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Complex Cyanides of Copper(II)

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Electron spin resonance and optical spectra of the unstable purple species produced by reaction of $\mathrm{Cu^{II}}$ and $\mathrm{CN^-}$ are studied at low temperature in various solvents. The species is shown to be the square-planar complex $[\mathrm{Cu(CN)_4}]^{2-}$. The delocalization of the electron "hole" may give an explanation of the instability of the complex.

1. Introduction

When an aqueous solution of $\mathrm{Cu^{II}}$ is added to a solution containing cyanide ions, one normally observes the formation of a brownish yellow precipitate which decomposes into cuprous cyanide and cyanogen gas according to the equation

$$\mathrm{Cu^{2+}} + 2\mathrm{CN^-} \longrightarrow \mathrm{Cu(CN)_2} \longrightarrow \mathrm{CuCN} + {}^1/_2\mathrm{(CN)_2} \qquad (1.1)$$

Other compounds have been, however, reported to form in such solutions. The first such observation was made by Moles and Izaguirre.[1] These authors concluded from a study of the conductivity, freezing points, viscosity, and heats of reaction that the following compounds were formed: $[\mathrm{Cu(CN)_4}]\mathrm{K_2}$, colorless and soluble; $[\mathrm{Cu(CN)_4}]\mathrm{Cu}$, a yellow prcipitate; and $[\mathrm{Cu_2(CN)_8}]\mathrm{CuK_2}$, a purple, soluble compound. At a later date, Glasner and Asher[2] attributed the purple color to the complex anion, $[\mathrm{Cu(CN)_4(CNH)}]^{2-}$. Several kinetic studies of the decomposition reaction were made under varying conditions.[3-6] The results of such studies are compatible with the existence of a labile intermediate species $[\mathrm{Cu(CN)_4}]^{2-}$ without giving a positive proof of its existence. In an article on complex cyanides, Griffith[7] cites a personal communication by Evans, who observed the formation of the purple complex in methanol at −70°.

2. Experimental Section

Solutions of the purple species were obtained in methanol of analytical quality, after elimination of reducing agents;[8] solutions in dimethylformamide (DMF), Baker Analyzed, and distilled water were also obtained. Cupric chloride was of Merck analytical quality and was dehydrated following the technique of Vanino.[9] Potassium cyanide of analytical quality was used without further purification.

Methanol Solutions.—Samples were prepared mixing a 0.016 *M* copper solution with 0.27 *M* cyanide solution at the melting temperature of methanol. The samples for epr spectroscopy were prepared in quartz tubes pouring one solution, cooled down to slightly above the melting point of the solvent, on top of the other solution kept as a solid; the tube was then slightly warmed, thoroughly mixed, and refrozen. The resulting purple samples could be kept indefinitely at liquid nitrogen temperature.

DMF Solutions.—Owing to the lower solubility of KCN in this solvent, the solutions used had to be more dilute; $\mathrm{CuCl_2}$ was 0.01 *M* and KCN was 0.015 *M*. The method of preparation was similar in other aspects.

Aqueous Solutions.—These were prepared from 0.25 *M* $\mathrm{CuCl_2}$ and 1.5 *M* KCN. The water solutions were exceedingly unstable, and extensive decomposition occurred before the sample could be frozen.

Electron paramagnetic resonance spectra were obtained with a Varian V-4500 spectrometer with 100-kc field modulation, at a microwave frequency of about 9.1 kMc.

Optical spectra were measured on a Perkin-Elmer 137-UV spectrometer at −40 to −30° using two low-temperature cells with quartz windows, with path lengths of 1 and 4 cm, respectively.

3. Results

(a) Electron Paramagnetic Resonance. (i) Methanol Solutions.—A series of spectra was obtained at liquid nitrogen temperature, for varying ratios of cyanide to copper concentrations. The ratio $[\mathrm{CN^-}]/[\mathrm{Cu^{2+}}]$ was varied between 200 and 5.5. The spectra are roughly independent of this ratio. A typical spectrum is shown in Figure 1. Under the conditions used for the preparation of the samples, the samples were usually glassy and transparent. When the samples were cooled more slowly, there appeared a different kind of spectrum, which we call the "anomalous" spectrum, which is discussed below.

We also obtained a series of spectra of the liquid solution at −60, −50, and −38° (Figure 2). In these solutions the anisotropy is averaged out by molecular tumbling, and the spectrum consists of four hyperfine components, at approximately equal spacings, but of different widths.

The solution spectra were measured and yielded the following values: $g_0 = 2.075 \pm 0.001$ and $A_0 = (58 \pm 1) \times 10^{-4}\ \mathrm{cm^{-1}}$.

The spectra of the vitreous samples show the typical shape of an anisotropic spectrum with approximately axial symmetry. The low-field end of the spectrum shows in quite good resolution three of the four hyperfine components expected for $I^{\mathrm{Cu}} = {}^3/_2$. The separation of the lines yielded the value for $|A|$, the component of the hyperfine splitting tensor in the direction of the symmetry axis. The line at the extreme left of the spectrum appears as a resolved doublet (Figure 1b). This is attributable to the two isotopes of copper, $^{63}\mathrm{Cu}$ and $^{65}\mathrm{Cu}$, both with $I = {}^3/_2$, and with a relative abundance of 69 and 31%. The shapes of

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[1] E. Moles and R. Izaguirre, *Anal. Soc. Espan. Fis. y Quim.*, **19**, 33 (1921).

