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Preparation and Crystal Structure of Manganese(II) Isothiocyanate Tetrahydrate

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Crystals of $Mn(NCS)_2 \cdot 4H_2O$ were isolated from an aqueous solution obtained by mixing solutions of barium thiocyanate and manganese(II) sulphate tetrahydrate. The crystals are monoclinic with $a = 7.827(7)$, $b = 9.208(1)$, $c = 7.456(5)$ Å, $\beta = 112.57(5)^\circ$, space group $P2_1/c$. The structure consists of discrete centrosymmetric trans-*$[Mn(NCS)_2(H_2O)_4]$ octahedra linked by hydrogen bonds.*

Introduction

There is increasing interest in the co-ordination chemistry of manganese in the +2, +3, and +4 oxidation states. This stems, in part, because manganese complexes are being examined as models for both respiratory proteins [1, 2] and photosystem II of the green plant chloroplast [3, 4].

We have a particular interest in the tertiary phosphine complexes of manganese(II), $MnX_2(PR_3)$ [5–8] and $MnX_2(PR_3)_2$ [9], as these compounds can reversibly bind small molecules such as dioxygen [5–7] and carbon monoxide [8] under very mild conditions. These compounds are highly unusual and, whilst the factors which activate them towards the relatively weak chemical binding of small molecules are not fully understood, it is clear that the $3d^5$ configuration and manganese(II) (*i.e.* $3d^5$ iron(III) complexes are inactive), and the presence of a manganese–phosphine linkage are necessary.

In order to understand the structural and electronic aspects of this system better we have begun a basic investigation of manganese(II) salts and their simple complexes, which includes EXAFS [10] and X-ray diffraction techniques [7, 9]. An examination of the literature reveals little about the structural chemistry of manganese(II) in aqueous media, or of the hydrated salts in the solid state. We have recently shown [10] that the predominant manganese species in aqueous $MnBr_2$ solution has the stoicheiometry $[MnBr_2(H_2O)_4]$.

Very few simple salts or aquo complexes of manganese(II) have been fully characterised by X-ray diffraction techniques. Two chlorides, $MnCl_2 \cdot 2H_2O$ and $MnCl_2 \cdot 4H_2O$, have been studied. The latter is discrete *cis*-$[MnCl_2(H_2O)_4]$ [11] and the former also contains *cis*-chlorines in a polymeric chain arrangement of *trans*-$MnCl_4(H_2O)_2$ octahedra sharing edges [12]. We here wish to report the preparation and crystal structure of manganese(II) isothiocyanate tetrahydrate which consists of discrete centrosymmetric *trans*-$[Mn(NCS)_2(H_2O)_4]$ octahedra, in contrast to the two *cis*-chlorides [11, 12].

Experimental

Preparation of Manganese(II) Isothiocyanate Tetrahydrate

Barium thiocyanate dihydrate (1157 g, 4.0 mol) was dissolved in distilled water (*ca.* 2 l), and the solution assayed for barium. A solution of manganese(II) sulphate tetrahydrate (892 g, 4.0 mol) in distilled water (*ca.* 2 l) was similarly prepared and assayed for sulphate. As a result of these assays the barium thiocyanate solution (1990 cm^3) was placed in a round bottom flanged flask (10 l) equipped with a mechanical stirrer and the means to maintain a dinitrogen atmosphere (it is not known if the dinitrogen atmosphere is necessary, but we thought it prudent to carry out all operations under dinitrogen). A further 2 l of distilled water was added. The manganese sulphate solution (1922 cm^3) was added rapidly (<5 min) with stirring, resulting in the precipitation of barium sulphate. Stirring was continued for 4 h, after which the mixture was allowed to settle overnight. (The clear pale pink supernatant liquor was tested for the presence of Ba^{2+} and $SO_4{}^{2-}$ which were found to be absent.)

The clear pale pink solution was decanted, filtered (Whatman filter tube 1A), and concentrated on a rotary evaporator until the first signs of a solid were noticed as a yellow ring on the flask.

The solution changed from pale pink, through blue to green as the manganese thiocyanate concentration increased. On cooling the solution (*ca.* 450 cm^3) the mass of crystals which formed was filtered off and placed in a desiccator over anhydrous calcium chloride.

