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Preliminary communication

STRUCTURAL CHARACTERIZATION OF $[Rh_2(PPh_3)_4(\mu\text{-}Cl)(\mu\text{-}SO_2)_2]_2(SO_4)$, WHICH CONTAINS A NOVEL SYNERGIC BRIDGING MODE FOR THE SO_2 LIGAND

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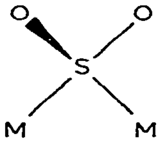
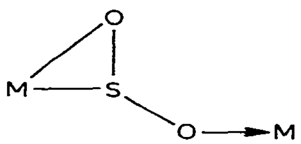
Summary

The structural characterization of $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SO_2)_2(PPh_3)_4]_2(SO_4)$ by single crystal X-ray diffraction techniques has demonstrated that this complex contains two identical square-pyramidal rhodium(I) units linked by a chloro and two sulphur dioxide bridging ligands. The SO_2 ligand adopts a novel bridging mode involving dative bonds from rhodium to sulphur and oxygen to the second rhodium atom.

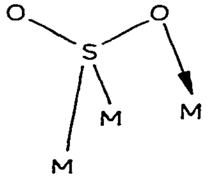
In the majority of polynuclear bridged SO_2 complexes the SO_2 ligand functions as a two electron bridging ligand I utilising only the orbitals on the sulphur atom [1,2]. Recently two examples of SO_2 acting as a four electron bridging ligand have been reported. Jarvinen, Kubas and Ryan [3] have demonstrated that in $[Mo(CO)_2(py)(SO_2)(PPh_3)]_2$ the SO_2 ligand bridges the two molybdenum atoms by bonding to one through an η^2-S,O linkage and the second through an oxygen atom, as shown schematically in II. Briant et al. [4] have established that in $[Rh_4(\mu\text{-}CO)_4(\mu\text{-}SO_2)_3(P(OPh)_3)_4]$ two of the SO_2 ligands bridge three metal atoms in the manner depicted in III, whilst the third SO_2 ligand adopts the more conventional bridging mode I. In this communication we report structural evidence for a fourth type of bridging mode for the SO_2 ligand.



(I)



(II)



(III)

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When SO_2 is bubbled through a solution of $[Rh(\eta\text{-}C_8H_{12})(PPh_3)_2]^+$ prepared in situ [5] by the addition of a stoichiometric amount of PPh_3 to a suspension of $[RhCl(\eta\text{-}C_8H_{12})]_2$ in methanol the solution takes on a red appearance and addition of a methanolic solution of $NaClO_4$ results in the separation of orange crystals of $[Rh_2Cl(SO_2)_2(PPh_3)_4]ClO_4$ together with a very small quantity of crystals of similar appearance which were shown by a single crystal X-ray diffraction study to be $[Rh_2Cl(SO_2)_2(PPh_3)_4]_2(SO_4)$. Bulk samples of the orange crystals obtained from this reaction gave satisfactory chemical analyses for the formulation $[Rh_2Cl(SO_2)_2(PPh_3)_4]ClO_4$ (Found: C, 56.5; H, 3.9; Cl, 4.8; S, 4.3. $C_{72}H_{60}Cl_2O_4P_2Rh_2S_2$ calcd.: C, 56.9; H, 3.9; Cl, 4.6; S, 4.2%), are diamagnetic and behave as 1/1 electrolytes in nitrobenzene solutions (Λ_M 20.2 l^{-1} cm^{-2} mol^{-1}). In addition to those bands characteristic of PPh_3 the infrared spectrum of $[Rh_2Cl(SO_2)_2(PPh_3)_4]ClO_4$ as a nujol mull showed bands at 1100(br,s) and 620(sh,s) cm^{-1} which were assigned to $\nu(ClO_4)$ and $\delta(ClO_4)$ respectively, and 1155(sh,s) and 890(br,s) cm^{-1} which were attributed to the coordinated SO_2 ligands. The frequencies of the latter lie outside the range normally associated with the SO_2 bridging mode illustrated in I (1240—1135 and 1085—975 cm^{-1}). The observed SO_2 frequencies do however lie close to the range reported for $\eta^2\text{-}SO_2$ complexes (1160—1100 and 950–850 cm^{-1}) [2], and are reminiscent of the frequencies observed for $[Rh_4(CO)_4(SO_2)_3(P(OPh)_3)_4]$ (i.e. 1102 and 977 cm^{-1}). A few crystals suitable for a single crystal X-ray crystallographic analysis were obtained from the reaction and shown to have identical melting point (165–166°C and infrared characteristics to those of the bulk sample.

