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# ELECTRON SPIN RESONANCE OF TRAPPED ELECTRONS IN IRRADIATED SODIUM NITROPRUSSIDE

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We have found that powdered sodium nitroprusside irradiated with 2-MeV electrons from a linear accelerator becomes strongly paramagnetic. The radiation-induced defects were investigated by ESR with a Varian spectrometer at 9000 Mc/sec.

The spectrum observed exhibits an intense line at $g \sim 2$ with a six-line structure, not well resolved. Solution of the irradiated solid in dimethylformamide shows a well-resolved resonance triplet with $\langle g \rangle = 2.025$ for the central line and an hyperfine splitting of 14.7 G. This spectrum arises from the interaction of an unpaired electron with the $^{14}N$ nucleus of NO and coincides in every respect with the well-known spectrum of

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$|FeI(CN)_5NO|^{3-}$ obtained by electrolytic reduction of the nitroprusside ion. [1]

These results lead to the conclusion that, in consequence of the irradiation, a secondary electron is trapped in an antibonding orbital of the diamagnetic $|FeII(CN)_5NO|^{2-}$, forming the paramagnetic $|FeI(CN)_5NO|^{3-}$, with the $3d^7$ spin-paired configuration for the central ion.

The crystal structure of $Na_2|FeII(CN)_5NO|\ 2H_2O$ has been recently determined[2] and shows the existence of four Fe's in each unit cell, forming linear FeII-NO bonds in two different orientations A and B with respect to the crystalline axes (Fig. 1). A and B are fourfold symmetry axes of the $|FeII(CN)_5NO|^{2-}$ anion which lay in two parallel planes, perpendicular to the c axes and form an angle $\varphi = 110^{\circ}45'$ between them.

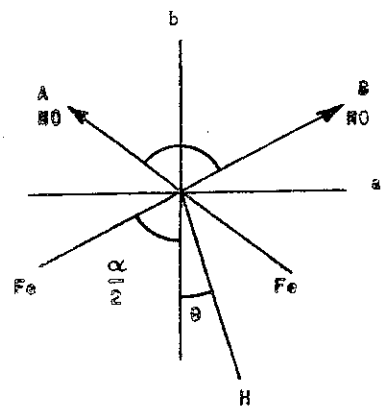


Fig. 1. Relative orientation of the Fe-NO directions in the ab plane.

Single crystals of sodium nitroprusside were irradiated and mounted in such a way that they could be rotated around the c axis, keeping the magnetic field H always in the ab plane. In such conditions the spectrum exhibits a six-line structure resulting from two well-resolved resonance triplets (Fig. 2).

The obsevred variations of the gyromagnetic factor g and of the hyperfine splitting A agree with those calculated from the equations

$$g = \left[ g_{||}^2 \cos^2\left(\tfrac{1}{2}\alpha \pm \theta\right) + g_{\perp}^2 \sin^2\left(\tfrac{1}{2}\alpha \pm \theta\right)\right]^{\frac{1}{2}},$$

$$A = \left[ (g^2/g_{||}^2)\, A_{||}^2 \cos^2\left(\tfrac{1}{2}\beta \pm \theta\right) + (g^2/g_{\perp}^2)\, A_{\perp}^2 \sin^2\left(\tfrac{1}{2}\beta \pm \theta\right)\right]^{\frac{1}{2}},$$

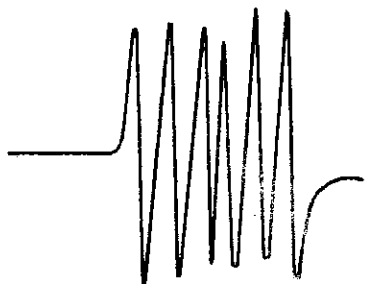

FIG. 2. ESR spectrum of electron-irradiated $Na_2|FeII(CN)_5NO| \cdot 2H_2O$ at an angle $\theta = 50^\circ$.

with $g_{||} = 2.0069$ (along the FeII-NO direction), $g_{\perp} = 2.0374$ (perpendicular to the FeII-NO direction), $\alpha = 102^\circ 15'$, $A_{||} = 16.31$ G, $A_{\perp} = 14.16$ G, and $\beta = 128^\circ$.

The difference between the angle of the two hyperfine axes of the FeI-NO centers ($\beta = 128^\circ$) and that of the original FeII-NO directions ($\varphi = 110^\circ 45'$) could be due to some deviation of linearity of FeII-NO bonds.

On the basis of previous results we have proposed the $e(\pi^b)^4(b_2)^2(a_1)^1$ configuration giving a $^2A_1$ ground state for the $|FeI(CN)_5NO|^{3-}$ molecule, with the unpaired electron in the $d_z^2$ orbital.[3,4] First-order perturbation theory gives for the $^2A_1$ ground state[5]: $g_{||} = 2.0023$, $g_{\perp} = 2.0023 + (6\lambda/\Delta)$, where $\lambda$ is the spin-orbit coupling constant and $\Delta$ the difference in energy between the $^2A_1$ ground state and the $^2E$ excited state.

Comparison with the experimental $g_{||} = 2.0069$ strongly supports the assignment of the unpaired electron in the $d_z^2$ orbital.

The experimental $g_{\perp} = 2.0374$ is fitted by $\lambda = 50$ cm$^{-1}$ and $\Delta = 8.100$ cm$^{-1}$, which are perfectly reasonable values.[6]

We are grateful to the referee who called out attention for the values of anisotropic ESR tensor components of $|FeI(CN)_5NO|^{3-}$ measured in a frozen solution of the complex,[7] which are, within the experimental error, identical to those obtained by us.

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