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A New Bridging Geometry for Sulphur Dioxide in $[Mo(CO)_2(PPh_3)$-(pyridine)$(\mu$-$SO_2)]_2$·$2CH_2Cl_2$; *X*-Ray Crystal Structure

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Summary In CH_2Cl_2 solution the complex *cis,trans*-$Mo(CO)_2(PPh_3)_2$(pyridine) $(\eta^2$-$SO_2)$ (**1**) reacts to give a dinuclear complex (**2**); an *X*-ray crystal structure determination shows that the molybdenum atoms are bridged by two SO_2 ligands that are co-ordinated to one metal through the sulphur atom and one oxygen atom and to the second metal *via* the remaining oxygen atom.

All the *X*-ray structure determinations so far reported of complexes containing one or more bridging SO_2 ligands show SO_2 bonding to two metal atoms through the sulphur atom.[1] We have obtained the dinuclear complex $[Mo(CO)_2(PPh_3)$-(pyridine)$(\mu$-$SO_2)]_2$·$2CH_2Cl_2$ (**2**) and have established its molecular structure by single-crystal *X*-ray methods. The complex exhibits a new bridging geometry for SO_2 that is also the first example of metal co-ordination of all three of its atoms.

Addition of SO_2 to the complex *cis,trans*-$Mo(CO)_2(PPh_3)_2$-$(MeCN)_2$ yields *cis,trans*-$Mo(CO)_2(PPh_3)_2(MeCN)(\eta^2$-$SO_2)$.[2] The co-ordinated acetonitrile of this complex can be replaced by other ligands giving *cis,trans*-$Mo(CO)_2(PPh_3)_2(SO_2)L$ in which the bonding mode of the SO_2 (η^1-planar or η^2) varies with L.[2] For L = pyridine an η^2-SO_2 complex (**1**) is obtained, but (**1**) is unstable in CH_2Cl_2 solution, losing PPh_3 and forming crystals of (**2**) in about an hour at room temperature. The i.r. spectrum (Nujol mull) of (**2**) shows ν(CO) bands at 1937 and 1788 cm^{-1} and $\nu(SO_2)$ bands at 1043 and 919 cm^{-1}. The position of the low-energy S–O stretch is similar to that for other η^2-SO_2 complexes of Mo [the parent complex (**1**) shows $\nu(SO_2)$ at 1130 and 905 cm^{-1}], but the high-energy band is at least 60 cm^{-1} below that for other Mo η^2-SO_2 complexes.[2,3] This provided the first indication that co-ordination of the terminal oxygen of the η^2-SO_2 was occurring and led us to undertake a single-crystal *X*-ray diffraction study of (**2**).

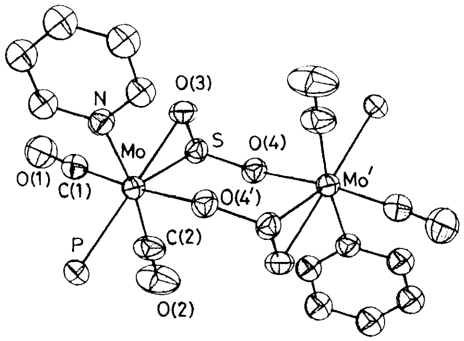

Figure. *X*-Ray structure of $[Mo(CO)_2(PPh_3)(pyridine)(\mu$-$SO_2)]_2$·$2CH_2Cl_2$; hydrogen atoms, phenyl rings, and CH_2Cl_2 of solvation have been omitted for clarity. Primed and unprimed atoms are related by the centre of symmetry. Distances and angles: Mo–C(1) 1·894(9), Mo–C(2) 1·994(10), Mo–P 2·528(2), Mo–N 2·287(6), Mo–O(3) 2·192(5), Mo–S 2·419(2), Mo–O(4′) 2·239(5), S–O(3) 1·523(6), S–O(4) 1·500(5), C(1)–O(1) 1·175(10), C(2)–O(2) 1·156(10), Mo–Mo′ 4·561(1) Å; C(1)–Mo–C(2) 87·4(4). C(1)–Mo–(P) 93·4(3), C(1)–Mo–N 90·7(3), C(1)–Mo–O(3) 93·8(3), C(1)–Mo–S 88·8(3), C(1)–Mo–O(4′) 171·7(3), Mo–S–O(4) 116·2(2), O(3)–S–O(4) 111·7(3), S–O(4)–Mo′ 140·0(3)°.