Crystal data. The structure was determined from 3582 unique reflections having $I > 3\sigma(I)$ and refined to $R = 0.079$. $M = 1513.4$, triclinic a 13.803(4), b 15.405(7), c 19.030(8) Å, α 108.97(4), β 97.73(3), γ 89.96(4)°, U 3788 Å^3, $Z = 2$, D_c 1.31 g cm^{-3}, μ(Mo-K_α) 6.57 cm^{-1}, $F(000)$ 1542, Mo-K_α 0.71069 Å; Space group $P\bar{1}$.

The single crystal structural analysis established the presence of the dimeric $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SO_2)_2(PPh_3)_4]^+$ cation anticipated on the basis of chemical analysis and spectroscopic measurements, but the electron density associated with the counteranion in a difference Fourier electron density map was approximately half of that anticipated for ClO_4^-. We were therefore forced to conclude that the X-ray crystallographic analysis had been performed on a "rogue" crystal of the related sulphato complex $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SO_2)_2(PPh_3)_4](SO_4)_{1/2}$ despite our efforts to confirm that the crystals used in the X-ray analysis were identical in their physical properties to the bulk sample of $[Rh_2Cl(SO_2)_2(PPh_3)_4$ (ClO_4). There is some precedence in the literature for the formation of sulphato complexes from the aerial oxidation of SO_2 in the presence of platinum metal complexes [6].

The molecular structure of $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SO_2)_2(PPh_3)_4]_2(SO_4)$ illustrated in Fig. 1 may be described in terms of two identical square pyramidal rhodium(I) units joined together by two bridging SO_2 ligands and a bridging chloro ligand. The SO_2 ligands occupy apical sites of the square-pyramids and are coordinated to the rhodium atoms in a pyramidal mode [1], with the O–S–O planes making angles of 133(±4)° to the best least squares planes passing through the basal ligands of the square-pyramids (i.e. P(2),P(1),Cl,O(21) and

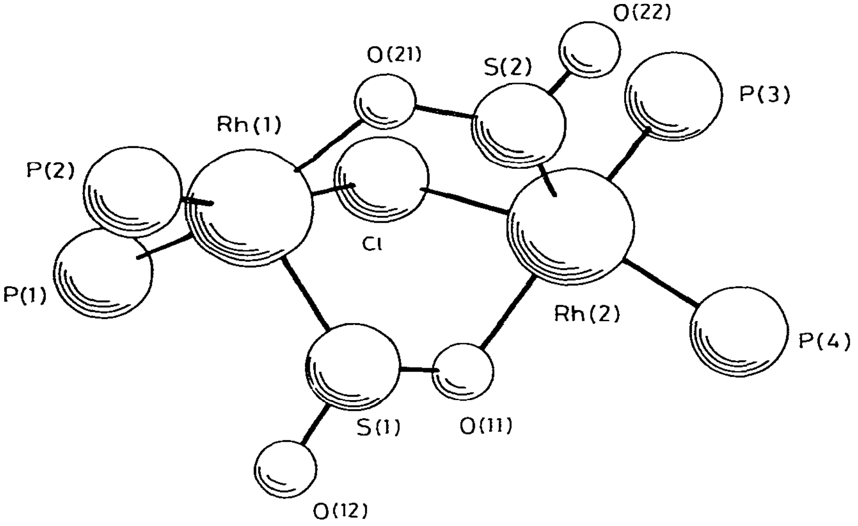
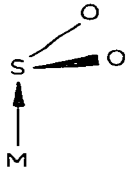
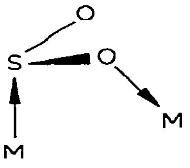


