

967. *Properties of Pentacyanonitrosylferrates.*

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Electron-spin resonance (e.s.r.) and visible absorption spectra of blue solutions obtained by photo-irradiation of solutions of disodium pentacyanonitrosylferrate in *NN*-dimethylformamide are identical with the spectra obtained from an electrolytically reduced solution of disodium pentacyanonitrosylferrate in *NN*-dimethylformamide. The products of photo-irradiation of tetrabutylammonium pentacyanonitrosylferrate in a variety of donor solvents yield e.s.r. spectra which are similar to those obtained from electrolytically reduced solutions in *NN*-dimethylformamide. It is concluded that irradiated solutions of pentacyanonitrosylferrate in electron-rich solvents contain $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$. Electrolytically and photochemically generated samples of labelled $[\text{Fe}^{13}\text{C}(\text{CN})_5\text{NO}]^{3-}$ were studied, and the hyperfine interactions are discussed with reference to a particular energy level scheme. The small axial ^{13}C hyperfine interaction is interpreted as indicative of a $b_{1(x^2-y^2)}$ ground state orbital for the ion $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$.

RECENT studies on nitrosyl co-ordination compounds such as $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$,¹⁻³ bis(*NN*-dimethyldithiocarbamato) nitrosyliron(II)^{4,5} (this compound will subsequently be referred to as $\text{FeNO}(\text{DTC})_2$), and the $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ anion⁶ have provided a guide for the understanding of the electronic energy level scheme prevailing in these substances. In particular, Gray, Bernal, and Billig⁴ have presented a molecular orbital diagram (Fig. 1), which is of a general nature and applicable to the class of compounds $\text{L}_5\text{M}-\text{NO}$ where L is any ligand. This diagram was derived for axial complexes under the assumption that the M-NO bond is the dominant interaction in the ligand field. The other five ligands act as perturbations, more or less strong, which modify the spacing of the energy levels to different degrees, depending on the specific case. This model has been applied to some of these compounds. Preliminary results have already been presented for two nitrosyls of iron^{4,6} and the delocalisation of the unpaired electron in certain metal-nitrosyl complexes has been discussed.

The preparation and detailed spectral data on $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ will be described. Hitherto, only a summary⁶ has been given of the results obtained on the product of the one-electron reduction of the nitroprusside ion $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ in *NN*-dimethylformamide. The previous work has been extended to include reduced samples of nitroprusside containing ^{13}C ligands.

The e.s.r. spectrum of material obtained by the method given by Manchot, Merry, and Woringer⁷ for the preparation of $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ will be discussed in connection with the relation of this material to the anion obtained electrolytically. Also,

¹ Bernal and Harrison, *J. Chem. Phys.*, 1961, **34**, 102.

² Bernal and Harrison, *J. Chem. Phys.*, 1963, **38**, 2581.

³ Gray and Ballhausen, *J. Chem. Phys.*, 1962, **36**, 1151.

⁴ Gray, Bernal, and Billig, *J. Amer. Chem. Soc.*, 1962, **84**, 3404; Gibson, *Nature*, 1962, **196**, 64.

⁵ Bernal and Gray, to be published.

⁶ Bernal and Hockings, *Proc. Chem. Soc.*, 1962, 361.

⁷ Manchot, Merry, and Woringer, *Ber.*, 1912, **45**, 2869.

e.s.r. and visible absorption data concerning the nature of the species studied by Baudisch⁸ will be presented.

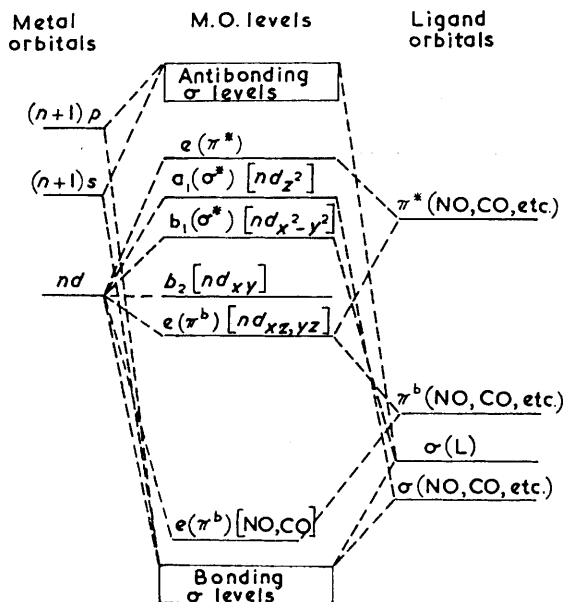


FIG. 1. Energy level scheme for L_5M-NO complexes.

