The X-Ray Crystal Structure of $[Mn_2(\mu\text{-}LL)_4(NCS)_2](NCS)_2$ [LL = $Ph_2P(O)(CH_2)_3P(O)Ph_2$], a Dinuclear Complex that reversibly absorbs Five Molecules of Sulphur Dioxide

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The X-ray crystal structure of the dinuclear complex, $[Mn_2(\mu\text{-}LL)_4(NCS)_2](NCS)_2$, is reported; this cage molecule reversibly binds sulphur dioxide in a 1 : 5 cage : sulphur dioxide ratio.

The reaction of macrocyclic ligands with metal ions is growing in importance in academic and industrial chemistry. Areas as diverse as biological inorganic chemistry, catalysis, separation and encapsulation processes, and small molecule binding and activation now involve these cyclic ligand systems.[1-9]

Whilst Beer's group[10] and others[11] have designed and synthesised macrocyclic compounds containing the ferrocene moiety external to the macrocycle, examples of systems in which a transition metal is an integral part of the macrocyclic ring are almost unknown. One such has recently been reported by Nixon and co-workers, *viz*: the novel bimetallic $[\{CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2\}_2]$, which contains a 14-membered ring.[12] We now report the self-assembly of a unique metal-containing dinuclear complex, $[Mn_2(\mu\text{-}LL)_4(NCS)_2](NCS)_2$, **1** [LL = $Ph_2P(O)(CH_2)_3P(O)Ph_2$], a cage containing four chains linking two pentacoordinate manganese(II) atoms and containing 16-membered rings.

Complex **1** can be synthesised either by reacting anhydrous manganese(II) isothiocyanate with 1,3-bis(diphenylphosphinyl)propane (mole ratio 1 : 2) in acetone–methanol or by dissolving $Mn(LL)(NCS)_2$ in acetone and slowly evaporating the solution.†

The molecular structure is shown in Fig. 1. $[Mn_2(\mu\text{-}$

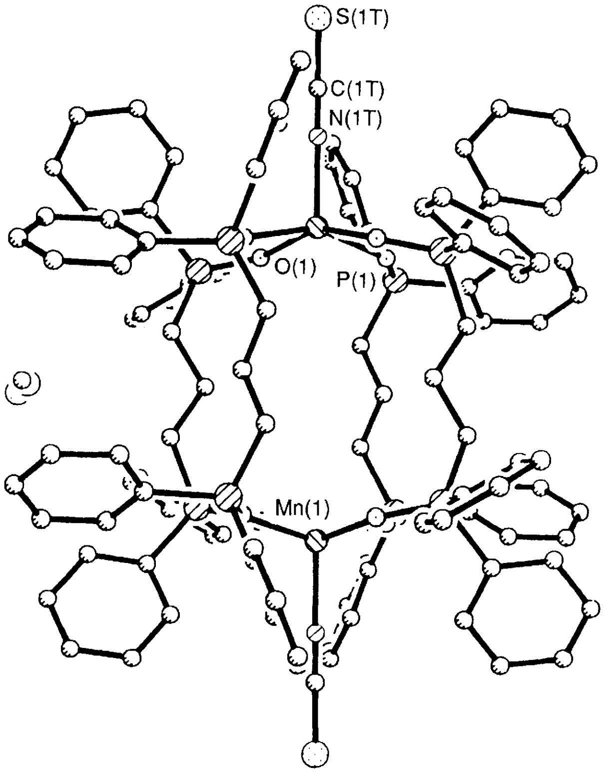

Fig. 1 The molecular structure of $[Mn_2(\mu\text{-}LL)_4(NCS)_2](NCS)_2$ showing atomic numbering. Bond lengths: Mn(1)–N(1T) 2.086(14), Mn(1)–O(1) 2.130(5), O(1)–P(1) 1.504(5), C(1T)–N(1T) 1.135(19) Å. Bond angles: O(1)–Mn(1)–N(1T) 102.8(1), P(1)–O(1)–Mn(1) 140.3(3), C(1T)–N(1T)–Mn(1) 180.0(1), N(1T)–C(1T)–S(1T) 180.0(1)°. The hydrogen atoms have been omitted for clarity.

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† *Crystal data*: $C_{112}H_{104}Mn_2N_4O_8P_8S_4$, $M = 2118$, tetragonal, $a = b = 14.939(5)$, $c = 25.621(8)$ Å, $V = 5718(2)$ Å^3, $F(000) = 2536$, $Z = 2$, $D_c = 1.23$ Mg m^{-3}, space group $I4/m$, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.69 mm^{-1}. The intensities of 5270 reflections with $5.5 < 2\theta < 15.5°$ were measured using a Nicolet R3m diffractometer. Of these 1417 were unique with $F > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-squares analysis to $R = 0.089$ and $R_w = 0.089$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been desposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$LL)_4(NCS)_2]^{2+}$ is a highly symmetrical entity and exhibits a central mirror plane. The molecule consists of two five-coordinate manganese centres bridged by four LL ligands. The fifth coordination site on each manganese atom is occupied by an isothiocyanate group, while the two remaining isothiocyanate counter-ions are disordered in the crystal lattice.

As its structure suggests, $[Mn_2(\mu\text{-}LL)_4(NCS)_2](NCS)_2$ was found to be a 2:1 electrolyte in nitromethane (Λ_m = 119 ohm^{-1} cm^2 mol^{-1}). A variable temperature magnetic susceptibility measurement showed that the magnetic moment is independent of temperature and that there is no interaction between the manganese atoms (6.00 μ_B at 296 K and 5.97 μ_B at 77 K). The IR spectrum failed to distinguish between *N*-bound and ionic isothiocyanate, showing only a single broad ν_{CN} absorption at 2060 cm^{-1}.

We are engaged in an extensive study of the binding and activation to oxidation of sulphur dioxide when complexed to manganese(II)[13,14] and iron(III)[15] complexes of triphenylphosphine oxide and triphenylarsine oxide. For example, we have shown that $[Mn(OPPh_3)_4(NCS)_2]$ binds SO_2 to form $[Mn(OPPh_3)_4(NCS)_2(SO_2)]$;[14] solutions of the latter complex in the presence of air under ambient conditions result in the production of the sulphuric acid derivative $[(Ph_3PO)(Ph_3POH)HSO_4]$, which we characterised by single X-ray diffraction. The reaction of **1** with sulphur dioxide has been studied in the solid state by monitoring the change in mass of the complex when exposed to an atmosphere of SO_2.

A total of 5 moles of SO_2 are absorbed per mole of complex, and the colour changes from white to pale-yellow. The IR spectrum of the SO_2-adduct exhibits a split ν_{CN} at 2060 cm^{-1} but this does not indicate whether the sulphur dioxide is bound to the *N*-bound isothiocyanate, to the ionic isothiocyanate or to both. Charge-transfer species between SCN^- and SO_2 have been reported both in solution[16] and in the solid state[17] and work in this laboratory suggests that SO_2 can bind to terminally coordinated NCS in other manganese(II) complexes[18].

The IR spectrum also shows a weak ν_{SO} absorption at 1325 cm^{-1}. The observation that this band is lost and the colour reverts to the original white when a vacuum is applied, or when the adduct is exposed to the atmosphere, suggests that much of the SO_2 is not strongly bound but simply sitting inside the cage-like structure. Further exposure to sulphur dioxide regenerates the SO_2 adduct, showing that the reaction is reversible. At no time do we observe any oxidation of the SO_2 when the adduct complex is exposed to moist air.

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