

Behaviour of Metal–Sulfoxide Complexes in Aqueous Solution: Base-Labilisation of S-Bound Dimethyl-sulfoxide

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Introduction

It is well established that alkyl sulfoxides, R_2SO , can bind to metals through either the oxygen or sulfur atom [1]. The factors which dictate the donor atom chosen, and the subsequent stereochemistry, include the size of the R group, the size of the central metal ion and general considerations of the class 'a' or class 'b' character of the metal.

Thus, while $[PtCl_2(DMSO)_2]$, (DMSO = dimethylsulfoxide), and $[PtCl_2(MBSO)_2]$, (MBSO = 3-methylbutylsulfoxide), have both sulfoxides bound through the sulfur atom, the sterically more demanding MBSO ligand results in a *trans* configuration whereas the DMSO complex is *cis*. Similarly, $[Pd(DMSO)_4]^{2+}$ has been shown to have two sulfur-bound *trans* to two oxygen-bound sulfoxides while $[Pd(MBSO)_4]^{2+}$ results in a complex with all four ligands bound through oxygen [2]. The effect of the metal ion may be gauged by comparison of *trans*- $[FeCl_2(DMSO)_4]^+$, all oxygen-bound [3] and *cis*- $[RuCl_2(DMSO)_4]$, with three sulfur and one oxygen-bound ligand [4]. We now wish to report on the behaviour of some DMSO complexes in aqueous solution and the unusual base-labilization of sulfur-bound dimethylsulfoxide.

Experimental

The ruthenium complexes were prepared by standard literature methods. 1H N.M.R. spectra were recorded on a Varian XL-100 machine and all chemical shift values are relative to the sodium salt of 3-trimethylsilylpropane sulfonic acid. The 2% OD^-/D_2O solutions were prepared by suitable dilution of a standard 30% $NaOD/D_2O$ solution purchased from Fluka AG, Switzerland. The concentration of metal complex in each experiment was kept at $5 \times 10^{-2} M$.

Results and Discussion

The complexes studied were *cis*- $[RuCl_2(DMSO)_4]$, I, and $[Ru(DMSO)_6](BF_4)_2$, II. The crystal structure

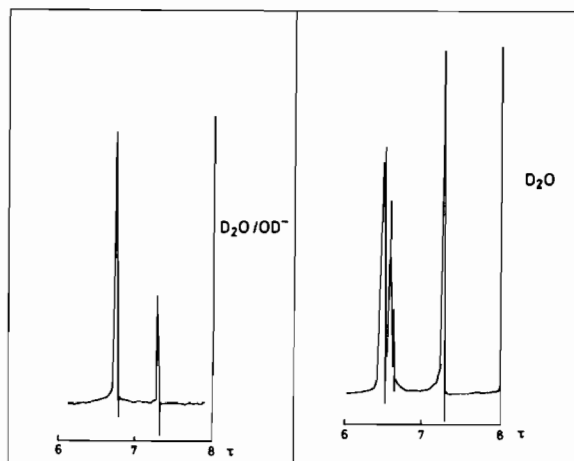


Fig. 1. 1H NMR spectra of $[RuCl_2(DMSO)_4]$ in aqueous solution.

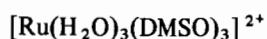
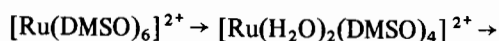
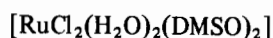
of I shows the presence of three sulfur- and one oxygen-bound sulfoxide [4]. The 1H N.M.R. spectrum of I in D_2O shows 5-line pattern with bands at 6.51, 6.53, 6.58, 6.62 and 6.66 τ , attributed to the methyl protons of the S-bound ligands, and a singlet at 7.3 τ , attributed to free DMSO, with total intensity ratio of 3:1. Upon addition of OD^- , or upon dissolution of the complex in a 2% OD^-/D_2O solution the spectrum changes markedly as shown in Fig. 1. The multiplet is now replaced by a singlet at 6.78 τ with integrated intensity of 3:1 relative to free DMSO at 7.3 τ .

With increasing temperature this ratio varies until at 82 $^\circ C$ the integrated intensity is 1:1 indicating labilisation of a second sulfoxide ligand. The variable temperature spectrum of I in neutral D_2O also shows a variation in intensity ratio until at 82 $^\circ C$ the ratio is 2:1 explained by the presence of a mixture at 3:1 and 1:1 isomers. The methyl resonance pattern consists of a 5-line pattern with slight changes in the relative intensity of the bands, the resonances at 6.51 and 6.53 τ decreasing while the band at 6.66 increases in intensity. Upon cooling to ambient temperature, (32 $^\circ C$), neither spectrum is reversible.

A similar situation occurs for the cation $[Ru(DMSO)_6]^{2+}$, II. This species is of interest because, while the crystal structure shows the presence of three sulfur- and three oxygen-bound sulfoxides in a *cis*-configuration, the 1H N.M.R. spectrum in D_2O at room temperature shows the presence of four sulfur-bound ligands [5]. The spectrum of II in OD^-/D_2O at 32 $^\circ C$ shows two singlets at 6.8 τ and 7.3 τ with intensity ratio of 1:1, presumably due to the $[Ru(DMSO)_3(H_2O)_3]^{2+}$ cation. The spectrum of II in neutral D_2O shows a three-line pattern at 6.51,

6.58 and 6.62 τ and a singlet at 7.3 with an intensity ratio of 2:1. Upon raising the temperature the ratio again varies until at 82 °C the observed proportion is 1:1. In this case the basic three-line pattern for the methyl resonances remains unaltered. As in the case of I, the spectrum is not reversed upon cooling to room temperature.

The results outlined above indicate that for M-DMSO species the choice of donor atom, and thus subsequent lability, may be influenced in aqueous medium by the presence of base. Thus, an extra DMSO ligand is labilised either by base or by increase of temperature:



The exact natures of the species formed in solution are under investigation as well as the extension of these observations to other metal systems. The ruthenium-sulfoxide complexes are active

homogeneous hydrogenation catalysts [5] and the ability to create labile sites by suitable selection of reaction conditions should be an asset in the design and evaluation of similar complexes as potential catalysts.

Acknowledgements

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