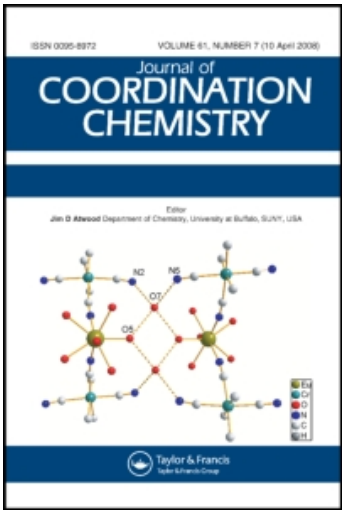

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ESR STUDY OF IRRADIATED PENTACYANONITROSYL COBALTATE (II)

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ESR STUDY OF IRRADIATED PENTACYANONITROSYL COBALTATE (II)

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An ESR study of γ-irradiated pentacyanonitrosyl cobaltate (II) shows the presence of two paramagnetic species. One, with $g_{\|} = 2.005$, $g_{\perp} = 2.172$, $A_{\|}$ 81.3 and $A_{\perp} = -26.2 \times 10^{-4}$ cm^{-1}, is the well-known d^7 species $Co(CN)_5^{3-}$. The second shows $g_{\|} > g_{\perp}$ and much lower ^{59}Co hyperfine interactions. The ESR parameters are shown to be consistent with those predicted for the species $[Co(CN)_5NO]^{4-}$ with C_s symmetry, a bent Co–N–O bond, and a d_{π} configuration with the odd electron in an a' orbital formed by mixing the cobalt $d_{x^2-y^2}$ and d_{z^2} orbitals. Theoretical arguments are advanced to show that, in general, small metal hyperfine splittings in low symmetry ions do not necessarily establish that the unpaired electron is in a ligand-dominated orbital.

INTRODUCTION

ESR studies of Co(II) species in irradiated Co(III) complexes have yielded quite interesting results and have permitted characterization of the electronic and molecular structures of several new complexes. Irradiation of $K_3Co(CN)_6$ by electrons from a linear accelerator[1] produced two types of Co(II) species in one of which cobalt (II) is bonded through nitrogens of two cyanide ligands to form $[Co(II)(CN)_4(NC)_2]^{4-}$ and in the second through normal cyanide bonding. Lin *et al.*[2] irradiated $K_3Co(CN)_6$ with 50 kV X-rays and found a species with a d^7 configuration with the odd electron in a d_{z^2} orbital as a result of weak tetragonal distortion. Similar results were obtained in the study[3] of the thermal decomposition of powder samples of $K_6Co_2(CN)_{12}$. In all these cases (except the ion which shows ^{14}N hyperfine splitting) the species responsible for the paramagnetic resonance has been identified as the pentacyanocobaltate (II) ion $[Co(CN)_5]^{3-}$. In a recent work[4] the $[Co(CN)_5]^{3-}$ species produced by irradiation of the solid has been compared with that formed by reduction of the $[Co(CN)_6]^{3-}$ in solution and the importance of the specific interaction in the axial coordination site shown. Fujiwara *et al.* have recently reported the results of irradiating sixty-seven cobalt (III) complexes and have discussed the electronic and spin states of the "hot" cobalt (II) ions produced. In most of the cases the cobalt (II) species are present with spin state S = 1/2.

In this work we report the production of the species $[Co(CN)_5]^{3-}$ in a different starting material, the potassium salt of pentacyanonitrosyl cobaltate (II). This result indicates that the metal-nitric oxide bond is weak, as had been proposed by Manoharan[6] for species with the $[d^6(\pi^*NO)^2]$ configuration. Evidence for a second, new species, with low cobalt hyperfine splitting constants, has also been obtained and the nature of this species and its structure are discussed from the molecular-orbital point of view.

