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The X-ray Molecular Structure of (η^6-*p*-Cymene)-(dimethylsulphoxide-*S*)dichloroosmium(II)

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Recently we have reported the synthesis of a rather wide range of *p*-cymeneosmium(II) complexes including methyl [1] and hydride [2, 3] derivatives. Interestingly, the *p*-cymene, which is the most labile ligand in the analogous ruthenium(II) complexes [4], appears quite difficult to displace or attack by nucleophiles when it is bonded to osmium.

We here report the crystal structure of (p-MeC_6H_4-$CHMe_2$)Os(Me_2SO)Cl_2, a complex with rather interesting features regarding the π-arene ligand and with a *S*-coordinated Me_2SO. Its IR spectrum shows the ν(SO) absorption at 1120 cm^{-1}, which is rather high for a *S*-coordinated Me_2SO (the related complex (p-$MeC_6H_4CHMe_2$)Os(Me_2SO)(Me)Cl shows the ν(SO) at 1088 cm^{-1} [1], quite consistent with *S*-bonded Me_2SO [5]). This structural determination clearly shows that the position of the IR band is influenced by factors other than the precise mode of ligation of the Me_2SO.

Experimental

The synthesis of the title compound has been reported [1]. Yellow–orange crystals of suitable quality were grown by slow diffusion of diethyl ether vapour through a concentrated dichloromethane solution.

Crystal Data: $C_{12}H_{20}Cl_2OOsS$, $M = 473.46$, triclinic, space group $P\bar{1}$, $a = 7.8395(52)$, $b = 9.3667(48)$, $c = 10.8467(60)$ Å, $\alpha = 106.931(38)$, $\beta = 94.296(49)$, $\gamma = 99.959(49)^\circ$, $U = 743.8$ Å^3, $Z = 2$, $D_c = 2.122$ g cm^{-3}, $F(000) = 451.88$, Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 90.65$ cm^{-1}. Unit-cell parameters were obtained from a least-squares fit of the setting angles of 25 well centered reflections. X-ray reflection data in the range $3.5 \leqslant 2\theta \leqslant 50^\circ$ were collected on a Nicolet R3M four-circle automatic diffractometer from a block-shaped crystal measuring approximately $0.04 \times 0.08 \times 0.15$ mm. 2366 independent reflections with $I \geqslant 3\sigma(I)$ were obtained and corrected for Lorentz and polarisation effects. An empirical absorption correction based on ϕ-scans of 9 reflections was also applied. The maximum and minimum transmission factors obtained were 0.346 and 0.209. The structure was solved by Patterson and difference-Fourier methods and refined by cascade blocked-diagonal matrix least-squares with weights $w_i = 1/[\sigma^2(F_i) + 0.00042F_i^2]$ to a final R value of 0.0355. The non-hydrogen atoms were refined with independent positional and anisotropic thermal vibration parameters. Sufficient hydrogen atoms were located from a low-angle difference Fourier synthesis to define approximate torsion angles for all the methyl groups. All hydrogen atoms were constrained to ride on the adjacent heavy atom with calculated bond lengths and angles; the hydrogen (isotropic) vibration parameters were fixed at 1.2 times the U_{eq} values for their respective neighbours.

The parameter shifts obtained on the final cycle of refinement were, in all cases, less than 0.02 of the corresponding e.e.d.s. A final difference Fourier synthesis showed no peak higher than 1.5 e Å^{-3} and none which could be interpreted as an atom. The final analysis of variance against sin θ and against $|F|$ showed no unusual features; neither did the normal probability plot. The SHELXTL [6] suite of crystallographic programs was used throughout. The atomic coordinates are listed in Table I. Further information is available, see 'Supplementary Material'.

Results and Discussion

A view of the complex with the numbering system of the atoms is shown in Fig. 1. Selected bond dis-

TABLE I. Atomic Coordinates ($\times 10^4$)

Atom	x	y	z
Os	7044(1)	6872(1)	7389(1)
S	7142(3)	8226(2)	9570(2)
O	7861(9)	9863(7)	9930(6)
Cl(1)	4188(3)	7430(3)	7112(2)
Cl(2)	5652(3)	4681(3)	7924(2)
C(1)	7825(10)	8000(9)	5962(7)
C(2)	9130(10)	8540(8)	7067(7)
C(3)	9901(10)	7490(10)	7549(8)
C(4)	9372(11)	5908(10)	6913(8)
C(5)	8100(12)	5400(9)	5786(8)
C(6)	7338(11)	6407(10)	5318(7)
C(7)	6953(11)	9103(11)	5485(9)
C(8)	7230(15)	10686(12)	6452(11)
C(9)	7500(13)	9127(15)	4178(11)
C(10)	10115(15)	4793(13)	7447(11)
C(11)	5157(14)	7997(12)	10233(9)
C(12)	8406(15)	7456(12)	10534(9)

