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LETTER

Novel elimination reaction of a hydroxyethyl group in a manganese complex. Formation of a binuclear manganese(II) complex with a Robson-type macrocyclic ligand

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Binuclear manganese complexes are of current interest because such systems are known to exist at the active site of some manganese-containing enzymes [1]. As part of the continuing study on binuclear manganese complexes, we recently reported the synthesis and characterization of a binuclear manganese(II) complex using a binucleating ligand, 2,6-bis[*N*-(2-pyridylethyl)-iminomethyl]-4-methylphenol [2]. The complex has a phenoxo-bridged binuclear structure containing five- and six-coordinate environments in the same molecule. This is a novel example of manganese complexes, because five-coordination is rare for manganese(II) [3]. We may expect that further introduction of a coordinating group at an apical position makes it possible to form a five-coordinate binuclear manganese complex. As such a ligand, we have used the Schiff base derived from the condensation of 2-(3-aminopropylamino)-ethanol and 2,6-diformyl-4-methylphenol in the hope of obtaining five-coordinate species, [Mn_2LX] (**1**), shown in Scheme 1. However, we found that reaction of 2,6-diformyl-4-methylphenol and 2-(3-aminopropyl-amino)ethanol in the presence of Mn(II) template ion leads to the formation of a binuclear manganese(II) complex with a Robson-type macrocyclic ligand [4], [$Mn_2L'(N_3)_2$] (**2**). We herein report the preparation, X-ray crystal structure, electronic spectra and magnetic property of this complex.

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The binuclear complex **2** was isolated as follows. 2,6-Diformyl-4-methylphenol (33 mg, 0.2 mmol) and 2-(3-aminopropylamino)ethanol (47 mg, 0.4 mmol) were dissolved in absolute methanol (6 ml), then manganese(II) acetate tetrahydrate (98 mg, 0.4 mmol) was added. The mixture was stirred for a while. To the resulting dark brown solution was added a methanol solution (3 ml) of sodium azide (52 mg, 0.8 mmol). The yellow crystals which formed were collected by filtration, washed with methanol, and dried *in vacuo* over P_2O_5 (yield 14 mg). A satisfactory analysis (C, H, N) was obtained.

The structure of **2** was determined by X-ray crystallography**. A perspective view of **2** is illustrated in Fig. 1. The essentially planar macrocyclic ligand is formed in the complex. The complex is crystallographically centrosymmetric and each manganese atom is coordinated to two bridging phenoxide oxygens and two imine nitrogens from the macrocycle. The coordination sphere is completed by an azide nitrogen. The metal atom is therefore five-coordinate and the geometry may be described as a square pyramid. The Mn atom is displaced by 0.67 Å on either side of the ligand plane. The Mn–O (phenoxide) (2.113(5), 2.114(4) Å) and Mn–N (imine) (2.153(6), 2.192(5) Å) lengths are typical for Mn(II) [2]. The structural feature is similar to those of binuclear manganese(II) complexes with Robson-type macrocyclic ligands which have been recently reported [5–7]. The electronic spectrum of **2**[†] shows no appreciable absorption in the region below 20×10^3 cm^{-1}, indicating the electronic configuration of the manganese(II) ion is of high-spin [8]. The magnetic susceptibility was measured over the temperature range 80–300 K. The room temperature moment (5.84 BM) falls in the range expected for a high-spin d^5 ion.