EXPERIMENTAL

Materials.—Hydrated crystals of reagent grade sodium nitroprusside, $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ were used without further purification. The crystals were crushed to a fine powder which was dissolved in *NN*-dimethylformamide. The solvent was of a quality suitable for spectroscopic purposes.

In order to examine nitroprusside in a series of solvents in which the sodium salt was insufficiently soluble, a specimen of tetrabutylammonium nitroprusside was prepared. This was obtained by the action of a solution of tetrabutylammonium iodide upon a suspension of silver nitroprusside. The product was isolated in the form of brown crystals giving the typical reactions of a nitroprusside and soluble in *NN*-dimethylformamide, acetonitrile, acetylacetone, cyclopentanone, pyridine, benzaldehyde, and *NN*-dimethylaniline.

Two methods were used to prepare paramagnetic species containing ^{13}C . The first was the electrolytic reduction of sodium ^{13}C nitroprusside in the presence of potassium ^{13}C cyanide. The reduction will be described subsequently. Sodium nitroprusside in which about 30% of the molecules were heavily labelled with ^{13}C cyanide ligands was used in the second method. The starting material for the synthesis of the labelled nitroprusside was potassium 87% ^{13}C cyanide and this was converted into sodium 87% ^{13}C ferrocyanide. To the material containing ^{13}C some ^{12}C ferrocyanide was added as a carrier so that $^{13}C : ^{12}C$ became 1 : 2, and then the mixture was converted into sodium nitroprusside by the action of sodium nitrite in the presence of barium chloride and carbon dioxide.⁹

Preparation of Paramagnetic Species.—(1) *Electrolytic reduction.* The cell consisted of two compartments separated by a fritted glass disk of fine porosity and had a mercury cathode. The electrolyte solution was $5 \times 10^{-3}M$ in $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ and $5 \times 10^{-2}M$ in tetrabutylammonium iodide, which was used as a supporting electrolyte, in *NN*-dimethylformamide. During electrolysis the colour of the solution changed from very pale pink to blue. The samples used for both e.s.r. and optical measurements were taken with a syringe to reduce contact with air.

The electrolytic preparation of paramagnetic species containing ^{13}C was accomplished by exposing 2 ml. of an aqueous solution, which was 0.25M in $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ and 1.5M

⁸ Baudisch, *Science*, 1948, **108**, 443.

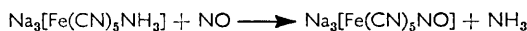
⁹ Palmer, "Experimental Inorganic Chemistry," University Press, Cambridge, 1954, p. 524.

in potassium [¹³C]cyanide, to the light from a 60 w incandescent lamp for a period of 2½ hr.,¹⁰ after which the solution was made up to 50 ml. with *NN*-dimethylformamide. The solubility of potassium cyanide in *NN*-dimethylformamide is low and some of the cyanide came out of solution. The liquid was reduced at a mercury cathode and the e.s.r. spectrum was then obtained.

(2) *Photo-irradiation.* Solutions were irradiated by the output from an induction-coupled plasma torch using argon and powered by a 10 kw, 5 Mc./sec. generator. The maximum total radiant energy output from a 2 cm. diameter plasma sphere was measured by a thermopile to be 1500 w. In the range 4000—3100 Å, the power was 230 w, and between 3100—2400 Å was 75 w. Solutions were irradiated for approximately 1 minute at a distance of about 1 cm. from the plasma. Specimens were kept at room temperature by water cooling and irradiated in optical cells or fused silica capillaries for spectral examination.

Solutions irradiated and then examined for e.s.r. included sodium nitroprusside in *NN*-dimethylformamide and in water, and tetrabutylammonium nitroprusside in acetylacetone, cyclopentanone, pyridine, benzaldehyde, p-nitrobenzaldehyde, and *NN*-dimethylaniline.

