Effect of Solvents and Lewis Bases on the Pentacyanocobaltate(II) Anion

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The e.s.r. spectra of $[Co(CN)_5]^{3-}$ in the presence of various bases are very similar, showing small effects due to weak interactions. With pyridine and diethylamine, hyperfine coupling to N (11.5 and 11.25 G) suggests a stronger interaction. With triphenylphosphine the unpaired electron density in the metal $3d_{z^2}$ orbital is reduced to only 39% whilst that in a *p* orbital on phosphorus is in excess of 46%. This substantial delocalisation is associated with a considerable ' flattening ' of the phosphine ligand. In the presence of triphenylarsine and triphenylstibine, complete reduction of the base takes place. The quadrupole coupling constant, Q', for $[Co(CN)_5]^{3-}$ is -2.5×10^{-4} cm^{-1}, from which it is deduced that the orbital coefficient β_2^2 for the d_{xy} orbital is 0.85.

THERE has been considerable interest in the cyanide complexes of cobalt since they lend themselves so well to e.s.r. measurements. Electrons are readily added to salts of the diamagnetic $[Co(CN)_6]^{3-}$ anion on irradiation.[1-6] A feature of interest is the detection of superhyperfine coupling to two equivalent nitrogen atoms which is attributed to bending of the cyanide ligand in the lattice.[1,5] Irradiation of $[Co(CN)_6]^{3-}$ substituted into alkali-halide host lattices causes some exchange of halide ion with the cyanide ligands to yield species of the type $[CoBr_2(CN)_4]^{4-}$.[4] The very air-sensitive $[Co(CN)_5]^{3-}$ has been studied only in water, methanol, and acetonitrile,[2,7,8] and no systematic study has been made of the interaction of solvent or Lewis bases with the vacant sixth co-ordination site. This complex lends itself to such a study by e.s.r. spectroscopy because the unpaired electron is in the $a_1(d_{z^2})$ orbital which is potentially capable of interacting directly with axial ligands.

EXPERIMENTAL

Solutions of lithium pentacyanocobaltate(II) in ethanol were prepared by the reaction of anhydrous cobalt(II) chloride with lithium ethoxide and hydrogen cyanide in ethanol under nitrogen. Portions of the solution were transferred to e.s.r. sample tubes together with aliquot portions of various Lewis bases or solutions of Lewis bases in ethanol.[9] All operations were in a dry oxygen-free atmosphere.

E.s.r. spectra were recorded at 77 K using a Varian E-3 spectrometer calibrated against diphenylpicrylhydrazyl. Spectra were simulated on a CDC 72 computer using a program described previously.[10]

RESULTS AND DISCUSSION

The analysis of the spectrum of $[Co(CN)_5]^{3-}$ and related species is now generally understood. The ion is low spin d^7 having C_{4v} symmetry and with the unpaired electron in an $a_1(d_{z^2})$ molecular orbital. The spin-Hamiltonian parameters may be deduced from the equations given by Griffith [11] which reduce to, in first order, (1)—(4), where the symbols have their usual meaning. We have used these equations in the detailed analysis of our spectra. Certain problems arise in the use of these equations, namely the uncertainty in the signs of $A_{\parallel}$ and $A_{\perp}$. No isotropic data are available

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since in fluid solution only a single broad line is obtained. The coupling constant $A_{\parallel}$ has to be positive to give the

$$g_{\parallel} = 2 \tag{1}$$

$$g_{\perp} = 2 + 6\lambda/[\Delta E(d_{z^2} - d_{xz,yz})] \tag{2}$$

$$A_{\parallel} = P\,[-\,\kappa + \tfrac{4}{7} - \tfrac{1}{7}\Delta g_{\perp}] \tag{3}$$

$$A_{\perp} = P\,[-\,\kappa - \tfrac{2}{7} + \tfrac{15}{14}\Delta g_{\perp}] \tag{4}$$

required positive values of P, but $A_{\perp}$ can be positive or negative. We have considered each case in turn.