Crystal data for **2: $Mn_2O_2N_{10}C_{24}H_{26}$, formula weight = 596.4, triclinic, space group $P\bar{1}$, $a = 9.342(2)$, $b = 9.801(2)$, $c = 7.636(4)$ Å, $\alpha = 110.37(3)$, $\beta = 92.77(3)$, $\gamma = 78.26(2)°$, $V = 641.5(4)$ Å^3, $Z = 1$, $D_m = 1.57$, $D_c = 1.54$ g cm^{-3}, μ(Mo Kα) = 9.89 cm^{-1}, $R = 0.054$, $R_w = 0.066$. A total of 2238 reflections was measured in the range $1 \leqslant 2\theta \leqslant 50°$; 1533 with $I \geqslant 3\sigma(I)$ were assumed observed. For **3**: $BrMnO_4N_2Cl_2H_{20}$, formula weight = 391.2, orthorhombic, space group *Pbca*, $a = 18.497(2)$, $b = 7.869(1)$, $c = 21.050(2)$ Å, $V = 3063.8(6)$ Å^3, $Z = 8$, $D_m = 1.71$, $D_c = 1.70$ g cm^{-3}, μ(Mo Kα) = 34.25 cm^{-1}, $R = 0.044$, $R_w = 0.046$. A total of 5783 reflections was measured in the range $1 \leqslant 2\theta \leqslant 64°$; 2298 with $I \geqslant 3\sigma(I)$ were assumed observed. For the determination of both structures, intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods and refined by the full-matrix least-squares methods using the SDP program package. In the case of **2**, the carbon atom C9 of the macrocycle showed some disorder. This has been modelled and the occupancies refined to 50:50 for positions C9 and C9'.

†Diffused reflectance spectra: **2**: 371, 470(sh) nm; **3**: 237, 384, 587 nm. Solution spectra: **2** in DMSO: 383 nm ($\epsilon = 13\,300$); **3** in methanol: 243 ($\epsilon = 19\,100$), 376 ($\epsilon = 4080$), 546 ($\epsilon = 238$) nm.

H₃L

2

H₂L″

3
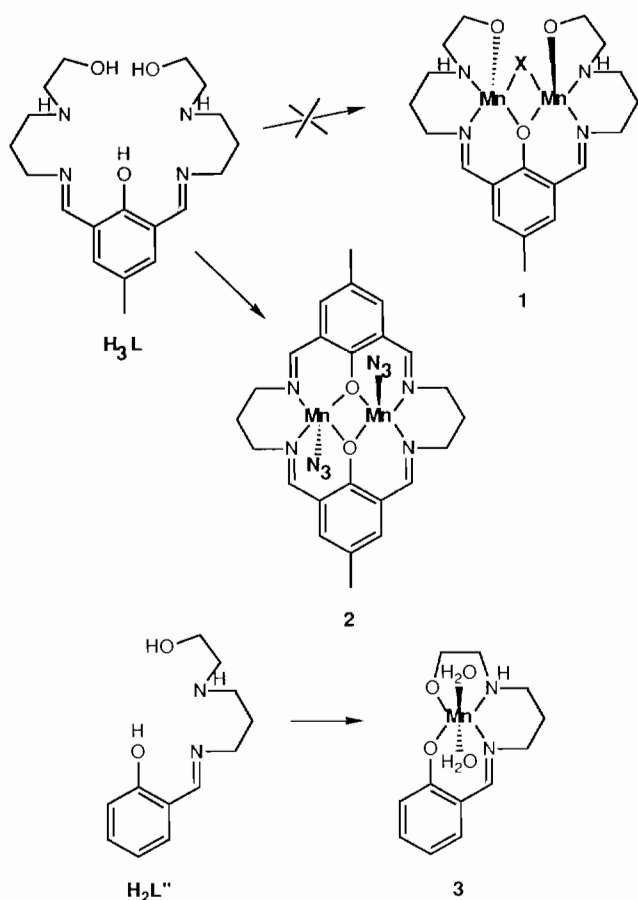
Scheme 1.
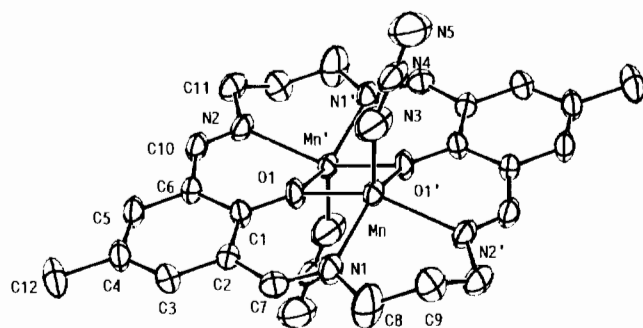
Fig. 1. Perspective view of [Mn₂(L′)(N₃)₂] (**2**). Selected bond distances (l/Å) and angles (ϕ/°) are: Mn–Mn′ 3.311(1), Mn–O1 2.114(4), Mn–O1′ 2.113(5), Mn–N1 2.153(6), Mn–N2′ 2.192(5), Mn–N3 2.043(9); Mn–O–Mn′ 103.1(2).