(3) *Chemical reaction.* The preparation of Na₃[Fe(CN)₅NO] was described by Manchot, Merry, and Woringer,⁷ who used the reaction



in aqueous solution with acetic acid to absorb the liberated ammonia. Nitric oxide was passed through a solution that was 10⁻²*M* in both Na₃[Fe(CN)₅NH₃] and acetic acid and under nitrogen. Several colour changes were observed: the solution became brown-red and then blue-green before finally depositing a blue precipitate. The brown-red solution was rapidly transferred to a specimen tube and examined by e.s.r. In view of the observed instability of the solution, optical measurements were not attempted.

Spectral Measurements.—Optical. The optical measurements were made in a Cary model 14M spectrophotometer over the frequency range 10,000—33,000 cm.⁻¹, 1 cm. fused silica cells being used.

Microwave. The e.s.r. measurements were made in a Varian spectrometer with 100 kc./sec. modulation. The magnetic field measurements were calibrated by means of a proton-resonance gaussmeter coupled to a counter. The modulation amplitude was about 0.32 gauss.

RESULTS AND DISCUSSION

The visible absorption spectrum of the blue solution obtained by the electrolytic reduction of sodium nitroprusside in *NN*-dimethylformamide showed an absorption band at 16,500 cm.⁻¹ (half-height width of 4200 cm.⁻¹), which was estimated, from coulometric considerations, to have a molar extinction coefficient, ϵ , of 1500. There was possibly another absorption band in the region of 25,000 cm.⁻¹ ($\epsilon \sim 5000$), but this was not clearly resolved. The spectrum of a photo-irradiated solution of sodium nitroprusside in *NN*-dimethylformamide showed an absorption band at the same frequency and of the same half-width as that found in the electrolytically reduced material.

The electrolytically reduced solution of sodium nitroprusside in *NN*-dimethylformamide exhibited strong e.s.r. absorption, as shown in Fig. 2. The three absorption lines are of equal intensity and approximately evenly spaced. Details of the spectral results are given in the Table.

The e.s.r. spectrum of the photochemically prepared species in *NN*-dimethylformamide showed the same triplet as that given by the electrolytically reduced solution and was also the same in the solvents acetylacetone and pyridine. In cyclopentanone, the triplet was observed to have a strong line superimposed on the low field component. In water, the photo-irradiated solution gave a single broad line of moderate intensity. The aqueous solution obtained by the method of Manchot, Merry, and Woringer also showed a single broad line, but this was of low intensity and decayed completely within 10 minutes.

A solution in *NN*-dimethylformamide, reduced electrolytically in the presence of potassium [¹³C]cyanide gave the e.s.r. spectrum shown in Fig. 3. Photo-irradiation of

¹⁰ MacDiarmid and Hall, *J. Amer. Chem. Soc.*, 1953, **75**, 5204.

sodium [^{13}C]nitroprusside in *NN*-dimethylformamide produced a solution having an e.s.r. spectrum shown in Fig. 4. The triplet of Fig. 2 has superimposed upon it the hyperfine line structure of Fig. 3. The simultaneous appearance of both spectra occurred because the specimen contained [^{12}C]nitroprusside and [^{13}C]nitroprusside. It is seen that both the

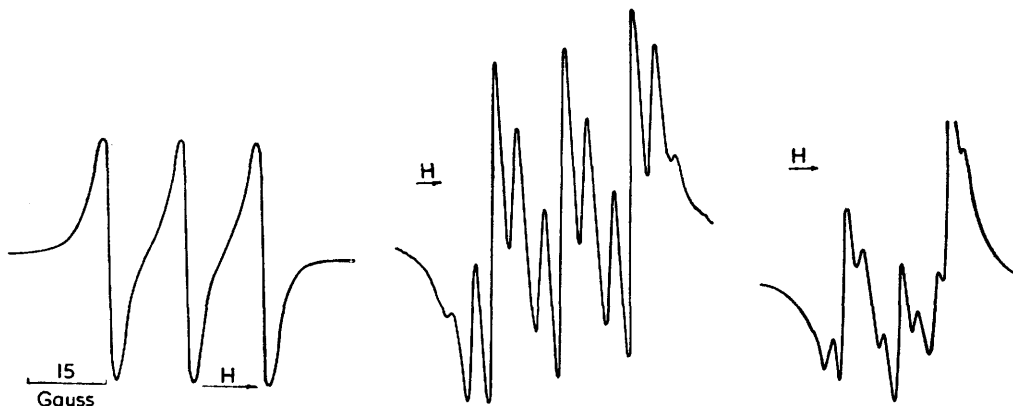


FIG. 2.