[2] A. Glasner and K. R. S. Asher, *J. Chem. Soc.*, 3296 (1949).

[3] F. R. Duke and W. G. Courtney, *J. Phys. Chem.*, **56**, 19 (1952).

[4] N. Tanaka, M. Kamada, and T. Murayama, *Bull. Chem. Soc. Japan*, **31**, 895 (1958).

[5] J. H. Baxendale and D. T. Westcott, *J. Chem. Soc.*, 2347 (1959).

[6] R. Paterson and J. Bjerrum, *Acta Chem. Scand.*, **19**, 729 (1965).

[7] W. P. Griffith, *Quart. Rev.* (London), **16**, 188 (1962).

[8] J. N. Pearce and F. S. Mortimer, *J. Am. Chem. Soc.*, **40**, 509 (1918).

[9] L. Vanino, "Handbuch der präparativen Chemie," F. Enke, Stuttgart, 1923–1925.

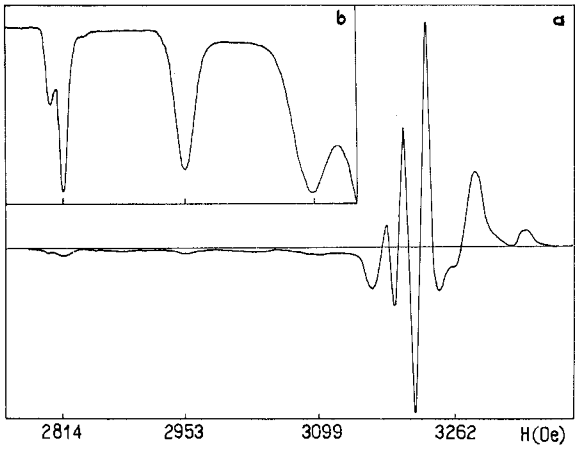

Figure 1.—(a) Electron paramagnetic resonance spectrum of the purple species in methanol at 77°K. (b) The low-field part of the spectrum under higher gain.

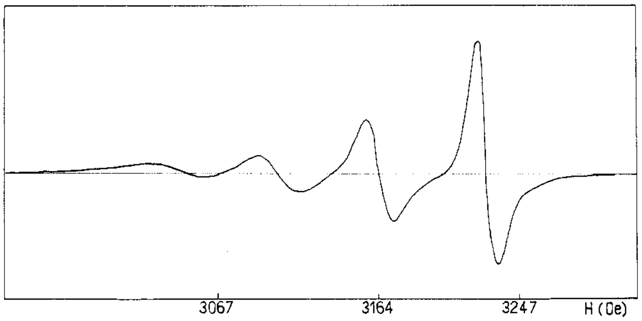

Figure 2.—Electron paramagnetic resonance spectrum of the liquid methanol solution at −50°.

these components are similar to that of the absorption lines,[10] so that they can be integrated after a graphical resolution. The ratio of these areas yields 35 and 65%, in good agreement with the relative abundances. The ratio of the hyperfine splittings of both isotopes obtained from the spectrum is 1.09 ± 0.06, which agrees with the ratio of the magnetic moments, which is 1.12.

From the "parallel" portion of the spectrum we obtain the following values for $g_{\|}$ and $|A|$: $g_{\|} = 2.160 \pm 0.009$, $|A^{63}| = (150 \pm 3) \times 10^{-4}$ cm^{-1}, and $|A^{65}| = (143 \pm 3) \times 10^{-4}$ cm^{-1}.

The "perpendicular" part of the spectrum is not so well resolved as is the "parallel" part. Therefore we prefer to obtain the values of $g_\perp$ and $|B|$ remembering that $g_0 = {}^1/_3(g_{\|} + 2g_\perp)$ and $A_0 = {}^1/_3(A + 2B)$, from which we obtain $g_\perp = 2.032 \pm 0.006$, $|B^{63}| = (17 \pm 3) \times 10^{-4}$ cm^{-1}, and $|B^{65}| = (16 \pm 3) \times 10^{-4}$ cm^{-1}. Using the positions and separations of the lines in the "perpendicular" part of the "solid" spectrum, these values were tested for consistency by a theoretical calculation of the spectrum following the method of Kivelson and Neiman.[11]

The perpendicular part of the spectrum consists of four lines of varying intensities and widths, but with approximately equal separations. The assumption that the unequal spacing of the lines is due to the combined effect of the quadrupole interaction and second-order hyperfine splitting[12] allowed us to obtain an estimate of the quadrupole coupling constant Q' as seen below.

