Electron-gain and -loss Centres in Irradiated Potassium Tetracyanocuprate(I) †

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Exposure of $K_3[Cu(CN)_4]$ to ^{60}Co γ-rays at 77 K gives an electron-gain centre, thought to be $Cu(CN)_3{}^{3-}$, having a planar structure with *ca.* 70% of the extra electron localised in the $4p_z$ orbital on copper. This is compared with the centres considered to be $Ag(CN)_3{}^{3-}$, $Zn(CN)_3{}^{2-}$, $Cd(CN)_3{}^{2-}$, and $Hg(CN)_3{}^{2-}$. The electron-loss centre undergoes a series of alterations on warming, one of the species apparently being the five-co-ordinate $Cu(CN)_5{}^{3-}$ with a d_{z^2} ground state.

THE number of reports concerning copper(II) compounds with cyanide ions is meagre, probably because of the redox reaction between the two species which is facile in aqueous solution. One species formed at low temperatures is a purple complex which is considered to be $Cu(CN)_4{}^{2-}$ and spectroscopic evidence indicates that it approaches square-planar stereochemistry.[1] E.s.r. parameters reported for this species are the following: $g_{\parallel} = 2.146$, $g_{\perp} = 2.033$, $A_{\parallel} = 190$ G,‡ $A_{\perp} = 26$ G (aqueous glass); $g_{\parallel} = 2.160$, $g_{\perp} = 2.033$, $A_{\parallel} = 151$ G, $A_{\perp} = 20$ G (methanolic glass). More recent studies concerning the oxidation of cyanide ion in the presence of Cu^{2+} have led to similar e.s.r. parameters being assigned to $Cu(CN)_4{}^{2-}$ in frozen aqueous solution.[2]

Both of the previous studies mentioned a second spectrum due to a copper(II) species which is observed at low temperatures when the $CN^-:Cu^{II}$ ratio is greater than 4 : 1. Suggested as having more than four co-ordinated cyanide ligands, this species has $g_{\perp} = ca.$ 2.1 and $A_{\perp} = ca.$ 64 G.[1]

One of us had carried out an e.s.r. study of the radiolysis products of $K[Ag(CN)_2]$,[3] and it seemed of interest to extend this to a study of potassium cyanocuprates(I). Three different potassium solids involving cyanocuprate(I) anions have been isolated previously. Both $K[Cu(CN)_2]$ and $K[Cu_2(CN)_3]\cdot H_2O$ were found to contain polymeric anionic chains.[4,5] However, $K_3[Cu(CN)_4]$ is monomeric, having two formula units per unit cell, with the copper(I) atom at the centre of a regular tetrahedron.[6] The potassium ion is surrounded by six nitrogen atoms in a distorted octahedral environment. A more recent crystal-structure determination [7] is in agreement with this, except that a seventh nitrogen atom, further away from the copper ion than the other six, was found. However, this is probably involved in the 'co-ordination sphere' of the potassium ions. The two polymeric salts gave weak, poorly defined spectra which we do not consider further.

EXPERIMENTAL

The different potassium solids were prepared by slow evaporation (*i.e.* room temperature) of stoicheiometric mixtures of reagent grade CuCN and KCN in aqueous solution. Only $K_3[Cu(CN)_4]$ was submitted for partial elemental analysis (C. H. N. Analysis Ltd., South Wigston, Leicester (Found: C, 16.6; N, 19.4. Calc. for $C_4CuK_3N_4$: C, 16.8; N, 19.65%).

Finely powdered solids were irradiated at 77 K in a Vickrad ^{60}Co source at a dose rate of 1.7 Mrad h^{-1} for up to 2 h. Dilute solutions in the various solvents were irradiated at 77 K as small spherical beads. E.s.r. spectra were measured on a Varian E3 spectrometer at 77 K. Samples were annealed in the insert Dewar flask after decanting the liquid nitrogen and were recooled to 77 K whenever the continuously monitored spectra showed significant changes.