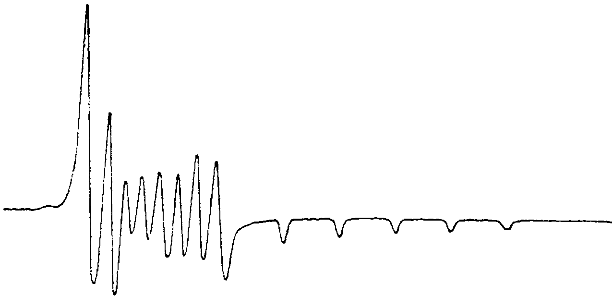

FIGURE 1 E.s.r. spectrum of $[Co(CN)_5]^{3-}$ in ethanol at 77 K

With some added bases, the spectra at 77 K were similar to that shown in Figure 1. They were readily interpreted in terms of an axially symmetric species with hyperfine coupling to ^{59}Co ($I = \frac{7}{2}$). With other added bases, namely pyridine, diethylamine, and triphenylphosphine, there was a further splitting of the parallel features showing coupling to ^{14}N ($I = 1$) or ^{31}P ($I = \frac{1}{2}$) (Figures 2 and 3). In the case of pyridine and diethylamine, the perpendicular cobalt features collapsed to a single line. When triphenylarsine or triphenylstilbine were added the spectra were very complex but showed no sign of coupling to cobalt. We have been unable to interpret these fully. Different preparations of the $[Co(CN)_5]^{3-}$ solution behaved differently towards added base. Some solutions with NEt_2H, C_5H_5N, $AsPh_3$, and $SbPh_3$ showed spectra typical of solutions with no added base. A similar observation was made by Maher[8] with acetonitrile solutions, who attributed the effect to different numbers of cyanide groups in the complex since it seemed to be associated with ratios of CN : Co of 5 : 1 or 3 : 1. No detailed formulation of the complexes was made, but they seem to have different stabilities in the presence of bases.

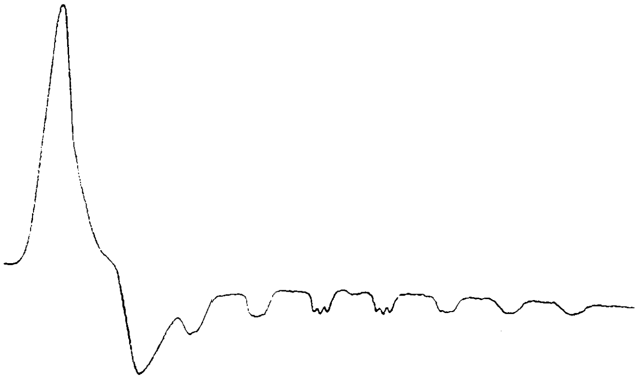

FIGURE 2 E.s.r. spectrum of $[Co(CN)_5]^{3-}$ in ethanol with added diethylamine at 77 K

The results can be grouped into three types which represent weak and strong interactions of $[Co(CN)_5]^{3-}$ with base and electron transfer. We consider each in turn.

Weakly interacting Bases.—When dimethyl sulphoxide, dimethylformamide, and NEt_3 were added to $[Co(CN)_5]^{3-}$ in ethanol, and for $[Co(CN)_5]^{3-}$ in ethanol or water, the spectra were almost identical. The parameters are given in Table 1. We do not believe that it is realistic to interpret the small changes in parameters from one spectrum to another since the differences arise from small changes in the energy of the molecular orbitals which themselves are dependent on small changes in the σ and π bonding in the molecule caused by weak interactions with the bases and solvent. From the spin-Hamiltonian parameters, assuming $A_{\parallel}$ and $A_{\perp}$ are both positive, we find that $\kappa = 0.083$ and $P = 176 \times 10^{-4}$ cm^{-1}. With $A_{\perp}$ negative, $\kappa = -0.424$ and $P = 84 \times 10^{-4}$ cm^{-1}. Knowing that the value of P

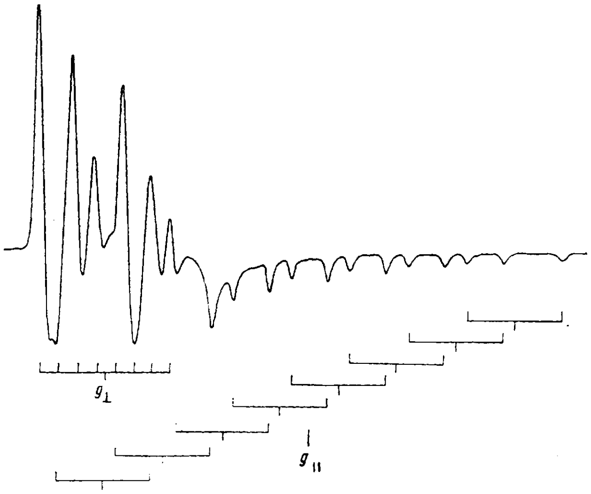

FIGURE 3 E.s.r. spectrum of $[Co(CN)_5]^{3-}$ in ethanol with added triphenylphosphine at 77 K

TABLE 1

Spin-Hamiltonian parameters of $[Co(CN)_5]^{3-}$ in the presence of various bases

