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Synthesis, crystal structure, and magnetic property of a rarely seen $\mu_{1,1}$-OMe-bridged dimeric manganese(III) complex derived from 2-[1-(2-methylaminoethylimino)ethyl]phenol

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ABSTRACT

A novel $\mu_{1,1}$-OMe-bridged dimeric manganese(III) complex with the tridentate Schiff base ligand 2-[1-(2-methylaminoethylimino)ethyl]phenolate has been prepared and structurally characterized. The magnetic property of the complex shows the presence of ferromagnetic interaction mediated by double methoxy bridges.

Considerable attention has been focused on the polynuclear manganese complexes due to their wide applications in magnetic [1–4] and catalytic fields [5–7]. The preferred way to construct polynuclear complexes is the use of suitable bridging groups, such as N_3^-, NCS$^-$, $N(CN)_2^-$, dicarboxylate, 4,4′-bipy, *etc.* [8–10]. The methanol is a common used solvent for the preparation of complexes. In addition, the methanol can also acts as coligand in the self-assembly of complexes [11–13], however, the $\mu_{1,1}$-OMe-bridged complexes with transition metal atoms are very rare. The mere examples of $\mu_{1,1}$-OMe-bridged dinuclear manganese(III) complexes show interesting magnetic properties [14,15]. Schiff bases bearing two or three donor atoms are a kind of versatile ligands in the construction of polymeric structures of complexes [16,17]. During the search of literature, only one $\mu_{1,1}$-OMe-bridged manganese(III) complex with Schiff base ligand was reported [18]. In this paper, a new $\mu_{1,1}$-OMe-bridged dimeric manganese(III) complex, $[Mn_2L_2(\mu_{1,1}\text{-OMe})_2(NCS)_2]$, where L is the deprotonated form of 2-[1-(2-methylaminoethylimino)ethyl]phenol (HL; Scheme 1), was prepared and structurally characterized. The magnetic property of the complex was studied.

The Schiff base ligand HL was prepared by the reaction of 2-acetylphenol with *N*-methylethane-1,2-diamine in methanol [19]. The complex was readily prepared by the reaction of the Schiff base ligand, ammonium thiocyanate, and manganese chloride in methanol [20]. The molecular structure of the complex is shown in Fig. 1. X-ray crystallography [21] reveals that the complex is a similar $\mu_{1,1}$-OMe-bridged centrosymmetric and dimeric compound. The inversion center is located at the midpoint of the two Mn atoms. The Mn···Mn distance is 3.236(1) Å. The Schiff base serves as a tridentate ligand to form five- and six-membered chelate rings with Mn atom in the complex. The coordination geometry around the metal center in the complex can be best described as a distorted octahedron, with the three donor atoms of the Schiff base ligand and one methoxy O atom defining the equatorial plane, and with the symmetry-related methoxy O atom and one thiocyanate N atom occupying the two axial positions. The Mn atom in the complex lies 0.168(2) Å from the least-squares plane defined by the equatorial donor atoms, in the direction of the axial thiocyanate ligand.

The four equatorial coordinate bond distances in the complex are shorter than the two axial bonds, which are caused by the Jahn–Teller effects. The bond distances and bond angles in the complex are typical, and are comparable to those observed in other similar manganese(III) complexes with Schiff bases [22,23].

In the crystal structure of the complex, there forms four intermolecular N–H···O hydrogen bonds in each dimer. The dimeric manganese(III) complex molecules are stacked *via* weak π···π interactions along the *a* axis with no other obvious short contacts, as shown in Fig. 2.

In the i.r. spectra of the complex, the middle band centered at 3135 cm^{-1} is assigned to the vibration of the N–H groups. The strong absorption band at 1620 cm^{-1} is assigned to the C=N groups. The intense band indicative of the thiocyanate ligands is located at 2044 cm^{-1}. The weak bands in the region 300–600 cm^{-1} for the complex may be assigned to the Mn–O and Mn–N vibrations.

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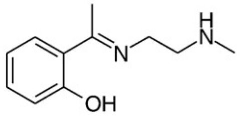

Scheme 1. The Schiff base HL.

Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the complex (Fig. 3). The first step started at about 168 °C and was completed at about 218 °C, corresponding to the loss of the methoxy ligands. The observed weight loss of 9.2% is equal to the calculated value. The second step, from 259 °C to 479 °C, corresponds to the loss of the thiocyanate ligands. The observed weight loss of 17.7% is close to the calculated value (17.3%). The third step, from 480 °C to 771 °C, corresponds to the loss of the Schiff base ligands. The observed weight loss of 49.0% is close to the calculated value (49.6%), and the formation of the final product (Mn_2O_3). The total weight loss of 77.8% is close to the calculated value (76.1%).

The temperature dependence of the χT product and inverse magnetic susceptibility ($1/\chi$) for the complex at 1000 Oe in the temperature range 2–300 K is shown in Fig. 4. The χT value of 7.3 $cm^3\ mol^{-1}\ K$ at 300 K, corresponding to the two isolated Mn(II) of $S = 5/2$ with significant orbital contribution. Upon cooling, the χT values gradually increased to a sharp maximum of 12.3 $cm^3\ mol^{-1}\ K$ around 9.8 K, and then dropped rapidly. This behavior of the complex indicates predominant ferromagnetic interaction within the dinuclear, and intercluster antiferromagnetic interactions. The magnetic susceptibility data above 70 K were fitted by the Curie–Weiss law, which gave a Curie constant of 6.97 $cm^3\ mol^{-1}\ K$ and a Weiss temperature of 10.9 K. The positive Weiss temperature confirms the dominant intra-chain ferromagnetic interactions bridged *via* oxygen atoms.

In summary, the present paper reports the synthesis, crystal structure, thermal stability and magnetic property of a novel $\mu_{1,1}$-OMe-bridged centrosymmetric and dimeric manganese(III) complex with tridentate Schiff base 2-[1-(2-methylaminoethylimino)ethyl]phenol. The methanol solvates act as interesting bridging groups for the self-assembly of the complex. The thermal stability of the complex was studied, which agreed well with the component of the complex. The magnetic property of the complex shows the presence of ferromagnetic interaction mediated by double methoxy bridges.

Acknowledgements

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Appendix A. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre (CCDC – 855110). Copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

