

An ESR study of $[V(CN)_5NO]^{4-}$ in γ irradiated $K_3V(CN)_5NO_2 \cdot 2H_2O$

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An ESR study of $[\text{V}(\text{CN})_5\text{NO}]^{4-}$ in γ -irradiated $\text{K}_3\text{V}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}^*$

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An ESR study of electron damaged $\text{K}_3\text{V}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ shows the presence of a d^5 species $[\text{V}(\text{CN})_5\text{NO}]^{4-}$ with the spin Hamiltonian parameters $g_{\parallel} = 1.974$, $g_{\perp} = 2.0007$, $A(^{51}\text{V}) = -116.03 \times 10^{-4} \text{ cm}^{-1}$, $B(^{51}\text{V}) = -43.76 \times 10^{-4} \text{ cm}^{-1}$, $A(^{14}\text{N}) = -1.8 \times 10^{-4} \text{ cm}^{-1}$, and $B(^{14}\text{N}) = -6.42 \times 10^{-4} \text{ cm}^{-1}$. Results of a simplified semiempirical molecular orbital approach have been used to correlate the experimental spin Hamiltonian parameters of the isoelectronic d^5 series from vanadium to iron. In addition, the ligand hyperfine splittings due to ^{14}N have been explained on the basis of a configuration interaction mechanism.

INTRODUCTION

Electronic structures of transition metal pentacyanonitrosyls have been fairly well established.^{1,2} Of these, chromium and manganese form well-characterized d^5 complexes and their ESR spectra have been extensively studied.¹⁻¹¹ Electronic structural information has been derived from the observed spin Hamiltonian parameters and, in general, is in accordance with the energy level scheme proposed by Manoharan and Gray¹ based on semiempirical molecular orbital methods. Recently, Bloom *et al.*¹² have identified the isoelectronic d^5 complex $[\text{Fe}(\text{CN})_5\text{NO}]^{4-}$ in γ -irradiated anhydrous $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ making use of the expected variations in the spin Hamiltonian parameters in the isoelectronic sequence. Of the first row transition metal ions, vanadium also forms a pentacyanonitrosyl complex¹³ $\text{V}(\text{CN})_5\text{NO}^{3-}$, but a stable d^5 ion has not been reported and attempts in these laboratories to prepare it have met with failure. We report here, however, an ESR study of a d^5 pentacyanonitrosyl of vanadium produced by irradiation damage of the vanadium (I) salt $\text{K}_3\text{V}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$. We also attempt to explain the electronic structures in the d^5 isoelectronic sequence of pentacyanonitrosyls from vanadium to iron and to account for the observed spin densities on the nitrogens.

EXPERIMENTAL

Potassium pentacyanonitrosyl vanadate (I), $\text{K}_3\text{V}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$, was prepared by the method of Griffith *et al.*¹³ The orange crystalline powder was dried and irradiated using either the 1 meV electron beam of a GE resonant transformer or a ^{60}Co γ -ray source. ESR spectra were obtained at X-band using Varian V-4500 and Varian E-4 spectrometers. Measurements were made both at 77°K and at room temperature. All attempts to grow single crystals of suitable size for ESR work failed and it was also found that the aqueous solution of the complex tended to decompose with time.

RESULTS

The X-band ESR spectrum of electron irradiated $\text{K}_3\text{V}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ at 77°K is shown in Fig. 1. The room temperature spectrum was identical, as were the

spectra obtained on γ -irradiation of the powder, except that the resolution appeared to be somewhat better for the electron damaged complex.

The general features of the spectrum are characteristic of an axially symmetric, randomly oriented $S = \frac{1}{2}$ system with parallel and perpendicular sets of hyperfine lines from interaction with the ^{51}V nucleus, as described by the spin Hamiltonian¹⁴

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

where g_{\parallel} , g_{\perp} , A , and B are the principal values of the g and ^{51}V hyperfine interaction tensors for a system with axial symmetry and Q' is the quadrupole coupling constant for the vanadium nucleus. These parameters were obtained by use of the usual second-order expressions¹⁴; Q' is small and was neglected.