Base	$g_{\parallel}$	$g_{\perp}$	$10^4 A_{\parallel}(^{59}Co)$/ cm^{-1}	$10^4 A_{\perp}(^{59}Co)$/ cm^{-1}	
EtOH	2.012	2.181	82.8	30.5	
SMe_2O	2.012	2.180	82.8	30.5	
$HCONMe_2$	2.008	2.188	80.9	28.3	
NEt_3	2.013	2.193	81.3	28.9	
NEt_2H	2.002	2.315	93.5		$A_{\parallel}(^{14}N)$ = 11.25 G
C_5H_5N	2.004	2.315	92.5		$A_{\parallel}(^{14}N)$ = 11.5 G
PPh_3	2.020	2.225	87.7	30.45	$A_{\parallel}(^{31}P)$ = 150 G

for an electron entirely in a *d* orbital on cobalt is 255×10^{-4} cm^{-1}, then the population of the $3d_{z^2}$ orbital is 0.69 if $A_\perp$ is negative and 0.33 if $A_\perp$ is positive. The population figure of 0.33 for d_{z^2} is much too small and we take the value of 0.69 as correct, where it has been assumed that $A_\parallel$ and $A_\perp$ are of opposite sign. This is entirely consistent with related systems; *e.g.* in $[Fe(CN)_5(NO)]^{3-}$ the population of the unpaired electron is *ca.* 0.85.[12] This choice of signs for $A_\perp$ has been postulated by Symons and Wilkinson [4] and by Maher [8] for $[Co(CN)_5]^{3-}$, but Lin *et al.*[3] assumed that $A_\perp$ was positive. Recently Booth and Lin,[6] assuming that $A_\perp$ was negative, deduced from ^{13}C superhyperfine coupling to the axial ^{13}CN that the population in d_{z^2} was 0.78 and that in the 2*s* and 2*p* orbitals on ^{13}C the population was 10%. In all these systems we suggest the species present is $[Co(CN)_5]^{3-}$ with negligible difference in the interaction of solvent or base with the vacant sixth co-ordination position.

Stronger interacting Bases.—With added NEt_2H or C_5H_5N the spectra observed were very different. Each cobalt parallel feature was split into a triplet with separation 11.25 and 11.50 G respectively,* whilst the perpendicular cobalt features collapsed to a single line shifted to lower field (Figure 2). These spectra were similar to that of Maher [8] in his $[Co(CN)_5]^{3-}$–MeCN system, and show direct interaction of the unpaired electron with the nitrogen atom of one added base. Analysis of the spin-Hamiltonian parameters yielded the values for P and κ given in Table 2. We estimated the value of $A_\perp$(Co) from the linewidth, in those spectra where it was not resolved, as *ca.* 7 G; changes of ± 5 G do not alter the values of P and κ significantly. It is not possible to decide on the best values of P and κ since taking $A_\perp$ as negative or positive both gave consistent and reasonable values.

We propose that the species responsible for the signal is a weak adduct of the form $[Co(CN)_5L]^{3-}$ ($L = C_5H_5N$ or NEt_2H). Our results are very similar to those of Maher [8] for his system $[Co(CN)_5]^{3-}$–MeCN. It is interesting to compare the N hyperfine coupling in these systems (11.25—14.5 G) with that found in irradiated $[Co(CN)_6]^{3-}$ (*ca.* 3.5 G),[5] where an axial cyanide group has bent away from the principal axis and permitted some interaction of the unpaired electron with the nitrogen.

Electron Transfer.—With added PPh_3 the spectrum was quite different; hyperfine coupling to Co was resolved in the perpendicular region and the coupling to phosphorus ($A_\parallel$) was large (150 G). Since there was no superhyperfine coupling to P on the cobalt perpendicular features, the splitting must be small (<10 G). The coupling constant A_{iso}(P) is then *ca.* 43 or 57 G depending on whether $A_\perp(P) = -10$ or $+10$ G; $A_\parallel$ is of course positive since there must be direct electron interaction with P. It follows that $A_{aniso} = 107$ or 93 G respectively. Taking the value of 202 G as that for 100% occupancy of a 3*p* orbital on P and 3 676 G for 100% occupancy of the 3*s* orbital, it follows that the *s* and *p* characters of the electron interacting with P are 1.2 and 53% if $A_\perp$(P) is negative, and 1.5 and 46% if $A_\perp$(P) is positive. In either case, there is much delocalisation of the unpaired electron on to a *p* orbital on phosphorus. Furthermore, with effectively half an electron transferred to the phosphine, the latter is beginning to resemble $[PPh_3]^-$. Inspection of the Walsh [13] energy-level correlation diagram for pyramidal and planar AB_3 molecules shows that an unpaired electron in $[PPh_3]^-$ would be in a $7a_1$ molecular orbital. 'Flattening' of the molecule would stabilise this orbital; our $p : s$ ratio for the electron in the P orbital is *ca.* 30—45 : 1 [depending on the choice of value for $A_\perp$(P)] and shows that the electron is almost entirely *p* in character. This is evidence for significant 'flattening' of the molecule with the angle C–P–C *ca.* 120° and Co–P–C *ca.* 90°.

