

On the Paramagnetic Resonance Spectrum of the $\text{Cr}(\text{CN})_5\text{NO}_3^-$ Ion

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Citation: *The Journal of Chemical Physics* **38**, 2581 (1963); doi: 10.1063/1.1733545

View online: <http://dx.doi.org/10.1063/1.1733545>

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unenriched sample or by studying an enriched sample of known enrichment. Preliminary studies by the former method favor the conclusion that all five cyanides have nearly identical C^{13} hyperfine coupling constants, since the intensity of the satellites seems to be more nearly 5% than 4%. Studies are now being made in an attempt to resolve this question using enriched samples.² In addition, the kinetics of the exchange reaction are being investigated and will be reported later.²

It is perhaps somewhat surprising that both axial and equatorial cyanide ions should have the same value of $A(C^{13})$ in view of the pronounced deviation $Cr(CN)_5NO^{3-}$ ion from octahedral symmetry.³ However, CN^- and NO^+ have rather similar chemical effects as ligands,⁴ and the fact that the axial CN^- does not appear to be exceptionally labile makes it equally surprising that $A(C^{13})$ should be vanishingly small for the axial cyanide.

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¹ I. Bernal and S. E. Harrison, *J. Chem. Phys.* **34**, 102 (1961).

² Brock Spencer and R. J. Myers (personal communication).

³ H. B. Gray and C. J. Ballhausen, *J. Chem. Phys.* **36**, 1151 (1962).

⁴ F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* (John Wiley & Sons, Inc., New York, 1958), p. 177.

On the Paramagnetic Resonance Spectrum of the $Cr(CN)_5NO^{3-}$ Ion

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(Received 5 November 1962)

IN connection with a recent study¹ on the $[Fe(CN)_5NO]^{3-}$ anion, we were led to re-examine the ESR spectrum of $Cr(CN)_5NO^{3-}$, in which we since have found an error in our original assignment of the ^{53}Cr hyperfine splitting constant. This was brought about by the appearance of a ^{13}C line in the ESR spectrum. We have verified that the line in question is due to ^{13}C by high-resolution studies on the low-field side of the spectrum. There we found the weak satellite due to the ^{13}C splitting of the ^{53}Cr lines. The lines in question are shown in Fig. 1.

As a result of these measurements and other studies carried out on samples which had been labeled with $K^{13}CN$, we have drawn some conclusions, the details of which will be the subject of a forthcoming report.²

(1) The ^{53}Cr splitting is, as stated by Hayes,³ approximately 18.5 G rather than 13.8 G, as we said earlier, in a previous communication.⁴

(2) Hayes correctly infers that there is a line due to ^{13}C near the central triplet. However, there are four

equivalent, equatorial, ligands and only one axial CN . Consideration of the intensity of the lines from the two cases affords an opportunity to distinguish between them. This should be particularly clear in the case of a compound enriched with ^{13}C .

In an unenriched sample, it is possible to differentiate between the two cases only by means of the intensity of the lines. The reason for this is because ^{13}C exists in nature only to the extent of about 1% and the number of molecules containing multiple substitution is too small to be useful here. Using ^{13}C in natural abundance, the ^{13}C doublet that arises from the equatorial ligands should have 4% of the intensity of the adjacent ^{53}Cr or ^{52}Cr lines, depending on its origin. This is shown to

