

## Synthesis and Structural Studies of $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$ : a 3D Coordination Polymer of Mn(II) with 1,3-Bis(4-pyridyl)propane

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The single crystal X-ray data of a novel 3D coordination polymer of Mn(II) with 1,3-bis(4-pyridyl)propane (bpp) and anionic chloride ligands,  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$ , show that the coordination environment around the Mn(II) is a distorted octahedral. The thermal stability of the compound was studied by thermal gravimetric and differential thermal analyses. The luminescent spectrum of the compound in solution indicates intense fluorescent emission at 368 nm.

**Keywords:** Manganese(II), 1,3-Bis(4-pyridyl)propane, Coordination polymer, Cl...H-C interaction, Fluorescent emission, Thermal stability

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### INTRODUCTION

In recent years, much interest has been focused on the design and synthesis of supramolecular compounds due to their remarkable structure motifs and potential applications in ion exchange, as porous materials and molecular adsorbents [1-7]. In the process of fabricating these kinds of complexes, some organic N-donors such as bipyridine and related species [8-19] are often chosen as rigid 'tectons' to bind the metal centers. The metal-organic coordination polymers [20-23] of 4,4'-bipyridine (4,4'-bipy) [24-26] and 1,3-bis(4-pyridyl)propane (bpp) ligands [27-32] have attracted continuous attention in recent years. A subtle change in the use of conformationally flexible ligands as spacers in the design and construction of coordination polymers may lead to new polymeric networks. Recently, bpp ligands were used with nickel, cobalt, cadmium, zinc and copper ions to form

new metal-organic coordination polymers [33-37]. As a continuation of these works, we herein report the solid state structure of  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$  as a new three-dimensional coordination polymer.

### EXPERIMENTAL

#### Materials and Methods

IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The thermal measurements were performed using a simultaneous thermal gravimetric-differential thermal analyzer. The luminescent properties were measured with a Shimadzu RF-5000 spectrofluorophotometer.

Crystallographic measurements were made at 298(2) K using a Siemens R3m/V diffractometer. The intensity data were collected within the range  $1.26 \leq \theta \leq 25.01^\circ$  using

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graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Accurate unit cell parameters and orientation matrix for data collection were obtained from the least-squares refinement. Intensities of 5740 unique reflections were measured, of which 4973 with  $I > 2\sigma(I)$  were used in the refinement. The structure has been solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$ . The molecular structure plots were prepared using ORTEPIII [38], and WinGX [39] was used as an interface during the structure solution procedure. The anisotropic crystal dimensions and the poor quality of the

crystal resulted in high R values for this compound. Crystal data and structure refinement are given in Table 1. Selected bond lengths and angles are given in Table 2. Anisotropy thermal parameters observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. The ORTEP diagram and perspective view of the packing are shown in Figs. 1 and 2.

### Preparation of $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$

An aqua solution (10 ml) containing manganese(II)

**Table 1.** Crystal Data and Structure Refinement for  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$

Empirical formula	$\text{C}_{26}\text{H}_{28}\text{Cl}_2\text{MnN}_4$
Formula weight	522.36
Temperature	298(2) K
Wavelength	0.71073 $\text{\AA}$
Crystal system	Tetragonal
Space group	$I4_1/a$
Unit cell dimensions	$a = 17.4501(9)\text{\AA}$ $b = 17.4501(9)\text{\AA}$ $c = 42.568(2)\text{\AA}$
Volume	12962.3(11) $\text{\AA}^3$
Z	16
Density (calculated)	1.071 $\text{Mg m}^{-3}$
Absorption coefficient	0.589 $\text{mm}^{-1}$
$F(000)$	4336
Crystal size	0.38 $\times$ 0.29 $\times$ 0.25 $\text{mm}^3$
Theta range for data collection	1.26 to 25.01 $^\circ$
Index ranges	$-16 \leq h \leq 20$ $-19 \leq k \leq 20$ $-42 \leq l \leq 50$
Reflections collected	34113
Independent reflections	5740 [ $R(\text{int}) = 0.0383$ ]
Completeness to theta = 25.01 $^\circ$	100%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on $F^2$
Max. and min. transmission	0.38 and 0.29
Data/restraints/parameters	5740/0 /299
Goodness-of-fit on $F^2$	1.207
Final R. [ $I > 2\sigma(I)$ ]	$R1 = 0.1410$ , $wR2 = 0.3918$
R indices (all data)	$R1 = 0.1519$ , $wR2 = 0.3995$
Largest diff. peak and hole	1.456 and -0.971 e. $\text{\AA}^{-3}$

