# Unstable Intermediates. Part 169.[1] Electron-gain and -loss Centres in Irradiated Potassium Dicyanoargentate(I)

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Exposure of $K[Ag(CN)_2]$ to $^{60}Co$ $\gamma$-rays at 77 K gives two paramagnetic species, A and B. Species A, having $g_{\parallel}$ 2.001, $g_{\perp}$ 2.006, $A_{\parallel}(^{109}Ag)$ 60 G, and $A_{\perp}(^{109}Ag)$ 30 G, is identified as an electron-gain centre, $[Ag(CN)_2]^{2-}$, with the extra electron in a $\sigma^*$ orbital with $4d_{z^2} + 5s$ character on silver and considerable density on the ligands. Species B, having $g_x$ 2.091, $g_y$ 2.051, $g_z \geqslant 2.008$, $A_x(^{109}Ag)$ 42 G, $A_y$ 34 G, and $A_z \leqslant 65$ G, is thought to be the electron-loss centre, $Ag[CN]_2$, with the hole largely localised in silver (again, $4d_{z^2} \pm 5s$); on annealing above 77 K, centre B acquired axial symmetry ($g_{\perp}$ 2.078, $A_{\perp}$ 29 G). Solutions in methanol give a poorly defined centre similar to A at 77 K. On annealing, a new species having $A_{\text{iso.}}(^{109}Ag)$ 155 G and $A(^{14}N)$(one) 17.3 G with $g_{\text{av.}}$ 2.002 is obtained. This is tentatively identified as $[Ag(CN)]^-$ and reasons for the large hyperfine coupling to $^{14}N$ are discussed.

It is now well established that metal ions having a . . . $d^{10}$ configuration and largely ' ionic ' ligands readily add an extra electron to give . . . . $d^{10}s^1$ centres.[2-4] In the other extreme, if the ligands have low-lying acceptor orbitals, the electrons may add to these, and exhibit only a weak interaction with one or more of the cations.[5] Yet again, covalent compounds containing these metals may behave in a manner similar to corresponding non-metallic compounds. Thus, for example, a range of covalent organotin compounds [6] gave electron-gain centres such as $[SnR_4]^{-\cdot}$ and $SnR_3^{\cdot}$ with magnetic properties resembling those of the corresponding phosphoranyl and phosphoryl radicals.[7-9]

Recently it has been found that electron attachment to $[Hg(CN)_4]^{2-}$ gives a centre with a relatively low isotropic hyperfine coupling to $^{199}Hg$ and a small anisotropy. Considerable spin density on the ligands was inferred.[10] In contrast, our own studies of $[Hg(SCN)_4]^{2-}$ indicate the formation of a centre more closely resembling aquated $Hg^+$.[11] Other related studies include those of Knight and Lin on matrix-isolated Cd[CN] and Hg[CN] molecules.[12] The metal hyperfine coupling constants

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[1] Part 168, S. P. Mishra and M. C. R. Symons, *J.C.S. Dalton*, 1976, 1622.

[2] R. S. Eachus and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1329, 1336.

[3] M. C. R. Symons and J. K. Yandell, *J. Chem. Soc.* (*A*), 1971, 760.

[4] R. J. Booth, H. C. Starkie, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2233.

[5] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Dalton*, 1974, 2247; 1975, 553.

[6] S. A. Fieldhouse, A. R. Lyons, H. C. Starkie, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 1966.

[7] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

[8] A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738.

[9] I. S. Ginns, S. P. Mishra, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2509.

[10] J.-I. Isoya and S. Fujiwara, *Bull. Chem. Soc. Japan*, 1972, **45**, 2182.

[11] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Dalton*, 1976, 1565.