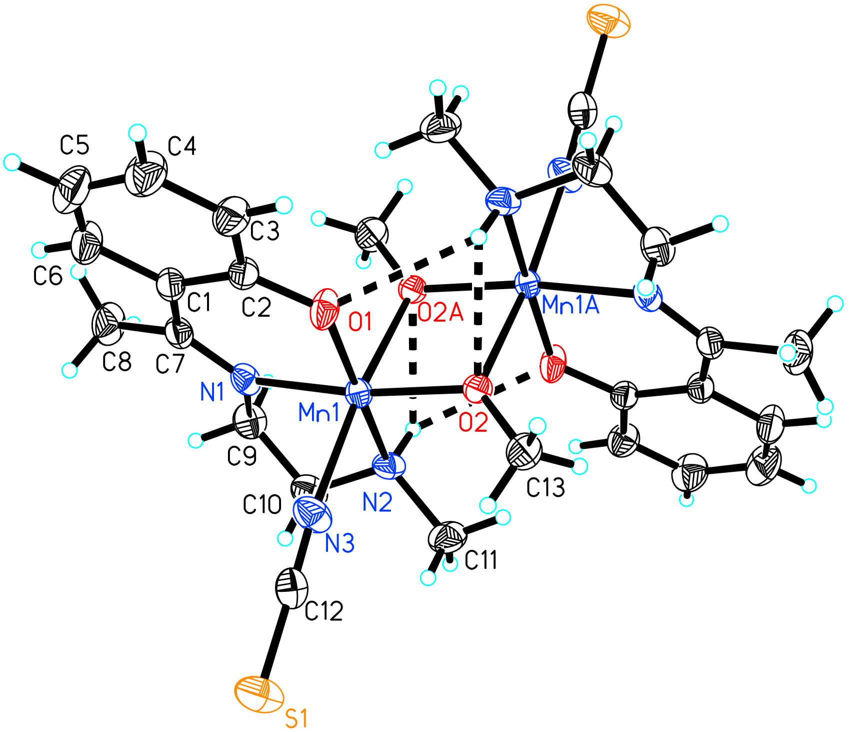

Fig. 1. A perspective view of the molecular structure of the complex with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix A or unlabelled are at the symmetry position $2 - x, -y, -z$. Selected bond lengths (Å) and bond angles (°): Mn1-O1 1.865(2), Mn1-O2 1.882(2), Mn1-O2A 2.279(2), Mn1-N1 2.017(3), Mn1-N2 2.069(3), Mn1-N3 2.200(3); O1-Mn1-O2 91.0(1), O1-Mn1-N1 91.1(1), O2-Mn1-N1 167.1(1), O1-Mn1-N2 171.6(1), O2-Mn1-N2 92.5(1), N1-Mn1-N2 83.8(1), O1-Mn1-N3 97.2(1), O2-Mn1-N3 100.2(1), N1-Mn1-N3 92.2(1), N2-Mn1-N3 89.7(1), O1-Mn1-O2A 91.6(1), O2-Mn1-O2A 78.4(1), N1-Mn1-O2A 88.9(1), N2-Mn1-O2A 81.7(1), N3-Mn1-O2A 171.2(1).

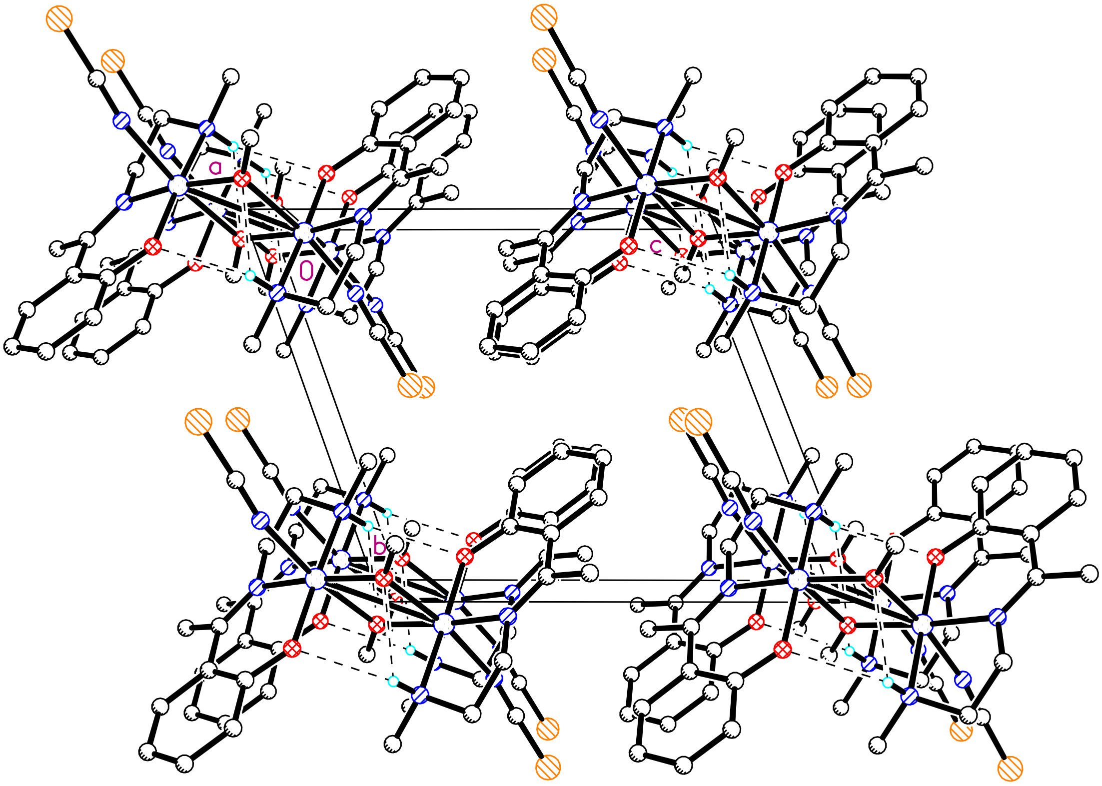

Fig. 2. Molecular packing of the complex, viewed along the *a* axis. Hydrogen bonds are shown as thin dashed lines.

