Electronic Structure of Nitroprusside Ion

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The bonding in the nitroprusside ion is described in terms of molecular orbitals. The very strong Fe–NO bond dominates the electronic structure of $Fe(CN)_5NO^{2-}$. A detailed SCCC–MO calculation of $Fe(CN)_5NO^{2-}$ gives the d-level ordering $z^2 > x^2 - y^2 > xy > xz,yz$. An important result is that the e level derived mainly from π^*NO is the lowest empty level in $Fe(CN)_5NO^{2-}$, lying between $x^2 - y^2$ and xy. The two absorption bands of $Fe(CN)_5NO^{2-}$ in the visible region are assigned using the derived energy level scheme. The assignments receive substantial support from the measured spectra of a single crystal of $Na_2Fe(CN)_5NO \cdot 2H_2O$ using polarized light and the glass spectrum of $[(n\text{-}C_4H_9)_4N]_2[Fe(CN)_5NO]$ at liquid nitrogen temperature. The assignments of the high-energy bands are also discussed.

Introduction

Nitric oxide forms many interesting complexes[2] with transition metal ions in which the distinguishing structural characteristic is a very short M–N bond,[3] indicating the electronic structure M≡NO. Formally the M≡NO bond is composed of one σ-bond, involving the nitrogen lone pair and available metal σ-orbitals, and two π-bonds, involving filled metal d_π-orbitals and the unusually stable π^*-level of NO. The ionization potential of the electron in the π^*-level of NO is approximately 74,000 cm.$^{-1}$.[4]

There have been many papers written on the electronic energy levels in metal nitrosyls,[5-11] and much disagreement exists. Thus we have chosen to investigate in considerable detail the parent member of the series of metal pentacyanonitrosyl $M(CN)_5NO^{n-}$ complexes, the nitroprusside ion $Fe(CN)_5NO^{2-}$.

In this paper we report a detailed molecular orbital calculation of $Fe(CN)_5NO^{2-}$. An interpretation of

the low- and high-intensity bands is presented which is consistent with the calculated energy levels, the measured spectra of a single crystal of $Na_2Fe(CN)_5NO \cdot 2H_2O$ using polarized light, and the spectrum of $[(n\text{-}C_4H_9)_4N]_2[Fe(CN)_5NO]$ in a glassy matrix at low temperature.

Structure of Nitroprusside Ion

The crystal structure of sodium nitroprusside $Na_2Fe(CN)_5NO \cdot 2H_2O$ has been determined by X-ray diffraction techniques.[12] The crystal is orthorhombic with space group D_{2h}^{12}-Pnnm. The structure of $Fe(CN)_5NO^{2-}$ in the crystal is shown in Figure 1. The nitroprusside ion in the crystal has approximately

Table I. Radial Functions

Iron	
$R(3d)$	$= 0.5366\Phi_3(5.35) + 0.6678\Phi_3(1.80)$
$R(4s)$	$= -0.02078\Phi_1(25.38) + 0.07052\Phi_2(9.75) -$
	$\quad 0.1744\Phi_3(4.48) + 1.0125\Phi_4(1.40)$
$R(4p)$	$= 0.01118\Phi_2(10.60) - 0.03833\Phi_3(4.17) +$
	$\quad 1.00067\Phi_4(0.80)$
$\Phi_n(\mu)$	$= N_\mu r^{n-1} e^{-\mu r}$

MO's for CN and NO[a]	
$\Psi(\sigma CN)$	$= -0.0943\Phi(1s_C;5.2309) + 0.0054\Phi(1s_C;7.9690)$
	$\quad +0.0950\Phi(2s_C;1.1678) + 0.2738\Phi(2s_C;1.8203)$
	$\quad +0.5613\Phi(2p_C;1.2557) + 0.1824\Phi(2p_C;2.7262)$
	$\quad -0.0508\Phi(1s_N;6.1186) + 0.0034\Phi(1s_N;8.9384)$
	$\quad +0.0547\Phi(2s_N;1.3933) + 0.1354\Phi(2s_N;2.2216)$
	$\quad -0.5192\Phi(2p_N;1.5058) - 0.1879\Phi(2p_N;3.2674)$
$\Psi(\pi^b CN)$	$= -0.4188\Phi(2p_C;1.2557) + 0.1361\Phi(2p_C;2.7262)$
	$\quad +0.5338\Phi(2p_N;1.5058) + 0.1932\Phi(2p_N;3.2674)$
$\Psi(\pi^* CN)$	$= 0.7535\Phi(2p_C;1.2557) + 0.2448\Phi(2p_C;2.7262)$
	$\quad -0.6505\Phi(2p_N;1.5058) - 0.2354\Phi(2p_N;3.2674)$
$\Psi(\sigma NO)$	$= 0.0217\Phi(1s_N;6.7) + 0.0192\Phi(1s_O;7.7)$
	$\quad +0.4727\Phi(2s_N;1.95) + 0.2368\Phi(2s_O;2.275)$
	$\quad +0.6149\Phi(2p_N;1.95) - 0.5794\Phi(2p_O;2.275)$
$\Psi(\pi^b NO)$	$= 0.5232\Phi(2p\pi_N;1.95) + 0.7508\Phi(2p_O;2.275)$
$\Psi(\pi^* NO)$	$= 0.8781\Phi(2p\pi_N;1.95) - 0.6936\Phi(2p_O;2.275)$