[12] L. B. Knight and K. C. Lin, *J. Chem. Phys.*, 1972, **56**, 6044.

were analysed in terms of an ionic bond, the electron being largely in an ($ns + np_z$) hybrid on the metal. Also, Kasai and McLeod[13] recently treated silver atoms with ethylene in a rare-gas matrix and obtained a most interesting complex in which the unpaired electron gave a remarkably weak interaction with $^{109}$Ag, the suggestion being that it was largely present in a $4d_{xy} + 5p_x$ orbital on silver with no 5s character. Electron loss from $Hg[CN]_2$ has been considered by Burroughs *et al.*,[14] who studied its photoelectron spectrum. They concluded that the first ionisation for this and related cadmium(II) species was from the $\delta$ rather than from the $\sigma$ orbital expected on simple theory, and as found for related zinc(II) complexes.[15] This was interpreted in terms of some $5d_{z^2} + 6s$ mixing of the type envisaged by Orgel.[16]

We have studied the effect of $\gamma$-rays on the $[Ag(CN)_2]^-$ ion because this commonly leads to the formation of electron-gain and electron-loss centres, and it was thought that an analysis of their e.s.r. spectra would shed further light on their structures.

## EXPERIMENTAL

Polycrystalline $K[Ag(CN)_2]$ was the purest commercial grade. Finely powdered samples were frozen to 77 K prior to irradiation in a Vickrad $^{60}$Co $\gamma$-ray source. Dilute solutions in methanol and $CD_3OD$ were prepared at low temperatures and directly frozen at 77 K in order to minimise solvolysis. Samples were irradiated for *ca.* 2 h at a dose rate of 1.7 MCi $h^{-1}$.

E.s.r. spectra were recorded on a Varian E3 spectrometer at 77 K. Samples were annealed in the insert Dewar flask with continuous monitoring of the e.s.r. spectra. Liquid nitrogen was added whenever significant spectral changes were observed. *Q*-Band spectra were recorded on a superheterodyne spectrometer constructed in these laboratories by Mr. J. A. Brivati. Diphenylpicrylhydrazyl (dpph) was used to obtain accurate *g* values.

## RESULTS AND DISCUSSION

Two major centres (A and B) were formed in $K[Ag(CN)_2]$ at 77 K. Their e.s.r. spectra at *X*- and *Q*-band frequencies are shown in Figures 1 and 2, and the derived data are given in the Table.

E.s.r. data for paramagnetic centres derived from the $[Ag(CN)_2]^-$ anions

| | | $^{109}$Ag Hyperfine coupling (G [a]) | | | | | |
|---|---|---|---|---|---|---|---|
| Centre | Structure | $A_x$ | $A_y$ | $A_z$ | $g_x$ | $g_y$ | $g_z$ |
| A | $[Ag(CN)_2]^{2-}$ | 30 | 30 | 60 [b] | 2.005 | 2.006 | 2.000 |
| B | $Ag[CN]_2$ | 42 | 34 | $\leqslant$65 [c] | 2.091 | 2.051 | $\geqslant$2.008[c] |
| C | $Ag[CN]_2$ | 29 | 29 | 65 | 2.078 | 2.078 | 2.000 |
| D | $[Ag(CN)]^-$ | 155 (iso)($^{14}$N, 17.3) | | | 2.002 | | |

[a] Errors *ca.* ±1 G. [b] Possible $^{13}$C coupling of *ca.* 180 G. [c] The features $A_z$ and $g_z$ were hidden by intense features from A.