We thus have a unique picture of a metal–phosphine complex with the PPh_3 group distorted towards planarity with the metal electron so delocalised on to the phosphorus that electron transfer is beginning to take place, according to (I). These results differ markedly from

$$Co^{II}(CN)_5\text{–}PPh_3 \longrightarrow Co^{III}(CN)_5\text{–}PPh_3^- \quad \text{(I)}$$

those for the various phosphine adducts of tetraphenylporphinecobalt(II) where the *s* character in the orbital of the co-ordinated phosphorus varies from 0.27—0.68.[14] However, these complexes are very different because of the extended π delocalisation into the porphine ring system which results in the relative energies of the porphine–phosphine complex being quite different from those in our adduct. It is interesting to see the trend in *s* and *p* character of the electron on phosphorus in porphine adducts with PMe_3 and PMe_2Ph where the $p : s$ ratios are 1.75 and 2.56 : 1 respectively. Triphenylphosphine was not studied, but presumably such an adduct, if capable of being formed, would have an even greater $p : s$ ratio. Triphenylphosphine–metal bonds are much longer than other phosphine–metal bonds, and this is consistent with an observed decrease in *s* character in the σ orbital and associated weakening of the Co–P bond.

Analysis of the cobalt hyperfine parameters yields the values of P and κ given in Table 2. The d_{z^2} population is either 80 or 39% depending on whether $A_\perp$(Co) is negative or positive respectively. Since the population on P is 47 or 54%, the population in the d_{z^2} orbital on cobalt must be 39%. This low value requires a positive value for A_{iso}, implying considerable 4*s* mixing into the ground state.

The effects of adding $AsPh_3$ and $SbPh_3$ may be readily explained. Electron transfer is now complete

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* 1 G = 10^{-4} T.

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and the products of reaction are a diamagnetic cobalt(III) cyanide and an arsine or stibine anion radical of undetermined structure. Electron transfer occurs more readily with these ligands because of their accessible π^* and d orbitals. The order of energy levels is such that the lowest empty As or Sb orbital lies between the Co d_{xy} and d_{z^2} orbitals.

TABLE 2

Calculated values of electron-population parameters for $[Co(CN)_5]^{3-}$ and various bases

	Assuming $A_\perp$(Co) negative				Assuming $A_\perp$(Co) positive			
Base	10^4P/cm^{-1}	κ	$-10^4\kappa P$ (A_{iso}) cm^{-1}	%d_{z^2} [a]	10^4P/cm^{-1}	κ	$-10^4\kappa P$(A_{iso}) cm^{-1}	%d_{z^2} [a]
None [b]	176	0.083	−15	69	84	−0.424	36	33
C_5H_5N [c]	208	0.083	−17	82	179	0.010	−18	70
PPh_3	202	0.106	−21	80	98	−0.356	35	39

[a] % Population in d_{z^2} orbital. [b] No added base, or addition of ' weakly interacting ' bases. [c] Diethylamine gives similar results.

Analysis of A_{iso}(Co).—Symons and Wilkinson [4] showed that a relation exists between A_{iso}(Co) and the co-ordination number of the complex; A_{iso} for six-co-ordination is *ca.* −30 to −45 G, *ca.* −5 to −25 G for five-co-ordination, and *ca.* 0 for four-co-ordination. This means that there is a steady increase in the 4s contribution to the orbital of the unpaired electron as the number of ligands is reduced from six to four. A semiquantitative estimate may be made of the 4s contribution if we set $A_{iso}(4s) = 1\,308 \times 10^{-4}$ cm^{-1} (value for electron entirely in 4s orbital) [15] and $A_{iso}(3d) = -90 \times 10^{-4}$ cm^{-1} (spin polarisation due to electron entirely in a 3d orbital).[16] If n = fraction of electron on cobalt, xn is the fraction of the 4s electron on Co and $(1 - x)n$ is the fraction of the 3d electron on cobalt. We can then write equation (5). For the

$$A_{iso}(\text{expt.}) = xn\,(A_{iso}, 4s) + (1 - x)n\,(A_{iso}, 3d) \quad (5)$$

weakly interacting bases, $x = 0.049$; for the stronger interacting bases, $x = 0.049$ or 0.045 depending on whether $A_\perp$(Co) is negative or positive. For the PPh_3 adduct, $x = 0.127$. The first two sets of values fit the theory for five-co-ordination well, and support our thesis that the bases interact relatively weakly. In the case of PPh_3 it is difficult to account for the big increase in 4s character unless there has been a structural change in the complex. This may well be the case since we have evidence that the complex formed depends on the preparation.