[a] Coordinate scheme as shown in Figure 1. The functions are normalized.

C_{4v} symmetry, with axial compression resulting from a very short Fe–N bond distance of 1.63 Å. This unusually short Fe–N distance confirms that the NO group is strongly bonded to the metal. The strong Fe–NO bonding probably dominates the over-all electronic structure of the nitroprusside ion. The Fe–N–O and Fe–C–N groupings are linear; the Fe atom is slightly displaced in the direction of the NO group from the plane of the four C atoms. The five C–N distances and the five Fe–C distances are not significantly different. The important bond dis-

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Table II. Orbital Transformations in C_{4v} Symmetry and Ligand–Ligand Overlap Corrections for H_{ii}

Irreducible representation	Row	Metal orbitals	Ligand orbitals	Ligand–ligand overlap corrections[a]
A_1	1	$3d_{z^2}, 4s, 4p_z$	σ_5	1.0
			σ_6	1.0
			$\frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$	1.1628
			$\frac{1}{2}(\pi^b_{1v} + \pi^b_{2v} + \pi^b_{3v} + \pi^b_{4v})$	1.0359
			$\frac{1}{2}(\pi^*_{1v} + \pi^*_{2v} + \pi^*_{3v} + \pi^*_{4v})$	1.0701
A_2	1	$\ldots$	$\frac{1}{2}(\pi^b_{1h} + \pi^b_{2h} + \pi^b_{3h} + \pi^b_{4h})$	0.9035
			$\frac{1}{2}(\pi^*_{1h} + \pi^*_{2h} + \pi^*_{3h} + \pi^*_{4h})$	0.8400
B_1	1	$3d_{x^2-y^2}$	$\frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$	0.8437
			$\frac{1}{2}(\pi^b_{1v} - \pi^b_{2v} + \pi^b_{3v} - \pi^b_{4v})$	0.9662
			$\frac{1}{2}(\pi^*_{1v} - \pi^*_{2v} + \pi^*_{3v} - \pi^*_{4v})$	0.9328
B_2	1	$3d_{xy}$	$\frac{1}{2}(\pi^b_{1h} - \pi^b_{2h} + \pi^b_{3h} - \pi^b_{4h}$	1.0780
			$\frac{1}{2}(\pi^*_{1b} - \pi^*_{2h} + \pi^*_{3b} - \pi^*_{4b})$	1.1108
E	1	$3d_{xz}, 4p_x$	$\pi^b_x(5), \pi^b_x(6)$	1.0
			$\frac{1}{\sqrt{2}}(\pi^b_{1v} - \pi^b_{3v})$	1.0
			$\frac{1}{\sqrt{2}}(\pi^b_{2h} - \pi^b_{4b})$	1.0
			$\pi^*_x(5), \pi^*_x(6)$	1.0
			$\frac{1}{\sqrt{2}}(\pi^*_{1v} - \pi^*_{3v})$	0.9942
			$\frac{1}{\sqrt{2}}(\pi^*_{2h} - \pi^*_{4b})$	1.0050
			$\frac{1}{2}(\sigma_1 - \sigma_3)$	0.9849
	2	$3d_{yz}, 4p_y$	$\pi^b_y(5), \pi^b_y(6)$	1.0
			$\frac{1}{\sqrt{2}}(\pi^b_{2v} - \pi^b_{4v})$	1.0
			$\frac{1}{\sqrt{2}}(\pi^b_{1b} - \pi^b_{3h})$	1.0
			$\pi^*_y(5), \pi_y^*(6)$	1.0
			$\frac{1}{\sqrt{2}}(\pi^*_{2v} - \pi^*_{4v})$	0.9942
			$\frac{1}{\sqrt{2}}(\pi^*_{1b} - \pi^*_{3b})$	1.0050
			$\frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4)$	0.9849

[a] For $H_{ii}(1 + 2x_i)/1 + x_i)$; corrections made as described in ref. 13.

tances (Å.) are: Fe–N, 1.63 ± 0.02; N–O, 1.13 ± 0.02; Fe–C, 1.90 ± 0.02; C–N, 1.16 ± 0.02.