EXPERIMENTAL

The compound $K_3Co(CN)_5NO \cdot H_2O$ was prepared by the method of Nast and Rhomer.[7] ESR spectra were obtained with a Varian-4500 X-band spectrometer using electron irradiated powdered samples. Measurements were made at 77°K, and at room temperature on fresh samples which had been irradiated at 77°K. Some irradiations were also made at 77°K of samples which had been previously heated to about 150°C to remove the water of crystallization. Single crystal measurements were not possible since the compound, precipitated as a powder, does not dissolve in any of the usual solvents without decomposition.

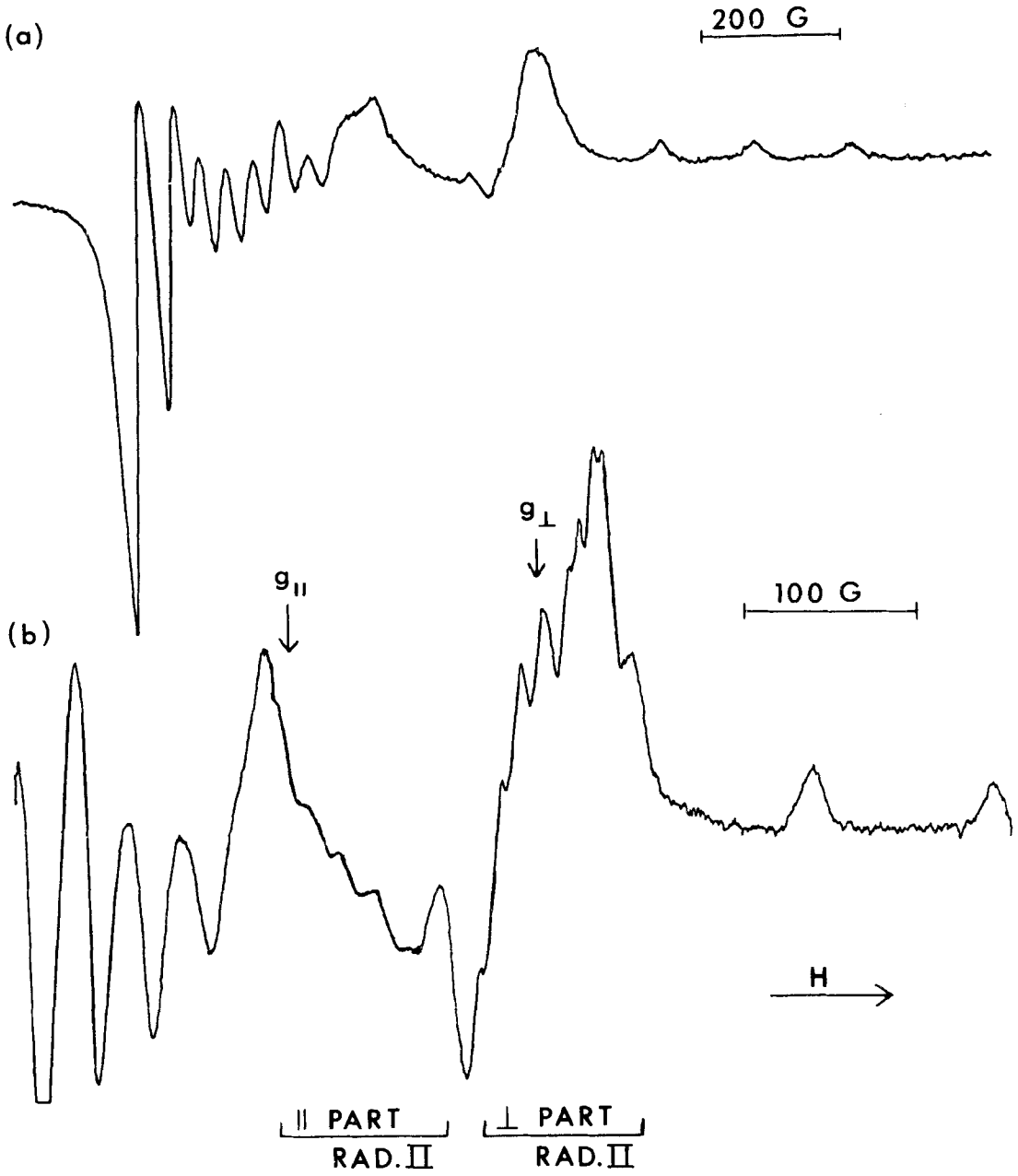

FIGURE 1 (a) X-band ESR spectrum of irradiated $K_3Co(CN)_5NO$ measured at room temperature; (b) X-band ESR spectrum at 77°K of irradiated $K_3Co(CN)_5NO$ showing the parallel and perpendicular sections corresponding to $Co(CN)_5NO^{4-}$