Fig. 1. Molecular structure of the $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SO_2)_2(PPh_3)_4]^+$ cation. For reasons of clarity the phenyl rings have been omitted. The oxygen atoms O(22) and O(12) are partially disordered about the planes Rh(2)S(2)O(21) and Rh(1)S(1)O(11). The oxygen atoms shown are those of the predominant (75%) configuration. Important bond lengths and angles: Rh(1)—S(1) 2.295(8), Rh(2)—S(2) 2.311(7), Rh(1)—Cl 2.384(7), Rh(2)—Cl 2.401(6), Rh(1)—O(21) 2.13(2), Rh(2)—O(11) 2.15(2), Rh(1)—P(1) 2.268(6), Rh(1)—P(2) 2.310(7), Rh(2)—P(3) 2.294(7), Rh(2)—P(4) 2.299(6), S(2)—O(21) 1.50(2), S(2)—O(22) 1.40(2), S(1)—O(11) 1.45(2), S(1)—O(12) 1.40(3) Å: O(21)—S(2)—O(22) 114(2), O(12)—S(1)—O(11) 116(2)°.

P(3),P(4),Cl,O(11)). Therefore the geometries about the individual rhodium atoms are closely related to those reported for the analogous rhodium(I) and iridium(I) complexes $[RhCl(CO)(SO_2)(PPh_3)_2]$ [7], $[IrCl(CO)(SO_2)(PPh_3)_2]$ [8], and $[RhCl(SO_2)(PPh_3)_2]_2$ [9], where the pyramidal SO_2 bonding mode may be accounted for in terms of the metal-SO_2 dative interaction illustrated in IV [1].



(IV)



(V)

The unique feature of the structure of $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SO_2)_2(PPh_3)_4]_2(SO_4)$ derives from the observation that the apical SO_2 ligands additionally function as bridging ligands to a second rhodium atom by utilizing a dative interaction between the lone pair on one of the oxygen atoms and the rhodium atom. These bridges are represented by the atom sequences Rh(2)S(2)O(21)Rh(1) and Rh(1)S(1)O(11)Rh(2) in Fig. 1. The resulting Rh(1)—O(21) and Rh(2)—O(11) distances of 2.13(2) and 2.15(2) Å, respectively, are comparable to the Rh—O distances reported for the coordination mode (III) in $[Rh_4(CO)_4(SO_2)_3$-

$(P(OPh)_3)_4]$ [4], viz. 2.35(2) and 2.29(2) Å. The μ-S,O coordination mode in $[Rh_2Cl(SO_2)_2(PPh_3)_4]_2(SO_4)$ results in a lengthening of S—O(Rh) relative to the uncoordinated S—O bond (see Figure legend) but the differences are on the verge of statistical significance. These bond length differences are of the same order of magnitude as those reported previously for $[Rh(NO)(SO_2)(PPh_3)_2]$ [10] and $[Rh_4(CO)_4(SO_2)_3(P(OPh)_3)_4]$ [4].

The bridging mode described above for SO_2 in $[Rh_2Cl(SO_2)_2(PPh_3)_4]_2(SO_4)$ may be represented by the canonical form illustrated in V and consequently represents an unusual example of a synergic bonding situation where the bridging ligand functions simultaneously as a Lewis acid (through sulphur) and Lewis base (through oxygen) to two metal atoms. There is no evidence of rhodium—rhodium bonding resulting from this bridging situation since the rhodium—rhodium internuclear distance is 3.543(6) Å.

The rhodium—sulphur (SO_2) distances of 2.311(8) and 2.295(7) Å are shorter than those reported previously for pyramidal SO_2-rhodium(I) complexes [7,9], perhaps reflecting the effect of the synergic interaction described above.

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