Synthesis, structure and magnetic properties of a linear-chain manganese(II) complex [Mn(μ-Cl)$_2$(mppma)]$_n$, where mppma is N-(3-methoxypropyl)-N-(pyridin-2-ylmethyl)amine

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Abstract

N-(3-methoxypropyl)-N-(pyridin-2-ylmethyl)amine (abbreviated as mppma) and its complex [Mn(μ-Cl)$_2$(mppma)]$_n$ have been synthesized. Single-crystal X-ray diffraction analysis has revealed that in the complex, mppma acts as a didentate ligand bound to the Mn(II) ion through two nitrogen atoms; [MnCl$_2$(mppma)] units are connected by double chloride bridges to form one-dimensional zigzag chains of edge-sharing distorted MnCl$_4$(mppma) octahedra. The temperature-dependent magnetic susceptibility data have been explained with Fisher model, with parameters $J = -0.25$ cm^{-1} and $g = 1.99$, indicating weak antiferromagnetic coupling.
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1. Introduction

The preparation and magnetic properties of polynuclear transition metal complexes are of considerable interest to the field of molecular magnetism [1,2]. A number of one-dimensional chain manganese(II) coordination polymers have been reported. The magnetic behaviour of these compounds is dependent on the bridging and terminal ligands involved. Most magnetic studies of polymeric Mn(II) compounds have focused on complexes with bridging carboxylate ligands [3–10]. Relatively few investigations of the structure and magnetic properties of halogen-bridged Mn(II) polymers have been carried out [11–14]. In addition to their magnetic interest, chloride-bridged Mn(II) compounds are attractive for the study of the role of chloride anions in the assembly of manganese ions in photosynthetic water oxidation systems [11]. In this paper, we present the synthesis of a new chelating ligand, N-(3-methoxypropyl)-N-(pyridin-2-ylmethyl)amine (mppma; Scheme 1), and its complex with MnCl$_2$. In the solid state, the structure of [Mn(μ-Cl)$_2$(mppma)]$_n$ consists of one-dimensional zigzag chains. Weak antiferromagnetic interactions occur between the metal ions within the chains.
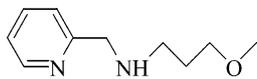
2. Experimental

2.1. General methods

All reagents were purchased from commercial sources and used as received. All the solvents were purified by regular methods. The syntheses were performed under an inert atmosphere of argon using standard Schlenk equipment. Infrared spectra were recorded on a Perkin–

Scheme 1. mppma.

Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 cm^{-1}, resp. 4 cm^{-1}). Magnetic susceptibility measurements (5–280 K) were carried out (at 1000 G) using a Quantum design MPMS-5 5T SQUID magnetometer. Data were corrected for the magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants. NMR spectra were recorded on a JEOL JNM FX-200 (200 MHz) instrument. C, H and N analyzes were performed with a Perkin–Elmer 2400 series II analyzer.

2.2. Synthesis

2.2.1. mppma

A solution of 2-pyridinecarboxaldehyde (1 ml, 10.5 mmol) and 1 equiv. of 3-methoxypropylamine (1.08 ml) in 80 ml of toluene was refluxed under argon overnight, in a flask equipped with a Dean-Stark assembly. The solvent was removed using a rotating evaporator, and to the residue oil was added 20 ml of methanol followed by 0.38 g (10 mmol) sodium borohydride in portions with stirring. Subsequently, the solution was continuously stirred for 5 h. Concentrated hydrochloric acid was added to destroy unreacted sodium borohydride until a pH of approximately 7 was reached. Sodium hydroxide (2 M) was then added to adjust the pH to approximately 11. The solvent was removed and the residue was extracted with 4 × 5 ml of diethyl ether. The extract was dried with anhydrous sodium sulfate. After removing the diethyl ether, the product was isolated as a brownish-red oil, yield 1.73 g, 91.5%. ^{1}H NMR (CDCl$_3$): δ (ppm) 8.55 (d, 1H, pyC6H), 7.64 (m, 1H, pyC4H), 7.30 (d, 1H, pyC3H), 7.15 (m, 1H, pyC5H), 3.91 (s, 2H, py–CH_2–N), 3.46 (t, 2H, CH_2–CH_2–O), 3.33 (2, 3H, O–CH_3), 2.74 (t, 2H, N–CH_2–CH$_2$), 2.11 (br, NH), 1.81 (m, 2H, CH$_2$–CH_2–CH$_2$). ^{13}C NMR (CDCl$_3$): δ (ppm) 159.9 (py$C$2), 149.2 (py$C$6), 136.3 (py$C$4), 122.2 (py$C$3), 121.8 (py$C$5), 71.2 (CH$_2$–CH$_2$–O), 58.6 (O–CH$_3$), 55.3 (py–CH$_2$–N), 46.9 (N–CH$_2$–CH$_2$), 30.1 (CH$_2$–CH$_2$–CH$_2$). IR: v (cm^{-1}) 2925 (m), 2828 (m), 1592 (m), 1570 (m), 1435 (m), 1386 (w), 1115 (s), 1048 (w), 994 (w), 758 (m), 631 (m), 533 (s).

