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LETTER

A novel thiolate-bridged polynuclear manganese(II) complex with 2-[2-(2-pyridyl)ethylamino]ethanethiol

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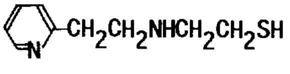
Metal complexes of thiolic ligands have attracted much attention in the last decade because the biological significance of metal thiolates has been recognized. However the chemistry of manganese thiolates is essentially undeveloped in confrast with the cases of Fe(II), Co(II), Ni(II) and Zn(II). In this study we have isolated a novel polynuclear manganese(II) complex by using a thiolic ligand, 2-[2-(2-pyridyl)ethylamino]ethanethiol (HL). This ligand was recently used for the preparation of some thiolate-bridged manganese(II) complexes by Handa *et al.* [1]. Based on the magnetic data, they proposed a binuclear structure, $[Mn_2(L)_2Cl_2]$, for the manganese(II) complex obtained from the reaction of equimolar amounts of $MnCl_2 \cdot 4H_2O$ and the thiolic ligand, HL. Contrary to their description, we have found that our complex prepared in a similar manner is the novel polynuclear complex, $[Mn(L)Cl(CH_3OH)]_n$ (**1**). We herein report the preparation, X-ray crystal structure, and magnetic properties of **1**.



HL

Experimental

Complex **1** was prepared as follows, all operations being performed under Ar using standard Schlenk techniques. A solution of $MnCl_2 \cdot 4H_2O$ (396 mg, 2 mM) in 6 ml of methanol was added to a methanol solution (4 ml) of HL [2] (365 mg, 2 mM) with stirring. Upon standing the solution for a few days pale brown crystals were deposited. They were collected by filtration (yield 141 mg).

The structure of **1** was determined by an X-ray structure analysis. Crystal data are: $C_{10}H_{17}ClMnN_2OS$, formula weight = 303.7, orthorhombic, $P2_12_12_1$ (No. 19), $a = 12.975(3)$, $b = 14.194(2)$, $c = 7.312(2)$ Å, $V = 1346.6(5)$ Å^3, $D_m = 1.49$, $D_c = 1.50$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 12.74 cm^{-1}. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Of the 2319 reflections ($1° \leqslant 2\theta \leqslant 60°$) measured, the unique 1050 reflections with $I \geqslant 3\sigma(I)$ were considered as observed. The structure was solved by the direct methods and refined by the full matrix least-squares method. All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in the least-squares calculation and fixed at their positions. The final residual values were $R = 0.047$ and $R_w = 0.052$.

Results and discussion

The complex essentially consists of a mononuclear $[Mn(L)Cl(CH_3OH)]$ unit. The structure of the unit is shown in Fig. 1. The thiolic ligand, L, forms a meridional chelate with thiolate sulfur, amino nitrogen, and pyridyl nitrogen atoms coordinated to the manganese atom (Mn–S 2.559(3), Mn–N1 2.295(7), Mn–N2 2.326(7) Å). The Mn–S distance falls in the range of those of the only one structure known as six-coordinate Mn(II) thiolate, $(PPh_4)_2[Mn_3(pdt)_5]$ (pdt^{2-} is propane-1,3-dithiolate) (2.554–2.677 Å) [3]. The Mn–N bond lengths compare well with the values usually observed for manganese(II) complexes (2.100(4)–2.380(4) Å) [4]. The manganese atom is further coordinated by the methanol oxygen atom and chloride ion at distances of 2.340(6) and 2.463(3) Å, respectively. In addition to these coordinations, a thiolate sulfur atom of a neighboring mononuclear unit approaches the manganese atom [Mn–S′ 2.642(3), Mn–Mn′ 4.669(2) Å, Mn–S′–Mn′ 127.7(1)° (primes refer to the equivalent position ($\frac{3}{2}-x$, $1-y$, $z-\frac{1}{2}$))] forming a distorted octahedron; thereby mononuclear units are linked in a helical chain parallel to the *c* axis throughout the crystal (Fig. 2). This Mn–S′ interaction is not weak because the Mn–S′ distance is comparable to those

