Nuclear Magnetic Resonance in Complexes exhibiting Second-order Paramagnetism

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WE have recently synthesised[1] several octahedral, neutral, paramagnetic complexes of $d^3(t_{2g}{}^3)$,$d^4(t_{2g}{}^4)$, and $d^5(t_{2g}{}^5)$ systems of ruthenium(III), osmium-(III) and -(IV), rhenium-(III) and -(IV), and iridium(IV) halides with tertiary phosphines and arsines, and have studied their magnetic properties and n.m.r. behaviour.

Their iridium(IV), osmium(III), and ruthenium(III) derivatives show very broad proton resonances which we have not been able to analyse, although in the case of [$RuCl_3(PMe_2Ph)_3$] the spectrum is consistent with local C_{2v} symmetry at the metal (meridianal structure). The spectra of [$ReCl_4(PR_2Ph)_2$] (R = Me, Et,[2] Pr^n, or Bu^n) are sharper (line widths ~5 Hz) but are still too broad for resolution of proton–proton couplings. However, the proton spectra of the d^4 systems [$ReCl_3(PR_2Ph)_3$] (R = Me,[2] Et,[2] Pr^n, or Bu^n) and [$OsCl_4L_2$] (L = PMe_2Ph, $PPr^n{}_2Ph$, $PBu^n{}_2Ph$, $PPr^n{}_3$, $AsPr^n{}_3$, or $AsMe_2Ph$) are sharp (line widths ~1 Hz) and shifted relative to those of diamagnetic analogues by several parts per million. The spectra have been completely assigned by double resonance techniques[3] and are consistent with meridianal structures for the Re^{III} compounds and *trans*-structures for the Os^{IV} phosphine compounds. Comparison of the methyl signals for [$OsCl_4(AsMe_2Ph)_2$] and [$OsCl_4(PMe_2Ph)_2$] (see Figure) shows a 1 : 2 : 1 splitting in the latter case, ascribed to "virtual coupling" to two mutually *trans* ^{31}P nuclei.[4] The rhenium compounds give

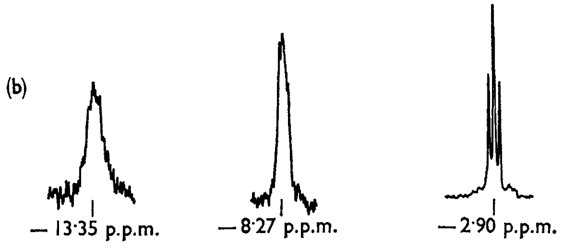

FIGURE. *The* 100 *Mc./sec.* ^1H *n.m.r. spectrum of* (a) $OsCl_4(AsMe_2Ph)_2$ *and* (b) $OsCl_4(PMe_2Ph)_2$ *in* $CDCl_3$ *solution at* 30° (*chemical shifts in p.p.m. with respect to tetramethylsilane*).

no indication of ^1H–^{31}P coupling, although both the rhenium and the osmium compounds exhibit the expected proton–proton coupling.

The lack of ^1H–^{31}P coupling as in the rhenium compounds has been attributed[2] to fast relaxation of the ^{31}P nuclei caused by an electron–nucleus interaction. This should lead to broader ^{31}P resonances for Re^{III} as compared to Os^{IV}, and we have not been able to detect ^{31}P resonances over an extended range for Re^{III} compounds (presumably the resonances are too broad) whereas lines have been observed for osmium(IV) compounds at approximately 1200 p.p.m. to high field of phosphoric acid. This is the first reported shift for ^{31}P in a paramagnetic phosphine complex.

The osmium(IV) compounds have room-temperature magnetic moments of approximately 1·5 B.M., comparable with those of K_2OsX_6 ($X = F$, Cl, Br or I) which have been shown to have "temperature-independent" susceptibilities.[5] In the absence of spin–orbit coupling, the ground state would be $^3T_{1g}(t_{2g}{}^4)$ and the complexes would have magnetic moments of about 2·8 B.M. However, spin–orbit coupling, which is large for Os^{IV} ($\zeta \sim 4000$ cm.$^{-1}$), gives a diamagnetic ground state ($J = 0$). A small admixture of a related higher state ($J = 1$) by a second-order Zeeman effect accounts for the observed susceptibilities and for the magnitudes of the chemical shifts, which, although larger than diamagnetic shifts, are nevertheless an order of magnitude smaller than the shifts of complexes with first-order paramagnetism. The magnetic moments of the rhenium d^4 compounds which have been studied[6] are also small ($\zeta \sim 2500$ cm.$^{-1}$) and similar arguments apply. The difference in the relaxation times for Os^{IV} and Re^{III} is presumably related to the difference in the spin–orbit coupling constants.

The chemical shifts are, in some cases, temperature dependent, as are the ^{59}Co chemical shifts produced by second-order paramagnetic effects in Co^{III} (d^6) complexes. This effect may be rationalised either by a change in the Boltzmann distribution between the ($J = 0$) and ($J = 1$) states or between the vibrational levels of the ground state.[7] An excited state has also been suggested to account for the anomalous fluorine chemical shifts[8] in the ion $OsF_6{}^{2-}$. Whatever the mechanism, the susceptibilities (sometimes called "temperature-independent" in these systems) must, in fact, be temperature-dependent, although to an extent less than the sensitivity of the bulk susceptibility measurements.

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