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Thermal gravimetric analysis and differential thermal analysis, Fig. 1, revealed three main endothermic processes: (i) m. pt. 42 °C; (ii) dehydration at 135 °C; (iii) decomposition of the anhydrous salt at 432 °C, and a slight exotherm at 442 °C.

A pale green crystal fragment (0.5 × 0.5 × 0.3 mm) was sealed in a Lindeman tube and examined on a CAD4 diffractometer fitted with a graphite monochromator.

Crystal Data

$Mn(NCS)_2 \cdot 4H_2O$, $M_r = 243.14$, monoclinic, $P2_1/c$, $a = 7.827(7)$, $b = 9.208(1)$, $c = 7.456(5)$ Å, $\beta = 112.57(5)^\circ$, $V = 496.2$ Å^3, $Z = 2$, $D_x = 1.63$ Mg m^{-3}, $F(000) = 242$, Mo Kα, $\lambda = 0.71069$ Å, $\mu = 1.77$ mm^{-1}, T = 293 K, $R = 0.039$ for 1370 reflections with $F > 3\sigma(F)$.

Lorentz and polarization, but not absorption corrections were applied. Examination of the reflections for systematic absences and the application of statistical tests on quasinormalized structure factors E(hkl) established the space group as $P2_1/c$. The phase problem was solved by Patterson and Fourier techniques, allowing the asymmetric unit to be identified as half the title molecule, with the Mn atom situation on the crystallographic inversion centres at 1/2, 1/2, 1/2 and 1/2, 0, 0. Full matrix least squares refinement was applied by means of SHELX [13] treating the heavy atoms anisotropically and the hydrogen atoms isotropically ($w = 0.0911/\sigma^2(F) + 0.0006\ F^2$). Fluctuations in the final difference Fourier map did not exceed ±0.5 e Å^{-3} except near Mn. Scattering factors were taken from International Tables for X-ray Crystallography [14] and all calculations were performed on the joint CDC7600/ICL1906A computers at the University of Manchester Regional Computing Centre.

Results and Discussion

Although some standard reference texts [15, 16] describe the crystalline hydrate of manganese(II) isothiocyanate as the trihydrate, $Mn(NCS)_2 \cdot 3H_2O$, the material prepared as described in the Experimental Section is indubitably a tetrahydrate, as shown by Karl Fischer water analysis and thermal analyses, Fig. 1. Manganese(II) isothiocyanate tetrahydrate is pale green and is very deliquescent.

The behaviour of the aqueous solutions of manganese(II) isothiocyanate on concentration is remarkable. Dilute (*ca.* 2 *M*) solutions are pale pink, typical of manganese(II) high-spin hexacoordinate aquo complexes. As the solution is concentrated a pale slate blue colour develops and gradually intensifies to a deep royal blue, which in turn changes to a deep green at high concentrations near to crystallisation (>10 *M*).

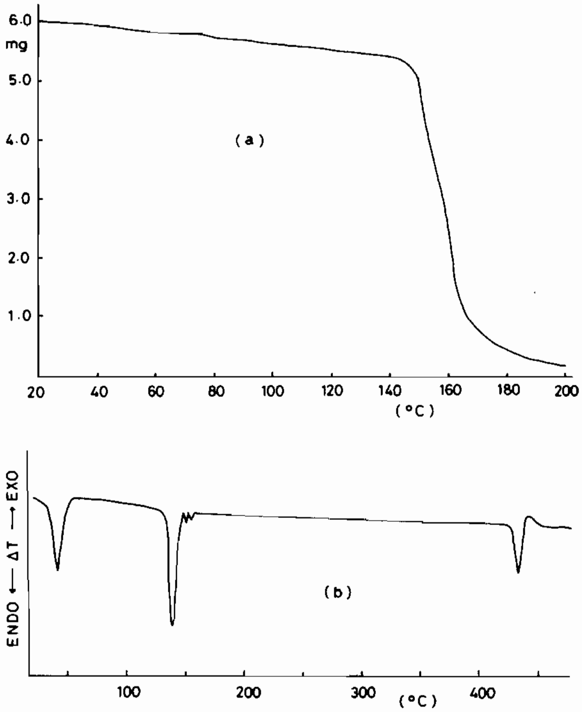

Fig. 1. (a) Thermogravimetric analysis of $Mn(NCS)_2 \cdot 4H_2O$; (b) differential thermal analysis of $Mn(NCS)_2 \cdot 4H_2O$.