The calculation of the theoretical spectrum was performed assigning different values of $g_{\|}$, $g_\perp$, A, and B. It turns out that the line for $M_I = -{}^3/_2$ shows a second "anomalous" maximum.[11,13] For $M_I = -{}^1/_2$ there also appears a second maximum very near to the principal one leading to an abnormal increase in the intensity of this line, which is the most intense in the spectrum. The best fit with the observed spectrum is obtained for the following values of the parameters of the spin Hamiltonian

$$g_{\|} = 2.160 \quad |A| = 143 \times 10^{-4}\ \text{cm}^{-1}$$
$$g_\perp = 2.033 \quad |B| = 21 \times 10^{-4}\ \text{cm}^{-1}$$
$$Q' = 4 \times 10^{-4}\ \text{cm}^{-1}$$

Table I shows the fit between the observed and calculated line positions. If our interpretation of the spectrum is correct, the line at highest field is the envelope of the two calculated maxima for $H = 3247$ and 3280 oersteds, which is reasonable in view of the width of this line and the calculated line shape for $M_I = -{}^3/_2$. We see that the values of $g_{\|}$, $g_\perp$, and A agree with the values given earlier. Only B, whose determination is most subject to error, deviates from the value calculated indirectly more than is warranted by the experimental error.

TABLE I

LINE POSITIONS (OERSTEDS) OF THE EPR SPECTRUM IN METHANOL

Obsd	Calcd
2814	2813
2955[a]	2955
3097[a]	3097
3179	3178
3198	3197
3223	3222
3269[b]	3247
	3280

[a] Corrected for ^{33}Cu. [b] Broad line, probably envelope of the calculated positions at 3247 and 3280 oersteds.

(ii) **DMF Solutions.**—In this solvent, the spectra of the frozen solution are similar to those in methanol. No satisfactory spectra in liquid solution could be obtained in this case, owing to the combination of the high melting point, the high electric conductivity of the solvent, and the low solubility of the reagents in it.

The values of $g_{\|}$ and A were obtained as described for the methanol solutions. Since the spectra in both solvents are quite similar, $g_\perp$ and B were obtained by comparison. The values obtained in this fashion are

$$g_{\|} = 2.158 \pm 0.009 \quad |A| = (139 \pm 3) \times 10^{-4}\ \text{cm}^{-1}$$
$$g_\perp = 2.032 \pm 0.006 \quad |B| = (16 \pm 3) \times 10^{-4}\ \text{cm}^{-1}$$

(iii) **Aqueous Solutions.**—In this solvent, the spectra of the frozen solutions are somewhat different from

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[10] J. A. Weil and H. G. Hecht, *J. Chem. Phys.*, **38**, 281 (1963).

[11] R. Neiman and D. Kivelson, *ibid.*, **35**, 156 (1961).

[12] W. Low, "Paramagnetic Resonance in Solids," Academic Press Inc., New York, N. Y., 1960.

[13] H. R. Gersman and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

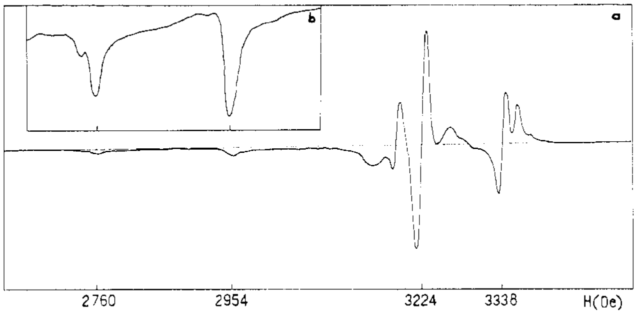

Figure 3.—(a) Electron paramagnetic resonance spectrum of the purple species in water at 77°K. (b) As in Figure 1.

those in methanol and DMF although the general features are similar (Figure 3). The high-field line is different, as are the separations between the more intense lines and as are their widths. Also in this case it is impossible to obtain useful spectra for the liquid solution. The parameters of the spin Hamiltonian obtained as in DMF are

$$g_{\parallel} = 2.146 \qquad |A| = 190 \times 10^{-4}\ \text{cm}^{-1}$$
$$g_{\perp} = 2.033 \qquad |B| = 27 \times 10^{-4}\ \text{cm}^{-1}$$

We performed the theoretical calculation of this spectrum as outlined above for the methanol solution. The second-order correction for the values cited above amounts to −4.8 oersteds for $M_I = \pm{}^3/_2$ and −11.5 oersteds for $M_I = \pm{}^1/_2$. The value of Q' was taken as 4×10^{-4} cm^{-1} as for methanol. The absorption curve was calculated taking the second-order and quadrupole effects into consideration. Best fit between calculated and observed line positions was obtained for

$$g_{\parallel} = 2.146 \qquad |A| = 185 \times 10^{-4}\ \text{cm}^{-1}$$
$$g_{\perp} = 2.033 \qquad |B| = 27 \times 10^{-4}\ \text{cm}^{-1}$$

in excellent agreement with the values measured directly. The peaks appearing at the high-field end of the spectrum correspond to the anomalous line shape for $M_I = -{}^2/_3$, which in this case does not coincide with the normal peak. The weaker absorption corresponds to the anomalous peak of the $M_I = -{}^2/_3$ component of the spectrum of the less abundant isotope, ^{65}Cu. This assignment was made from the value $|A^{65}| = 204 \times 10^{-4}$ cm^{-1} calculated from the observed value of $|A|$ and the ratio of the magnetic moments of both isotopes.