2.2.2. [Mn(μ-Cl)$_2$(mppma)]$_n$

Manganese(II) chloride dihydrate (40.5 mg, 0.25 mmol) and mppma (91.2 mg, 0.51 mmol) were dissolved in 1 ml of anhydrous methanol and heated at 50 °C under argon for 4 h. After cooling, 50 ml of diethyl ether was added and the off-white precipitate was collected,

yield 72.0 mg, 94.1% (based on Mn). Colourless needles of X-ray quality were obtained by vapour diffusion of diethyl ether into a methanolic solution of the product. Anal. Calc. for C$_{10}$H$_{16}$Cl$_2$MnN$_2$O: C, 39.24; H, 5.27; N, 9.15. Found: C, 39.49; H, 5.99; N, 9.67%. IR: v (cm^{-1}) 3282 (m), 2924 (w), 2874 (m), 2832 (w), 1607 (s), 1484 (m), 1434 (s), 1120 (vs), 1092 (s), 1086 (s), 1050 (m), 1020 (m), 959 (vs), 883 (s), 780 (s), 642 (s), 479 (m), 440 (m), 418 (m), 338 (m).

2.3. Crystal structure determination and refinement

Intensity data for a single crystal were collected using graphite-monochromated Mo Kα radiation, on a Nonius KappaCCD diffractometer with a rotating anode. An empirical absorption correction was applied using PLATON/DELABS (0.634–0.912 transmission) [15]. The structure was solved by direct methods using SHELXS97, and was refined on F^2 by least-squares procedures using SHELXL97 [16]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms, and in particular H18 on the secondary amine nitrogen, were positively identified in a difference map. Hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Structure validation and molecular graphics preparation were performed with the PLATON package [15]. Crystal data and details of the structure determination are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopy

The mppma ligand was synthesized according to the general procedure for preparing a Schiff base and its corresponding amine, using sodium borohydride as the reductant. Although a 1:2 ratio of Mn(II) to mppma was applied, the elemental analyzes and X-ray structure revealed that mppma coordinates to Mn(II) in a 1:1 ratio.

The IR spectrum of free mppma has a characteristic ether band at 1115 cm^{-1}. In the spectrum of [Mn(μ-Cl)$_2$(mppma)]$_n$, this very strong band is located at nearly the same position, 1120 cm^{-1}. Since coordination of the ether oxygen to a metal nucleus normally results in an obvious red shift [17], it can be concluded that the ether oxygen does not coordinate to Mn(II), which is confirmed by the X-ray structure.

Table 1
Crystal data and details of the structure determination for [Mn(μ-Cl)$_2$(mppma)]$_n$

Empirical formula	$C_{10}H_{16}Cl_2MnN_2O$
Formula weight	306.09
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	6.7865(2)
b (Å)	11.0911(3)
c (Å)	16.9764(6)
β (°)	100.932(1)
V (Å^3)	1254.62(7)
Z	4
D_{calc} (g cm^{-3})	1.620
$F(0\,0\,0)$	628
μ (cm^{-1})	14.58
Crystal size (mm^3)	$0.06 \times 0.08 \times 0.54$
T (K)	150
Radiation (Å)	Mo Kα, 0.71073
θ_{min}, θ_{max} (°)	2.2, 27.5
Total data collected	11 449
Unique reflections, R_{int}	2823, 0.048
Observed data [$I > 2\sigma(I)$]	2131
Number of refined reflections, parameters	2823, 146
Weighting scheme	$w = 1/[(\sigma^2(F_o^2) + (0.0206P)^2 + 0.0178P]$, where $P = (F_o^2 + 2F_c^2)/3$
Final R, wR_2, S	0.0308, 0.0603, 1.02
Min. and max. residual density (e Å^{-3})	−0.30, 0.47

