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The first structurally characterised example of a manganese(II) complex with monodentate thione ligands; the crystal and molecular structure of *trans*-dichloro{tetrakis(2(1*H*)-pyridinethione-*S*)}manganese(II)

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Abstract

The reaction of 2(1*H*)-pyridinethione (HL) with manganese(II) chloride in ethanolic solution results in the formation of the yellow octahedral complex $[Mn(HL)_4Cl_2]$; the crystal and molecular structure of the complex reveals that the two chloride ligands occupy *trans* axial sites and the four thione ligands are *S* bonded in the equatorial positions (crystallographic data: space group $C2/c, a=13.038(1)$, $b=11.184(1), c=17.353(1)$ Å, $\beta=104.61(1)°$, $Z=4$, 1940 reflections with $F \geq 4\sigma(F), R=0.029$).

Introduction

The versatile ligand 2(1*H*)-pyridinethione (HL) has been shown to form complexes with a wide range of transition metals [1] in which it exhibits a variety of bonding modes including monodentate S-bonded HL, S-bonded L, S-bridging HL, S-bridging L, *N,S*-chelating L and *N,S*-bridging L. Manganese(II) is a ‘hard’ metal ion [2] and many complexes with 0 and *N* donor ligands are known [3]. Manganese(II) complexes with ‘soft’ phosphine ligands have been shown to possess a number of interesting and potentially useful properties [4], and these observations prompted us to investigate manganese(II) complexes in the course of our investigations with the ambidentate *NS* donor ligands [5].

Experimental

Infrared spectra were recorded in compressed KBr pellets on Perkin-Elmer 983 or 1710 spectrophotometers; magnetic moments were measured at room temperature using a Johnson Matthey MSB1 susceptibility balance. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on Kratos MS-902, MS-30 or MS-890 spectrometers, with 3-nitrobenzyl alcohol as the matrix for the FAB spectra. 2(1*H*)-Pyridinethione was used as supplied by Aldrich.

Synthesis of trans-$[Mn(HL)_4Cl_2]$

A solution of 2(1*H*)-pyridinethione (0.347 g, 3.1 mmol) and $MnCl_2 \cdot 4H_2O$ (0.103 g, 0.52 mmol) in ethanol (50 cm’) was heated to reflux for 4 h, after which period the yellow solution was concentrated in *vacuo* and allowed to cool, when yellow blocks of the product separated (0.19 g, 60%). *Anal.* Found: C, 40.5; H, 3.4; N, 9.6. Calc. for $C_{20}Cl_2H_{20}MnN_4S_4$: C, 40.3; H, 3.4; N, 9.4%, FAB-MS: *m/z* 596. IR: v 1576(vs), 1140(s), 729(s) cm^{-1}.

X-ray crystallography of trans-$[Mn(HL)_4Cl_2]$

A pale yellow crystal obtained from methanol was mounted on a glass fibre. All geometric and intensity data were taken from this crystal using an automated four-circle diffractometer (Stoe-Siemens) operating in the 24-step ω-θ scan mode (ω step width 0.04°, step time 0.5-2.0 s per step, graphite-monochromated Mo *Kα* radiation). Pertinent crystallographic data are given in Table 1.

Centrosymmetric direct methods were used to locate the Mn, Cl and S atoms, followed by Fourier difference techniques for the remaining non-hydrogen atoms. Hydrogen atoms were placed in idealised positions (C-H, 1.08 Å) with a common isotropic thermal parameter and allowed to ride on the relevant heavier atom. The weighting scheme $\omega^{-1}=\sigma^2F+0.00102F^2$ gave satisfactory agreement analyses. The final converted residuals were $R=0.029$, $R'=0.035$. A final Fourier difference map showed no residual electron density above c. 0.25 $Å^{-3}$.