(iv) **Anomalous Spectra.**—We mentioned above, in connection with the measurement of the spectra of frozen solutions in methanol, that, depending on the rate of freezing of the samples, in some instances we obtained a type of spectrum different from those discussed above, which we call the "anomalous" spectrum (Figure 4d). In one case it was possible to obtain a whole series of spectra intermediate between both forms, from the same sample, varying the rate of freezing (Figure 4). These intermediate spectra can be interpreted as a superposition of the two extreme cases, the normal spectrum of Figure 1 and the anomalous spectrum (Figure 4d).

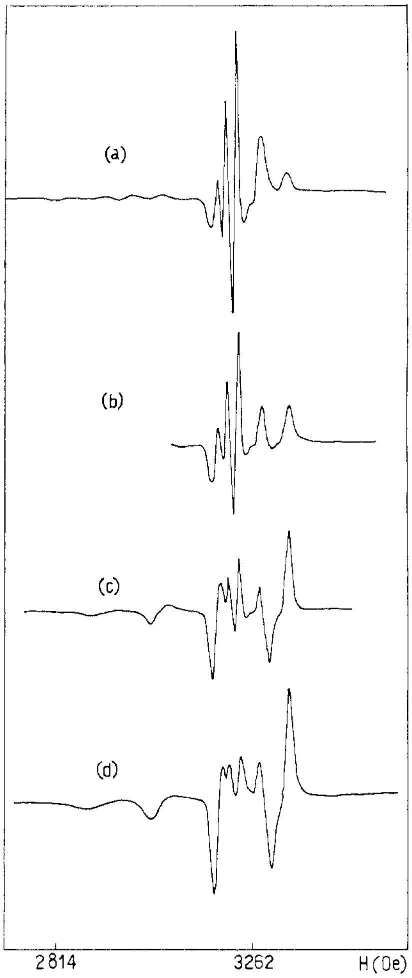

Figure 4.—Transition from the normal (a) to the "anomalous" spectrum, obtained varying the freezing conditions; solvent, methanol; temperature, 77°K. (d) is the "anomalous" spectrum, with small residual peaks due to a small contribution of the normal spectrum.

From a number of experiments performed under different conditions, using as a solvent methanol to which glycerine had been added to ensure the formation of low-temperature glasses for all rates of cooling, we draw the conclusion that the anomalous spectrum tends to appear more easily at very high [CN$^-$]/[Cu^{2+}] ratios, under conditions allowing the establishment of equilibria whose attainment might be slow.

The anomalous spectrum is nearly isotropic. Its g value is approximately 2.1, and it presents a hyperfine splitting of 65×10^{-4} cm^{-1}.

(b). **Optical Spectra.** (i) **Methanol Solutions.**—These were obtained from 0.012 M CuCl$_2$ and 0.3 M KCN stock solutions. The spectrum shows a very broad band with maximum absorption at about 550 mμ and a narrow band at about 280 mμ. The molar extinction coefficients are about 220 and 3900, respectively. The position of the bands does not change significantly when the ratio [CN$^-$]/[Cu^{2+}] is varied between 4 and 1000.

(ii) **Methanol–Water Solutions.**—Since it was not possible to obtain optical spectra in liquid water solutions, we investigated the effect of water on the optical spectra of the complex using mixtures with varying water content, compatible with obtaining freezing points below −30° at which temperature the spectra were taken. There always appears the band at about 550 mμ, still broader in the presence of water. There also appears a new, weaker band at 420 mμ, and the ultraviolet band appears at 280–290 mμ.

(iii) **DMF Solutions.**—At room temperature there appears a band at 490 mμ. At 375 mμ there appears a peak whose intensity diminishes with the time. Conversely, a peak at 295 mμ grows with time, showing an isobiestic point at 335 mμ. At −30° there appears a band at about 470 mμ, which shifts slightly toward longer wavelengths at increasing $[CN^-]/[Cu^{2+}]$ ratio.

4. Coordination Number and Symmetry

To our knowledge, little use has been made of epr data in transition metal complexes to decide between alternative structures. Pauling[14] was the first to suggest the use of magnetic susceptibilities as a diagnostic method for structure determinations. Ito and Ito[15] calculated magnetic susceptibilities for different configurations using a formula due to Van Vleck. This work was completed by Boudreaux[16] for trigonal and C_{4v} symmetry (square pyramid) taking spin–orbit coupling into account. However, as we shall see, paramagnetic resonance measurements are much more precise than bulk magnetic susceptibilities and may lead to much more definite results.

We shall now attempt to determine the structure of the purple cyanocupric complex using the spectroscopic information described above. Our model of the complex must account for the following facts. (a) The epr spectra are almost completely independent of the solvent. The data for methanol and DMF are identical within the experimental error, and those for water are but slightly different. (b) The epr spectra are almost completely independent of the ratio $[CN^-]/[Cu^{2+}]$. (c) The epr spectra show axial symmetry with $g_{\parallel} > g_{\perp} > 2$. (d) The optical spectra depend very markedly on the solvent.

