Slow Inversion about Sulphur in Certain Inorganic Complexes observed by Nuclear Magnetic Resonance

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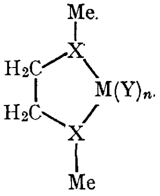
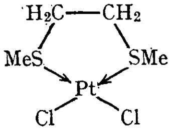
As part of a study of coupling constants from the metalloid or metal in the ring respectively to the ring protons and the side-chain protons, we have prepared a number of inorganic ring compounds illustrated by (I), where M has a spin $\frac{1}{2}$. In the particular case of (II)[1] we expected to observe a triplet for the methyl-proton resonance, the two outer lines due to molecules of the complex containing ^{195}Pt (34% abundance, spin $\frac{1}{2}$), and the inner line from the methyl-protons in molecules containing platinum isotopes of zero spin. However, the spectrum in hexadeuterodimethyl sulphoxide contained two such triplets, both with $J_{\text{Pt-H}}$ equal to 48·0 ± 0·5 c./sec. On warming, these two triplets converged, and at 95° coalesced to the single triplet (doublet + singlet) expected for the methyls of (II). Cooling restored the original double triplet. The permanence of the triplet on heating, and the invariance of the platinum–proton coupling constant shows that (II) does not dissociate on heating, and we conclude that these are two isomers of the complex in equilibrium.

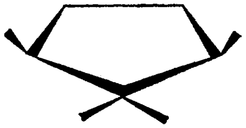


(I)

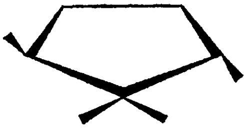


(II)

We believe this isomerism to be due to the projection of the sulphur-methyl groups on the same side (III), or different sides (IV) of the ring. Whilst methyl-protons in (III) would be in identical environments, as also would those of (IV), it would be expected that the methyl-proton environments in (III) and (IV) respectively would be slightly different.



(III)



(IV)

In the case of the corresponding palladium complex the methyl resonance is a broad singlet at 40°. On cooling, however, the resonance does split into a doublet, confirming the presence of isomers (III) and (IV) for palladium as well as platinum. In the case of the platinum complex it is difficult to estimate the relative intensities of the two triplets, but in the case of palladium the doublet is not symmetrical, indicating that population of the two forms (III) and (IV) at any time is not equal. That one form is favoured in solution over another is not unreasonable, and preliminary estimations using a variety of the accepted formulae[2,3] for such calculations indicate an energy barrier to their interconversion of about 5 Kcal. for the platinum complexes, and a slightly lower value for those of palladium.

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[2] J. A. Pople, W. G. Schneider, and H. T. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw Hill, New York, 1959.

[3] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, 1959, **30**, 899.