RESULTS

A. *The Species* $[Co(CN)_5]^{3-}$

The room temperature X-band ESR spectrum of a sample of $K_3Co(CN)_5NO\cdot H_2O$, which had been heated at 150°C before irradiation, is shown in Figure 1(a). Spectra were also taken of $K_3Co(CN)_5NO\cdot H_2O$ and $K_3Co(CN)_5NO\cdot D_2O$ which had not been heated and these are essentially the same as Figure 1. Hyperfine splitting from interaction of the odd electron with one ^{59}Co ($I = 7/2$) nucleus is seen and the general features of the spectrum are characteristic of a randomly oriented $S = 1/2$ system with axial symmetry, from which one can readily calculate g- and A-tensors with the aid of the spin Hamiltonian

$$\mathcal{H} = \beta[g_\parallel H_z S_z + g_\perp(H_x S_x + H_y S_y)] + AI_z S_z + B[I_x S_x + I_y S_y] + Q'[I_z^2 - I(I+1)/3], \quad (1)$$

where $g_\parallel$, $g_\perp$, A and B are the principal values of the g and hyperfine interaction tensors for a system with axial symmetry and $Q' = Q_{zz} - 1/2(Q_{xx} + Q_{yy})]$ is for the cobalt nucleus.

The nuclear hyperfine line positions in the $g_\parallel$ region can be fitted to the equation

$$H_\parallel = H_\parallel^0 - AM_I - [\beta^2 g_\perp^2/2H_\parallel^0 g_\parallel^2][I(I+1) - M_I^2] \quad (2)$$

while all the resonance field positions in the $g_\perp$ region, except the two at lowest field, can be fitted to the equation

$$H_\perp = H_\perp^0 - BM_I - [(A^2 g_\parallel^2 + B^2 g_\perp^2)/4H_\perp^0 g_\parallel^2][I(I+1) - M_I^2] - M_I(Q'^2/2B)[2I(I+1) - 2M_I^2 - 1], \quad (3)$$

where $H_\parallel^\circ = h\nu^\circ/g_\parallel\beta$, $H_\perp^\circ = h\nu^\circ/g_\perp\beta$, Q' is the quadrupole interaction term as defined above, S and I are the electron and nuclear spin operators, and M_I is the z component of the nuclear spin. These results are in complete agreement with those of Tsay *et al.*[4] for $[Co(CN)_5]^{3-}$ ion in irradiated $K_3Co(CN)_6$ and our measured spin Hamiltonian parameters are shown in Table I. Tsay *et al.* attributed the irregular spacings and exceptionally large intensities of the lowest field lines to angular anomalies[8] and this explanation presumably also holds here.

B. *The Species* $[Co(CN)_5NO]^{4-}$

In addition to the prominent ^{59}Co hyperfine structure on both the $g_\parallel$ and $g_\perp$ parts of the spectrum, a highly broadened extra absorption, extending from the higher field end of the perpendicular component to the central position of the parallel component, was noted as an additional feature. Whereas the $[Co(CN)_5]^{3-}$ portion of the spectrum remained unchanged on cooling the sample to 77°K, the broadened features showed resolved ^{59}Co hyperfine splitting. The broadened extra portion differs from that due to $[Co(CN)_5]^{3-}$ in that $g_\parallel > g_\perp$ and the ^{59}Co hyperfine splitting constants A and B are much smaller. The ESR spectrum of this second species is shown in Figure 1(b) and the corresponding spin Hamiltonian parameters, obtained by solving Equations (2) and (3), are listed in Table I.