Point b allows us to consider that only one species is present in concentrations sufficient to affect the spectra. (See the discussion of the anomalous spectrum, whose appearance is, within limits, concentration dependent.)

We analyze in turn the possible coordination numbers and different symmetries that are conceivable. We can exclude offhand the coordination numbers $n = 1$ and $n = 2$ for chemical reasons and because it would be very unlikely that species such as $[Cu(CN)]^+$ or $Cu(CN)_2$ would be the only ones present.

For $n = 3$, the only possibilities with axial symmetry correspond to point groups D_{3h} and C_{3v}. For D_{3h} without axial perturbation the electronic ground state of the d^9 system would be E' which under spin–orbit coupling splits into Γ_8 and Γ_9 of the double group, the first one lying lowest. For this situation one obtains the values $g_{\parallel} = 6$ and $g_{\perp} = 0$, in obvious disagreement with the facts.

If the central ion is not in the plane determined by the CN^- groups, one has point group C_{3v}. In this symmetry the copper d orbitals split into levels of symmetry A_1 and 2E. If the ground state were A_1, $g_{\parallel} = 2$ and $g_{\perp} = 2 - 6\lambda/\Delta$. For an E ground state, $g_{\perp}$ would be nearly zero, and $g_{\parallel}$ would vary between 4 and 6.

We point out that these calculations are made in a crude electrostatic crystal field scheme, which is sufficient at this point. The disagreement with experiment is obvious.

For $n = 4$, we consider the following possibilities: tetrahedral T_d, square-planar D_{4h}, distorted tetrahedral D_{2d}.

The tetrahedron can be discarded at once because it would be Jahn–Teller unstable, and, if it were not, it would give an isotropic g factor.

For a square-planar configuration the level B_{1g} would be lowest. In this case one obtains

$$g_{\parallel} = 2 - \frac{8\lambda}{\Delta} \qquad g_{\perp} = 2 - \frac{2\lambda}{\Delta'}$$

with $\Delta = E(B_{2g}) - E(B_{1g})$ and $\Delta' = E(E_g) - E(B_{1g})$. Since the spin–orbit constant λ is negative, we have $g_{\parallel} > g_{\perp} > 2$ in accordance with experiment. Furthermore, in this configuration one would expect solvent molecules to interact with the d_{z^2} (a_{1g}) and to a small extent d_{xz} and d_{yz} (e_g) orbitals. Such an interaction would not much affect the g values but would strongly affect the electronic excitation spectra. Thus, this model is fully in accordance with the experimental facts.

The case of D_{2d} symmetry can be treated as a perturbation either of the tetrahedron or of the square-planar case. The ground state in this case is again the $d_{x^2-y^2}$ level (B_1 of D_{2d}). The expressions for $g_{\parallel}$ and $g_{\perp}$ are the same as in the square-planar case.

If the configuration is not very different from the tetrahedral one, it would be difficult to explain the solvent dependence of the optical spectra, in part, for sterical reasons. If we allow the solvent molecules to approach the central atom closely enough to allow a strong interaction, the CN^- will tend to approach the planar disposition to reduce the ligand–solvent interaction. However, if this is the case, this flattening of the complex would depend on the nature of the solvent. This flattening would in turn affect the energy levels and modify the values of the crystal field splitting parameters Δ and Δ'. Thus the values of the g factors might be expected to be far more solvent dependent than is the case. There remains then the possibility of a nearly but not quite planar configuration; this will be discussed further below.

The other possibility for $n = 4$ is a trigonal pyramid of symmetry C_{3v} which has been discussed above.

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(14) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(15) K. Ito and T. Ito, *Australian J. Chem.*, **11**, 406 (1958).

(16) E. Boudreaux, *Trans. Faraday Soc.*, **59**, 1055 (1963).

For $n = 5$, there are two possible configuratious: the trigonal bipyramid of point group D_{3h}, and the square pyramid C_{4v}.

For the trigonal case, if we assume that the ligand–central atom distances are all equal, the level of A_1 symmetry is lowest and the g factors are $g_{\|} = 2$ and $g_{\perp} = 2 - 6\lambda/\Delta$, with $\Delta = E(E'') - E(E')$, which is in disagreement with the experimental facts.

If the bipyramid is flattened along the symmetry axis, the A_1 level would remain lowest, the levels E′ and E″ would exchange places, but we would still have $g_{\perp} > g_{\|} = 2$. If the bipyramid is axially elongated, the level scheme and g factors would be as discussed above for $n = 2$. This calculation also shows that we can eliminate the possibility of a plane-triangular configuration with an axial perturbation by solvent molecules.

For the square-pyramidal configuration of symmetry C_{4v} we may consider two cases; if the apical ligand is farther from the central ion than the other four, the ground state is B_1 and the level scheme is just as for the square-planar disposition, as are the calculated g values. Here we have another possibility requiring closer inspection.