**Table 2.** Bond Lengths and Bond Angles for  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$ 

	Bond lengths (Å)		Bond angles (°)
Mn1-N1	2.285(6)	N1-Mn1-N1 <sup>ii</sup>	92.6(3)
Mn1-N2 <sup>i</sup>	2.306(6)	N1-Mn1-N2 <sup>iii</sup>	177.8(2)
Mn1-Cl1	2.5079(19)	N1-Mn1-N2 <sup>i</sup>	87.5(2)
Mn2-N4 <sup>iii</sup>	2.295(9)	N2 <sup>iii</sup> -Mn1-N2 <sup>i</sup>	92.4(3)
Mn2-N3	2.305(8)	N1-Mn1-Cl1	91.40(17)
Mn2-Cl2	2.512(3)	N1-Mn1-Cl1 <sup>ii</sup>	89.47(17)
		N2 <sup>iii</sup> -Mn1-Cl1	90.84(17)
		N2 <sup>i</sup> -Mn1-Cl1	88.29(17)
		Cl1-Mn1-Cl1 <sup>ii</sup>	178.75(12)
		N4 <sup>i</sup> -Mn2-N4 <sup>iii</sup>	92.8(5)
		N4 <sup>iii</sup> -Mn2-N3	87.4(3)
		N4 <sup>iii</sup> -Mn2-N3 <sup>ii</sup>	177.9(3)
		N4 <sup>i</sup> -Mn2-Cl2	89.0(3)
		N4 <sup>iii</sup> -Mn2-Cl2	90.9(3)
		N3-Mn2-Cl2	88.9(2)
		N3 <sup>ii</sup> -Mn2-Cl2	91.2(2)
		Cl2-Mn2-Cl2 <sup>ii</sup>	179.89(17)

Symmetry transformations used to generate equivalent atoms: i:  $y+3/4, -x+3/4, z+3/4$ , ii:  $-x, -y+1/2, z$ , iii:  $-y+1/4, x+3/4, z+3/4$ .

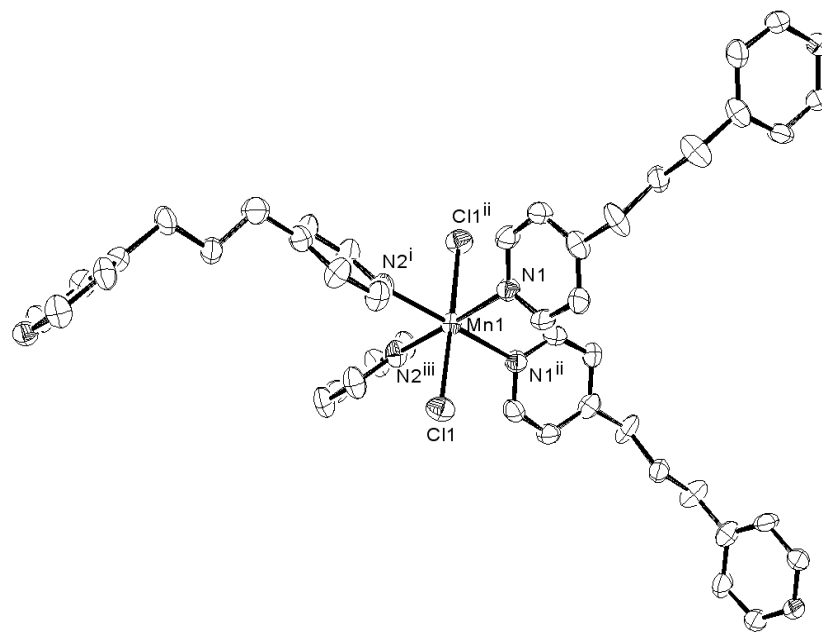
chloride (1 mmol, 0.126 g) was slowly added to 10 ml of a solution of bpp (2 mmol, 0.392 g). The mixture solution was left to stand at room temperature for approximately two days, after which colorless crystals were obtained, d.p. > 300 °C. Yield: 0.261 g, 50%.  $\text{C}_{26}\text{H}_{28}\text{Cl}_2\text{MnN}_4$ : calcd.: C, 59.73; H, 5.36; N, 10.72; found C, 59.42; H, 5.78; N, 10.46%. IR (KBr,  $\text{cm}^{-1}$ ) selected bonds: 590(m), 794(s), 840(m), 1410(m), 1480(m), 1523(m), 1551(m), 1601(vs), 2933(w), and 3055(w).