3.2. Crystal and molecular structure of [Mn(μ-Cl)$_2$(mppma)]$_n$

In the crystal structure of the title complex, [MnCl$_2$mppma] units are linked by double μ$_2$-bridging chlorides to form one-dimensional zigzag chains that run along the a direction. The geometry of three monomeric units in the coordination polymer is shown
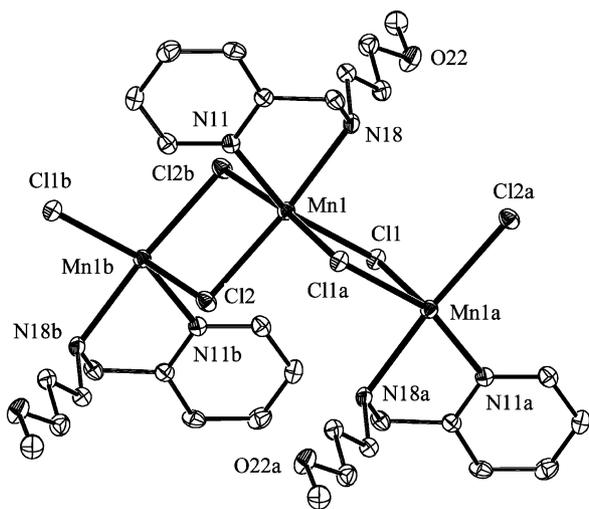

Fig. 1. ORTEP view (50% probability) of three monomeric units within a single chain of [Mn(μ-Cl)$_2$(mppma)]$_n$. Hydrogen atoms are omitted for clarity.

in Fig. 1. The crystal packing is shown in Fig. 2. Selected bond lengths, bond angles and torsion angles are given in Table 2.

The coordination sphere of Mn(II) is a distorted octahedron with four bridging chlorides and two nitrogens from mppma as vertices. The oxygen of mppma remains uncoordinated, in agreement with IR spectrum of the complex, most likely due to the weak coordinating ability of the ether oxygen in combination with the weaker six-membered chelate ring. The Mn$_2$Cl$_2$ diamond cores, which join inversion-related molecules, are strictly planar, as is also observed in the dimanganese(II) chloride complex [Mn$_2$(μ-Cl)$_2$(bpea)$_2$Cl$_2$] (bpea = N,N-bis(2-pyridylmethyl)ethylamine) [18].

It is interesting to compare the structure of the title complex with that of [Mn(μ-Cl)$_2$(bpy)]$_n$ (bpy = 2,2′-bipyridine), a similar chain complex of Mn(II) with the symmetric bpy ligand [19]. The two Mn−N distances in the bpy complex are 2.258(3) Å, while in the mppma complex the Mn(1)−N(11) and Mn(1)−N(18) distances are 2.2426(16) and 2.3381(16) Å, respectively, reflecting the stronger coordinating ability of the pyridine nitrogen vs. that of the nitrogen in the aliphatic secondary amine. Nevertheless, the ligand N−Mn−N bite angles of 73.26(6)° in [Mn(μ-Cl)$_2$(mppma)]$_n$ and 72.34(11)° in [Mn(μ-Cl)$_2$(bpy)]$_n$ are similar. The Mn−Cl distances in the mppma complex fall within a relatively small range, from 2.5265(6) to 2.5906(6) Å, while in the bpy complex the Mn−Cl distances are 2.481(1) and 2.662(1) Å. The Mn(II) ions within the chains of the bpy complex are equidistant, separated by 3.8352(7) Å; in the mppma complex, the intrachain Mn···Mn distances alternate between 3.7398(4) and 3.8399(4) Å. These intrachain Mn···Mn distances are comparable to those found in double chloride-bridged dimanganese(II) complexes [18,20], but shorter than the 3.94 Å distance observed in polymeric [Mn(μ-Cl)$_2$(tmen)]$_n$ (tmen = Me$_2$NCH$_2$CH$_2$NMe$_2$) [11].

No classical hydrogen bonds occur in the crystal structure of [Mn(μ-Cl)$_2$(mppma)]$_n$. There may, however, be some weaker N−H···Cl interactions, as the N(18)···Cl(1) distance is found to be 3.374(2) Å. The shortest interchain Mn···Mn distance is 9.2148(6) Å, which is quite large compared with that observed in Mn(II) chain complexes in which the chains are connected by hydrogen bonds [6,14].