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TABLE 1. Crystal data for *trans*-$[Mn(HL)_4Cl_2]$

Formula	$C_{20}Cl_2H_{20}MnN_4S_4$
Formula weight	570.48
Space group	*C2/c*
a (Å)	13.038 (1)
b (Å)	11.184(1)
c (Å)	17.353(1)
β (°)	104.61(1)
V (Å^3)	2448.5
Z	4
F(000)	1164
D_{calc}(g/cm^3)	1.55
Crystal size (mm)	$0.27 \times 0.35 \times 0.44$
μ(Mo Kα) (cm^{-1})	10.35
Data collection instrument	Stoe-Siemens
Radiation	Mo Kα ($\lambda = 0.7107$ Å)
Orientation reflections: no., range	60, $20 \leq 2\theta \leq 25°$
Data collection range	$5.0 \leq 2\theta \leq 50.0°$
No. unique data	4881
Total with $F \geq 4\sigma(F)$	1940
R	0.029
R'	0.035
Weighting scheme	$w = 1/[\sigma^2 F + 0.00102F^2]$

TABLE 2. Atomic coordinates ($\times 10^4$) for *trans*-$[Mn(HL)_4Cl_2]$

	x	y	z
Mn(1)	5000	5000	0
Cl(1)	4640(1)	4467(1)	1305(1)
S(1)	4119(1)	7029(1)	355(1)
S(2)	6958(1)	5776(1)	630(1)
C(1)	4154(2)	8200(2)	−274(1)
C(2)	5022(2)	8495(2)	−582(2)
C(3)	4976(2)	9468(2)	−1066(2)
C(4)	4069(2)	10186(2)	−1266(2)
C(5)	3235(2)	9895(2)	−966(2)
N(6)	3301(1)	8931(2)	−486(1)
C(7)	7123(2)	6504(2)	1512(1)
N(8)	6440(1)	6336(2)	1981(1)
C(9)	6513(2)	6912(2)	2678(1)
C(10)	7306(2)	7710(2)	2957(1)
C(11)	8043(2)	7899(2)	2508(1)
C(12)	7954(2)	7314(2)	1807(1)

For the solution and refinement of the structure neutral-atom scattering factors were taken from ref. 6. All computations were carried out on the University of Cambridge IBM 3081 computer using modified versions of SHELX 76 [7]. Positional parameters are presented in Table 2, and bond distances and angles in Table 3.

Results and discussion

The reaction of manganese(II) chloride with 2(1*H*)-pyridinethione in ethanol results in the formation of pale yellow solutions from which pale yellow crystals of composition $\{MnCl_2(HL)_4\}$ are obtained upon concentration. We have not isolated other products from this reaction. The IR spectrum of the yellow product exhibits NH absorptions at 3172 cm^{-1} and C=S absorptions at 1140 cm^{-1}, whilst the FAB-MS (in 3-nitrobenzyl alcohol matrix) showed peaks at m/z 569 ($\{MnCl_2(HL)_4\}$) and m/z 458 ($\{MnCl_2(HL)\}$). The complex is paramagnetic with a magnetic moment $\mu_{eff} = 5.97$ BM, which is extremely close to the expected spin-only value of 5.92 BM. These observations suggest an octahedral manganese(II) centre with the HL ligands coordinated through sulfur in the thione tautomer. The complex is stable in aqueous or alcoholic solution, and is indefinitely stable in air. Although a number of manganese complexes containing thiolate ligands have been structurally characterised, there is only a single example of a manganese(II) complex with neutral *S* donor ligand (an *ONS* donor pyridoxal thiosemicarbazone) [8] and none with monodentate *S* donors, although a number of examples of manganese(III) complexes with cyclic thioethers have been reported. In order to confirm the presence of *S* bonded thione ligands in $[Mn(HL)_4Cl_2]$ we have determined the crystal and molecular structure of the complex.

The molecular structure of the complex $[Mn(HL)_4Cl_2]$ is shown in Fig. 1; the manganese atom sits on a crystallographic centre of symmetry. The manganese atom is in a six coordinate S_4Cl_2 environment, with each of the 2(1*H*)pyridinethione ligands acting as a neutral monodentate *S* donor. The two chloride ligands are arranged *trans* to each other in the axial sites as required by the crystallographically imposed symmetry, and the four thione ligands occupy the equatorial sites. The two Mn–Cl bonds (2.498(1) Å) are typical. There are two shorter (2.656(1) Å) and two longer (2.684(1) Å) Mn–S bonds with the equivalent lengths arranged *trans* to each other. The shorter Mn–S bonds are associated with thione ligands in which the NH is involved in a near-linear hydrogen bond to the axial chloride ligand (H(8)...Cl(1), 2.065(1) Å, ∠N(8)–H(8)...Cl(1), 174 °). The Mn–S bonds are significantly longer than those observed with the terdentate *ONS* donor pyridoxal thiosemicarbazone (2.477 Å) [8]. The remaining bond parameters within the structure do not deviate significantly from the idealised values. In conclusion, we have demonstrated that suitable monodentate *S* donor ligands may form stable complexes with manganese(II).