TABLE I
ESR spin Hamiltonian parameters[a] for the cobalt species

	$Co(CN)_5^{3-}$	$Co(CN)_5NO^{4-}$
$g_\parallel$	2.005 ± 0.002	2.075 ± 0.005
$g_\perp$	2.172 ± 0.005	1.998 ± 0.003
A	81.3 ± 1.0	15.9 ± 0.2
B	−26.2 ± 1.5	7.3 ± 0.1
Q'		0.9 ± 0.05

[a] A, B and Q' values are given in 10^{-4} cm^{-1}.

The species giving rise to this spectrum is not an F center of the type observed[4] in irradiated $K_3Co(CN)_6$ since the latter gives a sharp, strong feature with $g = 2.002$ at 77°K, which disappears on warming.

The general features of the ESR spectra of this species resemble those of the Class C series of irradiated Co(III) complexes studied by Fujiwara *et al.*[5] They attributed this type of spectrum to $[Co(III)L_5 - O_2^-]^{2+}$ complexes on the basis of their similarity to the spectra of the tetraphenylporphine Co(II) or N,N-ethylene-bis(3-methoxy-salicylideneiminato)Co(II) ions in pyridine after exposure to oxygen.[9,10] The unpaired electron was assigned to a ligand-dominated molecular orbital with only about 10% unpaired spin density in the cobalt orbitals. Similar spectra, with $g_\parallel > g_\perp$ and very low ^{59}Co nuclear hyperfine splittings, have been observed in other cobalt(II) species with O_2 bridges[3,11-13] or an O_2 adduct.[9,15-17] In all these, the dominating electron configuration has been considered to be $Co^{3+}O_2^-$ with the unpaired electron in a molecular orbital largely π^*O_2.

Irradiation of pentacyanonitrosyl cobaltate(II) under vacuum produces the same two species as were found with the sample which was not evacuated before irradiation. The presence of the second species even when the sample is under vacuum indicates that it is not an oxygen adduct. In fact the spectra of the second species seem to be much better resolved in the experiment using $K_3Co(CN)_5NO$ irradiated under vacuum.

Despite the similarities of the spectrum of Figure 1(b) to the cobalt (III)-superoxide-type spectra, it has certain striking differences, particularly the differences in line widths in the high-field region, and we attribute it to the species $[Co(CN)_5NO]^{4-}$ with a $[Co^{2+}NO^-]$ electron configuration and the odd electron mainly in the metal orbitals. The arguments supporting this assignment are given below.

DISCUSSION

A. *The Species $[Co(CN)_5]^{3-}$*

The spin Hamiltonian parameters we observe for $[Co(CN)_5]^{3-}$ in $K_3[Co(CN)_5NO]\cdot H_2O$ matrix are quite similar to those found for it in $K_3Co(CN)_6$ matrix[1-5] or in frozen ethylene glycol-water solutions.[4] The structure has been established as square pyramidal with the odd electron in a d_{z^2} orbital.[1-5] The absence of any substantial matrix effects on the ESR parameters supports the idea that there is no ligand in the sixth position.

B. *The Species $[Co(CN)_5NO]^{4-}$*

Ground state configuration and energy level diagram. Adding an electron to the original Co^{3+} d^6 species would give $[Co(CN)_5NO]^{4-}$ which could be formally written $Co^+\cdot NO$, $Co^{2+}NO^-$ or $Co^{3+}NO^{2-}$. The first and third structures would lead to a large ^{14}N hyperfine splitting[16] since the unpaired electron would be in a molecular orbital mainly π^*NO. Since no such hyperfine splitting is seen, even though the linewidths are sufficiently narrow that they should be observable, we conclude that the ground state configuration is $[Co(II)(CN)_5(NO)]^{4-}$ which we may write $d^7(\pi^*NO)^2$. It has been predicted[6] that such nitrosyl complexes, with more than six electrons, would have a bent M–N–O bond (M = transition metal ion) and our ESR data are in agreement with such a structure.