The magnetic susceptibility data were analyzed with the Van Vleck equation based on the Heisenberg model ($\mathscr{H} = -2JS_1S_2$ ($S_1 = S_2 = 5/2$) and the best fitting parameters are $J = +0.2$ cm^{-1} and $g = 2.00$. This suggests that there may be a weak ferromagnetic interaction. Similar interactions have been observed in the analogous binuclear manganese(II) complexes [5–7].

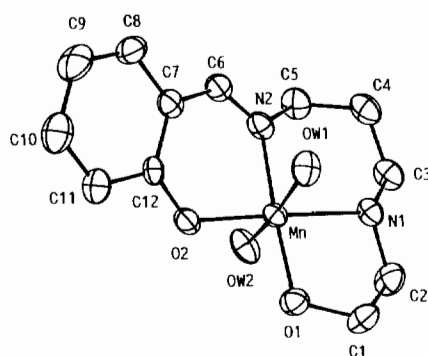The formation of the macrocyclic ligand indicates that an elimination reaction of a hydroxylethyl group

Fig. 2. Perspective view of the complex cation in [Mn(L″)(H₂O)₂]Br (**3**). Selected bond distances (l/Å) and angles (ϕ/°) are: Mn–O1 1.892(4), Mn–O2 1.871(4), Mn–N1 2.060(4), Mn–N2 2.013(5), Mn–OW1 2.278(4), Mn–OW2 2.253(4); N1–Mn–O1 84.7(2), N1–Mn–N2 92.1(2), N2–Mn–O2 91.1(2), O1–Mn–O2 92.1(2).

occurs during the template reaction of the Schiff base H₃L. In order to see if such an elimination reaction occurs in other systems, salicylaldehyde was allowed to react with 2-(3-aminopropylamino)ethanol in the presence of Mn(II) ion. A manganese(III) complex (**3**) was obtained as black crystals from the reaction mixture of salicylaldehyde (48 mg, 0.4 mmol), 2-(3-aminopropylamino)ethanol (47 mg, 0.4 mmol) and manganese(II) bromide tetrahydrate (228 mg, 0.8 mmol) in methanol (yield 82 mg). (A satisfactory analysis (C, H, N) was obtained.) The X-ray structure determination of **3** revealed that the hydroxylethyl group is not eliminated but the Schiff base, 1-(2-hydroxylethyl)amino-3-(salicylideneamino)propane, H₂L″, is formed (Fig. 2). The manganese atom is coordinated to the Schiff base ligand in *trans* configuration. The coordination geometry of the manganese atom is an elongated octahedron. The tetragonal elongation is attributable to the Jahn–Teller effect of a high-spin d⁴ ion [9–11]. Electronic spectra of **3** (see † p. 129) are consistent with the distorted octahedral manganese(III) ion. In this case, the formation of a stable 5–6–6 fused chelate ring may protect it from the elimination reaction. On the other hand, the formation of the Robson-type macrocyclic ligand in **2** may occur due to steric crowding of the hydroxy groups of H₃L or the great stability of the macrocyclic ligand L′, resulting in the elimination reaction of the hydroxy groups.

Acknowledgement

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