

The Electron Spin Resonance Spectra of Some Low-spin Cobalt(II) Complexes

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COBALT(II) forms a series of complexes $\text{Co}(\text{CNR})_4\text{X}_2$, [CNR = alkyl or aryl isonitrile, X = Cl, Br, or I]; these are paramagnetic with moments corresponding to one unpaired electron, and conductivity measurements on the methyl isonitrile derivatives in aqueous solution indicated a tetra-co-ordinated structure with ionic halide.¹ The e.s.r. spectra of

these compounds in various solvents (ethanol, acetone, methylene chloride) show hyperfine interaction from the two halogens (Figure) indicating some degree of covalency in the cobalt-halogen bond, and that the lifetime of the halide ion on the cobalt must be $\geq 10^{-8}$ sec. The addition of an excess of lithium halide to alcohol solutions

of the complexes causes some broadening of the hyperfine lines; this may be due to a change in the viscosity of the solution rather than to chemical exchange.² All the spectra are anisotropic, that is, the line-width depends upon the nuclear spin states of the halogens. For the ethyl, cyclohexyl, and *p*-tolyl isonitrile complexes, the hyperfine coupling constant for the iodide (two ¹²⁷I, $I = 5/2$), give eleven lines, areas 1:2:3:4:5:6:5:4:3:2:1) $A \sim 94$ gauss, for the bromide (two ^{79/81}Br, $I = 3/2$, give seven lines, areas 1:2:3:4:3:2:1) $A \sim 76$ gauss. In the chloride complexes a hyperfine interaction of ~ 14 gauss is resolvable, but since more than seven lines are observed (^{35/37}Cl, $I = 3/2$) there must be some splitting from the cobalt (⁵⁹Co, $I = 7/2$). Some cobalt hyperfine coupling is just resolvable for Co(CN·C₆H₁₁)₄I₂, $A \sim 16$ gauss, and although none was observed for the other bromide and iodide complexes, a strong asymmetry of the component lines indicates unresolved cobalt hyperfine coupling.

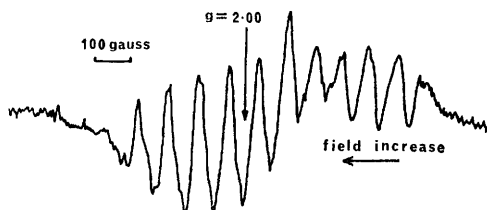


FIGURE. Di-iodotetra(cyclohexyl isonitrile)cobalt(II), 1.8×10^{-3} M, in acetone.

The g -factors of the complexes are illustrated by those for the *p*-tolyl isonitrile derivatives in methylene chloride, where $g_{\text{Cl}} = 2.091$, $g_{\text{Br}} = 2.076$, and $g_{\text{I}} = 2.044 (\pm 0.001)$. These values together with the fairly large hyperfine couplings allow a tentative assignment of the relative energies of the cobalt $3d$ -orbitals. For a low-spin Co^{II} complex $g = 2(1 + \zeta/\delta)$, where ζ is the spin-orbit constant and δ is the separation of the level having the unpaired spin and its neighbouring levels; ζ contains a contribution from the cobalt and from the ligands, it can be subdivided into $\zeta_{\pi\pi}$ and $\zeta_{\sigma\pi}$ representing π - π interaction and σ - π interaction of the metal d -orbitals.³ For $\zeta_{\pi\pi}$ the ligand contribution is positive, for $\zeta_{\sigma\pi}$ it is negative, thus the decrease in g for these complexes could conceivably be explained by a contribution from $\zeta_{\sigma\pi}$ increasing with the increasing spin-orbit constants of the halogens⁴ ($\zeta_{\text{Cl}} = 590 \text{ cm.}^{-1}$, $\zeta_{\text{Br}} = 2460 \text{ cm.}^{-1}$, $\zeta_{\text{I}} = 4060 \text{ cm.}^{-1}$). Thus the unpaired electron is probably in a d_{z^2} orbital, rather than a d_{xy} orbital, or the degenerate d_{zx} , d_{yz} . The order of the energy levels in increasing energy is probably $3d_{xy}$; $3d_{zx}$, $3d_{yz}$; $3d_{z^2}$; $3d_{x^2-y^2}$, this is in accord with previous assignments of the levels.⁵ The large hyperfine coupling accords with a σ -interaction with unfilled halogen s -orbitals, also $3d_{z^2}$ may mix with the $4s$ cobalt orbitals⁵, giving a direct hyperfine interaction with both the cobalt and the halogen. A more quantitative explanation of these data will be presented later.

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