The *X*-Ray Crystal Structure of *trans*-Bis(sulphur dioxide)tetrakis(triphenylphosphine oxide)manganese(II) Di-iodide, a Compound which undergoes Demi-reversible Binding of Sulphur Dioxide: the First Crystallographically Characterised Example of O-bonded Sulphur Dioxide in a Transition Metal Complex

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The *X*-ray crystal structure of the complex *trans*-$[Mn(OPPh_3)_4(SO_2)_2]I_2$ shows it to contain O-bonded sulphur dioxide groups; one of these can be lost to form $Mn(OPPh_3)_4(SO_2)I_2$, and the reaction is reversible.

In our investigations of the binding of small molecules by the MnX_2(phosphine) (X = halogen, pseudohalogen) complexes[1,2] relationships between the nature of the manganese complex and small molecule binding activity are emerging. For example, there are clearly defined reactions with dioxygen as the phosphine changes. Thus the $MnX_2(PMe_3)$ complexes react with dioxygen to oxidise the manganese to form $MnX_3(PMe_3)_2$ (plus inorganic products),[3] the $MnX_2(PR_3)$ complexes (PR_3 = *e.g.* PEt_3, $PPhMe_2$) bind dioxygen to form $MnX_2(PR_3)(O_2)$ and this reaction is reversible,[1] whereas the $MnX_2(PPh_3)$ complexes do not react with dioxygen even at $p(O_2) = 12$ atm.

The triphenylphosphine complex $MnI_2(PPh_3)$ reacts with sulphur dioxide to form a complex of stoicheiometry $MnI_2(PPh_3)(SO_2)_{2/3}$.[4] Therefore we have investigated manganese(II) compounds containing ligands other than those phosphines which normally induce small molecule binding activity, and examined their reaction with sulphur dioxide. We report here the synthesis and *X*-ray crystal structure of *trans*-bis(sulphur dioxide)tetrakis(triphenylphosphine oxide)manganese(II) di-iodide, $[Mn(OPPh_3)_4(SO_2)_2]I_2$, and the ability of this complex to lose one sulphur dioxide ligand to form $Mn(OPPh_3)_4(SO_2)I_2$. This reaction is reversible.

The compound $[Mn(OPPh_3)_4(SO_2)_2]I_2$, $\mu_{eff} = 6.0\ \mu_B$, is formed when anhydrous manganese(II) iodide and triphenylphosphine oxide (mol ratio 1 : 4) are stirred together in propyl acetate for 7 days. The resulting beige suspension is then saturated with sulphur dioxide gas and the resulting orange suspension is stirred for 2 days. The solid is then filtered off. Crystals were obtained by crystallisation from toluene.

Co-ordination complexes of sulphur dioxide have been known for a number of years and they have a wide range of geometries.[2] The monodentate oxygen-bonded mode generally occurs in complexes of main group metals, *e.g.* F_5SbOSO,[5] although there is one unconfirmed report of O-bonded sulphur dioxide in $Ni(AsF_6)_2(SO_2)_2$.[6] We report here the first crystallographically characterised example of O-bonded SO_2 in a transition metal complex.

Crystal data for $[Mn(OPPh_3)_4(SO_2)_2]I_2$, $C_{72}H_{60}I_2MnO_8P_4S_2$, $M = 1550.01$, triclinic, $a = 13.426(7)$, $b = 13.022(8)$, $c = 13.863(11)$ Å, $\alpha = 125.5(1)$, $\beta = 120.1(1)$, $\gamma = 83.2(1)°$, $U = 1655$ Å^3, $Z = 1$, $D_c = 1.55$ g cm^{-3}, space group $P\bar{1}$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu = 24$ cm^{-1}. The intensities of 9 051 reflections with $7 < 2\theta < 60°$ were measured using a Stoe STADI2 Weissenberg diffractometer; after correction for Lorentz, polarisation, and absorption effects, 5 281 data had $I > 3\sigma(I)$.

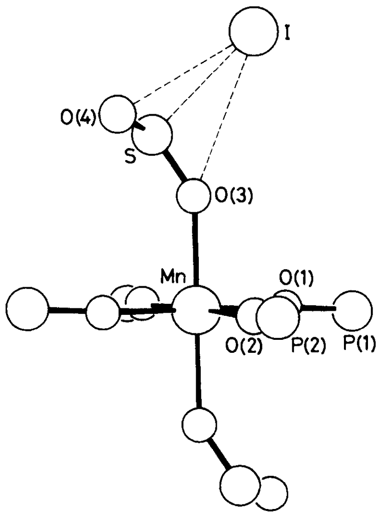

Figure 1. The molecular structure of $[Mn(OPPh_3)_4(SO_2)_2]I_2$, showing atomic numbering. Bond lengths: Mn–O(1) 2.084(3), Mn–O(2) 2.147(3), Mn–O(3) 2.282(4), P(1)–O(1) 1.498(3), P(2)–O(2) 1.485(3), S–O(3) 1.448(4), S–O(4) 1.410(6) Å. Angles: O(4)–S–O(3) 116.2(4), S–O(3)–Mn 146.9(3)°. The phenyl carbon atoms have been omitted for clarity and the position of only one iodide ion is shown. The Mn atom is at a centre of symmetry. Distances involving I^-: –S 2.859(2), –O(3) 3.39, –O(4) 3.345 Å.

In the final cycle of least squares refinement all non-hydrogen atoms were given anisotropic thermal parameters, $R = 0.050$ and $R_w = 0.055$.†

The molecular structure is shown in Figure 1. The manganese atom is at a centre of symmetry, and the two SO_2 groups are unambiguously O-bonded (Mn · · · S 3.59 Å). The SO_2 geometry is similar to that found in the adduct $SbF_5{\cdot}SO_2$, but with a smaller O–S–O angle and a larger M–O–S angle (119.2 and 138.9° respectively in $SbF_5{\cdot}SO_2$). There is a short cation–anion interaction involving the sulphur and iodine atoms which is considerably less than the formal sum of their van der Waal's radii (4.0 Å).

Each specific mode of sulphur dioxide co-ordination geometry exhibits particular diagnostic i.r. features, which have been summarised by Kubas for over 140 complexes.[7] The ν(S–O) bands expected for O-bonded SO_2 lie in the regions *ca.* 1300 and 1100 cm^{-1}.[5,7] In the i.r. spectrum of $[Mn(OPPh_3)_4(SO_2)_2]I_2$ the latter region is masked by ligand absorptions, but we do observe bands at 1234(s) and 1275(w) cm^{-1} assignable to ν(S–O).

When under vacuum for 2—3 h, or heated to 129 °C, the $[Mn(OPPh_3)_4(SO_2)_2]I_2$ complex loses one molecule of sulphur dioxide to form $Mn(OPPh_3)_4(SO_2)I_2$.‡ This complex melts at 148—150 °C without further loss of sulphur dioxide. The i.r. spectrum exhibits bands at 1279(w) and 1260(w) cm^{-1} assignable to ν(S–O). Upon exposure to sulphur dioxide in the solid state or in suspension in propyl acetate the original $[Mn(OPPh_3)_4(SO_2)_2]I_2$ is reformed. We have thus observed a unique example of demi-reversible co-ordination of sulphur dioxide.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Elemental analyses (C,H,S) are in excellent agreement with the proposed formulation.