Protonated Dimethyl Sulphoxide, $[Me_2SO \cdots H \cdots OSMe_2]^+$; a Novel Hydrogen-bridged Structure: *X*-Ray Crystal Structure of ***trans***-$[H(Me_2SO)_2][RhCl_4(Me_2SO)_2]$

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Summary Studies on salts of tetrachlororhodate(III) containing sulphoxide ligands show the existence of the hydrogen-bonded cation $[Me_2SO \cdots H \cdots OSMe_2]^+$ with a very short $O \cdots H \cdots O$ bond length of 2·42 Å.

PROTONATED sulphoxides are thought to play an important role in several organic reactions carried out in Me_2SO,[1] and in the acid-catalysed decomposition of sulphoxides,[2] but there is only indirect evidence for protonation (at oxygen) from studies using magic acid (HSO_3F–SbF_5);[3] spectroscopic evidence has also indicated adduct formation between several hydrogen donors and sulphoxides.[4] We have studied the complexes *trans*-$[H(R_2SO)_2][RhCl_4(R_2SO)_2]$, (**1**, R = Me, Pr^n) and find from a *X*-ray crystal structure determination that the complex (R = Me) contains the hydrogen-bridged cation $[Me_2SO \cdots H \cdots OSMe_2]^+$.

In attempts to synthesize Rh^I sulphoxide catalysts,[5] we added sulphoxides to aqueous propan-2-ol solutions of $RhCl_3{\cdot}3H_2O$, but use of dipropyl sulphoxide unexpectedly gave complex (**1**; R = Pr^n). Intense and broad i.r. bands (Nujol) at 1600—1100 and 900—600 cm^{-1}, that are not caused by the anion, as shown by the spectrum of the corresponding NEt_4^+ salt, suggested the presence of a hydrogen-bonded base in the cation.[6] The dimethyl sulphoxide analogue (**1**, R = Me), originally formulated[7] $H[RhCl_4(Me_2SO)_2]{\cdot}2Me_2SO$, showed the same i.r. features, and an *X*-ray crystal structure has confirmed the existence of the H-bonded cation.

Crystal data: $C_8H_{25}Cl_4O_4RhS_4$, monoclinic, space group $P2_1/n$, $a = 9{\cdot}217(8)$, $b = 16{\cdot}50(2)$, $c = 14{\cdot}03(1)$ Å, $\beta = 100{\cdot}73(6)^\circ$, $U = 2170{\cdot}8$ Å^3, $Z = 4$, $D_c = 1{\cdot}708$, $\mu = 16{\cdot}3$ cm^{-1} for Mo-$K_{\alpha 1}$ radiation. 2765 independent reflections ($2\theta \leqslant 45^\circ$) were measured on a 4-circle Picker FACS-I diffractometer using a crystal 0·32 × 0·25 × 0·20 mm, absorption being neglected. All H atoms were located from a difference map, though only the solvated H atom was refined (x, y, z, U). Use of 2184 observed reflections ($I > 2{\cdot}3\,\sigma_I$) gave $R = 0{\cdot}029$.†

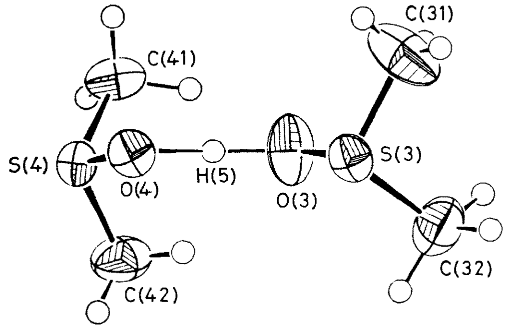

FIGURE. ORTEP diagram of the $[H(Me_2SO)_2]^+$ cation (50% ellipsoids, except H). Selected bond lengths (Å) and bond angles (°) are: S(4)–O(4), 1.531(4); O(4)–H(5), 1.25(5); H(5)–O(3), 1.18(5); O(3)–S(3), 1.536(4); ∠O(3)–S(3)–C(31), 102.6(3); ∠O(3)–S(3)–C(32), 103.2(3); ∠O(4)–S(4)–C(41), 105.2(2); ∠O(4)–S(4)–C(42), 105.7(2); ∠O(3)–H(5)–O(4), 173(5).

The molecular structure of the $[H(Me_2SO)_2]^+$ cation (Figure) reveals the short O ··· O distance of 2·420(5) Å [2·474(5) Å after correction for thermal motion if the two atoms are assumed to be moving independently]. The temperature factor for the solvated H atom is high, so the possibility of disorder involving two slightly asymmetric H positions cannot be excluded, though there is no elongation of the thermal ellipsoids of O(3) or O(4) along the S–O bonds. The average S–O bond length (1·533 Å), uncorrected for thermal vibration, is as expected somewhat larger than the corresponding value in crystalline Me_2SO (1·513 Å),[8] although oxygen co-ordination of Me_2SO to metals usually results in surprisingly little change in the S–O bond length.[9]

The geometry of the *trans*-$[RhCl_4(Me_2SO)_2]^-$ anion, containing *S*-bonded sulphoxides, is the same as reported for the sodium salt[10] but is more accurately determined; the average S–O bond length is now 1·460 Å, consistent with an increase in S–O bond order ($M \leftarrow S^- \equiv O^+$).

The ν(SO) of the cation, expected[11] at *ca.* 950 cm^{-1}, is not readily detected. There is a wide region of decreased intensity in the ν_a(OHO) envelope at 1100—900 cm^{-1}; the apparent borrowing of ν(SO) intensity may result from a Fermi resonance effect, suggested previously as a possible origin of transmission windows.[6] Similar spectral effects have been found with H-bridged cations of arsine- and pyridine-oxides,[12] and furnish evidence[13] for an *NN*-dimethylformamide (DMF) cation, $[H(DMF)_2]^+$. Some protonated chloroiridate complexes containing Me_2SO,[14] judging by the i.r. spectrum, must also contain the $[H(Me_2SO)_2]^+$ cation. The protonation at the oxygen in (**1**) has not been detected by studying shifts in the methyl n.m.r. resonance of Me_2SO; compatible solvents lead to elimination of HCl and formation of neutral *mer*-$[RhCl_3(sulphoxide)_3]$ complexes,[15] or simply displace the sulphoxide of the cation.

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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.

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