If the pyramid is flattened along the axis, the ground state becomes A_1 and the g values are $g_{\|} = 2$ and $g_{\perp} = 2 - 6\lambda/\Delta$.

For $n = 6$, the symmetry could be octahedral, a case which can be excluded owing to its Jahn–Teller instability and isotropy. A deformation of the octahedron may produce D_{4h} or D_{3d} symmetries.

For D_{4h}, if the resulting square bipyramid is elongated, we have the same situation and g values as discussed above. However, if the axial positions are occupied by CN^- groups, we could hardly explain the solvent effect on the optical spectra. The same would be true if the bipyramid were flattened. In this case, the g values would be as for C_{3v} symmetry.

For an octahedron with trigonal distortion the symmetry is D_{3d}. The ground state would be an orbital doublet split into two Kramers' doublets under spin–orbit interaction. The g factors of the ground state (Γ_4, Γ_5) are $g_{\|} = 6$ and $g_{\perp} = 0$, in disagreement with experiment.

There remains to discuss the possibility that the species be polymeric. This possibility can be ruled out on the basis of several arguments. On one side, the epr spectra show no indication of a direct Cu–Cu coupling. A polymeric species would then be possible only by the joining of Cu ions *via* bridging cyanide groups. It is quite difficult to see how such a species could show the axial symmetry displayed by the epr spectra. Furthermore, the results of kinetic studies are in contradiction with the assumption of a polymeric species: the decomposition reaction is second order with respect to the total Cu^{II} concentration, and also second order with respect to the complex.[5,6] Both conclusions would be contradictory if the complex were a polymer.

So we see that if we exclude some unlikely configuration like D_{5h} or C_{5v}, etc., which we do not take into consideration for chemical reasons, the only configurations compatible with all the experimental facts are D_{4h} (square planar), C_{4v} (square pyramid), or D_{2d} (flattened tetrahedron). These configurations are, of course, just the ones one might expect for a Cu^{II} complex on the basis of chemical arguments alone, as discussed below.

5. Discussion

As we mentioned in the Introduction, the previous work done on the Cu^{II}–CN^- system is conflicting and inconclusive. Moles and Izaguirre[1] found the purple color for $[CN^-]/[Cu^{2+}] = 2.7$ and report another colorless complex for $[CN^-]/[Cu^{2+}] = 4$. Their measurements were done at rather high temperatures, so that the instability makes these numbers somewhat doubtful.

In all of our experiments we found that the purple color appears when $[CN^-]/[Cu^{2+}] > 4$, under conditions corresponding to the colorless species of ref 1. One possibility that appears likely is that these authors never saw "our" purple species and that their results refer to a pink color which is obtained in water at 0° under certain circumstances and which is much more stable than the purple. Also the authors of ref 2 probably refer to a species different from ours. Their results were obtained only under conditions of low alkalinity, whereas we obtained the purple species with varying ease in liquid ammonia, methanol, DMF, and acetonitrile. These authors obtain a maximum absorption at 500 mμ for a ratio $[Cu^{2+}]:[H^+]:[KCN] = 1:0.5:5$. However, this is not sufficient to conclude that the species responsible for this absorption has the formula $[Cu(HCN)(CN)_4]^{2-}$ as they report. Also, the stability of their species seems to be greater than that of ours. Their species might again be the "pink" species described above, which shows an absorption peak at 520 mμ and yields no paramagnetic resonance signal.

All of the kinetic data on the reaction of CN^- with Cu^{II} under a variety of conditions are compatible with an intermediate species $[Cu(CN)_4]^{2-}$.[6]

The crude electrostatic model shows that the most favorable configurations are square planar for $n = 4$ and tetragonal for $n = 6$, and it can be seen that in most cases in which these configurations are not attained the cause can be found in steric effects of the ligand or of the packing in the crystal lattice.

The characteristics of CN^- as a ligand are well known. It figures at the strong-field end of the spectrochemical series, owing to the presence of empty π-antibonding orbitals of low energy.

We must now perform a closer examination of the three types of symmetry found to be compatible with our epr and optical data. The dependence of the optical spectra on the solvent indicates solvent coordination. This fact allows us to discard a large number of CN^- groups, as in a (distorted) octahedral coordination.

A pentacoordinated structure of C_{4v} symmetry cannot be excluded offhand, but it seems unlikely that the stability constant of such a species be large enough to explain the fact that this should be the only species present at low CN^- concentration. We may also compare the low stability of the similar species $[Ni(CN)_5]^{3-}$[17,18] and the lower tendency of Cu^{II} toward replacing axially coordinated solvent molecules by other ligands; in other words, an axial CN^- ligand would behave as a weaker ligand than a solvent molecule.

The remaining possibilities are D_{4h} and D_{2d} with $n = 4$. The distorted tetrahedron would be plausible for steric reasons alone. The effective radius of a freely rotating CN^- is comparable with (and intermediate between) Cl^- and Br^- ions, which form Cu^{II} complexes of D_{2d} symmetry. However, the real bonding distance for CN^- is probably much smaller than this, so that the steric factor may not be the determining effect in solution, favoring a planar structure which is more favorable from an electrostatic point of view. A small deviation from the square-planar symmetry is however quite likely and would provide an attractive explanation for the molar extinction coefficient of the optical band in the visible part of the spectrum, whose value is close to the upper limit of the range admitted for planar complexes. The final answer to this question would require a direct structural study and is outside the scope of the present work.

