (H_2L) (0.034 g, 0.1 mmol) in methanol (15 ml) to a solution of manganese nitrate tetrahydrate (0.050 g, 0.2 mmol) in methanol (10 mL). The mixture was refluxed with stirring for 3 h. Then potassium thiocyanate (0.780 g, 8 mmol) dissolved in water (2 ml) was added dropwise under constant stirring. A brown precipitate was obtained, washed with about 3 ml of methanol, dried, and rinsed with copious quantities of diethylether. Brown single crystals of the complex suitable for the X-ray structure determination were recrystallized from methanol by slow

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Table 1

Crystallographic and structure refinement of **1**^{a}

Empirical formula	$C_{23}H_{18}MnN_3O_4S$
Formula weight	487.40
Crystal system	Monoclinic
Space group	$P2_1/c$
a, b, c, Å; β, deg.	9.946(2), 12.889(3), 16.760(3); 102.78(3)
V, Å^3	2095.3(8)
Z	4
ρ_{calcd}, g/cm^3	1.545
$\mu(MoK_\alpha)$, mm^{-1}	0.767
Crystal size, mm	0.28×0.20×0.17
θ Range for data collection, deg.	2.10 to 29.25
Index ranges h, k, l	–13/13, –17/14, –21/22
Data / restraint / parameters	5621 / 0 / 291
T_{max} and T_{min}	0.8807 and 0.8140
Reflections collected (R_{int})	16477 (0.0890)
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0605$, $wR_2 = 0.1071$
R indices (all data)	$R_1 = 0.1361$, $wR_2 = 0.1265$
Largest diff. peak and hole, e/Å^3	0.599 and –0.338

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^{a} $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR_2 = [\Sigma(w(F_0^2 - F_c^2)^2)/\Sigma w(F_0^2)^2]^{1/2}$.

evaporation of the solvent at room temperature after two weeks. Anal. Calcd. for $C_{23}H_{18}MnN_3O_4S$ (%): C 56.68, H 3.72, N 8.62. Found (%): C 56.19, H 3.65, N 8.68. IR (KBr, υ/cm^{-1}): 2077 (NCS), 1596 (C=N).

X-ray crystallography. The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated MoK_α radiation. A colorless crystal with the dimensions of 0.28×0.20×0.17 mm was mounted on a glass fiber and used for data collection. Cell constants and the orientation matrix were obtained by the least squares refinement of diffraction data from 5621 unique reflections. Data were collected at a temperature of 298(2) K to a maximum 2θ value of 58.5° and in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA software package [20]. A numerical absorption correction was applied using X-RED [21] and X-SHAPE [22] software with the maximum and minimum transmissions of 0.8807 and 0.8140, respectively. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and subsequent difference Fourier maps, and then refined on F^2 by a full-matrix least squares technique using anisotropic displacement parameters [23]. All hydrogen atoms were located geometrically and then refined isotropically. Atomic factors are from International Tables for X-Ray Crystallography [24]. All refinements were performed with the X-STEP32 crystallographic software package [25]. Further details are summarized in Table 1. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 1046721, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

Complex **1** was synthesized from the reaction of $Mn(NO_3)_2\cdot 4H_2O$ with the N,N′-*O*-phenylenebis(4-methoxysalicylideneimine) Schiff base ligand in the presence of KSCN in a methanol/water solvent mixture.

Spectral characterization. The elemental analysis of the complex was entirely consistent with its proposed stoichiometry. FT-IR spectral data of the complex were compared with the free ligand. The N,N′-*O*-phenylenebis(4-methoxysalicylideneimine) ligand shows a broad band characteristic of the

Table 2

Selected bond lengths (Å) *and angles* (deg.) *for* **1**

Mn(1)—O(2)	1.858(2)	O(2)—C(6)	1.324(4)	O(2)—Mn(1)—O(3)	91.94(10)	N(3)—C(23)—S(1)	178.8(4)
Mn(1)—O(3)	1.868(2)	O(3)—C(22)	1.312(4)	O(2)—Mn(1)—N(1)	92.13(11)	C(2)—O(1)—C(1)	118.3(3)
Mn(1)—N(1)	1.976(3)	O(4)—C(19)	1.348(4)	O(3)—Mn(1)—N(1)	166.83(12)	C(6)—O(2)—Mn(1)	130.1(2)
Mn(1)—N(2)	1.991(3)	O(4)—C(20)	1.462(5)	O(2)—Mn(1)—N(2)	169.32(12)	C(22)—O(3)—Mn(1)	129.2(2)
Mn(1)—N(3)	2.166(3)	N(1)—C(8)	1.297(4)	O(3)—Mn(1)—N(2)	91.86(11)	C(19)—O(4)—C(20)	116.6(3)
S(1)—C(23)	1.626(4)	N(1)—C(9)	1.426(4)	N(1)—Mn(1)—N(2)	82.05(12)	C(8)—N(1)—Mn(1)	125.1(2)
O(1)—C(2)	1.355(4)	N(2)—C(15)	1.299(4)	O(2)—Mn(1)—N(3)	98.87(12)	C(9)—N(1)—Mn(1)	112.1(2)
O(1)—C(1)	1.437(5)	N(2)—C(14)	1.423(4)	O(3)—Mn(1)—N(3)	96.30(12)	C(15)—N(2)—Mn(1)	124.9(2)
				N(1)—Mn(1)—N(3)	95.44(12)	C(14)—N(2)—Mn(1)	111.3(2)
				N(2)—Mn(1)—N(3)	90.62(12)	C(23)—N(3)—Mn(1)	174.7(3)

OH group in the 3300—3500 cm^{-1} region. The disappearance of this band in the FT-IR spectra of the complex is indicative of the fact that the tetradentate N_2O_2 ligand is coordinated as dianions. The (C=N) band appearing at 1609 cm^{-1} in the ligand is shifted to lower frequencies by 13 cm^{-1} in the Mn complex (1596 cm^{-1}), indicating that the ligand is coordinated to Mn^{III} through the imino groups. Also, the infrared spectrum of the complex displays a strong band at 2077 cm^{-1}, which is characteristic of the C=N stretch for an N-coordinated thiocyanate ion. It is consistent with the X-ray analysis data.