RESULTS AND DISCUSSION

Pure samples of $K_3[Cu(CN)_4]$ were studied as fine powders and as single crystals. Typical e.s.r. spectra of the products of γ irradiation are shown in Figures 1 and 2. There are clearly two paramagnetic copper centres formed at 77 K. Species A has g values close to or less than that for free spin (2.0023) and is therefore thought to be an electron-gain centre. Species B behaves as a typical copper(II), $3d^9$ centre, except that it is changed irreversibly to C on annealing above 77 K, C also being an electron-loss copper centre. Species C was also formed when glassy solids of $K_3[Cu(CN)_4]$ containing an excess of cyanide ions were annealed above 77 K following exposure to γ-rays.

Species A, Identification and Structure.—Generally, when d^{10} transition-metal ions capture electrons, species with configurations close to $d^{10}s^1$ are formed. Had this occurred in our work, the copper(0) centre would have exhibited a very large isotropic hyperfine coupling, the e.s.r. spectrum usually containing diagnostic high-field features for the ^{63}Cu and ^{65}Cu isotopes (both having $I = \frac{3}{2}$). Such features were never detected in the present studies. In fact, the electron-excess centre exhibits only a small copper hyperfine coupling, which means either that the extra electron is largely delocalised on to the cyanide ligands, or that an outer $4p$ orbital has been favoured over the $4s$ orbital.

We therefore assume that the anisotropic coupling to copper is due to occupation of the $4p_z$ orbital. Using data calculated for unit occupancy of a $5p$ orbital on silver,[8] we find that for ^{63}Cu a coupling of *ca.* +57 G is expected. This gives *ca.* 77% $4p$ character. The isotropic coupling of *ca.* 44 G corresponds to only about 2% $4s$ character, which is about the value expected for spin

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† Taken as 'Unstable Intermediates,' Part 199. Part 198, M. C. R. Symons, *J. Chem. Res.*, 1981, (*S*) 286.

‡ Throughout this paper: 1 G = 10^{-4} T; 1 rad = 10^{-2} J kg^{-1}.