Nitrosyl complexes with bent M–N–O bonds have been intensively studied recently.[17-19] From a structural viewpoint NO^+ coordination is considered to give rise to a linear M–N–O bond and NO^- to a bent arrangement so we expect the nitrosyl bond in $[Co(CN)_5NO]^{4-}$ to be bent, resulting in C_s symmetry for the ion. The Pierpont-Eisenberg correlation diagram[17] gives the one-electron ordering

$$a''(yz) < a''(xy) < a'(xz) < a''(\pi^*NO) < a'(z^2) < a'(x^2-y^2)$$

while the calculation of Mingos[19] for $[Co(NH_3)_5NO]^{2+}$ suggests the ordering

$$a''(yz) < a''(xy) < a'(xz) < a'(\pi^*NO, z^2) < a''(\pi^*NO, yz) < a'(x^2-y^2) < a'(z^2, \pi^*NO).$$

The one electron energy of $e(\pi^*NO)$ for the assumed linear molecule in the latter calculation is extraordinarily low for a $\pi^*(NO)$ orbital containing two electrons and it would appear more reasonable for $b_1(x^2-y^2)$ to be lower. It is possible that the use of valence state ionization energies for the nitrosyl nitrogen and oxygen atoms (rather than for an NO molecule) led to too low an energy for $e(\pi^*NO)$ and a separate calculation for NO^- would be desirable. Also, in contrast to a bent $[Co(NH_3)_5NO]^{2+}$ ion, bent $[Co(CN)_5NO]^{4-}$ has much stronger equatorial bonds which will destabilize the (x^2-y^2) relative to the z^2 orbital. In the bent $[Co(NH)_3NO]^{2+}$ the cobalt-nitrogen (nitrosyl) bond distance[18] is 1.87 Å and the cobalt-nitrogen (NH_3) distance is 2.20 Å whereas in $[Co(CN)_5NO]^{4-}$ the Co–C and Co–N distances will be more or less the same.[20] The nature of the σ interactions will then decide the ordering of z^2 and (x^2-y^2) one-electron levels and z^2 will tend to be lowered since the overlap of an sp^2 hybridized NO^- orbital with z^2 will be much less than that of an sp^2 hybridized CN^- orbital with (x^2-y^2).

A reasonable energy level scheme for a bent $[Co(CN)_5NO]^{4-}$ system is shown in Figure 2 and is similar to that of Pierpont and Eisenberg.[17] This leads to an $[a''(xz)]^2[a''(xy)]^2[a'(yz)]^2[a''(\pi^*NO)]^2[a'(z^2)]^1$ ground state. It should, however, be remembered that since d_{z^2} and $d_{x^2-y^2}$ transform under the same irreducible representation in C_s symmetry, the orbital designations are somewhat arbitrary and both levels must be viewed as strongly antibonding σ^* levels based on the metal. As a result, the unpaired electron will actually be in a predominantly metal orbital with both z^2 and (x^2-y^2) character and the odd electron orbital should be written $[a'(x^2-y^2, z^2)]$.

Theory of g and A parameters. It might appear at first glance that the very low values for the ^{59}Co hyperfine splittings (Table I) require that the unpaired electron be in a predominantly ligand orbital. Although such an electron configuration does account for the ESR parameters of the $[Co^{3+}O_2^-]$-type complexes[9-15] it is by no means necessary in complexes of low symmetry. Both the low ^{59}Co hyperfine splittings and the anisotropic g values which are near the free spin value may be shown to be consistent with having the odd electron in a metal orbital of mixed z^2 and (x^2-y^2) character.

