SHORT PAPER

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Synthesis and crystal structure of [MnL(μ-Cl)MnCl$_3$]·H$_2$O L=N, N′-bis(2′-pyridine)methyl-1, 10-phenanthroline-2,9-dimethanamine

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The binuclear manganese(II) complex, [MnL(μ-Cl)MnCl$_3$]·H$_2$O (L=N, N′-bis- (2′-pyridine)methyl-1,10-phenanthroline-2,9-dimethanamine) was synthesised and its crystal structure was determined by X-ray diffraction methods.

Keywords: binuclear manganese (II) complex

1,10-phenanthroline has been extensively used as a ligand in both analytical and preparative coordination chemistry.[1] Most of the work on phenanthroline derivatives has been prompted by the intense current interest in their catalytic, redox, photoredox properties, biological activity, complexation activity, and in their novel supramolecular chemistry.[2-7] Pyridine and 1,10-phenanthroline, carrying N-donor atoms and being excellent π acceptors, have shown ability to stabilise low-valent metal complexes and have a marked influence on the coordination geometry. [8]

In seeking to extend the range of available chelating heteroatomic phenanthroline-based ligands, we have reported the synthesis of N,N′-bis(2′-pyridine)methyl- 1,10-phenanthroline-2,9-dimethanamine (L), together with its complexation properties with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)[9] by a pH potentiometric titration method. In this paper we report the crystal structure of the manganese(II) complex with N, N′-bis(2′-pyridine)-methyl-1,10-phenanthroline-2,9-dimethanamine(L).

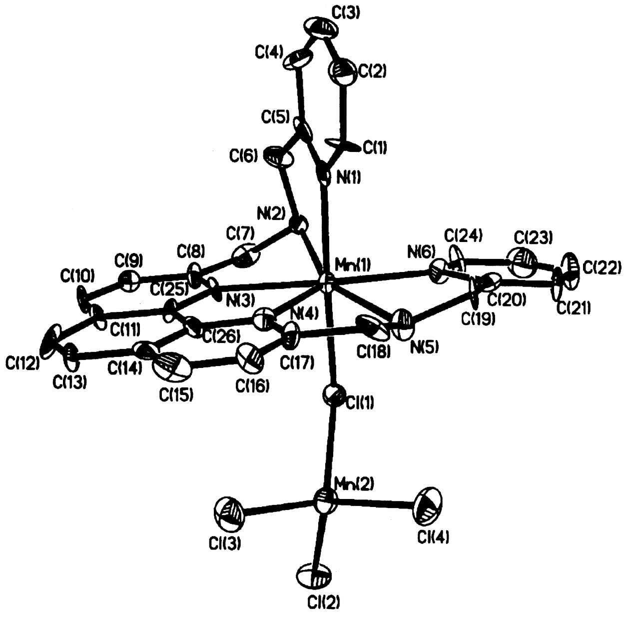

Fig. 1 Molecular structure of [MnL(μ-Cl)MnCl$_3$] with the atom-numbering scheme used. Selected bond lengths (Å): Mn(1)–N(1) 2.196(10), Mn(1)–N(3) 2.310(9), Mn(1)–N(4) 2.320(10), Mn(1)–N(5) 2.359(9), Mn(1)–N(6) 2.374(10), Mn(1)–N(2) 2.456(10), Mn(1)–Cl(1) 2.578(4), Mn(1)...Mn(2) 4.27, Mn(2)–Cl(4) 2.334(4), Mn(2)–Cl(3) 2.328(4), Mn(2)–Cl(2) 2.345(4), Mn(2)–Cl(1) 2.397(4).

A perspective view of the complex with the atoms labelling scheme is shown in Fig.1 and the selected bonds and angles are shown in Table 1. The crystal structure consists of the [MnL(μ-Cl)MnCl$_3$] molecular and a water molecule. In the binuclear complex the two metal ions are bridged by a chloride atom. The Mn(1)–Cl(1)–Mn(2) angle is 117.99(13)°. The Mn(1) atom is seven-coordinated by six nitrogen atoms of the ligand and a chloride atom. The bond lengths which range from 2.196(10) Å[Mn(1)-N(1)] to 2.578(4) Å [Mn(1)-Cl(1)], indicate a weak interaction of these six nitrogen atoms and chloride atom with the metal. The distance between Mn(1) and Mn(2) is 4.27 Å. The Mn(1) atom adopts a distorted pentagonal bipyramidal environment and the Mn(2) atom has a slightly distorted tetrahedral environment. One pyridine is almost parallel to the phenanthroline moiety of the ligand and another is vertical to the phenanthroline moiety.