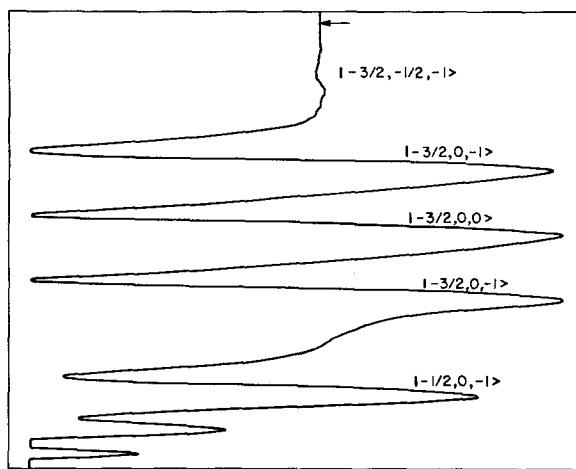


FIG. 1. Enlargement of the low-field region of the ESR spectrum of $Cr(CN)_5NO^{3-}$ showing the C^{13} splitting of the Cr^{53} lines. All the isotopes in question are in natural abundance. Note that the intensity ratio of the lines $| -\frac{3}{2}, -\frac{1}{2}, -1 \rangle$ and $| -\frac{3}{2}, 0, -1 \rangle$ is 4/100. Quantum numbers of zero for carbon and chromium refer to the isotopes ^{12}C and ^{53}Cr .

be the case in Fig. 1, where the weak low-field satellite is 4% of the ^{53}Cr lines. If the doublet were due to the axial ^{13}C , it would have only 1% of the intensity of the ^{53}Cr lines. One does not expect the axial ^{13}CN to have the same splitting as the equatorial ones since the ground state b_2 orbital containing the unpaired electron lies in the equatorial plane.

(3) We have observed the electron resonance behavior of solutions of $Cr(CN)_5NO^{3-}$ in which the CN ligands were exchanged with ^{13}CN . In this fashion we attempted to observe the axial ^{13}C splitting. The choice of this method was based on considerations of rates of exchange. It is well known⁵ that whenever a coordination compound has ligands of different strengths, there can occur *trans*-elimination reactions of a ligand. We considered this phenomenon in our previous communication,⁴ in connection with the shift of the first band in water solution. Because of the strength of the $M-NO$ ligand,^{1,6,7} the axial CN should exchange much more rapidly than the equatorial ligands, unless the

axial CN is also compressed. Basolo and Pearson⁵ rate the *trans*-eliminating power of CN⁻ and NO⁺ as about equal. However, in view of the short M-N distance,⁸ and the fact that NO⁺ and CN⁻ are isoelectronic, it is likely that the nitrosyl will cause the CN ligand *trans* to it to be displaced if the Cr-C bonds are all equal.

We have placed water solutions of K₃[Cr(CN)₅NO] in the presence of equimolar and of excess 87% K¹³CN. In neither case do we observe any difference in the ESR spectrum from that of a plain solution of [Cr(CN)₅NO]³⁻. This means that either (a) no measurable exchange of CN, axial or equatorial, takes place under these conditions over 41 h; or (b) ¹³CN exchange takes place in the axial positions *but* no hyperfine interaction is observed from this carbon. We have obtained ligand exchange by other means² and have observed the spectrum of a sample containing a mixture of singly and doubly substituted ¹³CN. The intensity ratios of the lines due to the two species (mono and di substituted with ¹³C) was 45/13. This ratio is what one would predict from simple collision theory for four equivalent sites if one knows that there is 45% single substitution. This suggests that no axial CN exchange took place since it is unlikely that no hyperfine splitting would be observed from the axial carbon.

(4) Let us identify the lines of a spectrum by their nuclear quantum number in the order of decreasing size of the hyperfine splitting constant; i.e., |Cr, C^a, N), where C^a is axial carbon and C^e is equatorial carbon. Let us also, arbitrarily, use negative values of the nuclear quantum numbers to label the low-field lines. Then, the weak low-field line due to ¹³C shown on Fig. 1 must be the - $\frac{3}{2}$, - $\frac{1}{2}$, -1 line. If it were, instead, the | - $\frac{3}{2}$, - $\frac{1}{2}$, 0) line, there would be another line (the | - $\frac{3}{2}$, - $\frac{1}{2}$, -1) line) 5.45 G down field from it where the arrow shows in the figure. Since such a line is not present in the observed spectrum, we assign this line to a ¹³CN carbon with a splitting of 11.90 G.