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TABLE 3. Bond distances (Å) and bond angles (°) for *trans*-[Mn(HL)$_4$Cl$_2$]

Mn(1)–Cl(1)	2.498(1)	Mn(1)–S(1)	2.684(1)
Mn(1)–S(2)	2.656(1)	C(1)–S(1)	1.713(2)
C(1)–C(2)	1.407(3)	C(1)–N(6)	1.354(3)
C(2)–C(3)	1.367(3)	C(3)–C(4)	1.399(3)
C(4)–C(5)	1.359(4)	C(5)–N(6)	1.351(3)
C(7)–S(2)	1.698(2)	C(7)–N(8)	1.363(3)
C(7)–C(12)	1.406(3)	C(9)–N(8)	1.351(3)
C(9)–C(10)	1.358(4)	C(10)–C(11)	1.398(4)
C(11)–C(12)	1.361(4)		
Cl(1)–Mn(1)–S(1)	78.7(1)	Cl(1)–Mn(1)–S(2)	94.9(1)
Cl(1)–Mn(1)–S(2a)	85.1(1)	Cl(1)–Mn(1)–S(1a)	101.3(1)
S(1)–Mn(1)–S(2)	93.0(1)	S(1)–Mn(1)–S(2)	93.0(1)
S(1)–Mn(1)–S(2a)	87.0(1)	Mn(1)–S(2)–C(7)	114.7(1)
Mn(1)–S(1)–Cl(1)	114.7(1)	S(1)–C(1)–N(6)	118.9(2)
S(1)–C(1)–C(2)	125.1(2)	C(1)–C(2)–C(3)	120.4(2)
C(2)–C(1)–N(6)	116.0(2)	C(3)–C(4)–C(5)	118.4(2)
C(2)–C(3)–C(4)	120.8(2)	C(1)–N(6)–C(5)	124.7(2)
C(4)–C(5)–N(6)	119.6(2)	S(2)–C(7)–C(12)	123.2(2)
S(2)–C(7)–N(8)	121.3(2)	C(7)–N(8)–C(9)	124.0(2)
N(8)–C(7)–C(12)	115.5(2)	C(9)–C(10)–C(11)	117.9(2)
N(8)–C(9)–C(10)	120.5(3)	C(7)–C(12)–C(11)	121.3(2)
C(10)–C(11)–C(12)	120.7(2)		

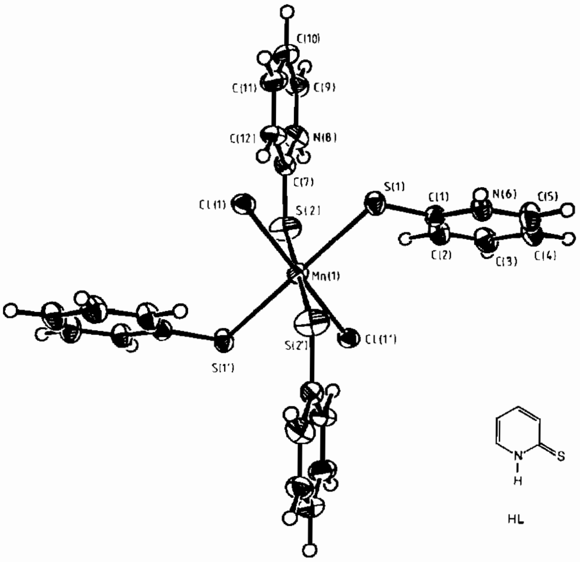

Fig. 1. The molecular structure of *trans*-[Mn(HL)$_4$Cl$_2$] showing the numbering scheme adopted.

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