

**THE PROTON MAGNETIC RESONANCE
CONTACT SHIFT STUDIES ON COBALT(II)
HALIDE COMPLEXES OF PYRIDINE N-OXIDE
AND DIPHENYL SULPHOXIDE**

Introduction

THIS investigation is carried out to arrive at the anion effect on the metal-neutral ligand bonding. In order to discuss these effects, the spin-delocalisation mechanisms that give rise to pmr contact shifts and the effects of halide anions on the cobalt-neutral ligand bonding must be considered. It has already been reported that the composition and configuration of Co(II) halide complexes of pyridine N-Oxide (PNO) and diphenyl sulphoxide (DPSO) vary depending on the nature of the halide anion¹⁻⁶. But very limited number of contact shift studies on cobalt(II) halide complexes with these ligands is reported⁷⁻³. Moreover, it will be interesting to know how the contact shift studies can be made use of, to predict the effect of the halide anions on the bonding of the metal to the various neutral monodentate ligands.

Experimental

Cobalt(II) halides and perchlorate complexes of (PNO) and (DPSO) were prepared by methods reported previously¹⁻⁶. Their configurations were assigned from their conductance, magnetic susceptibility, infrared and electronic spectral data. PMR contact shift measurements were made in 60 MHz Varian NMR spectrophotometer with 0.1 M solutions of the complexes containing a slight excess of the neutral ligand in CD₃CN. The results are given in Table I. The proton resonance shifts (Table I) are shifts in the resonance frequencies from their normal values in the absence of the paramagnetic complexes measured in cps with an error of ± 0.5 cps. Negative shifts indicate shifts to lower applied field.

Results and Discussion

In general, the delocalisation mechanism is understood if we consider the main effects that contribute to the observed pmr shifts of octahedral cobalt(II) complexes. Cobalt(II) unpaired electrons, two e_g and one t_{2g} electrons are responsible for the mechanism of spin delocalisation. The t_{2g} electrons can be transferred on to ligands only in the case where π bonds are formed between the metal ion and the ligand (π -delocalisation). The π -delocalisation mechanism is significant for planar ligands and usually dominant. It is present in the Co(II) complexes.

However, six-coordinated Co(II) complexes have a triply degenerate ground state which is expected to produce magnetic anisotropy and hence pseudo-contact shift. This is particularly significant in the case of distorted DPSO complexes. In the case of PNO complexes (O_h) substitution of the solvent can introduce significant pseudo-contact contribution even in the presence of rapid exchange.

According to Wayland and Drago⁹, the magnitude of metal-neutral ligand covalent character depends upon the energy of the metal halide valence orbitals. Application of their orbital bonding model leads to the prediction that the energy (destabilisation) of the MX_2 acceptor orbitals increases in the order $MCl_2 > MBr_2 > MI_2$. The magnitude of the metal-neutral ligand covalent character is thus expected to increase in the order $MCl_2 < MBr_2 < MI_2$. This will be observed only if there is an increase in ligand proton resonance shifts when the anion is changed from Cl^- to I^- . The coordinated anion may impart pseudo-contact shifts than the uncoordinated anion. Accordingly the observed shifts are expected to be

TABLE I

PMR shifts in ligand protons in Co(II) halide and perchlorate complexes with PNO and DPSO

Complexes	Stereo Chemistry	$\Delta\nu_\alpha$	$\Delta\nu_\beta$
1. $[Co(PNO)_6]^{2+} [CoCl_4]^{2-}$	Octahedral cation with tetrahedral anion	+ 14	+ 2
2. $[Co(PNO)_6] (ClO_4)_2$	Octahedral	+ 20	- 4
3. $[Co(PNO)_6] I_2$	Octahedral	+ 16	- 6
4. $[Co(PNO)_4 Br_2]$	Distorted octahedral	+ 18	+ 24
5. $[Co(DPSO)_2 Cl_2]$	Distorted tetrahedral	+ 6	+ 58
6. $[Co(DPSO)_4 I_2]$	Distorted octahedral	- 66	- 30
7. $[Co(DPSO)_6] (ClO_4)_2$	Octahedral	-166	- 78
8. $[Co(DPSO)_6]^{2+} [CoBr_4]^{2-}$	Octahedral cation with tetrahedral anion	- 93	-43