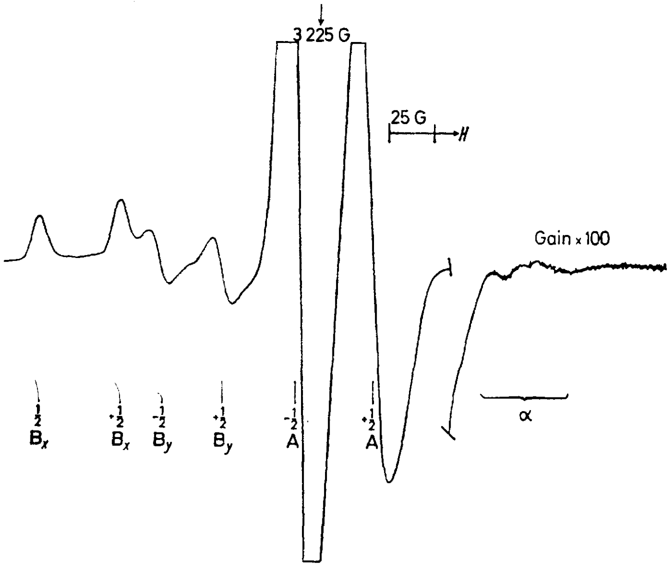

FIGURE 1 First-derivative *X*-band e.s.r. spectrum for $K[Ag(CN)_2]$ after exposure to $^{60}$Co $\gamma$-rays at 77 K showing features for centres A and B. An extra feature tentatively assigned to centre A containing $^{13}$C is also shown ($\alpha$)

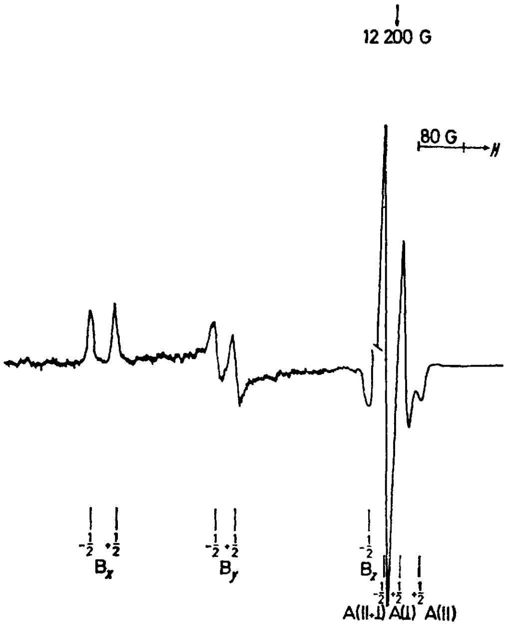

FIGURE 2 First-derivative *Q*-band e.s.r. spectrum for $K[Ag(CN)_2]$ after exposure to $^{60}$Co $\gamma$-rays at 77 K showing features for centres A and B

*Centre A*.—This is taken to be the major electron-gain centre, because one of the *g* values is less than that of the free-spin value and because centre B is clearly an electron-loss species. Also, a poorly resolved doublet of this type was obtained from solutions in methanol, and the formation of trapped electrons was strongly suppressed. Centre B was not formed. Since solid methanol readily forms trapped electron-loss centres ($\dot{C}H_2OH$) which were detected in high yield, we infer that centre A is, indeed, an electron-gain centre. Although

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[13] P. H. Kasai and D. McLeod, *J. Amer. Chem. Soc.*, 1975, **97**, 6602.

[14] P. Burroughs, S. Evans, A. Hamnett, A. F. Orchard, and N. V. Richardson, *J.C.S. Chem. Comm.*, 1974, 921.

[15] A. F. Orchard and N. V. Richardson, *J. Electron Spectroscopy*, 1975, **6**, 61.

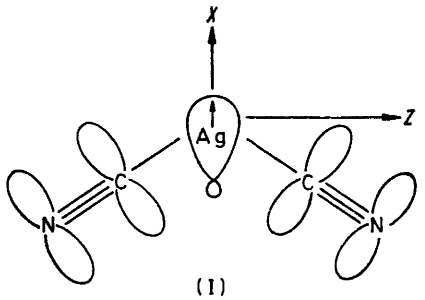
[16] L. E. Orgel, *J. Chem. Soc.*, 1958, 4186.

the e.s.r. spectrum at *X*-band was just a broad doublet (Figure 1), at *Q*-band a well defined shoulder could be seen, leading to the analysis given in Figure 2. Axial symmetry is assumed, but the features remain broad and this leaves room for small deviations from axial symmetry.