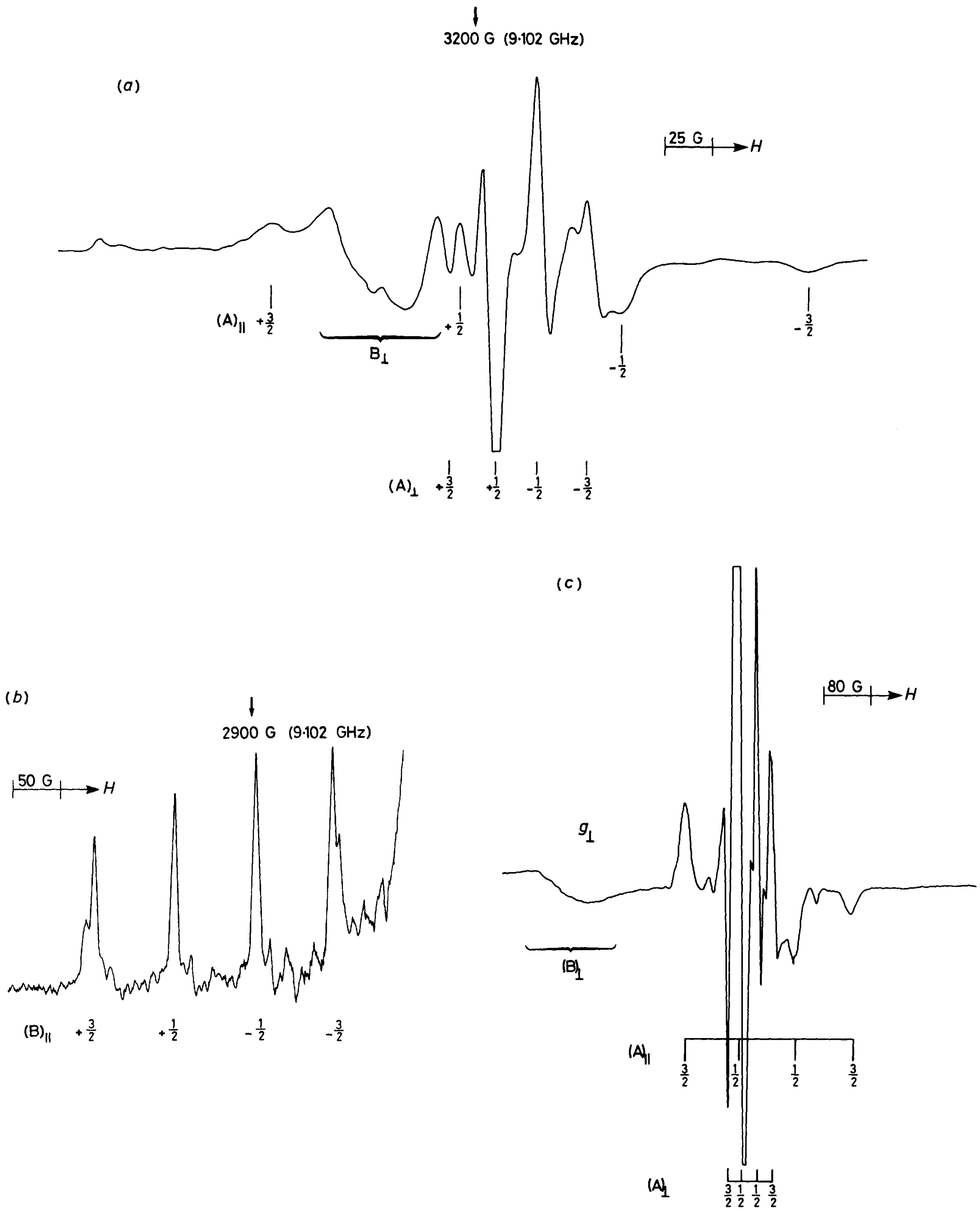


FIGURE 1 First-derivative powder spectra for $K_3[Cu(CN)_4]$ after exposure to ^{60}Co γ-rays at 77 K. (*a*) *X*-band showing features for species A, and the perpendicular feature for species B, (*b*) *X*-band showing the parallel features for B, and (*c*) *Q*-band, as for (*a*)

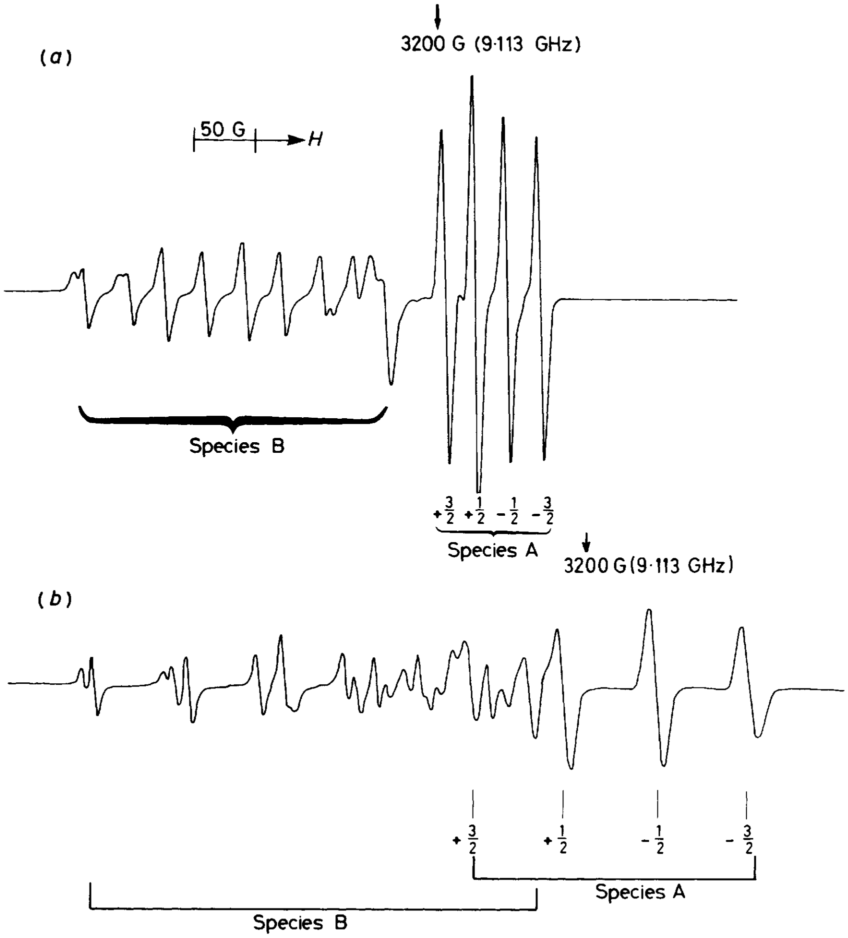
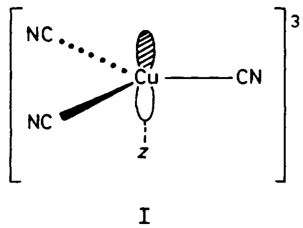