The perpendicular vanadium hyperfine lines were further resolved into equal intensity triplets arising from interaction of the unpaired electron with the single nitrogen nucleus of the NO ligand. The ^{14}N superhyperfine splitting is of the order of 6.8 G as expected for a d^5 complex.¹⁻¹² The parallel part of the spectrum did not show any further resolution but a reasonable estimate of the ^{14}N superhyperfine splitting was obtained from the linewidths of the parallel vanadium lines. Neither spectral abnormalities nor spectra due to additional vanadium-containing species were observed. The measured spin Hamiltonian parameters of the paramagnetic species produced by irradiation are listed in Table I.

DISCUSSION

The pentacyanonitrosyl of vanadium prepared by Griffith *et al.*¹³ was assigned the formula $\text{K}_5\text{V}(\text{CN})_5\text{NO} \cdot \text{H}_2\text{O}$ by them and, accordingly, the electronic spectra were interpreted by Manoharan and Gray² as arising from a $d^6(\text{NO}^+)$ configuration. Subsequently the crystal structure determination¹⁵ showed that the correct formula was $\text{K}_3\text{V}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$, giving it a $d^4(\text{NO}^+)$ configuration. A different assignment for the electronic spectra of this complex is therefore required.

The paramagnetic species produced in this investiga-

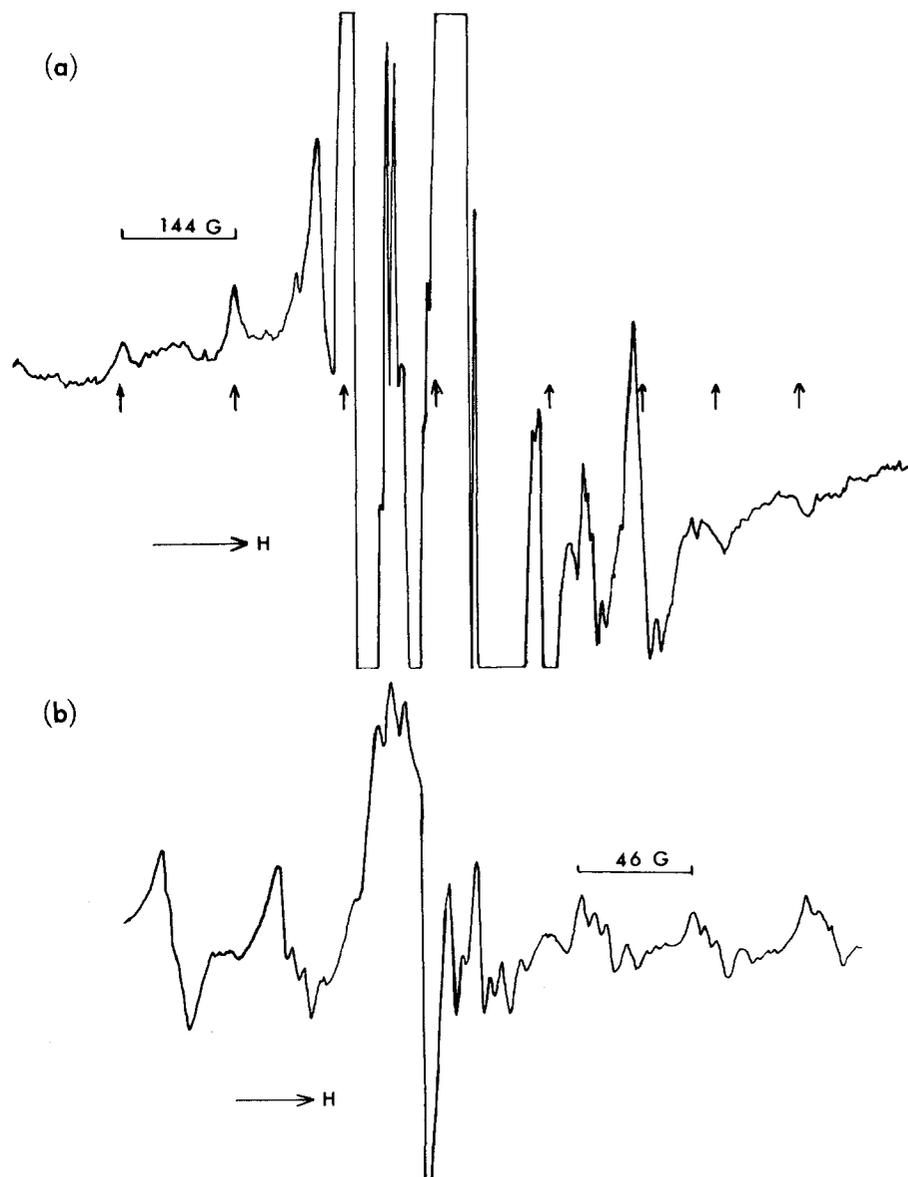


FIG. 1. (a) X-band ESR spectrum of electron irradiated polycrystalline $\text{K}_3\text{V}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$. The arrows indicate the eight lines of the parallel component. (b) The central portion of the above spectrum expanded to show the perpendicular component with resolved nitrogen superhyperfine structure.

tion by electron or γ irradiation of $\text{K}_3\text{V}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ appears to be the complex ion $\text{V}(\text{CN})_5\text{NO}^{4-}$ with configuration $d^5(\text{NO}^+)$. This identification is based on comparison of the observed g , $A(^{51}\text{V})$, and $A(^{14}\text{N})$ tensors with those reported for the known isoelectronic $d^5(\text{NO}^+)$ ions $\text{Cr}(\text{CN})_5\text{NO}^{3-}$, $\text{Mn}(\text{CN})_5\text{NO}^{2-}$, and $\text{Fe}(\text{CN})_5\text{NO}^{1-}$. The values we observe for the vanadium species fit into the sequence and complete the series from vanadium to iron as shown in Table I. The unpaired electron, by analogy with the isoelectronic chromium and manganese complexes,² will therefore have the odd electron in the $2b_2$ orbital with ground state 2B_2 .

Calculation of the molecular orbital coefficients in terms of the spin Hamiltonian parameters is extremely difficult for this case. The relevant equations have been given by Manoharan and Gray² for the chromium and manganese complexes based on the ordering of energy levels which they obtained¹ and including only the most important excitations. Neglecting some less important terms the following simplified versions of their expres-

sions may be written:

$$g_{\parallel} = 2.0023 - \frac{8\lambda(\beta_1^*\beta_2^*)^2}{\Delta E(2b_2 - 3b_1)} + \frac{8\lambda(\beta_1\beta_2^*)^2}{\Delta E(1b_1 - 2b_2)}, \quad (2)$$

$$g_{\perp} = 2.0023 - \frac{2\lambda(\beta_2^*\epsilon^*)^2}{\Delta E(2b_2 - 7e)} + \frac{2\lambda(\beta_2^*\epsilon)^2}{\Delta E(6e - 2b_2)}, \quad (3)$$

$$A = P[-(\beta_2^*)^2(\frac{2}{7} + \kappa) + (g_{\parallel} - 2.0023) + \frac{1}{7}(g_{\perp} - 2.0023)], \quad (4)$$

$$B = P[(\beta_2^*)^2(\frac{2}{7} - \kappa) + \frac{11}{14}(g_{\perp} - 2.0023)], \quad (5)$$

where β_1^* , β_2^* , and ϵ^* are the metal coefficients in the antibonding molecular orbitals $3b_1$, $2b_2$, and $7e$, and β_1 and ϵ are the coefficients corresponding to the orbitals $1b_1$ and $6e$, respectively; λ is the spin-orbit coupling constant; $P = 2g_n\beta_n\beta_e\langle r^{-3} \rangle_{3d}$; and κ is the Fermi contact interaction constant. The g values for all the d^5 nitrosyls are close to the free spin value as a result of the opposing spin-orbit coupling contributions involving excited states with electron transitions and hole transitions.