Only like signs for $A_{\parallel}$ and $A_{\perp}$ give reasonable values for $A_{\text{iso.}}$ and $2B$ (the parallel component of the dipolar coupling). The resulting isotropic coupling ($\pm 40$ G) is unusually large for a spin-polarisation effect (*ca.* +20 G being normal) * and hence it is assumed to stem from direct population of the 5*s* orbital on silver. Hence the negative signs are preferred (since the magnetic moments for $^{109}$Ag and $^{107}$Ag are negative). [These two isotopes have $I = \frac{1}{2}$ and are present in about equal abundance. They have very similar moments, and separate features were not resolved for centres A or B.] A search for features from radicals containing $^{13}$C revealed the high-field feature, α (Figure 1), which may well be the $M_I = +\frac{1}{2}$ ($^{109,107}$Ag), $M_I = -\frac{1}{2}$ ($^{13}$C) line. If this is so, then $A_{\text{iso.}}$($^{13}$C) is *ca.* 180 G, and the anisotropy is small.

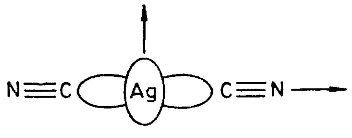
We consider two limiting possibilities for centre A, one being $[\text{NC–}\dot{\text{A}}\text{g–CN}]^{2-}$, with a C–$\dot{\text{A}}$g–C angle of less than 180°, and the unpaired electron in an in-plane pseudo-$\pi^*$ orbital having $5s + 5p_x$ character on silver, and the other being a linear or near-linear structure with the unpaired electron in a $\sigma_4^*$ orbital comprising the $4d_{z^2}$ and 5*s* orbitals on silver.

Structure (I) is based on analogy with the behaviour of radicals such as $\text{BH}_2^{\bullet}$ or $[\text{CO}_2]^{-\bullet}$ in which the central atom uses only its outer *s* and *p* orbitals for bonding. The latter is based on Orgel's model [16] for linear bonding in complexes of this type. Expectations for structure (I) are a large hyperfine coupling along the *x* axis with $g_x$ close to the free-spin value and small values for $A_y$ and $A_z$, with $g_z \gg 2.00$ and with $g_y$ intermediate between $g_x$ and $g_z$. The results are not in accord with this since $A_{\max.}$ coincides with $g_{\min.}$. A small admixture of suitable 4*d* orbitals is unlikely to modify this argument.



(I)

However, for structure (II), we expect $g_z$ to be close to 2.00 with $A_z$ large, and $g_x \approx g_y > 2.00$, with $A_x \approx A_y < A_z$. This fits reasonably well with the results. The hyperfine coupling constants can be used to estimate approximate orbital populations using the $A^0$ value for $^{109}$Ag in silver atoms and the $2B^0$ value calculated from the wavefunctions of Froese.[17] Since we expect a considerable 5*s* orbital admixture, we take negative signs for $A_{\parallel}$ and $A_{\perp}$. This leads to $a_{5s}^2 \approx 0.06$ and $a_{4d_{z^2}} \approx 0.45$. [If instead of using the calculated $2B^0$ value of −44.5 G we use the value of *ca.* −62 G obtained below, we have $a_{4d_{z^2}} \approx 0.32$.] Thus this model requires a large delocalisation on to the ligands, and we suggest that this is achieved partly by admixture of the [CN]⁻ σ* levels (Figure 3). [The $a_{5s}^2$ value is actually greater than this because the high *d*-orbital population will give rise to a negative spin density *via* spin polarisation of inner *s* orbitals.]