(5) The insistence in differentiating between the axial and the equatorial ligand ¹³C splitting is, aside from mere accounting, because it has a very strong bearing on the bonding picture prevailing in the nitrosyl compounds. In particular, it has a strong bearing on the ligand field scheme presented recently by Gray, Bernal, and Billig^{6a} who described the M-NO bond as similar to the VO bond.⁹ It will be shown in forthcoming publications^{2,7} that this representation predicts correctly the expected ¹³C (CN) and N (NO) splittings in Cr(CN)₅NO³⁻ and Fe(CN)₅NO³⁻.

Regarding the vanadyl system, Ballhausen and Gray⁸ used the fact that no N hyperfine splitting was observed in vanadyl porphines by some investigators¹⁰ to justify their assignment of the unpaired VO electron to a low-lying nonbonding *b*₂ orbital. We agree with the assignment but since the system Cr(CN)₅NO³⁻ also contains an unpaired electron in a low-lying nonbonding *b*₂ orbital, we feel that their argument cannot be correct in view of the fact that we observe a large equatorial

¹³C splitting. It is probably more correct to say that since vanadyl compounds give broad ESR lines, the N lines are blurred. In the Cr(CN)₅NO³⁻ the linewidth is unusually narrow for a transition metal compound in solution at room temperature (about 1 G).

¹ I. Bernal and E. F. Hockings, Proc. Chem. Soc., **1962**, 361. ¹³C splittings in this compound have also been observed here in a heavily labeled sample. These measurements will be reported elsewhere.⁶

² I. Bernal and S. E. Harrison, "ESR of ¹³C Enriched Pentacyanonitrosyl Cr(I)" (to be published).

³ R. G. Hayes, J. Chem. Phys. **38**, 2580 (1963) (preceding letter).

⁴ I. Bernal and S. E. Harrison, J. Chem. Phys. **34**, 102 (1961). ⁵ F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* (John Wiley & Sons, Inc., New York, 1958).

⁶ (a) H. B. Gray, I. Bernal, and E. Billing, J. Am. Chem. Soc. **84**, 3404 (1962); (b) I. Bernal and H. B. Gray, "Optical and ESR measurement on Fe nitrosyl dithiocarbamate" (to be published).

⁷ I. Bernal and E. F. Hockings "Optical and ESR measurements of pentacyanonitrosyl Fe(I)" (to be published).

⁸ They range from about 1.5 to 1.7 Å; see J. Lewis, Sci. Progr. (London) **47**, 506 (1959).

⁹ C. J. Ballhausen and H. B. Gray, Inorg. Chem. **1**, III (1962).

¹⁰ E. M. Roberts, W. S. Koski, and W. S. Caughey, J. Chem. Phys. **34**, 591 (1961).

Erratum: Spin Hamiltonian of Chromium (III) in a Cubic Field

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[J. Chem. Phys. **37**, 3020 (1962)]

EQUATIONS (2) and (3) are incorrect in this note. The correct expression for *u* is¹

$$u = -\frac{2}{15} \frac{5}{2} (g - 2.0023)^3.$$

This predicts a value of *u* = 7.6 × 10⁻⁷ for Cr(NH₃)₆³⁺ which is still too small to explain the observed value of *u*. The arguments and conclusions stated in the note are not affected by this error.

¹ F. S. Ham, G. W. Ludwig, G. D. Watkins, and H. H. Woodbury, Phys. Rev. Letters **5**, 468 (1960).

Erratum: Proton NMR Spectra of Disubstituted Benzenes

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[J. Chem. Phys. **37**, 2594 (1962)]

IN Table I, the subdeterminants should be indicated by grouping the entries thusly: 1S₂, (1S₁, 2S₁), (1S₀, 2S₀, 3S₀, 4S₀), (1S₋₁, 2S₋₁), 1S₋₂, (1A₁, 2A₁), (1A₀, 2A₀), (1A₋₁, 2A₋₁). In the listing of absorption (not adsorption) lines in Table II, the primes should be on the state symbols, not on their subscripts.

In line 8 of Table VII, the chemical shifts of *p*-bromoanisole should be 0.567 and -0.043 ppm.