Molecular Orbitals for $Fe(CN)_5NO^{2-}$

The coordinate system and the numbering used are shown in Figure 1. The method of calculation has been reported in detail in a previous paper.[13] The iron 3d-, 4s-, and 4p-orbitals were used for the calculation. Radial functions used for iron are those given by Richardson, et al.[14] The valence orbitals taken for CN were obtained from a separate molecular orbital calculation. The functions used for NO are those calculated by Brion, Moser, and Yamazaki.[15] The highest occupied σ-orbital and the π-bonding and π-antibonding orbitals of NO and CN were included in the final calculation of $Fe(CN)_5NO^{2-}$. The method of calculation of the CN functions is given in the Appendix. Table I gives the wave functions used in the MO calculation. Orbital transformations in C_{4v} symmetry are given in Table II. Ligand–ligand overlap corrections summarized in Table II were included in the calculation. The numerical values of the group overlaps G_{ij} for $Fe(CN)_5NO^{2-}$ are given in Table III.

The secular equations are of the order $8(a_1)$, $2(a_2)$, $4(b_1)$, $3(b_2)$, and $11(e)$. The eigenvalues and eigenvectors were obtained by solving the secular equation $|H_{ij} - G_{ij}E| = 0$ using an IBM 7094 program. The resonance integrals were approximated as $H_{ij} = -FG_{ij}(H_{ii}H_{jj})^{1/2}$ where H_{ii} and H_{jj} are the diagonal elements uncorrected for the ligand–ligand overlap.

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The first calculation was performed using $F = 2.00$ for all H_{ij}. The calculated level scheme was used to assign the spectrum of $Fe(CN)_5NO^{2-}$. After certain assignments were confirmed by measuring single crystal
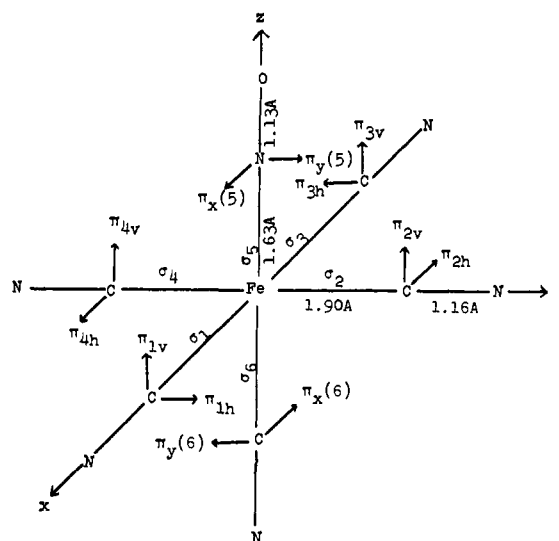
Figure 1. The structure of $Fe(CN)_5NO^{2-}$ and coordinate system for molecular orbitals.

spectra, the F factors were adjusted slightly to give calculated one-electron separations in very close agreement with the "observed" separations derived from the electronic spectrum. The adjusted F factors are 2.20 for the $\sigma(Fe-NO)$ and $\sigma(Fe-CN)$ interactions and 2.00 for all π–π and ligand–ligand interactions. As

Figure 2. Molecular orbital energy levels for $Fe(CN)_5NO^{2-}$.

usual, a Mulliken population analysis[16] was carried out for the occupied levels, yielding the effective charge and configuration of Fe. The calculation was repeated until a self-consistent charge and configuration (SCCC) for Fe was obtained. The final charge obtained for Fe in $Fe(CN)_5NO^{2-}$ is $+0.317$, with the configuration $3d^{6.983}4s^{0.449}4p^{0.251}$.