(II)

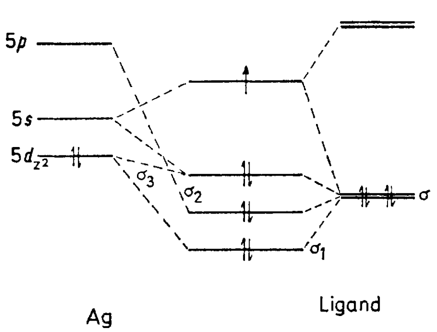


FIGURE 3 Energy-level diagram for $\text{K[Ag(CN)}_2]$

*Centres B and C.*—We consider first the axially symmetric centre, C, formed from B on slight annealing above 77 K. The $g_{\perp}$ shift was small and hence orbital magnetic contributions are also small. The form of the spectrum is that required for an electron in the $4d_{z^2}$ ($\sigma_3$) orbital rather than the normal $4d_{x^2-y^2}$ orbital found for most silver(II) complexes. In that case, the only acceptable sign combination is $A_{\perp} = +29$ G and $A_{\parallel} = -65$ G. These values lead to free-spin values for $A_{\text{iso.}}$ and $2B^0$ of −3 and −62 G. Thus the 5*s* population is reduced and the $4d_{z^2}$ population is increased relative to $\sigma_4^*$, as expected. [The value of −62 G is greater than the calculated $2B^0$ value of −44.5 G. We found a similar discrepancy for other silver(II) complexes, and hence all that can be said is that, for $\sigma_3$, delocalisation on to the ligands is small.]

The most probable structure for centre B is the same as C, but with a small deviation from axial symmetry imposed by the lattice. Relaxation to the preferred axial configuration then only occurs on annealing above 77 K. In view of our inability to estimate $A_z$ accurately, all that can be said is that the values obtained are reasonable. However, the photoelectron results [14,15] suggest that the alternative δ structure is possible for B and that the change B ⟶ C is really $\delta \longrightarrow \sigma_3$. This seems less probable, but the parameters obtained for B do not

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

[17] C. Froese, *J. Chem. Phys.*, 1966, **45**, 1417.

enable us to make a definitive distinction. For the $\delta$ structure, the unpaired electron is in the non-bonding $d_{x^2-y^2}$, $d_{xy}$ pair of orbitals which are degenerate for the linear molecule. These give rise to $\frac{5}{2}\Delta$ and $\frac{3}{2}\Delta$ levels which are well separated, but bending, which is now expected to occur, would at least partially quench the orbital angular momentum. Thus we predict, for this structure, $g_z \gg g_x \approx g_y \approx 2.00$. We see no reason why a second $g$ value should deviate from the free-spin value to any great extent, but this is not impossible. Similarly, the $A$ values can be shown to be possible for this model.

If species B has the $\sigma_3$ structure we need an initial asymmetry reflecting the crystal structure, which is lost during the annealing process. This is possible but must be small. On the other hand, if the $\delta$ structure were correct, we would need to say that electron loss under Frank–Condon conditions is from the non-bonding $d_{xy}$, $d_{x^2-y^2}$ orbitals followed, if necessary, by a bending distortion. On annealing, this structure changes irreversibly to the $\sigma_3$ structure. There is plenty of precedent for such behaviour. Thus we are unable to make a definitive distinction between the alternative structures for centre B, but favour the $\sigma_3$ structure.

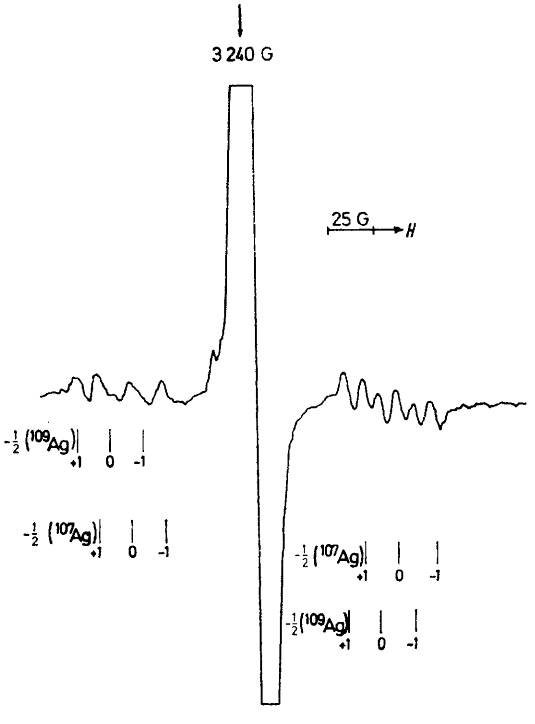
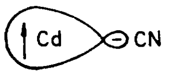