The spectra are practically independent of the $[CN^-]/(Cu^{2+}]$ ratio over the range studied. This is not surprising if we admit that the formation constant of $[Cu(CN)_5]^{3-}$ is small[19] since the range of cyanide concentrations was limited in our study by the solubility of the cyanide in the solvents used.

The Anomalous Spectrum.—The occurrence of the "anomalous" epr spectra together with the normal one in one and the same sample presents a problem. None of the alternative explanations of this effect explains all of the experimental facts. We discuss the various possibilities, but the subject obviously requires further experimental work.

If we assume that the phenomenon depends on the fashion in which the solvent freezes, we must consider two aspects: (a) the interaction of the solvent molecules with the complex which depends on the freezing process and (b) the segregation of the paramagnetic molecules during freezing.

The anomalous spectrum is almost isotropic. This means that the ligand field must be very nearly cubic. In this case the spacing of the B_{1g} and E_g levels diminishes, decreasing the value of the hyperfine constant B and increasing $g_\perp$; the parallel values would be less affected. On the other hand, the structure of the complex could be distorted toward a tetrahedral structure by steric factors. In this case it is difficult to see why these effects should be similar in different solvents.

The segregation of the paramagnetic species during freezing might be expected to produce in the first place a line broadening which is not observed. Furthermore, such a segregation would indicate a relatively easy crystallization of the complex with cations available in the solution. This tendency is in opposition to the fact that it was possible to obtain solid precipitates containing CN^- and Cu^{II} only with great difficulty. Besides, the spectra of such solids are completely different from the "anomalous" spectrum.

The anomalous spectrum can be produced equally in vitreous solutions containing glycerol and in methanol when it crystallizes, thus excluding the effect of the vitreous or crystalline structure of the solid solvent.

For methanol, it was easier to obtain the "anomalous" spectrum when the ratio $[CN^-]/[Cu^{2+}]$ was high, and its intensity relative to that of the normal spectrum was then greater. In glycerine at high CN^- concentration one always obtains the anomalous spectrum and the normal spectrum when $[CN^-]$ is low. The influence of $[CN^-]$ on the appearance of the anomalous spectrum is thus evident. This induces us to postulate that there are different species in equilibrium—the one which gives the normal spectrum predominating for the range of $[CN^-]/[Cu^{2+}]$ used in this work and a second one giving the "anomalous" spectrum at high values of this ratio and corresponding to a different coordination of Cu^{II}. However, this assumption does not explain the surprising fact that both spectra can be obtained in the same solution, depending on the cooling rate. If the equilibrium between both species were (a) strongly temperature dependent and (b) quite slow to adjust to a change in temperature, it could be that equilibrium is attained only for a slow cooling rate and that the high-temperature equilibrium is quenched by fast cooling. This explanation needs more experimental information to be really credible.

6. Bonding Parameters for Planar $[Cu(CN)_4]^{2-}$

With the available data of $g_{\|}$, $g_\perp$, A, and B, it is not possible to obtain all the necessary parameters that describe the bonding in the complex. If we adopt a MO–LCAO model with the usual meaning of the symbols,[13] the hyperfine splitting constants are given by

$$A = -P\left[\left(K_0 + \frac{4}{7}\right)\alpha^2 + 8\lambda_c(\alpha\beta_1)^2(E_{B_{2g}} - E_{B_{1g}})^{-1} + \frac{6}{7}\lambda_c(\alpha\beta)^2(E_{E_g} - E_{B_{1g}})^{-1}\right]$$

$$B = -P\left[\left(K_0 - \frac{2}{7}\right)\alpha^2 + \frac{11}{7}\lambda_c(\alpha\beta)^2(E_{E_g} - E_{B_{1g}})^{-1}\right]$$

In these expressions K_0 describes the contact hyperfine interaction in the free Cu^{2+} ion, whose spin–orbit constant is λ_c. α, β, and β_1 are the coefficients of $d_{x^2-y^2}$ (B_{1g}), $d_{xz,yz}$ (E_g), and d_{xy} (B_{2g}), respectively, in the LCAO expansion of the molecular orbitals of the symmetry type given. Using the measured values of A and B, and the values $\lambda_c = -828$ cm^{-1} and $K_0 = 0.43$, we obtain the expression: $\alpha^{-2} = 2.47 - 17.700 \times$

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[17] J. S. Coleman, H. Petersen, Jr., and R. A. Penneman, *Inorg. Chem.*, **4**, 135 (1965).

[18] R. A. Penneman, R. Bain, R. Gilbert, L. H. Jones, R. S. Nyholm, and R. K. N. Reddy, *J. Chem. Soc.*, 2266 (1963).

[19] D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961).