Experimental

MnCl$_2$·4H$_2$O 396mg (2mmol) in ethanol 20 cm^3 was added to a solution of L 473mg (1mmol) dissolved in ethanol 50 cm^3, and was slowly stirred at room temperature. After 4h, ethanol 50 cm^3 was removed under reduced pressure, and ether 30 cm^3 was added. The

Table 1 The selected bonds(Å) and angles(°)

Mn(1)–N(1)	2.196(10)	N(1)–Mn(1)–N(3)	94.5(4)
Mn(1)–N(3)	2.310(9)	N(1)–Mn(1)–N(4)	93.7(4)
Mn(1)–N(4)	2.320(10)	N(3)–Mn(1)–N(4)	69.2(4)
Mn(1)–N(5)	2.359(9)	N(1)–Mn(1)–N(5)	99.1(4)
Mn(1)–N(6)	2.374(10)	N(3)–Mn(1)–N(5)	135.9(4)
Mn(1)–N(2)	2.456(10)	N(4)–Mn(1)–N(5)	68.3(4)
Mn(1)–Cl(1)	2.578(4)	N(1)–Mn(1)–N(6)	90.1(4)
Mn(2)–Cl(4)	2.334(4)	N(3)–Mn(1)–N(6)	153.1(4)
Mn(2)–Cl(3)	2.328(4)	N(4)–Mn(1)–N(6)	137.1(3)
Mn(2)–Cl(2)	2.345(4)	N(5)–Mn(1)–N(6)	68.9(3)
Mn(2)–Cl(1)	2.397(4)	N(1)–Mn(1)–N(2)	74.3(4)
		N(3)–Mn(1)–N(2)	68.1(3)
		N(4)–Mn(1)–N(2)	134.3(4)
		N(5)–Mn(1)–N(2)	155.9(3)
		N(6)–Mn(1)–N(2)	87.8(3)
		N(1)–Mn(1)–Cl(1)	167.2(3)
		N(3)–Mn(1)–Cl(1)	85.1(3)
		N(4)–Mn(1)–Cl(1)	98.1(2)
		N(5)–Mn(1)–Cl(1)	89.9(3)
		N(6)–Mn(1)–Cl(1)	84.7(2)
		N(2)–Mn(1)–Cl(1)	93.8(2)
		Cl(4)–Mn(2)–Cl(3)	108.98(15)
		Cl(4)–Mn(2)–Cl(2)	117.71(16)
		Cl(3)–Mn(2)–Cl(2)	107.16(16)
		Cl(4)–Mn(2)–Cl(1)	103.38(14)
		Cl(3)–Mn(2)–Cl(1)	115.81(14)
		Cl(2)–Mn(2)–Cl(1)	104.11(13)
		Mn(2)–Cl(1)–Mn(1)	117.99(13)

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

solid products were filtered and washed with a small portion of cool ethanol and dried in a vacuum desiccator (435mg, 63%). Anal. for $C_{26}H_{26}Cl_4Mn_2N_6O$ Calcd. C, 45.20; H, 3.77; N, 12.17 %. Found: C, 45.09; H, 3.70; N, 12.23%. IR(KBr pellet) 3280, 2908, 1602, 1573, 1501, 1439, 860, 760 cm^{-1}.

The pale-yellow crystal suitable for X-ray diffraction was obtained by evaporation from a methanol solution of complex $[MnL(\mu\text{-}Cl)MnCl_3]\cdot H_2O$ at room temperature.

Crystallographic data: $[MnL(\mu\text{-}Cl)MnCl_3]\cdot H_2O$ Mr = 690.21, crystal size: 0.30 × 0.25 × 0.20 mm, monoclinic, space group $P2_1/c$, a = 11.890(5), b = 14.815(6), c = 17.860(8) Å, β = 104.116(9)°, z = 4, V = 3051(2) $Å^3$, Dc = 1.503 Mg/m^3, F000 = 1400, R = 0.0668, wR = 0.0868. Structural analyses for $[MnL(\mu\text{-}Cl)MnCl_3]\cdot H_2O$ was performed on a Bruker SMART diffractometer at 293(2) K with graphite-monochromated Mo $K\alpha(\lambda = 0.71073$ Å) by θ-2ω scan technique in the range $1.77 \le \theta \le 25.03°$. A total of 12310 reflections were collected, 5339 reflections with $I > 2\sigma(I)$ were used in the structure determination and refinement. The structure was solved by direct methods using the SHELXTL-97 package. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located theoretically and refined with riding mode position parameters and fixed isotropic thermal parameters.

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