FIGURE 2 Typical X-band single-crystal spectra for $K_3[Cu(CN)_4]$ after exposure to ^{60}Co γ-rays at 77 K showing features for species A, (a) close to perpendicular and (b) close to parallel

polarisation in a planar π radical. These calculations lead us to structure I for the electron-gain species. Electron capture probably leads to loss of one cyanide ion giving $Cu(CN)_3{}^{3-}$, which must be planar in view of the e.s.r. data. Delocalisation into the π or π^* cyanide orbitals then accounts for the extra *ca.* 23% spin density.



I

The fact that the g values are very close to 2.0023 means that this π level is remarkably isolated from neighbouring filled and vacant levels. This in turn means that the $4p_x$ and $4p_y$ orbitals must be strongly involved in bonding to the three in-plane cyanide ligands. Probably a reasonable model involves $4s4p^2$ hybridisation to give three covalent σ bonds to the cyanide ligands, with further bonding from the π orbitals.

Species B, Identification and Structure.—The form of the g-tensor components for this species suggests a predominantly $(d_{x^2-y^2})^1$ ground state for this complex. The parent $Cu(CN)_4{}^{3-}$ ions are tetrahedral at copper.[6,7] Loss of an electron must be accompanied by a Jahn–Teller distortion which in this case favours occupancy of the $d_{x^2-y^2}$ orbital and consequently a flattening of the tetrahedron. This flattening cannot be very extensive, since the parameters are markedly different from those for the equilibrium structure for $Cu(CN)_4{}^{2-}$ ions[1,2] (Table), which is itself probably not planar (see below). It therefore seems that the tendency to become planar is arrested, presumably as a result of resistance from the surrounding crystal matrix. We have shown previously that copper(II) complexes with a $(d_{x^2-y^2})^1$ ground state exhibit unusually small values for $A_\parallel$ when forced into a structure between planar and tetrahedral.[9] We suggested that this arises because of the direct admixture of the outer 4s orbital into the wavefunction which is allowed because of the low symmetry of these complexes. The present data are in fact quite close to those for Cu^{II} doped into $Zn[Cd(SCN)_4]$ and related hosts.[9] Using the standard equations where A and $2B$ are the ' free-spin ' isotropic and principal anisotropic hyperfine coupling

$$A_{\parallel}(\text{expt.}) = A + 2B(1 - \tfrac{7}{4}\Delta g_{\parallel} - \tfrac{3}{4}\Delta g_{\perp}) \qquad (1)$$

$$A_{\perp}(\text{expt.}) = A - B(1 + \tfrac{11}{4}\Delta g_{\perp}) \qquad (2)$$

constants corrected for g shift and orbital magnetism, and $\Delta g = g_{\text{expt.}} - 2.0023$, we find that $A = -31.5$ G and $2B = -103$ G. The latter corresponds to a $3d_{x^2-y^2}$ orbital population of *ca.* 44% using an atomic value of *ca.* 235 G. The former is numerically small compared with the ' normal ' spin-polarisation value of *ca.* —100 G. If the difference is assigned to outer 4*s*, orbital admixtures, then we require *ca.* 4% 4*s* character. If these computations are correct, then there is *ca.* 50% delocalisation onto the cyanide ligands in this unrelaxed complex.