The principal values of the ^{59}Co dipolar hyperfine interaction tensor may be derived from the equation

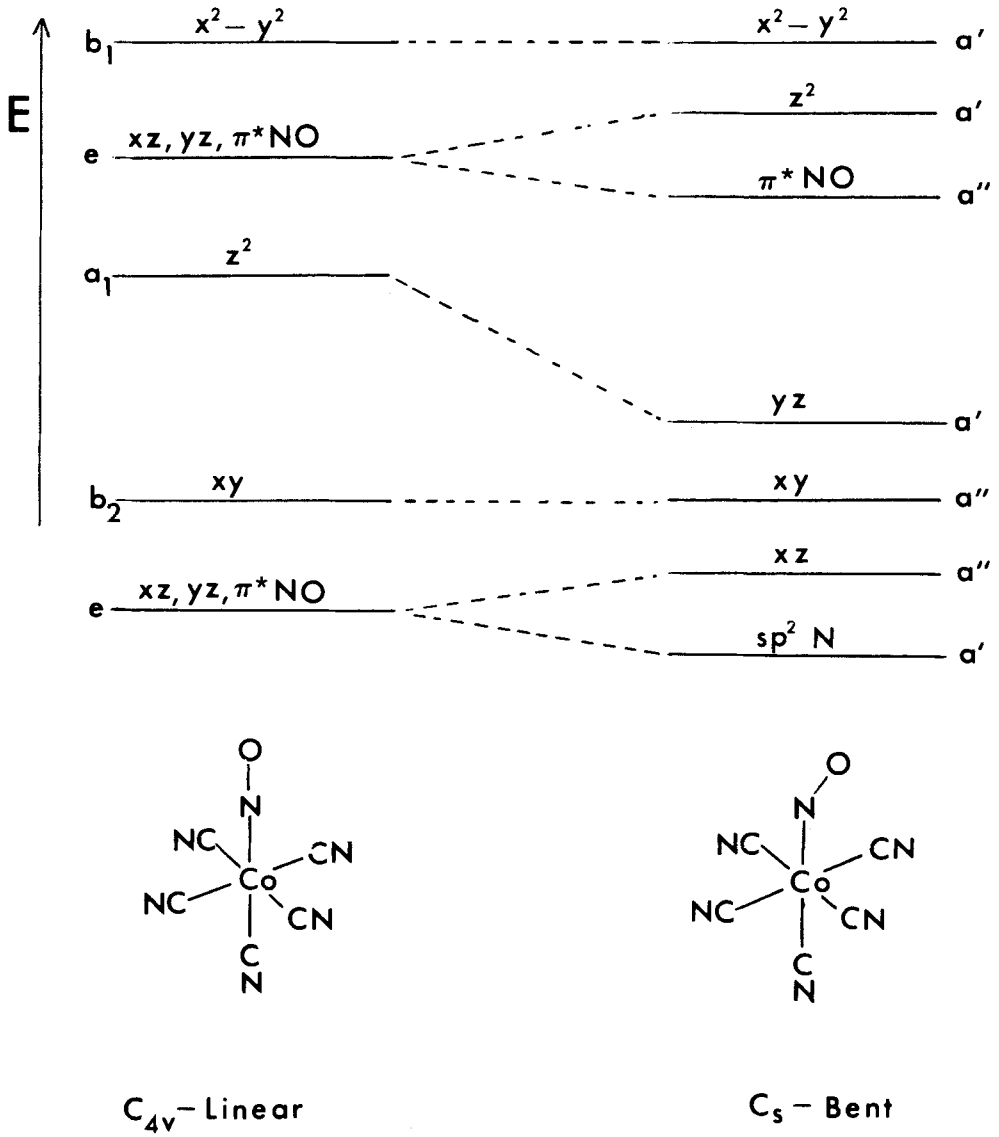

FIGURE 2 Proposed partial energy level diagram for the complex ion $[Co(CN)_5NO]^{4-}$ with linear and bent Co–N–O linkages.

$$P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle_{3d} \quad (4)$$

but the dipolar contribution to A_{zz} will differ for each d orbital[21] and is +4/7P for d_{z^2} but −4/7P for $d_{x^2-y^2}$ and d_{xy}. It may be noted that the value for $d_{x^2-y^2}$ has been erroneously applied in some calculations requiring the value for another orbital.