β_1^2/Δ, where $\Delta = E_{B_{2g}} - E_{B_{1g}}$. We do not know either β_1 or Δ with certainty. The optical transition observed in the visible region lies in the range expected for Δ, but we cannot assign it clearly to this transition because of its strong solvent dependence. It is likely that the relatively weak d–d transition is obliterated by a strong band. The value of β_1 probably lies between 0.8 and 1.0. If we admit that Δ is in the range between 17 and 25 kK, we obtain values for α between 0.71 and 0.84.

The ligand contribution α' to the ground state can be estimated from the normalization conditions; we may take for the overlap integral $\langle d_{x^2-y^2} | -\sigma_x \rangle = 0.17$ which is obtained considering the cyanide σ orbitals to be sp hybrids and taking the Cu–C distance to be 1.9 A, which is a weighted average of the metal–carbon distance for a number of complex cyanides of similar structure. This value gives for α' the limits $0.98 > \alpha' > 0.89$ for $0.71 < \alpha < 0.84$. The values of α' thus obtained are unusually high. They are quite reasonable, though, if we consider the great instability of the complex, which can thus be related to the large degree of delocalization of the "hole" in the d shell over the ligands.

If we use Kivelson's formula for α[19]

$$\alpha^2 = -\frac{A}{P} + (g_{\parallel} - 2) + \frac{3}{7}(g_{\perp} - 2) + 0.04$$

we obtain the value $\alpha = 0.78$, which lies midway between the limits found above.

7. Conclusions

The epr and optical spectra of the purple unstable species obtained adding CN$^-$ to Cu^{II} solutions in various solvents at low temperature can be interpreted as belonging to the essentially square-planar complex, $[Cu(CN)_4]^{2-}$. All of the experimental facts are satisfactorily accounted for by this interpretation. In particular, the theoretical interpretation of the parameters of the spin Hamiltonian yield a degree of delocalization of the electron "hole" which is higher than those observed for most other Cu^{II} complexes, a fact which may be correlated with the great instability of the species under study.

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The Electronic Spectra of Hexanitrometalates

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The charge-transfer spectra of the hexanitro complexes of Co^{3+}, Rh^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} are reported. Contrary to a previous interpretation, an analysis of the solid-state infrared spectra of the various $Co(NO_2)_6^{3-}$ salts indicates that the principal deviation from T$_h$ symmetry involves a rotation of the nitro groups about the Co–N axis. A molecular orbital energy level diagram which accounts for the charge-transfer spectra of the hexanitrometalates is presented. By means of this diagram the weak band at 21.5 kK in $Co(NO_2)_6^{3-}$ is shown to be an orbitally forbidden charge-transfer transition from a nonbonding oxygen orbital to the predominantly metal e$_g$ orbital. Proper assignment of this transition obviates anomalous spectroscopic properties previously attributed to the nitro group.

Although the nitro group is taken as a classic example of a π-acceptor ligand[2] and the prevailing theory of the *trans* effect is based upon its back-bonding ability,[3] recent evidence from the Mössbauer effect[4] attributes equal π-bonding ability to NO_2^- and NH_3. Electronic spectra also provide evidence which is seemingly contradictory in nature. Since d-to-d spectra are blue shifted from $Co(NH_3)_6^{3+}$ to $Co(NH_3)_5NO_2^{2+}$, it has been concluded that the nitrite ion provides a stronger field than NH_3.[5] However, the first band of $Co(NH_3)_6^{3+}$ *red* shifts on passing to $Co(NO_2)_6^{3-}$.[6] This anomaly has been interpreted as indicating coordination through oxygen in $Co(NO_2)_6^{3-}$,[5] but the absence of a metal–oxygen stretching fundamental at 1050 cm^{-1} makes such an explanation highly doubtful. The red shift of the first band on going from $Rh(NH_3)_6^{3+}$ to $Rh(NO_2)_6^{3-}$ only serves to compound the confusion.[7]

Recently Krause, Wickenden, and Ruggles (KWR)[8] have shown, in agreement with others,[9] that the infrared spectra of $M_3Co(NO_2)_6$ are dependent upon the cation M$^+$. They claim that the visible spectra show a similar dependence. The spectra of the Na$^+$ and K$^+$ salts are interpreted by KWR as arising from an axial elongation along two Co–N bonds. However, KWR conclude the cesium salt, $Cs_3Co(NO_2)_6$, has all Co–N bond lengths equal and derive values of the ligand field

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(1) Predoctoral National Science Foundation Fellow.

(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 853.

(3) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1963).

(4) E. Flück, *Advan. Inorg. Chem. Radiochem.*, **6**, 433 (1964).

(5) R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388 (1938).

(6) A. Kiss and D. Czeglédy, *Z. Anorg. Allgem. Chem.*, **235**, 407 (1938).

(7) H. Schmidtke, *Z. Physik. Chem.* (Frankfurt), **47**, 96 (1964).

(8) R. Krause, A. Wickenden, and C. Ruggles, *Inorg. Chem.*, **5**, 936 (1966).

(9) I. Nakagawa, T. Shimanouchi, and K. Yamasaki, *ibid.*, **3**, 772 (1964).