Crystal data: $C_{50}H_{40}Mo_2N_2O_8P_2S_2$·$2CH_2Cl_2$, triclinic, space group $P\overline{1}$ with a = 14.833(4), b = 9.264(2), c = 10.808(2) Å; α = 93.13(2), β = 98.23(2), γ = 110.54(1)°; Z = 1. The structure was solved by Patterson and difference Fourier techniques and refined to an unweighted R value of

0·064 for 3281 independent reflections. The octahedral co-ordination around the molybdenum atoms is shown in the Figure with selected distances and angles.† The SO_2 ligands are seen to bridge the molybdenum atoms by bonding to one metal through an η^2-S,O linkage and to the second metal through the other oxygen atom. As found for the analogous bond in other η^2-SO_2 complexes, the S–O(3)bond (1.52 Å) is lengthened relative to the S–O bonds in solid SO_2 (1·43 Å),[4] bridging SO_2 complexes (1·45—1·48 Å),[1] or η^1-planar SO_2 complexes (1·36—1·47 Å)[2,5] indicating a significant decrease in the S–O(3) bond order. Apparently, co-ordination of O(4) to the second Mo also lengthens the S–O(4) bond relative to terminal S–O linkages in η^2-SO_2 complexes (1·43—1·46 Å). The Mo–O(4) bond is nearly in the O(4)–S–O(3) plane and the Mo–O(4)–S angle is 140°. This closely resembles the SO_2 co-ordination geometry in the only structurally characterized O-bonded SO_2 complex, $SbF_5 \cdot SO_2$, where the Sb atom lies in the SO_2 plane and the Sb–O–S angle is 139°.[6] The O(4)–S–O(3) angle of 112° and the dihedral angle between the SO_2 and Mo–O–S planes of 97·5° are similar to those found for previously structurally characterized η^2-SO_2 complexes.[3] The η^2-S,O bond is oriented to place the sulphur atom near the better π-acceptor ligand (CO *vs.* pyridine) as observed in other structures of η^2-SO_2 complexes.[3] The structure indicates that rearrangement of the co-ordination geometry occurs in addition to phosphine loss during the formation of (**2**) from (**1**). The η^2-S,O bond is *trans* to a carbonyl in (**1**) but in (**2**) is *trans* to PPh_3.

Reaction of excess of pyridine with (**2**) at room temperature does not cleave the SO_2 bridge, but results in substitution of the PPh_3 with pyridine. The formation of (**2**) by displacement of PPh_3 and the apparent stability of the SO_2 bridge in the presence of excess of pyridine indicate that the terminal oxygen of an η^2-SO_2 ligand can possess considerable basicity, a feature we hope to exploit in further reactions of η^2-SO_2 complexes.

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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 Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] G. J. Kubas, *Inorg. Chem.*, 1979, **18**, 182, and references therein; M. Cowie and S. K. Dwight, *ibid.*, 1980, **19**, 209; N. J. Taylor, M. S. Arabi, and R. Mathieu, *ibid.*, p. 1740.

[2] G. J. Kubas, G. D. Jarvinen, and R. R. Ryan, submitted for publication.

[3] G. J. Kubas, R. R. Ryan, and V. McCarty, *Inorg. Chem.*, 1980, **19**, 3003.

[4] B. Post, R. S. Schwartz, and I. Fankuchen, *Acta Crystallogr.*, 1952, **5**, 372.

[5] R. R. Ryan and G. J. Kubas, *Inorg. Chem.*, 1978, **17**, 637; I. Ghatak, D. M. P. Mingos, M. B. Hursthouse, and K. M. A. Malik, *Transition Met. Chem.*, 1979, **4**, 260; P. Conway, S. M. Grant, A. R. Manning, and F. S. Stephens, *J. Organomet. Chem.*, 1980, **186**, C61; D. C. Moody and R. R. Ryan, *Inorg. Chem.*, 1979, **18**, 223; D. C. Moody, R. R. Ryan, and A. C. Larson, *ibid.*, p. 227.

[6] J. W. Moore, H. W. Baird, and H. B. Miller, *J. Am. Chem. Soc.*, 1968, **90**, 1358.