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 Me_2SO in square-planar platinum(II) complexes. Previously, cleavage of chloride bridges by Me_2SO has been observed in palladium complexes although no distinct species containing Me_2SO were isolated.[2] We have used heteronuclear double resonance experiments to identify positively three distinct species containing Me_2SO directly bound to platinum.

The proton resonances of the methyl groups in $[Me_2L]_2PtCl_2$ (L = S or Se) solutions in Me_2SO 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 ^{195}Pt ($I = \frac{1}{2}$, 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(Pt–S–Me)	J(Pt–SO–Me)	τ(Me_2S)	τ(Me_2SO)	Ξ(^{195}Pt)	δ(^{195}Pt) (p.p.m.)
cis-$(Me_2S)_2PtCl_2$	49·5	—	7·45	—	21,421,130	0
trans-$(Me_2S)_2PtCl_2$	41·6	—	7·56	—	21,423,880	−128
cis-Me_2SO,Me_2SPtCl_2[a]	50·8	22·1	7·41	6·51	21,420,970	+8
trans-Me_2SO,Me_2SPtCl_2[a]	50·8(?)	21·2	7·41	6·67	21,422,220	−51
$(Me_2SO)_2PtCl_2$	—	23·5	—	—	21,432,780	−544

[a] Designated on the basis of coupling constants and ^{195}Pt 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 $(CD_3)_2SO$ or free Me_2L. These observations are consistent with the following equilibrium:

$$[Me_2L]_2PtCl_2 + Me_2SO \rightleftharpoons MeSO,[Me_2L]PtCl_2 + Me_2L,$$

and the appearance of well resolved ^{195}Pt 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 ^{195}Pt 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 ^{195}Pt–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 $^{195}Pt \cdots H$ coupling constant in $(Me_2SO)_2PtCl_2$ 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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