Fractional atomic coordinates and vibrational parameters from the X-ray study are provided in Table I*. Selected bond lengths, angles and torsion angles are presented in Table II. Figure 2 shows a stereoscopic pair of the discrete *trans*-$[Mn(NCS)_2(H_2O)_4]$ units and indicates the atom numbering. Figure 3 shows how the discrete units of the complex are linked by hydrogen bonds.

TABLE I. Fractional Atomic Coordinates (×10^4) and Vibrational Parameters (Å^2 × 10^4) for all Atoms, with e.s.d. in Parentheses.

	x	y	z	$U/U_{eq}{}^a$
Mn	5000	5000	5000	414
S	9081(1)	743(0)	6797(1)	581
C	7734(2)	2169(2)	6366(2)	456
N	6769(2)	3156(2)	6026(2)	618
O(1)	3894(2)	4118(2)	2087(2)	598
O(2)	2809(2)	3839(1)	5718(2)	553
H(11)	3125(38)	4606(32)	1344(39)	515(60)
H(12)	3773(52)	2967(54)	1728(51)	1221(131)
H(21)	1894(40)	3840(38)	4711(47)	740(89)
H(22)	2595(39)	4391(34)	6435(40)	639(79)

$^aU_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

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*Full anisotropic vibrational parameters and the lists of structure factors are deposited.

TABLE II. Bond Lengths (Å), Angles (°) and Torsion Angles (°) with e.s.d. in Parentheses.

N–Mn	2.138(0.001)
O(1)–Mn	2.164(0.001)
O(2)–Mn	2.253(0.001)
C–S	1.637(0.002)
N–C	1.146(0.002)
H(11)–O(1)	0.784(0.028)
H(12)–O(1)	1.088(0.049)
H(21)–O(2)	0.814(0.030)
H(22)–O(2)	0.801(0.030)
O(1)–Mn–N	90.9(0.1)
O(2)–Mn–N	89.2(0.1)
O(2)–Mn–O(1)	90.7(0.1)
N–C–S	178.5(0.2)
C–N–Mn	171.9(0.1)
H(11)–O(1)–Mn	113.4(2.1)
H(12)–O(1)–Mn	125.2(1.9)
H(12)–O(1)–H(11)	114.4(2.5)
H(21)–O(2)–Mn	105.1(2.2)
H(22)–O(2)–Mn	103.3(2.0)
H(22)–O(2)–H(21)	106.2(2.9)
H(12)–O(1)–Mn–N	30(3)
H(11)–O(1)–Mn–N	-182(3)
H(21)–O(2)–Mn–N	-125(3)
H(22)–O(2)–Mn–N	124(3)
O(1)–Mn–N–C	35.1(0.2)
O(2)–Mn–N–C	125.8(0.2)

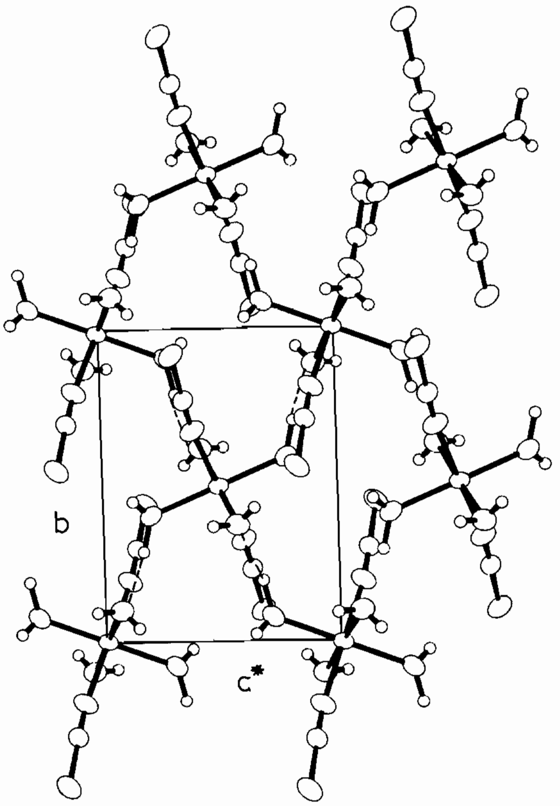

Fig. 3. ORTEP view down *a* showing packing and H-bonded sheet in bc plane.