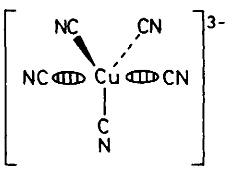
E.s.r. parameters for the electron-gain and -loss centres of $K_3[Cu(CN)_4]$ and for $Ag(CN)_3{}^{3-}$

	g Values (±0.002)		*A*(^{63}Cu)/G [a]	
Species	∥	⊥	∥	⊥
A	2.002	2.005	(+) 90 ± 1 [b]	(+) 23 ± 1 [b]
B	2.242	2.050 (*X*-band) 2.055 (*Q*-band) *ca.* 2.050 (crystal)	(±) 81.2 ± 1	(+) *ca.* 20 ±5
C	2.002	2.093	(+) 43 ± 1	(−) 130 ±1
D	2.165	2.032	(−) 140 ± 2	(±) 23 ± 2
			A(^{107}Ag)	
$Ag(CN)_3{}^{3-}$ [c]	2.001	2.006	(−) 60 ± 10	(−) 30 ± 10

[a] Experimental results taken directly from the e.s.r. spectra. [b] That these components have like signs was established by observing a reversible increase in $A_{\perp}$ and decrease in $A_{\parallel}$ on annealing (see M. C. R. Symons and I. Smith, *J. Chem. Soc., Faraday Trans. 1*, 1981, 2701). [c] Ref. 3. Previously thought to be $Ag(CN)_2{}^{2-}$.

Species C, Identification and Structure.—Surprisingly, on annealing above 77 K, this centre did not change into the ' normal ' near-planar complex that previously has been studied.[1,2] Instead, a spectrum similar to that shown in Figure 3 was obtained as the signal due to species B decayed. The data extracted from this spectrum for species C are given in the Table. These parameters are typical of a copper(II) complex with a d_{z^2} ground state. In particular, $g_{\perp} > g_{\parallel} \approx 2.0023$ is characteristic of such complexes.

Analysis of the data in the manner described above again indicates *ca.* 50% spin density on the copper atom, with a relatively small 4*s* contribution. Since it is well established that the thermodynamically stable structure for $Cu(CN)_4{}^{2-}$ ions has a $(d_{x^2-y^2})^1$ ground state, and since the primary product from γ-irradiation of $Cu(CN)_4{}^{3-}$ ions also has this configuration, we cannot accept the possibility that species C is some form of $Cu(CN)_4{}^{2-}$. Instead, we suggest that the complex is $Cu(CN)_5{}^{3-}$, having the trigonal-bipyramidal structure, II, shown below.



II

Such a complex is expected to have the required $(d_{z^2})^1$ configuration with axial symmetry. In the preparation of $K_3[Cu(CN)_4]$ an excess of cyanide ion was often used so that two possible processes can be envisioned for the formation of $Cu(CN)_5{}^{3-}$: either $Cu(CN)_4{}^{2-}$ ions react with unco-ordinated CN^- ions, or electron transfer can occur between $Cu(CN)_4{}^{2-}$ and $Cu(CN)_4{}^{3-}$ so that the

