

Replacement of π -Bonding Ligands by Dimethyl Sulphoxide in Square-planar Platinum(II) Complexes: a Chemical Application of Heteronuclear Double Resonance

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DIMETHYL SULPHOXIDE is often used as a solvent in n.m.r. spectroscopy for sparingly soluble materials, although it is recognised that its co-ordinating ability and high dielectric constant can cause large solvent shifts.¹ We now report the observation of ready reversible replacement of sulphur and selenium ligands by Me₂SO in square-planar platinum(II) complexes. Previously, cleavage of chloride bridges by Me₂SO has been observed in palladium complexes although no distinct species containing Me₂SO were isolated.² We have used heteronuclear double resonance

experiments to identify positively three distinct species containing Me₂SO directly bound to platinum.

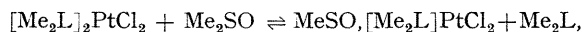
The proton resonances of the methyl groups in [Me₂L]₂PtCl₂ (L = S or Se) solutions in Me₂SO are at *ca.* τ 7.5, and are obscured by the solvent line, but there is also another resonance at τ 6.5 which is flanked by satellite peaks of *ca.* one quarter of its intensity. These can be removed by irradiation at the ¹⁹⁵Pt ($I = \frac{1}{2}$, abundance 34%) resonant frequency, so they clearly arise from a platinum-containing species. The line at τ 6.5 and its satellites are also present

N.m.r. parameters (Hz.) in platinum complexes

Species	$J(\text{Pt-S-Me})$	$J(\text{Pt-SO-Me})$	$\tau(\text{Me}_2\text{S})$	$\tau(\text{Me}_2\text{SO})$	$\Xi(^{195}\text{Pt})$	$\delta(^{195}\text{Pt})$ (p.p.m.)
<i>cis</i> -(Me_2S) ₂ PtCl ₂	49.5	—	7.45	—	21,421,130	0
<i>trans</i> -(Me_2S) ₂ PtCl ₂	41.6	—	7.56	—	21,423,880	-128
<i>cis</i> - $\text{Me}_2\text{SO}, \text{Me}_2\text{SPtCl}_2^a$	50.8	22.1	7.41	6.51	21,420,970	+8
<i>trans</i> - $\text{Me}_2\text{SO}, \text{Me}_2\text{SPtCl}_2^a$	50.8(?)	21.2	7.41	6.67	21,422,220	-51
(Me_2SO) ₂ PtCl ₂	—	23.5	—	—	21,432,780	-544

^a Designated on the basis of coupling constants and ¹⁹⁵Pt chemical shift.

in solutions of the complexes in methylene dichloride to which 5–10% Me_2SO has been added, and the intensity can be diminished by adding either $(\text{CD}_3)_2\text{SO}$ or free Me_2L . These observations are consistent with the following equilibrium:



and the appearance of well resolved ¹⁹⁵Pt satellites indicates that the lifetimes of the species are long on an n.m.r. time scale.

The reaction between equimolar amounts of Me_2S , Me_2SO , and K_2PtCl_2 in the presence of water yields the compounds listed in the Table. Only the last is insoluble in methylene dichloride and its spectrum was measured in D_2O .

The ¹⁹⁵Pt chemical shifts are accurate to ± 4 p.p.m. for the solutions examined, but are quite sensitive to changes of temperature and solvent. However, the values quoted for the first four species were obtained from a solution of a

mixture in methylene dichloride, and comparisons between them are probably valid.

There is evidence that vicinal ¹⁹⁵Pt–H coupling constants can be used to estimate the *trans*-effect and π -bonding ability of ligands, and if this is so the results indicate that these two parameters are similar for Cl^- and Me_2SO . The magnitude of the ¹⁹⁵Pt ··· H coupling constant in (Me_2SO)₂-PtCl₂ appears to support the view that there is a direct bond between platinum and sulphur in this compound.³ Our results are of practical significance because they show that there is a mechanism for conformational and other changes to occur readily in platinum(II) complexes in Me_2SO solution.⁴ More extensive studies of these and related systems are under way.

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