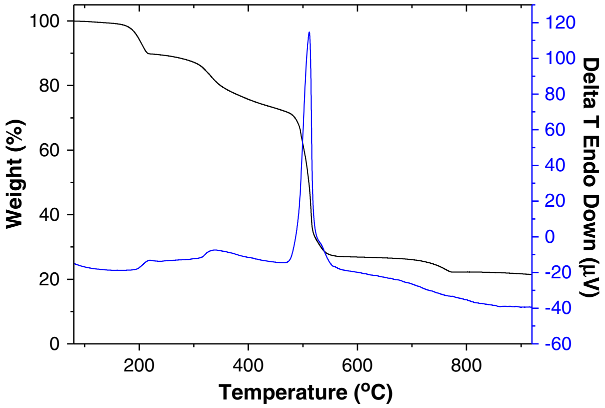

Fig. 3. DT-TGA curve of the complex.

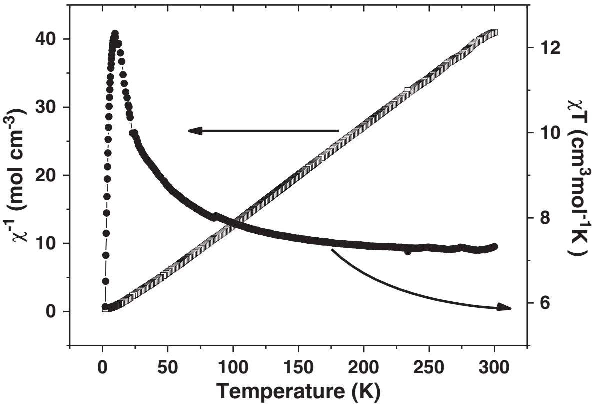

Fig. 4. Thermal variation of magnetic susceptibility, χT vs *T* (●) and χ^{-1} vs *T* (□) of the complex under an applied field of 1 kOe in the temperature range of 2–300 K.

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[19] 2-Acetylphenol and N-methylethane-1,2-diamine were purchased from Lancaster. The remaining reagents and solvents with AR grade were used as received. To the stirred methanolic solution (30 mL) of 2-acetylphenol (1.36 g, 10 mmol) was added a methanolic solution (20 mL) of N-methylethane-1,2-diamine (0.74 g, 10 mmol). The mixture was stirred at reflux for 30 min to give yellow solution. The solvent was evaporated to give yellow oil product of HL which was used to prepare the manganese complex without purification.

[20] To the stirred methanolic solution (30 mL) of HL (0.192 g, 1 mmol) and ammonium thiocyanate (0.076 g, 1 mmol) was added a methanolic solution (20 mL) of manganese chloride (0.126 g, 1 mmol). The mixture was stirred at room temperature for 30 min to give brown solution. Brown block-shaped single crystals of the complex, suitable for X-ray diffraction, were formed by slow evaporation of the solution in air for a few days. The crystals were isolated by filtration, washed with methanol, and dried in air. Yield: 55%. Anal. Calc. for $C_{26}H_{36}Mn_2N_6O_4S_2$: C 46.6, H 5.4, N 12.5%. Found: C 46.4, H 5.5, N 12.6%. IR data: 2044 (s), 1620 (s), 1599 (s), 1542 (m), 1468 (w), 1442 (m), 1382 (w), 1298 (m), 1276 (m), 1254 (w), 1202 (w), 1150 (w), 1130 (w), 1087 (w), 1046 (w), 1029 (w), 902 (m), 801 (m), 754 (s), 632 (m), 596 (w), 464 (m), 382 (w), 359 (w).

[21] The X-ray single crystal diffraction measurement was carried out at 298(2) K on a Bruker Smart 1000 CCD area diffractometer. The unit cell parameters and data collection was performed with MoKα ($\lambda = 0.71073$ Å) radiation. The crystal data and structural parameters for the complex: $C_{26}H_{36}Mn_2N_6O_4S_2$, M = 670.6, triclinic, space group P-1, $a = 6.9662(2)$, $b = 10.1460(3)$, $c = 11.3316(4)$, $\alpha = 69.685(2)°$, $\beta = 88.918(2)°$, $\gamma = 80.625(2)°$, $V = 740.44(4)$ ^{3}, $Z = 1$, $\rho_{calcd} = 1.504$ g cm^{-3}, $T = 298(2)$ K, μ(Mo Kα) = 1.036 mm^{-1}, $R_1 = 0.0466$, $wR_2 = 0.0966$.

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