Being a centric complex, $[Mn(NCS)_2(H_2O)_4]$ contains only two crystallographically distinct water ligands. They are in considerably different situations, displaying significantly different Mn–O bond lengths [Mn–O(1) = 2.164(1) Å, Mn–O(2) = 2.253(1) Å] and different rotational orientations about the Mn–O bonds (see Table II). The one, crystallographically distinct, hydrogen bond between the two water

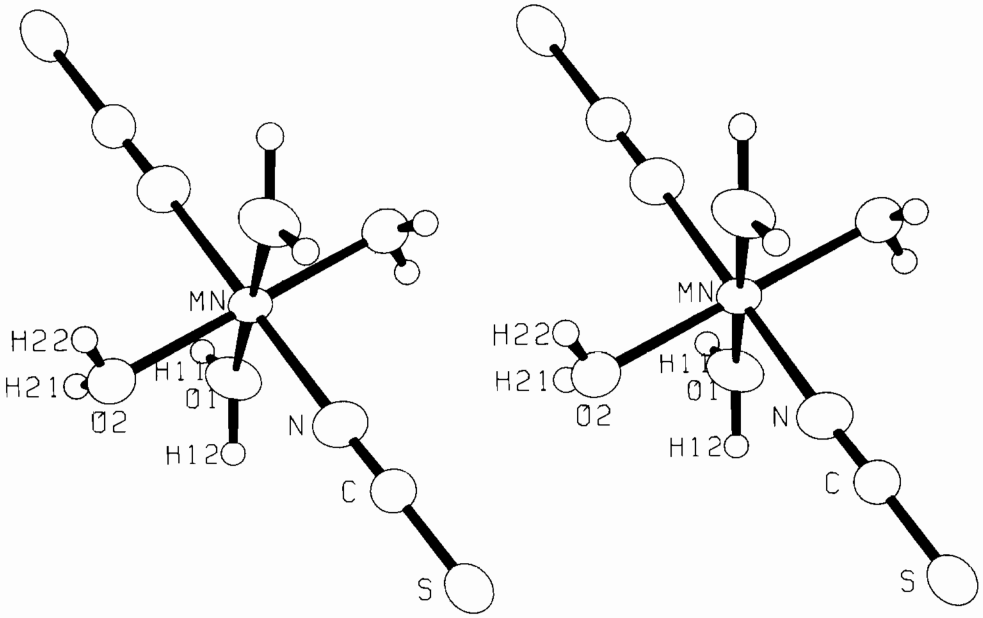

Fig. 2. ORTEP stereoscopic view with atoms depicted as 50% probability ellipsoids [17].

molecules emphasises their different roles. The longer Mn–O bond, Mn–O(2), appears weakened by the formation of the hydrogen bond, with H(12) approaching O(2) at 1.86(9) Å [O(1)···O(2) = 2.918(5) Å; O(2) at x, 1/2 – y, z – 1/2]. The nearly linear NCS ligand displays normal dimensions and is slightly inclined to the Mn–N bond (∠Mn–N–C = 171.9-(1)°). *Trans*-di-isothiocyanatotetra(urea)manganese-(II) also lies on a crystallographic inversion centre [18], however, ∠Mn–N–C is smaller at 147° and the ligands approach the Mn atom more closely: Mn–O = 2.03 and 2.04 Å, and Mn–N = 2.05 Å.

Although the manganese(II) halide tetrahydrates are also octahedral complexes, they are *cis* structures. However the Mn–O distances show good agreement with those in [$Mn(NCS)_2(H_2O)_4$] with a range 2.181(6) to 2.224(2) Å in [$MnCl_2(H_2O)_4$] [19] and 2.176(6) to 2.218(6) Å in [$MnBr_2(H_2O)_4$] [20].

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