FIG. 3.

FIG. 4.

FIG. 2. The e.s.r. spectrum of $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ at 9.492 Gc./sec.

FIG. 3. The e.s.r. spectrum of $[\text{Fe}(^{13}\text{C})_5(\text{NO})]^{3-}$ prepared by electrolytic exchange and reduction.

FIG. 4. The e.s.r. spectrum of $[\text{Fe}(^{13}\text{C})_5\text{NO}]^{3-}$ prepared by photochemical reduction.

electrolytic and photochemical methods of preparation of paramagnetic species containing [^{13}C] led to spectra in which each line of the original triplet (Fig. 2) is split into five hyperfine lines.

Spectral figures for reduced nitroprusside.

Method of preparation	Spectral region				
	Optical		Microwave		
	ν (cm^{-1})	ϵ	$a(^{14}\text{N})$ (gauss)	g	$a(^{13}\text{C})$ (gauss)
Electrolytic	16,500	1500	14.9	2.0253	4.6
Photochemical	16,500	—	14.7—15.0 *	2.0253	4.6 †

* Depending upon solvent. † In *NN*-dimethylformamide.

Nature of the Reduced Species.—The electrolytic reduction of sodium nitroprusside in aqueous solution at a dropping mercury electrode has been shown¹¹ to proceed in stages, of which the first is the addition of a single electron. Sodium nitroprusside can also be reduced by hydrogen in the presence of the enzyme hydrogenase,¹² to give blue solutions. Thus, the blue solutions here prepared both electrolytically and by photo-irradiation probably contain the anion $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$. This implies that irradiation causes the *NN*-dimethylformamide solvent to donate an electron to the nitroprusside ion. This is not improbable, since electron transfer is known¹³ to occur when strong electron-acceptors are dissolved in *NN*-dimethylformamide. The visible absorption spectrum can be compared with that of the dithiocarbamate complex, $\text{FeNO}(\text{DTC})_2$, as the compounds are iso-electronic and have the same effective symmetry. The dithiocarbamate showed⁴ an absorption band at $17,100 \text{ cm}^{-1}$ ($\epsilon = 1200$). As the nitrosyl group dominates the overall ligand field, the optical absorption spectrum should be similar for the two compounds,

¹¹ Kolthoff and Toren, *J. Amer. Chem. Soc.*, 1953, **75**, 1197.

¹² Krasna and Rittenberg, *J. Amer. Chem. Soc.*, 1955, **77**, 5295.

¹³ Rieger, Bernal, and Fraenkel, *J. Amer. Chem. Soc.*, 1961, **83**, 3918.

and the presence of the axial cyano-group in the reduced anion acts as a perturbation on the energy levels observed for the dithiocarbamate-complex. Thus, by analogy, the transition observed in the pentacyanonitrosylferrate at $16,500\text{ cm.}^{-1}$ is assigned as $b_1(\sigma^*) \rightarrow e(\pi^*)$.

The e.s.r. spectra of the reduced species in *NN*-dimethylformamide (Fig. 2) indicate that the species was paramagnetic with an electronic ground state that was orbitally non-degenerate. The three lines arise from interaction of the unpaired electron with the nucleus of the nitrogen of the nitrosyl ligand. Similar interactions have been observed in the anion pentacyanonitrosylchromate(II)¹ and in $\text{FeNO}(\text{DTC})_2$ ⁴. Since the reduction of nitroprusside is considered to be a single-electron reversible process, there would result a $3d^7$ configuration, which in C_{4v} symmetry becomes $e^4b_2^2b_1^1$ with an electronic ground state 2B_1 . This accords with the observed electron spin resonance.

The single broad line in the microwave spectrum of the aqueous solutions obtained by the action of nitric oxide on $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ suggests that the preparative methods used here did not give the reduced nitroprusside ion; it is, however, possible that the various relaxation mechanisms available to a sample undergoing decomposition may broaden the three component lines into a single line spectrum. Photo-irradiated solutions of sodium nitroprusside in water gave a single broad line resonance and contained a blue-green precipitate, which was probably Prussian blue. The paramagnetic species was not stable, but its lifetime was longer than that of the chemically generated species. The single broad line spectrum could be due to a species such as $\text{Fe}(\text{CN})_5\text{X}$ ($\text{X} = \text{OH}$ or H_2O), as such a compound would be iso-electronic with $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ and would be expected to give electron resonance absorption.