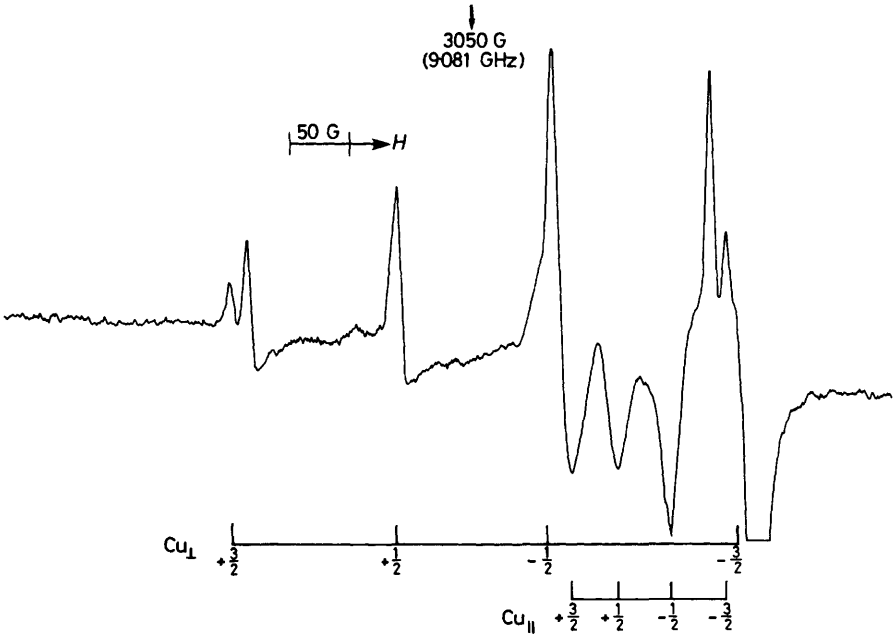


FIGURE 3 First-derivative *X*-band powder spectrum for irradiated $K_3[Cu(CN)_4]$ after annealing to convert species B into species C

' hole ' becomes mobile and can seek out $\mathrm{Cu(CN)_5}^{4-}$ ions [equation (3)]. Since the conversion into C is complete,

$$\mathrm{Cu(CN)_4}^{2-} + \mathrm{Cu(CN)_5}^{4-} \longrightarrow \mathrm{Cu(CN)_4}^{3-} + \mathrm{Cu(CN)_5}^{3-} \quad (3)$$

the latter process is clearly favoured. Also, recall that species A is formed with loss of CN^- so that CN^- ions are available from the initial radiation process.

Annealing to near room temperature resulted in the decay of species C, and the appearance of a novel species having three isotropic components with a splitting of 14 G and a *g* value of *ca.* 2.0035 (Figure 4). This has the e.s.r. properties of a rotating nitroxide radical ($\mathrm{R_2\dot{N}O}$), including the characteristic asymmetric line broadening. This spectrum broadened on cooling to 77 K, but we were unable to extract the anisotropic parameters. We are not able to offer a firm identification of this product.

Solutions of $\mathrm{K_3[Cu(CN)_4]}$.—Using excess of KCN to ensure complete conversion into $\mathrm{Cu(CN)_4}^{3-}$, aqueous and methanolic glasses gave solvent radicals together with $\mathrm{H\dot{C}N}^-$ and $\mathrm{H_2C\dot{N}}$ radicals formed from free cyanide ions.[10] On annealing, $\mathrm{H\dot{C}N}^-$ ions were converted into $\mathrm{H_2C\dot{N}}$, and on further annealing species C, thought to be $\mathrm{Cu(CN)_5}^{3-}$, was detected (Figure 3). When excess of cyanide was not present, methanolic glasses gave, after annealing, species D, whose e.s.r. spectrum is shown in Figure 5. This spectrum is clearly a copper(II) complex with the unpaired electron in a $d_{x^2-y^2}$ orbital. The parameters (Table) are quite close to those reported previously for $\mathrm{Cu(CN)_4}^{2-}$ complexes.