## RESULTS AND DISCUSSION

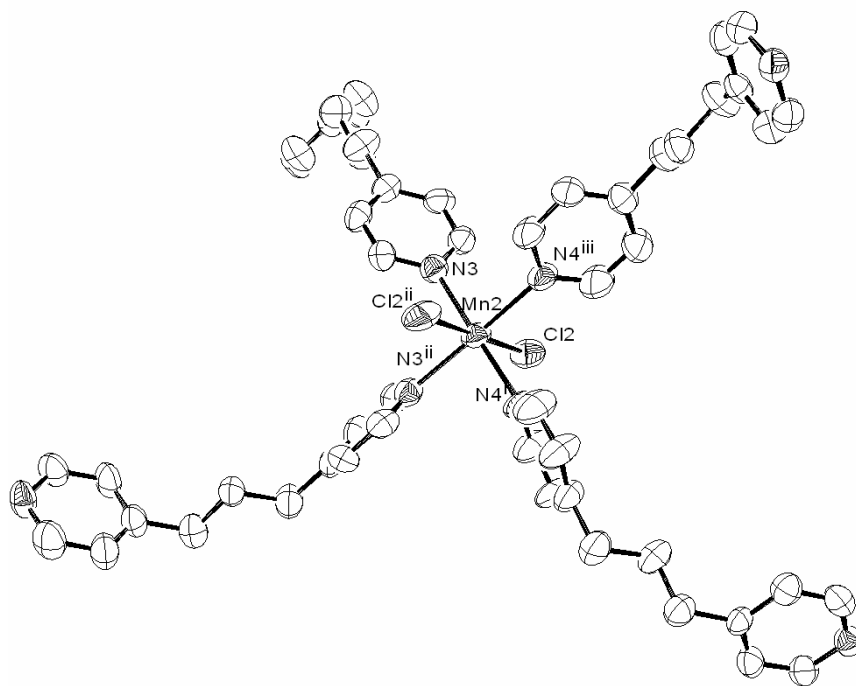
The reaction between bpp and manganese(II) chloride provided crystalline materials of  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$ . The IR spectrum of this complex shows absorption bands resulting from the skeletal vibrations of the aromatic rings in the 1400-1523  $\text{cm}^{-1}$  range. The relatively weak absorption bands at approximately 3055  $\text{cm}^{-1}$  are due to the C-H modes involving the aromatic ring hydrogen atoms. The C-H modes involving the aliphatic hydrogen atoms of the bpp ligand appeared at

2933  $\text{cm}^{-1}$ . Determination of the structure of  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$  by X-ray crystallography (Table 1) shows the complex in the solid state (Figs. 1 and 2) consisting of polymeric units. There are two types of Mn(II) ions with coordination numbers of six in addition to a  $\text{MnN}_4\text{Cl}_2$  sphere (Fig. 1). In the solid state, the complex consists of three-dimensional polymeric units that result from connecting the bpp ligands. The manganese atoms are linked by nitrogen and chlorine atoms that are six-coordinate with  $\text{N}_4\text{Cl}_2$  donor atom arrays. The manganese atoms are indeed bridged by the bpp ligand and produce three-dimensional solid state polymeric units. The coordination around Mn is a distorted octahedral with the four nitrogen atoms of the bpp ligand and the two chlorine atoms coordinate with the Mn atom. Two chlorine atoms are in the *trans* position [the angles Cl2-Mn2-Cl2<sup>ii</sup> (ii:  $-x, -y+1/2, z$ ) = 179.89(17) and Cl1-Mn1-Cl1<sup>ii</sup> (ii:  $-x, -y+1/2, z$ ) = 178.75(12)°].

There are three conformations of the bpp ligand. This flexible ligand usually assumes TT, TG or GG conformations



**a**

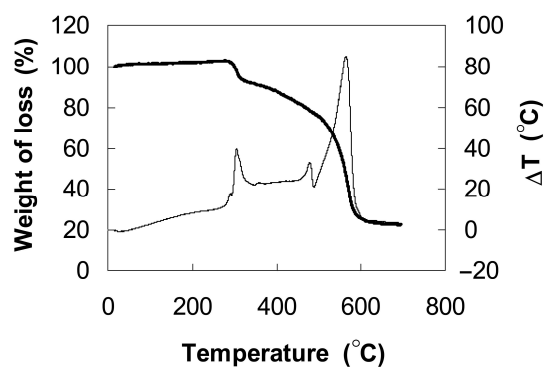


**b**

**Fig. 1.** ORTEP diagram and schematic representation of Mn(II) environments for  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$ :  
a) Mn1 and b) Mn2.