TABLE I. Experimental and calculated spin Hamiltonian parameters for isoelectronic d^5 pentacyanonitrosyls.

	$\text{V}(\text{CN})_5\text{NO}^{4-}$		$\text{Cr}(\text{CN})_5\text{NO}^{3-}$		$\text{Mn}(\text{CN})_5\text{NO}^{2-}$		$\text{Fe}(\text{CN})_5\text{NO}^{1-}$	
	Obs.	Calc. ^a	Obs. ^b	Calc. ^c	Obs. ^b	Calc. ^c	Obs.	Calc. ^a
g_{\parallel}	1.974	1.961	1.972	1.987	1.992	2.000	2.014	1.983
g_{\perp}	2.007	1.995	2.004	2.004	2.031	2.022	2.072	2.078
g_{av}	1.996		1.994		2.018		2.053	
$A(M)^d$	-116.03	-101.6	30.75		-148.8		...	-17.7
$B(M)$	-43.76	-36.8	11.14		-34.7		...	+3.5
$A(^{14}\text{N})$	(-)1.84		-2.66 ^e		(-)1.78		(-)1.84	
$B(^{14}\text{N})$	(-)6.42		-6.64 ^e		(-)4.5		(-)2.75	
$A_s(^{14}\text{N})_{\text{obs}}$			-4.90 ^f					
Ref.	This work		2,4		2,6		7	

^aCalculated in this investigation.^bOther experimental values are in Refs. 3-12 for $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and $\text{Mn}(\text{CN})_5\text{NO}^{2-}$.^cCalculated values from Reference 2.^dAll hyperfine splitting values are in units of 10^{-4} cm^{-1} .^eThe signs have been determined experimentally (see Refs. 6 and 8).^fReference 4.

We feel that no useful purpose would be served in attempting to calculate the molecular orbital parameters from the ESR data using Eqs. (2)-(5) since the molecular orbitals are quite involved.^{1,2} However, as has been pointed out by Manoharan and Gray,² it may be worthwhile to use these equations to correlate the experimental spin Hamiltonian parameters with a set calculated using the MO coefficients and transition energies obtained from a semiempirical calculation. For this purpose we have performed the same type of Wolfsberg-Helmholz MO calculation on $\text{V}(\text{CN})_5\text{NO}^{4-}$ and $\text{Fe}(\text{CN})_5\text{NO}^{1-}$, as employed by Manoharan and Gray² for $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and $\text{Mn}(\text{CN})_5\text{NO}^{2-}$, so that the entire series of d^5 pentacyanonitrosyls may be compared. The wavefunctions for V^0 and Fe^{2+} employed were those of Richardson *et al.*¹⁶ The MO coefficients and transition energies obtained from the calculations were substituted into Eqs. (2)-(5) to obtain the calculated spin Hamiltonian parameters shown in Table I. The P values used were those for V^0 and Fe^{2+} from McGarvey,¹⁷ the spin-orbit coupling constants ($\lambda = 85.7 \text{ cm}^{-1}$ for V^0 and $\lambda = 345 \text{ cm}^{-1}$ for Fe^{2+}) were from Dunn,¹⁸ and the Fermi contact constants κ were calculated from the expression $A_{\text{iso}} = -P\kappa$, where A_{iso} is the isotropic hyperfine interaction obtained by averaging the anisotropic values. In the case of iron no hyperfine splittings have been reported and κ was therefore estimated as 0.2 by extrapolation from the values 0.79, 0.6, and 0.39 obtained for V, Cr, and Mn.