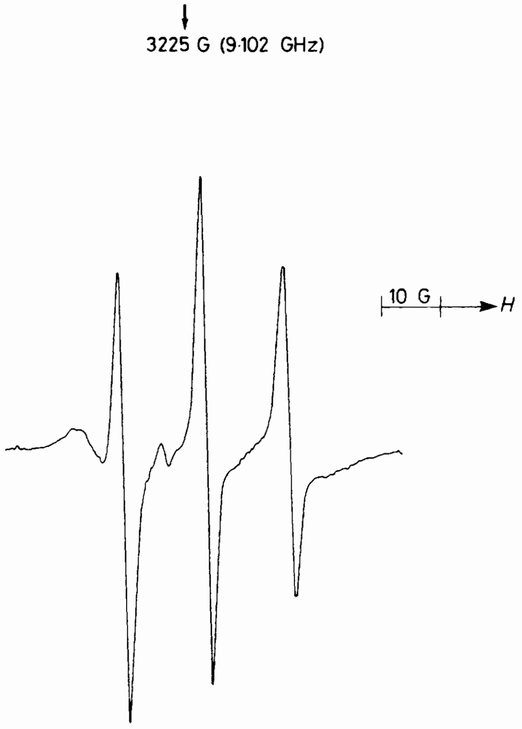


FIGURE 4 As Figure 3, after further annealing, showing the unidentified isotropic triplet

It is worth noting that if these data are included in Figure 5 of ref. 9 which correlates $A_{\parallel}$ and $g_{\parallel}$ for a range of copper(II) complexes, the results still indicate marked deviation from planarity. Also, when the corrected hyperfine coupling constants are analysed in the manner indicated above, we find *ca.* 61% spin density on copper. This implies unusually extensive delocalisation onto the ligands, and supports the concept that $\mathrm{Cu(CN)_4}^{2-}$ ions are not planar. This is also supported by the relatively low magnitude for A_{iso} of -44 G, which suggests admixture of the 4*s* orbital of *ca.* 3%.

Conclusions.—The most remarkable result is the

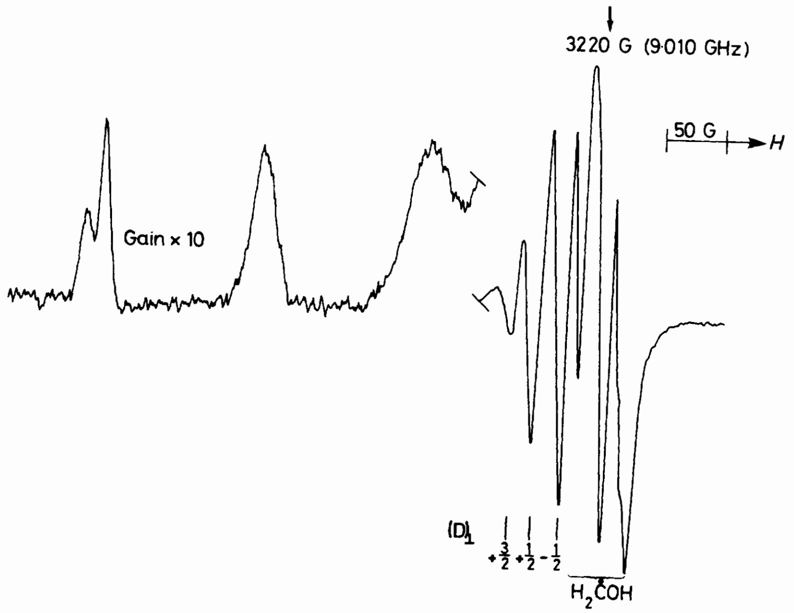


FIGURE 5 First-derivative *X*-band spectrum for a dilute solution of $\mathrm{K_3[Cu(CN)_4]}$ in $\mathrm{CH_3OH}$ after irradiation at 77 K and annealing to reduce the intensity of the signals for solvent radicals

detection of an electron-gain centre having the extra electron in a $4p$ orbital on copper rather than in the $4s$ orbital. Furthermore, the very small value for Δg shows that the half-occupied p orbital is well removed from the other two p orbitals, which must, therefore, be involved in strong bonding. These requirements seem to be fulfilled by the planar anion, $\mathrm{Cu(CN)_3^{3-}}$. This anion is isostructural with $\mathrm{Zn(CN)_3^{2-}}$, $\mathrm{Cd(CN)_3^{2-}}$, and $\mathrm{Hg(CN)_3^{2-}}$, which we have tentatively suggested[9] are the species formed in γ-irradiated salts of $\mathrm{Zn(CN)_4^{2-}}$, $\mathrm{Cd(CN)_4^{2-}}$, and $\mathrm{Hg(CN)_4^{2-}}$.[11] The species detected were