Oxidation Product of the Donor.—Photo-excitation of solutions of nitroprusside is thought to lead to simple electron transfer reactions. With *NN*-dimethylformamide, acetylacetone, and pyridine the cation radical forms of the donor molecule are not expected to be stable. With aromatic species such as benzaldehyde, *p*-nitrobenzaldehyde, or dimethylaniline one might expect e.s.r. lines due to their cations, but this was only observed with cyclopentanone. This ketone has also been observed to give e.s.r. lines when used as a donor to organic compounds.¹⁴ It is concluded that, for all the other cases, the generated cation decomposes or polymerizes to diamagnetic species.

The only effect that was observed in the e.s.r. upon changing the donor was a slight variation in the constant of the nitrogen hyperfine splitting. This effect is probably due to a solvent perturbation of the nitrosyl group; such solvent effects upon the hyperfine splittings of polarizable substances are well documented for the vanadyl system¹⁵ and for organic free radicals.¹⁶

The g-Factor.—The electronic energy levels in the systems $\text{FeNO}(\text{DTC})_2$ and $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ are probably similar, since they both have dominant axial ligand fields created by the M-NO interactions. The *g*-factors should also reflect this similarity, since the spin-orbit admixtures of excited states with the ground states would be similar. The detailed visible absorption spectrum of $\text{FeNO}(\text{DTC})_2$ permitted⁴ the prediction of the anisotropic components of the tensor to be 2.04 and 2.02 for the parallel and perpendicular directions, respectively. The usual averaging of the two components leads to a calculated value of $g = 2.027$, and this is in agreement with the measured value of 2.025. This agreement supports the suggestion that $\text{FeNO}(\text{DTC})_2$ and $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ have similar level schemes.

Species Containing ¹³CN.—The crystal structure of sodium nitroprusside was recently studied by Manoharan and Hamilton,¹⁷ who found that there is a short Fe-N distance of 1.6 Å and five Fe-C bonds with approximately equal bond lengths of 1.91 Å. Consequently,

¹⁴ Lagercrantz and Yhland, *Acta Chem. Scand.*, 1962, **16**, 1807.

¹⁵ Bernal and Rieger, *Inorg. Chem.*, 1963, **2**, 256.

¹⁶ Gendell, Freed, and Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2832.

¹⁷ Manoharan and Hamilton, *Inorg. Chem.*, 1963, **2**, 1043.

if the five Fe-C bonds are equal in $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$, the labelled compounds should show hyperfine lines from the axial ^{13}C together with hyperfine lines from the equatorial ^{13}C groups. However, no axial components were observable in any of the experiments, whether electrolytic or photochemical. Labelled paramagnetic species gave e.s.r. spectra that showed only a series of five hyperfine lines arising from the four equatorial ligands; this indicates either that the axial CN ligand leaves the complex upon reduction, or that the electron-spin interaction with the axial ^{13}C nucleus is not observed.

The electrolytic exchange experiments could conceivably produce a mixture of partially labelled complexes. If 50% of the ions were mono-substituted and 15% di-substituted with ^{13}C ligands in the equatorial positions, there could arise a spectrum that would resemble Fig. 3. For that case, the value of $a(^{13}\text{C})$ would be 9.2 gauss. However, the spectrum of reduced nitroprusside synthesized from K^{13}CN shows that $a(^{13}\text{C})$ is 4.6 gauss.

The d.c. polarographic measurements of Kolthoff and Toren¹¹ indicate that the first reduction wave of the nitroprusside ion is a reversible, one-electron process. Although loss of the axial CN ligand could take place by means of a relatively slow, secondary process, there is no direct evidence for this.

If no axial CN elimination occurs during the reduction of the nitroprusside ion and the five CN ligands are assumed to remain approximately equivalent, the hyperfine splitting arising from the axial ^{13}C is smaller than the line widths of the resolved components. From a consideration of line width and resolution, the maximum value for the axial hyperfine splitting is 3 gauss. This would suggest that the ordering of the orbital energy levels is that shown in Fig. 1. In particular, the ground state orbital is a metal $3d_{z^2-y^2}$ orbital rather than $3d_{z^2}$. The latter assumption would lead to an axial hyperfine splitting that would be larger than the equatorial splitting, and this is apparently not the case.

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