Although valid criticisms have been raised against the Wolfsberg-Helmholz procedure,¹⁹⁻²² the salient features of some of the ground and excited state properties of transition metal complexes can often be obtained by this method, particularly for an isoelectronic sequence. As shown in Table I, the observed ordering of the g and metal hyperfine splitting values is reproduced reasonably well by the values calculated here, particularly considering the simplicity of the MO calculation and the approximations involved in using Eqs. (2)-(5).

We may compare the covalency, as measured by the transfer of spin density from the metal d_{xy} orbital, in $\text{VO}(\text{CN})_5^{3-}$ and $\text{V}(\text{CN})_5\text{NO}^{4-}$, where each has a 2B_2 ground

state. Decomposing the ^{51}V hyperfine interaction tensors for each in the usual way, we obtain $A_{\text{iso}} = -77.16 \times 10^{-4} \text{ cm}^{-1}$, $A_{\text{aniso}}(^{51}\text{V}) = -59.9 \times 10^{-4} \text{ cm}^{-1}$ for $\text{VO}(\text{CN})_5^{3-}$ using the data of Kuska and Rogers,²³ and $A_{\text{iso}} = -67.8 \times 10^{-4} \text{ cm}^{-1}$, $A_{\text{aniso}}(^{51}\text{V}) = -48.2 \times 10^{-4} \text{ cm}^{-1}$ for $\text{V}(\text{CN})_5\text{NO}^{4-}$. Values of $f_{d_{xy}} = (-59.6 / -73.6) \times 100 = 81\%$ for $\text{VO}(\text{CN})_5^{3-}$ and $f_{d_{xy}} = (-48.2 / -70.7) \times 100 = 68\%$ for $\text{V}(\text{CN})_5\text{NO}^{4-}$ are then obtained using the Hartree-Fock values $A_{\text{aniso}}^0 = 70.67$ and $-73.63 \times 10^{-4} \text{ cm}^{-1}$ for the charge states V^0 and V^{+2} , respectively.²⁴ Although the formal charge on vanadium in $\text{VO}(\text{CN})_5^{3-}$ is 4+, the effective charge is probably closer to 2+, while a formal charge of zero for $\text{V}(\text{CN})_5\text{NO}^{4-}$ appears to be reasonable. The covalency is therefore somewhat larger in the case of $\text{V}(\text{CN})_5\text{NO}^{4-}$.

The unpaired electron of $\text{V}(\text{CN})_5\text{NO}^{4-}$ is in the $2b_2$ MO; hence, the unpaired spin density cannot be placed directly on ^{14}N of nitric oxide, since the nitrogen orbitals do not contribute to the $2b_2$ linear combination. However, the hyperfine interactions of the unpaired electron in the nitrogen orbitals (A_s , $A_{p\sigma}$, $A_{p\pi}$) may be explained by a configuration interaction mechanism.²⁵ Appropriate excited state configurations are obtained by the promotion of an electron from a filled bonding orbital to an unfilled antibonding orbital of the same symmetry. Since $2s$ and $2p\sigma$ orbitals of nitric oxide span the a_1 representation, excited states to be considered are of the type $\dots (na_1)^2 \dots (2b_2)^1 \dots (na_1)^1 \dots (2b_2)^1 (5a_1)^1$, where n will be lower than 5 since $5a_1$ is the first unfilled anti-

TABLE II. Values of $f_{p\pi}$ and $\Delta E(6e \rightarrow 7e)$ in $d^5 \text{M}(\text{CN})_5\text{NO}^{n-}$ ions.