$$\mathrm{Hg(CN)_4^{2-} + e^- \longrightarrow \dot{H}g(CN)_3^{2-} + \dot{C}N^-} \qquad (4)$$

originally thought to be the electron-capture centres $\mathrm{Zn(CN)_4^{3-}}$, $\mathrm{Cd(CN)_4^{3-}}$, and $\mathrm{Hg(CN)_4^{3-}}$, but we argued that the relatively low s character and high p character in the orbital of the unpaired electron was in better accord with the tricyano-derivatives.[12]

If this is accepted, then these anions must be pyramidal, in contrast with the copper derivative, which is planar. There is in fact a possible trend towards planarity implied by the decrease in s character of the extra electron, on going from the mercury to the zinc derivative. This trend follows Pauling's electronegativity rule,[13] and can be compared with our results for $\mathrm{R_3Al^{\bullet-}}$, $\mathrm{R_3\dot{S}i}$, and $\mathrm{R_3P^{\bullet+}}$ alkyls,[14] in which the s-orbital character and the estimated p/s ratio fall steadily.

It is interesting to compare our results with those of Kasai and McLeod[15] for alkyne compounds of copper and silver. Complexes containing only one ligand have very high atomic s character, but those with two organic ligands have almost pure p character on the metal.

We must also compare this work with our earlier results for γ-irradiated $\mathrm{K[Ag(CN)_2]}$ and its solutions.[3] This study also resulted in an electron-loss d^9 derivative, and an electron-gain centre exhibiting very low s character. We considered two structures for the electron-gain centre, one being $\mathrm{Ag(CN)_2^{2-}}$ with C–Ag–C angle of <180°, the unpaired electron being in an sp^n hybrid on silver, the other being a linear structure with a $(d_{z^2})^n s$ hybrid on silver. In view of the large $4d$–$5s$ separation for silver, we now consider the latter structure to be unlikely. In view of the marked similarity of the e.s.r. parameters for this centre and species A [$\mathrm{\dot{C}u(CN)_3^{3-}}$] shown in the Table, we now suggest that this species may well have been $\mathrm{\dot{A}g(CN)_3^{3-}}$, also formed either by addition of $\mathrm{CN^-}$, or from some $\mathrm{Ag(CN)_3^{2-}}$ present in the system. The magnitude of the anisotropic coupling of 20 G quoted in ref. 3 is too great, if our estimated unit population of *ca.* 9.5 G for a $5p$ silver orbital (^{109}Ag) is correct.[8] However, the error in the anisotropy is very great, even for the Q-band spectrum, and using the presently estimated error limits we find a lower limit of *ca.* 6.7 G, corresponding to 70% $5p$-orbital population, which is quite reasonable. We note that the $5s$ character of *ca.* 6% lies between those for the copper and zinc derivatives, as expected on electronegativity grounds.

The other result which is of interest is the formation of the d_{z^2} copper(II) species upon annealing. It seems that the tendency for $\mathrm{Cu(CN)_4^{2-}}$ ions to relax from the initial tetrahedral configuration on electron capture is strongly resisted by environmental forces. Preliminary studies with $\mathrm{Na_3[Cu(CN)_4]}$ have indicated that species C is not formed upon exposure of this solid to γ-rays.[16] However, in the crystalline $\mathrm{K_3[Cu(CN)_4]}$ (single crystals and powder) conversion into species C, thought to be $\mathrm{Cu(CN)_5^{3-}}$, occurs before full relaxation towards planarity can occur. Our solution results strongly support the idea that $\mathrm{Cu(CN)_5^{4-}}$ ions can be formed in the presence of excess of cyanide ions.

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