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On the Interaction between Pentacyanocobaltate(II) Anion and Triphenylphosphine

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A recent report of the interaction of various bases with ethanolic solutions of pentacyanocobaltate anion suggested that there was considerable delocalisation of the unpaired electron onto the phosphorus of the triphenylphosphine [1]. Further analysis of the spectrum in the $g_\perp$ region where there is considerable overlap between the eight lines due to the ^{59}Co nucleus (I = 7/2) each split by the interaction with ^{31}P (I = 0.5), suggests that the value for $A_\perp$ (^{31}P) should be considerably increased. The figure shows the spectrum of a frozen ethanolic solution at 77 K which was analysed by computer simulation using the following spin Hamiltonian parameters:
$g_\parallel$ = 1.993, $g_\perp$ = 2.169, $A_\parallel$ (^{59}Co) = 82 G, $A_\perp$ (^{59}Co) = 30 G, $A_\parallel$ (^{31}P) = 150 G and $A_\perp$ (^{31}P) = 120 G.

Analysis of the ^{31}P hyperfine tensor shows that the 3*s* character is 3.5% and 3*p* character 9.9% with the *p*:*s* ratio = 2.8. Analysis of the ^{59}Co hyperfine tensor using the standard equations for a d^7 ion with unpaired electron in an a_1 orbital (C_{3v} symmetry) shows that, with negative $A_\perp$, there is slightly less spin density in the d_{z^2} orbital and more delocalised onto the axial ligand (P of triphenylphosphine) than is the case when the only axial ligand is CN (from ^{13}C h.f.s.) – see Table.

The *p*:*s* ratio of the unpaired electron on phosphorus is close to that expected for a ligand having a lone pair with approximately sp^3 hybridisation. These results are very similar to those reported for the interaction of phenyldimethylphosphine with tetraphenylphosphinecobalt(II) [3] where a *p*:*s* ratio of 2.56 was found.

TABLE. Calculated Values of Electron Population Parameters for $[Co(CN)_5]^{3-}$ and Various Bases.

Base	10^4P/ cm^{-1}	κ	$-10^4\kappa P(A_{iso})$/ cm^{-1}	$\%d_{z^2}$	% Ligand
PPh_3 [1]	171	0.065	−11	67	13.4
None [2]	176	0.083	−15	69	10(CN)
C_5H_5N [1]	208	0.083	−17	82	–

1 J. B. Raynor and R. L. Nye, *J. Chem. Soc. Dalton*, 504 (1976).
2 R. J. Booth and W. C. Lui, *J. Chem. Phys.*, *61*, 1226 (1974).
3 B. B. Wayland and M. E. Abd-Elmageed, *J. Am. Chem. Soc.*, *96*, 4809 (1974).

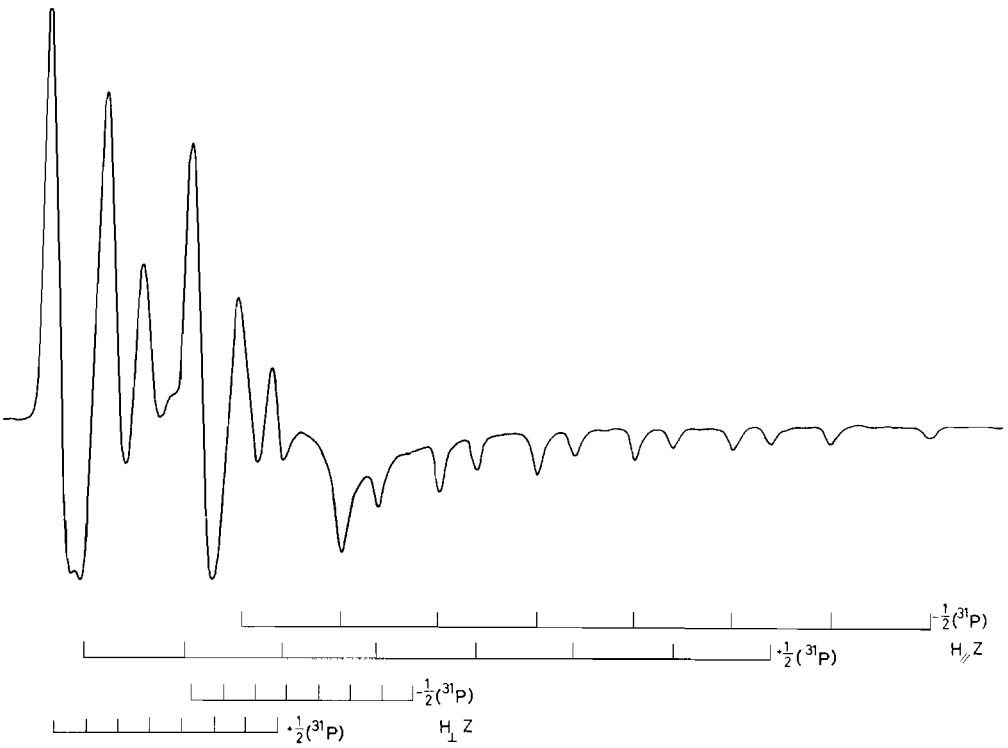

Figure. E.s.r. spectrum of $[Co(CN)_5]^{3-}$ in ethanol with added triphenylphosphine at 77 K.