FIGURE 4 First-derivative $X$-band e.s.r. spectrum for a dilute solution of $K[Ag(CN)_2]$ in $CD_3OD$ after exposure to $^{60}Co$ $\gamma$-rays at 77 K and slight annealing, showing features assigned to species C

*Centre D.*—This centre (Figure 4) was formed, probably from centre A, when irradiated methanolic solutions were slightly annealed above 77 K. The pair of nearly isotropic sextets are well accounted for in terms of one silver atom ($^{109}Ag + ^{107}Ag$) and one nitrogen. In addition to this centre, weak features for $[HCN]^-$ ($[DCN]^-$) and $H_2CN$ ($D_2CN$) were obtained. This accords with our results for aqueous cyanide glasses,[18] and suggests the presence of some free cyanide ions. One apparently reasonable structure for centre D is $[Ag(CN)]^-$, formed either from solvated Ag[CN] or from $[Ag(CN)_2]^{2-}$ [equation (1)]. The difficulty with

$$[Ag(CN)_2]^{2-} \longrightarrow [Ag(CN)]^- + [CN]^- \qquad (1)$$

this formulation is the large coupling to $^{14}N$. The species $[Ag(CN)]^-$ is isoelectronic with Cd[CN], studied by Knight and Lin.[12] This species showed a higher spin density on the metal and no resolved coupling to $^{14}N$. The orbital envisaged for Cd[CN] is an *s-p* hybrid as indicated in (III). Such a non-bonding orbital is not available for $[Ag(CN)_2]^-$, but is for Ag[CN], and it is hard to understand why the present results are so different from those for Cd[CN] if $[Ag(CN)]^-$ is a correct formulation.



(III)

In previous work on irradiated cyanides[19] we frequently detected hyperfine coupling to $^{14}N$, but this was small (*ca.* 2—3 G) and could be understood in terms of a small deviation from linear co-ordination for one of the cyanide ligands. In order to achieve a coupling as large as 17.5 G, complete inversion to give $[Ag(NC)]^-$ would be required. This is unprecedented and, so far as we can judge, unreasonable.

An alternative structure for $[Ag(CN)]^-$ that would still be expected to have a large isotropic hyperfine coupling to silver is the bent anion, $Ag\text{–}\dot{C}\text{–}N^-$, isostructural with $H\text{–}\dot{C}\text{–}N^-$.[20] In this case, the electron is formally localised on carbon, but is delocalised into the Ag–C $\sigma$ bond and on to nitrogen by both $\pi$ and $\sigma$ mechanisms. A coupling of 17.5 G is still large compared with 6.9 G for $[HCN]^-$, but is certainly possible. We favour this bent structure, and recall that a similar dichotomy has arisen for the structures of the cyanogen halide anions. Thus, FCO[21] and ClCO[22] have e.s.r. spectra characteristic of the expected bent structures, but the isostructural $[BrCN]^-$ anion has a linear $\sigma^*$ structure.[23]

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[18] I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1972, 185.

[19] M. C. R. Symons and J. G. Wilkinson, *J.C.S. Dalton*, 1972, 1086.

[20] K. D. J. Root, M. C. R. Symons, and B. C. Weatherby, *Mol. Phys.*, 1966, **11**, 161.

[21] F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, 1965, **43**, 462; 1966, **44**, 4626.

[22] F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, 1972, **56**, 6251.

[23] S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1974, 1280.