3.3. Magnetic behaviour

Plots of the temperature dependence of the molar magnetic susceptibility (χ_M) and effective magnetic moment (μ_{eff}) per one [MnCl$_2$(mppma)] unit are shown in Figs. 3 and 4, respectively. The μ_{eff} value at 300 K is 5.68 BM, close to the spin-only value of 5.92 BM expected for an uncoupled high-spin Mn(II) ion. When the temperature is lowered, the μ_{eff} value remains
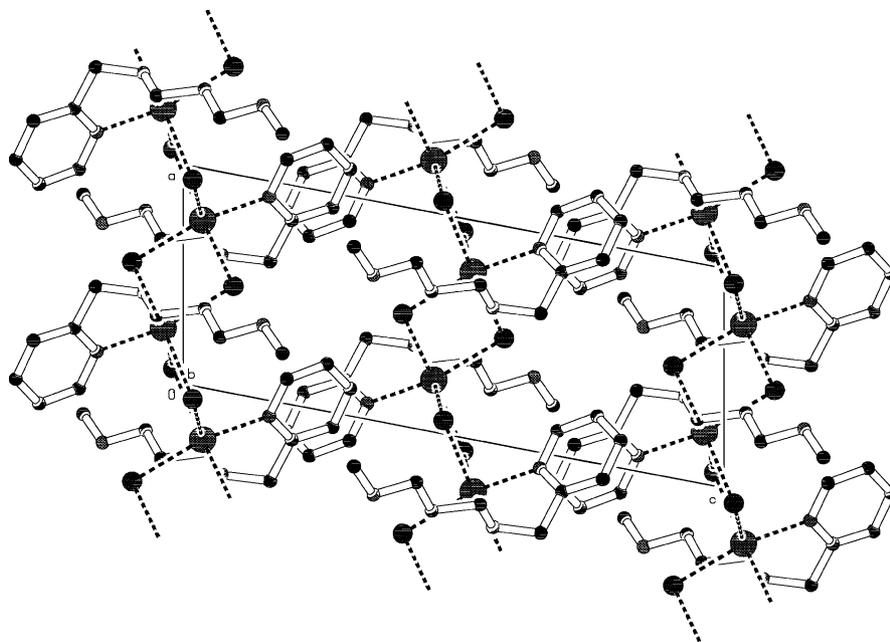
Fig. 2. PLATON view of the crystal lattice of [Mn(μ-Cl)$_2$(mppma)]$_n$, showing the one-dimensional chains that propagate along the *a* direction.

relatively constant to 50 K and then decreases sharply to 3.57 BM at 2 K, as a result of weak antiferromagnetic spin-exchange interactions between the Mn(II) ions through the double chloride bridges.

Since the coordination environment of each Mn(II) ion is equivalent, the difference between the two

Table 2
Selected bond lengths (Å), bond angles (°) and torsion angles (°) in [Mn(μ-Cl)$_2$(mppma)]$_n$

Bond lengths			
Mn(1)–Cl(1)	2.5265(6)	Mn(1)–Cl(2)	2.5503(6)
Mn(1)–Cl(1)[a]	2.5811(6)	Mn(1)–Cl(2)[b]	2.5906(6)
Mn(1)–N(11)	2.2426(16)	Mn(1)–N(18)	2.3381(16)
Bond angles			
Cl(1)–Mn(1)–Cl(2)	100.085(19)	Cl(1)–Mn(1)–Cl(1)[a]	85.863(18)
Cl(1)–Mn(1)–Cl(2)[b]	97.053(18)	Cl(2)–Mn(1)–Cl(1)[a]	90.729(18)
Cl(2)–Mn(1)–Cl(2)[b]	83.355(18)	Cl(1)[a]–Mn(1)–Cl(2)[b]	173.774(19)
Cl(1)–Mn(1)–N(11)	160.95(4)	Cl(1)–Mn(1)–N(18)	87.73(4)
Cl(2)–Mn(1)–N(11)	98.83(4)	Cl(2)–Mn(1)–N(18)	171.54(4)
N(11)–Mn(1)–Cl(1)[a]	91.67(4)	N(11)–Mn(1)–Cl(2)[b]	87.34(4)
N(18)–Mn(1)–Cl(1)[a]	86.58(4)	N(18)–Mn(1)–Cl(2)[b]	99.00(4)
N(11)–Mn(1)–N(18)	73.26(6)	Mn(1)–Cl(1)–Mn(1)[a]	94.137(18)
Mn(1)–Cl(2)–Mn(1)[b]	96.645(18)	Mn(1)–N(11)–C(12)	116.93(12)
Mn(1)–N(11)–C(16)	124.61(13)	Mn(1)–N(18)–C(17)	105.88(11)
Mn(1)–N(18)–C(19)	114.57(11)		
Torsion angles			
Mn(1)–N(18)–C(17)–C(12)	−45.04(16)	Mn(1)–N(18)–C(19)–C(20)	−76.66(16)
C(17)–N(18)–C(19)–C(20)	162.71(15)	C(19)–N(18)–C(17)–C(12)	80.51(19)