Complex	$f_{p\pi} (^{14}\text{N})$ percent	$\Delta E(6e \rightarrow 7e)$ (in cm^{-1})
$\text{V}(\text{CN})_5\text{NO}^{4-}$	8.0 ^a	14 300 ^b
$\text{Cr}(\text{CN})_5\text{NO}^{3-}$	7.3	22 200 ^c
$\text{Mn}(\text{CN})_5\text{NO}^{2-}$	3.9	25 960 ^c

^aUsing Hartree-Fock values of A_{aniso}^0 from Ref. 24.^bCalculated value using Wolfsberg-Helmholz approximations.^cExperimental value as assigned in Ref. 2.

bonding molecular orbital. Because of the various contributions involved, it will be difficult to calculate theoretical values of the spin densities on nitrogen. However, from the experimental nitrogen hyperfine splitting values we can calculate the spin densities in the nitrogen orbitals. The isotropic splitting $A_s = \frac{1}{3}(A_{zz} + A_{xx} + A_{yy}) = -4.89 \times 10^{-4} \text{ cm}^{-1}$ leads (using the value²⁶ $A_{\text{iso}}^0 = 514 \times 10^{-4} \text{ cm}^{-1}$) to a spin density in the nitrogen $2s$ orbital $f_s = 100 \times (4.89/514) = 0.95\%$ for $\text{V}(\text{CN})_5\text{NO}^{4-}$ and, since $\text{V}-\text{N}-\text{O}$ is approximately linear for d^5 systems, we can safely conclude that $f_{p\sigma} = 0.95\%$ since sp hybridized orbitals of NO will be involved in σ bonding with the metal orbitals. Values of $f_s = f_{p\sigma}(^{14}\text{N})$ are then 0.95%, 1.03%, and 0.67%, respectively, for the vanadium, chromium, and manganese pentacyanonitrosyls (Table I). Assuming that $A_{rx} = A_{ry}$, and correcting for the dipolar term A_d , the nitrogen tensor may be decomposed as follows:

$$A_{zz} = A_s + 2(A_d + A_{p\sigma} - A_{p_r})$$

and

$$A_{xx} = A_{yy} = A_s - (A_d + A_{p\sigma} - A_{p_r}).$$

Then if $f_s = f_{p\sigma} = 0.95\%$, $A_{p\sigma} = -0.0095 \times 15.89 \times 10^{-4} = -0.15 \times 10^{-4} \text{ cm}^{-1}$, $A_d = g\beta g_n \beta_n R^{-3} = +0.4 \times 10^{-4} \text{ cm}^{-1}$, and we obtain $A_{p_r} = -1.275 \times 10^{-4} \text{ cm}^{-1}$ for the ligand hyperfine contribution from the unpaired spin density in the $2p_x$, $2p_y$ orbitals of nitrogen; by the same method we obtain values of A_{p_r} for $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and $\text{Mn}(\text{CN})_5\text{NO}^{2-}$ of $1.16 \times 10^{-4} \text{ cm}^{-1}$ and $0.62 \times 10^{-4} \text{ cm}^{-1}$, respectively. The respective unpaired spin densities in the p_r orbitals are $f_{p_r} = 7.3$ and 3.9% . Again, since the mechanism of spin density transfer would depend on configuration interactions, the most important contributor to spin density in the $2p_r$ orbitals of NO is the excited state configuration $\dots (6e)^4(2b_2)^1 \rightarrow \dots (6e)^3(2b_2)^1(7e)^1$.

The magnitude of the spin density will be inversely proportional to the excitation energy,^{21,22} i. e., to $\Delta E(6e \rightarrow 7e)$. These energy values are 14 300, 22 200, and 25 960 cm^{-1} , respectively, for the vanadium, chromium, and manganese complexes. While the first one is a calculated $6e \rightarrow 7e$ separation by the MO method, the latter two are observed values assigned for these transitions.² Accordingly, the magnitudes of the calculated values of $\%f_{p_r}$ decrease from vanadium to manganese as found in Table II. This again is in fairly good agreement with the nature of energy levels and their separations as calculated from the Wolfsberg-Helmholtz method.

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