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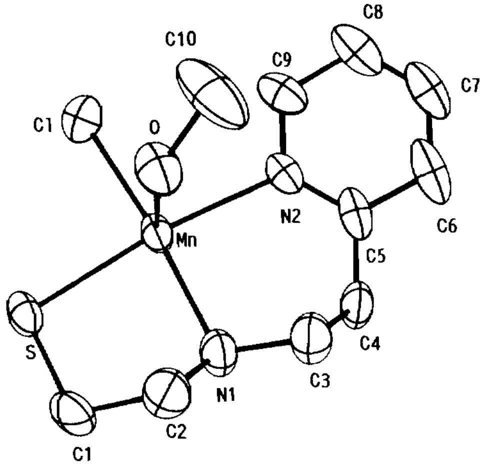

Fig. 1. Perspective view of $[Mn(L)Cl(CH_3OH)]$ unit. Selected bond lengths (l (Å)) and angles (ϕ(°)): Mn–S 2.559(3), Mn–N1 2.295(7), Mn–N2 2.326(7), Mn–Cl 2.463(3), Mn–O 2.340(6); S–Mn–N1 79.5(2), S–Mn–N2 163.1(2), S–Mn–Cl 94.2(1), S–Mn–O 86.3(2), N1–Mn–N2 88.4(3), N1–Mn–Cl 172.8(2), N1–Mn–O 85.7(3), N2–Mn–Cl 97.1(2), N2–Mn–O 81.0(2), Cl–Mn–O 90.5(2).

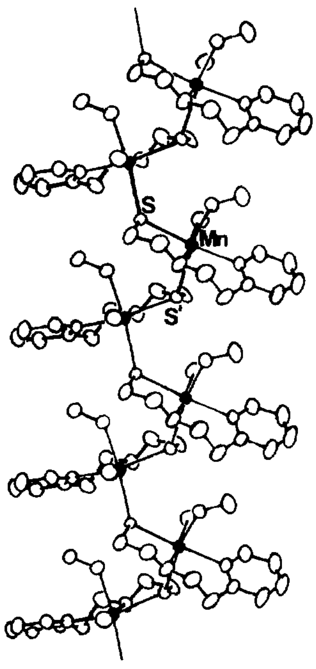

Fig. 2. Polymeric structure of $[Mn(L)Cl(CH_3OH)]_n$.

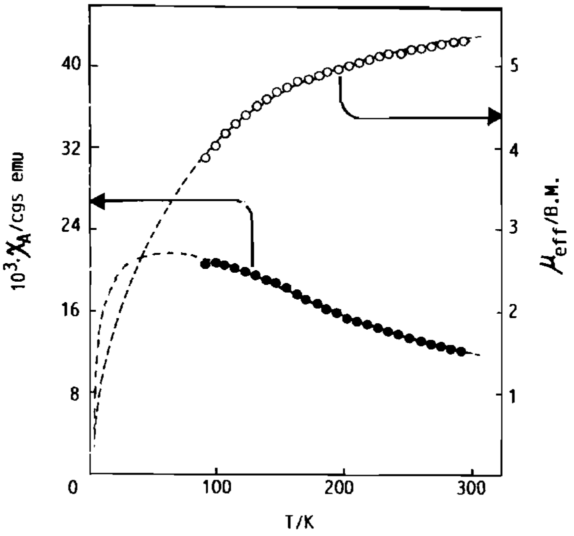

Fig. 3. Variable-temperature magnetic susceptibility data for $[Mn(L)Cl(CH_3OH)]_n$.

for the six-coordinate Mn(II) thiolate [3] and the manganese atom is displaced by 0.17 Å from the mean (S–N1–N2–Cl) plane toward the approaching thiolate sulfur S′. Thus the structure of the complex may be best described as a novel polynuclear helical chain.

The diffuse reflectance spectrum of **1** shows no appreciable absorption in the visible region, indicating the electronic configuration of the manganese(II) ion is of high spin. However, the room temperature magnetic moment of **1** (5.30 BM/Mn) is lower than the spin-only value (5.92 BM/Mn) for a high-spin d^5 system. The magnetic susceptibilities were measured over the temperature range 80–300 K. Surprisingly the magnetic susceptibility data could be explained by the dimer equation ($S_1 = S_2 = 5/2$) based on the Heisenberg model ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$) in the same way as that for Handa's compound [1]. The broken curve in Fig.3 was calculated by using the parameters, $J = -7.8\ \mathrm{cm}^{-1}$ and $g = 2.0$ ($N\alpha = 0$). This result shows that the limited magnetic data cannot provide definite evidence for the molecular structures of manganese thiolates. Further studies on thiolate-bridged manganese complexes with this type of thiolic ligands are in progress.

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