Quadrupole Coupling.—Computer simulation of the e.s.r. spectrum of $[Co(CN)_5]^{3-}$ in ethanol has permitted a determination of the quadrupole coupling constant Q', where it was found to be $\pm 2.5 \times 10^{-4}$ cm^{-1}. Because the perpendicular region of the spectrum in C_5H_5N and NEt_2H was not resolved, Q' could not be determined. We were unable to get a value for Q' with sufficient accuracy in the triphenylphosphine complex to make worthwhile deductions. Whilst the sign of Q' cannot be determined directly from powder data, it can often be deduced from other evidence (see below). Because of the axial symmetry of the molecule, the asymmetry parameter η is zero. The interpretation of the electric-field gradient is straightforward: [10] since s electrons do not contribute to the electric-field gradient, we need only consider 3d and 4p electrons. The indirect effects of 4s populations can safely be ignored since we have shown that they are not more than 4.9%.

Utilising the relation (6) of the field gradient to the

$$q_{n,l,m} = q_{n,l,0}\{1 - [3m^2/l(l + 1)]\} \quad (6)$$

angular momentum,[17] where n, l, and m are the principal, angular-momentum, and magnetic quantum numbers respectively, we can write expression (7) for q_{zz} in terms

$$q_{zz} = q_{3,2,0}(3d_{z^2} + 3d_{xz,yz} - 3d_{x^2-y^2,xy}) + q_{4,1,0}(4p_z - 4p_{y,x}) \quad (7)$$

of the number of various types of d and p electrons. It follows from this equation that the experimental electric-field gradient, $q_{\text{expt.}}$, is related to the populations of the d orbitals by the more useful expression (8),

$$eQq_{\text{expt.}}/h = (eQq_{\text{atom}}/h)(n_{z^2} + \tfrac{1}{2}n_{xz,yz} - n_{x^2-y^2,xy}) \quad (8)$$

where the unit of eQq/h is Hz; n is defined as the fraction of each electron which is localised in each orbital. The magnitude of the term involving p orbitals is likely to be small; in this work we ignore it.

The value [10] for the field-gradient contribution of one cobalt 3d_{z^2} electron has been calculated; the value of the product $eQq_{\text{atom}}/h = -343$ MHz. This neglects the Steinheimer correction and a small contribution from spin–orbit coupling; for comparative purposes and for estimating relative changes in electron distribution in cobalt complexes, it is more than adequate. The parameter Q' used in the spin Hamiltonian is related to Q by expression (9). Hence our experimental value of

$$Q' = \frac{3eQq}{4I(2I - 1)} \quad (9)$$

Q' (2.5×10^{-4} cm^{-1}) is equivalent to a value for eQq/h of ±210 MHz (since we do not know the sign of Q'). The nomenclature and units of quadrupole couplings are notoriously varied; [18] we use frequency for the energy unit for consistency with pure n.q.r. measurements.

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To a first approximation which assumes no metal–ligand covalency, the complex can be considered as having electrons entirely in the d orbitals, *viz.* $(d_{xz,yz})^4$, $(d_{xy})^2$, $(d_{z^2})^1$. By using equation (8), an expected experimental value of eQq/h would be -343 MHz. This is so different from our experimental value that significant covalency needs to be invoked. In our calculations, we assume that the deep seated bonding b_2 and e_g molecular orbitals (in C_{4v} symmetry) have negligible metal character. From our e.s.r. results, the metal population in the a_1 $(3d_{z^2})$ molecular orbital is 0.69. Using the population $\beta^2 = 0.81$ in d_{xz} (or d_{yz}) calculated from the e.s.r. data by Booth and Lin,[6] we calculate that the population in the d_{xy} orbital is 0.85 if $(eQq/h)_{\text{expt.}}$ is negative or 1.46 if $(eQq/h)_{\text{expt.}}$ is positive. This latter result is absurd, and so we conclude that Q' is negative. The population of 0.85 in d_{xy} is close to that calculated by Manoharan and Gray[19] for $[\mathrm{Fe(CN)_5(NO)}]^{2-}$, and shows as expected that the d_{xy} orbital is little influenced by axial substituents.

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