**Fig. 2.** View of 3D-network down the  $a$  axis of  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$ .



**Fig. 3.** Thermal behavior for  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$ : (—) TGA, (---) DTA.

with quite different N-to-N distances (within the 6.7-10.1 Å range) [14]. The TT and TG conformations have been fairly widely encountered and such structures tend to pack efficiently, whereas the GG conformations are quite rare in the context of coordination polymers [30-31]. Self-assembly of the bpp ligand in this complex is the TG conformation type with a N-to-N distance of 9.777 and 9.781 Å (Fig. 1).

A general search was also made for non-classical C-H...Cl approaches in this compound. The interesting feature of this complex is that there are C-H...Cl interactions, with weak hydrogen bonding between the hydrogen atoms of the aromatic rings of the bpp ligand and coordinated chlorine atoms belonging to the adjacent complexes. In this complex, there are two types of C-H...Cl interactions with the distances of Cl...HC(py) equal to 2.597 and 2.764 Å {HC(py)...Cl = 3.402 and 3.684 Å and  $\angle \text{Cl}\cdots\text{H}-\text{C} = 124.15$  and  $169.64^\circ$ }. The C-H...Cl distance range in this compound is much shorter than that reported for similar compounds [40-41], which suggests strong interactions within this class of weak noncovalent contacts. There are edge-to-face  $\pi$ - $\pi$  stacking interactions [42] between the parallel aromatic rings that belong to the adjacent chain in this complex. In the crystal reported here, the interplanar distance is *ca.* 3.76 Å.

A search of the Cambridge Structural Database revealed the structure of a closely related 3D coordination polymer of bpp and  $\text{CuCl}_2$ ,  $[\text{Cu}(\mu\text{-bpp})_2\text{Cl}_2]_n \cdot 2.75\text{H}_2\text{O}$  [43]. The copper centers are octahedral with *trans* chlorides and four molecules of bpp in the equatorial positions that bridge the copper centers, very similar to the compound reported here. The structure of  $[\text{Cu}(\mu\text{-bpp})_2\text{Cl}_2]_n \cdot 2.75\text{H}_2\text{O}$  consists of four interpenetrating 3D diamond-like networks; however, no such interpenetration was found in the compound  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$ .

The fluorescence spectra of the bpp ligand and the complex  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$  in MeOH show a broad emission band with the maximum intensity at 368 nm upon excitation at 295 nm. This fluorescent emission can be tentatively assigned to the intraligand fluorescence emission, since a similar emission at 348.2 nm upon excitation at 295 nm can also be observed for the free bpp. Generally, the intraligand fluorescence emission wavelength is determined by the energy gap between the  $\pi$  and  $\pi^*$  molecular orbitals of the free ligand, which is simply related to the extent of  $\pi$  conjugation in the

system. Thus the unexpected slightly red-shifted emission of the compound  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$  probably results from the coordination of the bpp ligand in solution effecting the fluorescent properties. In order to examine the thermal stability of the compound  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$ , thermal gravimetric and differential thermal analyses were carried out between 30 and 700 °C (Fig. 3). The thermal gravimetric curve of  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$  indicates that this compound does not melt and is stable up to 310 °C, at which temperature it begins to decompose. The release of the two bpp ligands and decomposition of the compound take place at 310-590 °C with three exothermic effects at 320, 475 and 580 °C (Fig. 3). The solid residue formed at approximately 600 °C is suggested to be MnO (observed: 15.50, calcd.: 13.80%). From the thermal gravimetric analysis, up to a temperature of 310 °C, no reduction in weight is observed, indicating that  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$  does not contain any solvent molecules, unlike the closely related 3D coordination polymer  $[\text{Cu}(\text{bpp})_2\text{Cl}_2]_n \cdot 2.75\text{H}_2\text{O}$ .

In summary, a new 3D manganese(II) chloride polymer based on a flexible ligand,  $[\text{Mn}(\mu\text{-bpp})_2\text{Cl}_2]_n$ , has been demonstrated. This compound is stable up to a temperature of 310 °C and displays luminescence in the solution state at room temperature.

## SUPPLEMENTARY MATERIAL

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 293276.

## ACKNOWLEDGEMENTS

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