The admixture of z^2 orbital with $(x^2 - y^2)$ orbital is allowed by group theory in low symmetries such as C_s because both orbitals belong to the same irreducible representation. Qualitatively it occurs because adding d_{z^2} to $d_{x^2-y^2}$ increases the charge density in one lobe of $d_{x^2-y^2}$ while decreasing it in the other.[22] Using the crystal field approach we may write the wave function for the odd electron orbital as

$$\psi = a\phi_{x^2-y^2} + b\phi_{z^2} \quad (5)$$

with $a^2 + b^2 = 1$. In MO theory there would be a ligand component but we use crystal field theory here for simplicity and write the spin Hamiltonian parameters (rejecting smaller terms which will make only small contributions) in the form

$$g_{\parallel}: g_z = 2.0023\,[1 + 4\lambda a^2/(E_\psi - E_{xy})] \quad (6)$$

$$g_{\perp}: \begin{cases} g_x = 2.0023\,[1 - \lambda(a - \sqrt{3}b)^2/(E_\psi - E_{yz})] & (7) \\ g_y = 2.0023\,[1 - \lambda(a + \sqrt{3}b)^2/(E_\psi - E_{xz})] & (8) \end{cases}$$

$$A: A_z = P[-\kappa - (4/7)(a^2 - b^2)] \quad (9)$$

$$B: A_x = A_y = P[-\kappa + (2/7)(a^2 - b^2)]. \quad (10)$$

These expressions, plus the normalization equation, will allow us to make an estimate of the mixing coefficients a and b. Using the experimental values of A and B in Eqs. (9) and (10), along with the value $P=0.0254\ cm^{-1}$ calculated[21] from Hartree-Fock wave functions for Co^{2+}, we obtain $a = 0.664$ and $b = 0.748$. An unpaired electron occupying an orbital formally z^2, but with a large $(x^2 - y^2)$ contribution in accordance with the energy level scheme of Figure 2, will therefore lead to the observed low ^{59}Co hyperfine splittings.

An estimate of the spin-orbit coupling constant λ may now be obtained from the observed g values. We use the value of $(E_{z^2} - E_{xy}) \cong 23000\ cm^{-1}$, found by Alexander and Gray[23] for $[Co(CN)_5]^{3-}$, in $(E_\psi - E_{xy})$ in Eq. (6); this should be a good estimate since the ground state here has considerable z^2 character. This leads to $\lambda = 480\ cm^{-1}$ compared to $\lambda = 533\ cm^{-1}$ for the free Co^{2+} ion and gives an estimate of the metal character of the odd electron orbital of about 90% in good agreement with the earlier assumption that this must be a highly anti-bonding σ-metal orbital.

The value of κ is now found from Eq. (9) and (10) to be -0.03. In several dipositive cobalt systems studied[2,4] it has varied from -0.333 to $+0.325$ and hence our calculated value of κ is not unreasonable.

Because there will be a sizeable energy difference between the $a''(xz)$ and $a'(yz)$ orbitals, g_x and g_y should have similar values corresponding to the observed single value for $g_\perp$; however, in the absence of optical data no estimate of $g_\perp$ can be made.

These arguments have been given in detail to establish that small metal hyperfine splittings in low symmetry systems do not necessarily mean that the unpaired electron is in a ligand-dominated molecular orbital and the ratio P/P_0 (where P_0 is the calculated anisotropic splitting for the free ion with the odd electron in a single d orbital) will not give the correct orbital delocalization where there is an admixture of d orbitals. It seems likely that the less abundant radical in irradiated $K_3Co(CN)_5NO$ is such a low symmetry species, $[Co(CN)_5NO]^{4-}$, with low ^{59}Co hyperfine splittings but large metal d character for the odd electron orbital.

C. *Mechanism of formation of paramagnetic products*

Since the spectrum of $[Co(CN)_5]^{3-}$ is the stronger one we suggest that the radical ions are formed by electron attachment followed by decomposition of the electron adduct:

$$[Co(CN)_5NO]^{3-} + e \rightarrow [Co(CN)_5NO]^{4-}$$

$$[Co(CN)_5NO]^{4-} \rightarrow [Co(CN)_5]^{3-} + NO^-$$

and that the decomposition is favored.

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