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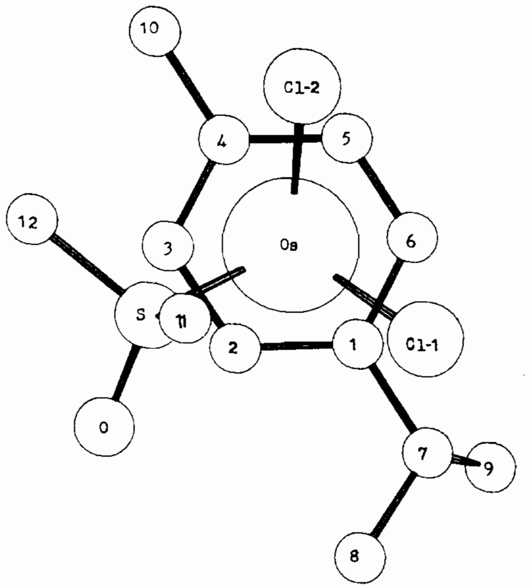

Fig. 1. A view of the complex (p-$MeC_6H_4CHMe_2$)OS(Me_2SO)Cl_2 along the line passing through the centroid (G) of the p-cymene ring and the osmium atom. Selected bond distances (Å) and angles (°): Os–S 2.324(2), Os–Cl(1) 2.402(2), Os–Cl(2) 2.399(3), Os–C(1) 2.180(9), Os–C(2) 2.181(8), Os–C(3) 2.194(8), Os–C(4) 2.203(9), Os–C(5) 2.196(9), Os–C(6) 2.198(8), S–O 1.461(7), S–C(11) 1.768(11), S–C(12) 1.768(12), C(1)–C(2) 1.423(10), C(1)–C(6) 1.420(11), C(1)–C(7) 1.519(14), C(2)–C(3) 1.436(13), C(3)–C(4) 1.411(11), C(4)–C(5) 1.425(11), C(4)–C(10) 1.509(19), C(5)–C(6) 1.390(14), C(7)–C(8) 1.514(13), C(7)–C(9) 1.517(16), S–Os–Cl(1) 85.7(1), S–Os–Cl(2) 86.5(1), Cl(1)–Os–Cl(2) 87.0(1), G–Os–S 128.4(1), G–Os–Cl(1) 127.8(1), G–Os–Cl(2) 127.2(1), Os–S–O 115.6(3), Os–S–C(11) 116.1(3), Os–S–C(12) 109.3(3), C(11)–S–C(12) 99.3(5), O–S–C(11) 107.1(5), O–S–C(12) 108.0(4).

tances and angles are given in the caption of Fig. 1. The osmium atom has an approximately octahedral coordination, with the p-cymene ligand occupying three coordination sites [averaged Os–C(1–6) 2.192(8), Os–G 1.672(3) Å] and the other three sites filled by two chlorine atoms and the sulphur atom of a Me_2SO ligand. The staggered mutual disposition of the p-cymene ring carbons with respect to the other ligands agrees with that found in the complex (p-$MeC_6H_4CHMe_2$)Ru(PPh_2Me)Cl_2 [7].

As in (p-$MeC_6H_4CHMe_2$)$_2Os_2Cl_4$ [8] or in [(p-$MeC_6H_4CHMe_2$)Ru(pyrazine)$_2$]Cl]PF_6 [9], the p-cymene ring in the title complex can be considered planar (maximum deviations of the carbon atoms from the mean plane ±0.013(8) Å]. This is in contrast to the p-cymene in the complex (p-$MeC_6H_4CHMe_2$)Ru(PPh_2Me)Cl_2 which adopts a boat conformation [7]. Both the methyl and isopropyl substituents of (p-$MeC_6H_4CHMe_2$)Os(Me_2SO)Cl_2 are bent towards the osmium (deviations from the ring plane 0.065(8) Å for C(10) and 0.080(8) Å for C(7)]. With the sole exception of the complex [(p-$MeC_6H_4CHMe_2$)$_2Os_2$(μ-H)(μ-OH)(μ-HCO_2)] PF_6 in which one of the methyls is bent away from the osmium [3], in all the other reported structures of p-cymene complexes [7–11] both the methyl and isopropyl groups are bent towards the metal. The p-cymene ring in the title complex is not regular, with carbon–carbon distances varying from 1.390(14) to 1.436(13) Å, the longest ones being those *cis* to the chlorine (C(1)–C(6) 1.420(11), C(4)–C(5) 1.425(11) Å) and Me_2SO (C(2)–C(3) 1.436(13) Å) ligands. The osmium–carbon bond distances are not regular either, varying from 2.180(9) Å for Os–C(1) to 2.203(9) Å for Os–C(4), but the distortion is apparently unrelated to the extraannular substitution. The Me_2SO ligand adopts a distorted tetrahedral coordination around the sulphur atom, with a S–O bond distance of 1.461(7) Å.

Supplementary Material

Complete tables of interatomic distances, angles, observed and calculated structure factors, isotropic and anisotropic temperature factors and hydrogen coordinates have been deposited with the Editor-in-Chief.

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