[a] 1−x, 1−y, −z.
[b] 2−x, 1−y, −z.

intrachain Mn⋯Mn distances is quite small and the interchain Mn⋯Mn distance is quite large. The magnetic susceptibility data may be analyzed according to Fisher's formula for an infinite linear chain of magnetically coupled classical spins scaled to a spin value of 5/2 [2,6,21]:

$$\chi = \frac{Ng^2\beta^2 S(S+1)}{3kT}\frac{1+u}{1-u}$$

$$u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{JS(S+1)}{kT}\right]^{-1}$$

where N is Avagadro's number, β the Bohr magneton and k Boltzman's constant. An excellent fit to the experimental data was obtained (Fig. 3), giving parameters $J = -0.255(0)$ cm^{-1} and $g = 1.990(1)$, with an
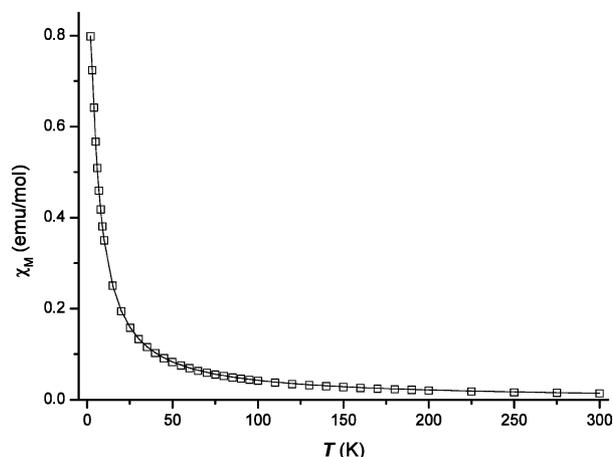

Fig. 3. Plot of molar magnetic susceptibility vs. temperature. Solid line is the best fit described in the text.
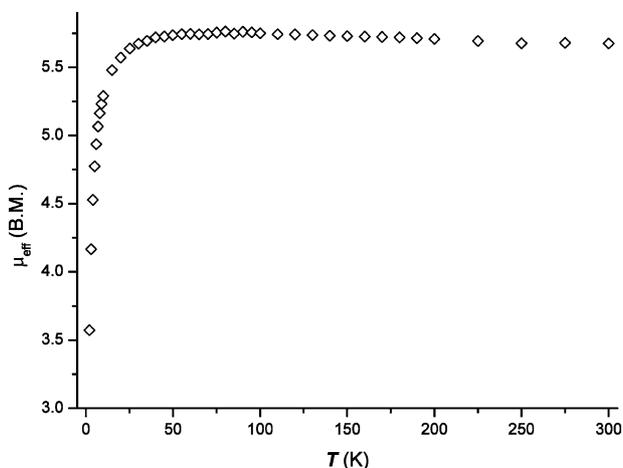
Fig. 4. Plot of the experimental effective magnetic moment vs. temperature.

agreement factor of $R = 9.9 \times 10^{-7}$ (R is defined as $\Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma[(\chi_M)_{obs}]^2)$ and a coefficient of determination of $r^2 = 0.99998$.

The fact that the magnetic data can be well described without considering other factors, such as the alteration in the exchange due to alternating metallic distances, or the local anisotropies of Mn(II), suggests that such effects, if present, are too small to be detected.

The low value of J, i.e., the weak antiferromagnetic exchange coupling in $[Mn(\mu\text{-}Cl)_2(mppma)]_n$, can be compared with that for other double chloride-bridged polymeric Mn(II) chains $[Mn(\mu\text{-}Cl)_2(4\text{-}CNpy)_2]_n$ ($J = -0.57$ cm^{-1}) [14] and $[Mn(\mu\text{-}Cl)_2(tmen)]_n$ (estimated $J = 0$ cm^{-1}) [11], or other types of Mn(II) chains for which J values in the range -0.20 to -0.74 cm^{-1} have been reported [4,6,7,20]. Such low J values might be the result of a combination of ferro and antiferromagnetic interaction [22].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 203689. Copies of this information may 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/conts/retrieving.html).

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