A Reassignment of the Structure of $MCl_3(SEt_2)_3(M = Ir, Rh, and Ru)$

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Summary The compounds $MCl_3(SEt_2)_3$, (M = Ir, Rh, and Ru) have been reassigned a *mer*-configuration on the basis of ^1H n.m.r. measurements.

IN the course of our investigation of the co-ordinating ability of ligands containing donor atoms of Group VIB[1] we have prepared $IrCl_3(SEt_2)_3$. This complex was originally assigned the *fac*-configuration[2] on the basis of its ^1H n.m.r. spectrum in $CDCl_3$ at 60 MHz. Subsequently *X*-ray powder measurements have shown that the corresponding sulphide complexes of rhodium and ruthenium also have the same configuration.[3] We find, however, that the ^1H n.m.r. spectrum of $IrCl_3(SEt_2)_3$ in nitrobenzene at 60 and 100 MHz is consistent with the compound having a *mer*-configuration.

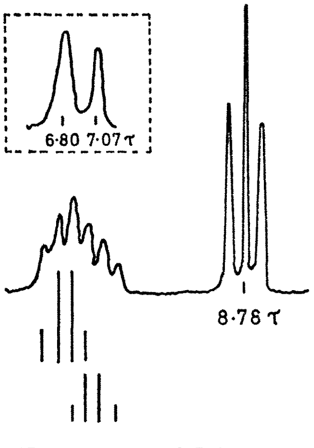

FIGURE 1. 60 MHz *spectrum of* $IrCl_3(SEt_2)_3$ *in nitrobenzene*

The *fac*-isomer should show a single methylene quartet and a single methyl triplet resonance, whereas the compound under consideration shows two methylene quartets and the methyl triplet (Figure 1). The latter can be resolved into two triplets at 100 MHz (Figure 2) as would be expected for a *mer*-configuration. Assignment of this structure was confirmed by double resonance. Irradiation at the centre of the central methyl resonance at τ 8·78 caused the methylene resonance to collapse into two single peaks at τ 6·80 and

7·07 (Figure 1, inset). Both compounds isolated from nitrobenzene and $CDCl_3$ had similar m.p.s and i.r. spectra.

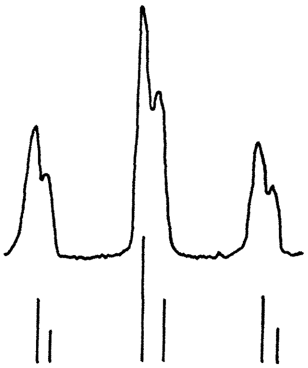

FIGURE 2. *Expanded* 100 MHz *spectrum of the methyl resonances of* $IrCl_3(SEt_2)_3$ *in nitrobenzene*

Kauffman *et al.*[2] reported the dipole moment of $IrCl_3(SEt_2)_3$ in benzene as 5·2 D whereas the dipole moment of 6·85 D [4] for *mer*-$IrCl_3(PEt_3)_3$ is consistent with the value expected from simple geometric arguments based on the dipole moment of 10·7 D for *cis*-$PtCl_2(PEt_3)_2$.[5] If we neglect any effect of assymetry of the sulphide ligand and assume that the Cl–Ir–SEt_2 and the Cl–Pt–SEt_2 moments are of the same order of magnitude, simple geometrica) arguments[6] and a value of 9·5 D for *cis*-$PtCl_2(SEt_2)_2$[7] can be used to predict a dipole moment of 6·7 D for the *mer*- and 11·6 D for the *fac*-isomers respectively of $IrCl_3(SEt_2)_3$. Hence the reported dipole moment is consistent with the complex having the *mer*-configuration.

Similar dipole moment and ^1H n.m.r. results[8] have been found for $IrBr_3(SEt_2)_3$, $RhCl_3(SEt_2)_3$, and $RhBr_3(SEt_2)_3$ indicating a common *mer*-configuration.

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