Crystal structure description. Complex **1** crystallizes in the monoclinic system, with the $P2_1/c$ space group and four molecules in the unit cell ($Z = 4$). The selected bond lengths and angles are listed in Table 2. The molecular structure of **1** with the atom numbering scheme is shown in Fig. 1. The asymmetric unit of **1** comprises a manganese Schiff base complex in which the Mn(III) atom is coordinated by the N_2O_2 unit of the tetradentate Schiff base ligand and an NCS$^-$ ligand (Fig. 1). The manganese(III) ion has a distorted octahedral geometry in which the equatorial coordination plane is composed of the N_2O_2 donor atoms of the tetradentate ligand. Two axial positions are occupied by one nitrogen atom from the NCS$^-$ anion and one sulfur atom of a neighboring thiocyanate ligand with a weak Mn···S secondary bonding interaction (3.137 Å). In the equatorial coordination plane the Mn—O distances (Mn(1)—O(2) = 1.858(2), Mn(1)—O(3) = 1.868(2) Å) and Mn—N distances (Mn(1)—N(1) = = 1.976(3), Mn(1)—N(2) = 1.991(3) Å) are within the same ranges as those observed in other related Mn^{III} complexes of the N_2O_2 Schiff base ligands [16]. As shown in Fig. 1, the thiocyanate ion is coordinated to Mn(III) via the N(3) atom. The Mn(1)—N(3) bond (2.166(3) Å) is longer than Mn—N bonds in the equatorial plane. This effect should be due to the Jahn—Teller effect in the high-spin Mn^{3+} d^4 system. Another axial position is used for the Mn···S secondary bonding interaction (3.137 Å) which is much longer than the normal Mn—S bond [12]. The Mn(l)—N(3)—C(23) and N(3)—C(23)—S(1) angles are 174.7(3)° and 178.8(4)°, respectively, showing that four atoms, namely, Mn(1), N(3), C(23), and S(1) are not collinear. The N—C—S angle (178.8(4)°) indicates that the NCS ligand is linear. The [Mn(L)(NCS)] units are joined together by Mn···S SBI to form infinite zigzag chains (Fig. 2).

In summary, new manganese(III) complex [Mn(L)(NCS)] (**1**) was synthesized and characterized. Complex **1** was structurally characterized by

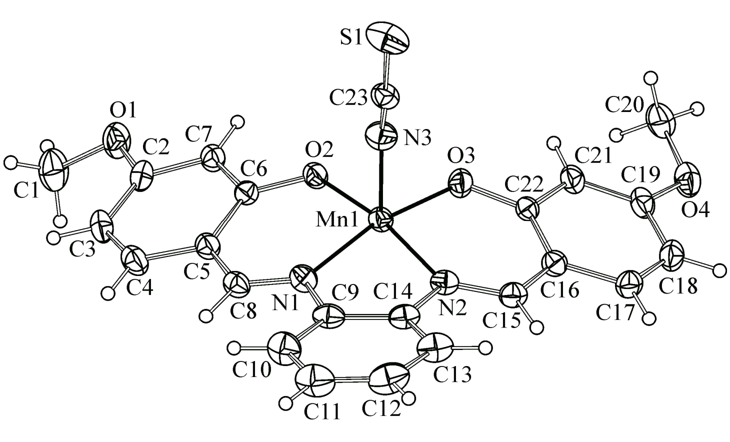

Fig. 1. ORTEP view of complex **1** with the atom numbering scheme.
Thermal ellipsoids are at 30 % probability level

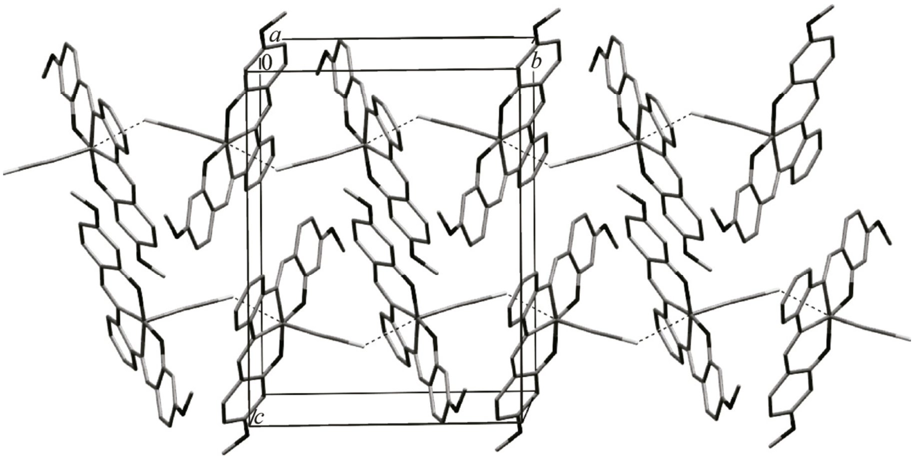

Fig. 2. A view of the polymeric structure of **1**. Secondary bonding interaction (Mn···S) is shown as dotted lines

single-crystal X-ray diffraction. The crystal structure of complex **1** consists of polymeric 1D chains linked by the Mn···S secondary bonding interaction.

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