The Coulomb integrals H_{ii} for the atomic orbitals of iron were taken as the valence orbital ionization potentials (VOIP's). The iron VOIP's have been tabulated elsewhere.[17] The H_{ii}'s for NO and CN were calculated from the ionization potentials and appropriate spectroscopic transition energies of these molecules.[18] The ligand Coulomb integrals were corrected for ligand–ligand overlap. Uncorrected H_{ii}'s are given in Table IV. The final calculated MO eigenvectors for $Fe(CN)_5NO^{2-}$ are given in Table V.

Discussion

Order of Levels. The calculated one-electron MO energy levels for $Fe(CN)_5NO^{2-}$ are given in Table VI. A diagram of the energy levels is given in Figure 2. By including the σ-, π^b-, and π^*-orbitals for both CN and NO, we obtained the d-orbital ordering suggested earlier.[7] There is net axial destabilization of the $5a_1(z^2)$ orbital and this results in the ordering $5a_1$ $(z^2) > 3b_1(x^2 - y^2)$. It should be noted, however, that $5a_1(z^2)$ and $3b_1(x^2 - y^2)$ are not substantially different in

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Table III. Group Overlap Integrals[a]

A₁	$G_{A_1}(3d, \sigma_{NO})$	= 0.1996
	$G_{A_1}(3d, \sigma_{CN\ comb})$	= -0.1202
	$G_{A_1}(3d, \sigma_{CN})$	= 0.1314
	$G_{A_1}(4s, \sigma_{NO})$	= 0.2406
	$G_{A_1}(4s, \sigma_{CN\ comb})$	= 0.4803
	$G_{A_1}(4s, \sigma_{CN})$	= 0.2625
	$G_{A_1}(4p, \sigma_{NO})$	= 0.1564
	$G_{A_1}(4p, \sigma_{CN})$	= 0.0941
	$G_{A_1}(\sigma_{NO}, \sigma_{CN\ comb})$	= 0.1246
	$G_{A_1}(\sigma_{NO}, \sigma_{CN})$	= 0.0186
	$G_{A_1}(\sigma_{CN}, \sigma_{CN\ comb})$	= 0.1513
	$G_{A_1}(4p, \pi^b_{comb})$	= 0.3700
	$G_{A_1}(4p, \pi^*_{comb})$	= 0.2987
	$G_{A_1}(\pi^b_{comb}, \pi^*_{comb})$	= 0.0507
A₂	$G_{A_2}(\pi^b_{comb}, \pi^*_{comb})$	= -0.1251
B₁	$G_{B_1}(3d, \sigma_{CN\ comb})$	= 0.2447
	$G_{B_1}(\pi^b_{comb}, \pi^*_{comb})$	= -0.0484
B₂	$G_{B_2}(3d, \pi^b_{comb})$	= 0.1678
	$G_{B_2}(3d, \pi^*_{comb})$	= 0.2389
	$G_{B_2}(\pi^b_{comb}, \pi^*_{comb})$	= 0.0938
E[b]	$G_E(3d, \pi^b_x(6))$	= 0.0874
	$G_E(3d, \pi^b_{v\ comb})$	= 0.1237
	$G_E(3d, \pi^b_x(5))$	= 0.0979
	$G_E(3d, \pi^*_x(6))$	= 0.1267
	$G_E(3d, \pi^*_{v\ comb})$	= 0.1797
	$G_E(3d, \pi^*_x(5))$	= 0.1417
	$G_E(4p, \pi^b_x(6))$	= -0.1884
	$G_E(4p, \pi^b_x(5))$	= 0.1116
	$G_E(4p, \pi^b_{h\ comb})$	= -0.2664
	$G_E(4p, \pi^*_x(6))$	= -0.1549
	$G_E(4p, \pi^*_x(5))$	= 0.0814
	$G_E(4p, \pi^*_{h\ comb})$	= -0.2197
	$G_E(4p, \sigma^b_{comb})$	= 0.1351
	$G_E(\pi^b_x(6), \pi^b_{v\ comb})$	= 0.0609
	$G_E(\pi^b_x(6), \pi^b_x(5))$	= -0.0010
	$G_E(\pi^b_x(6), \pi^b_{h\ comb})$	= 0.0338
	$G_E(\pi^b_x(6), \pi^*_{v\ comb})$	= 0.0759
	$G_E(\pi^b_x(6), \pi^*_x(5))$	= -0.0015
	$G_E(\pi^b_x(6), \pi^*_{h\ comb})$	= 0.0419
	$G_E(\pi^b_{v\ comb}, \pi^b_x(5))$	= 0.0681
	$G_E(\pi^b_{v\ comb}, \pi^*_{v\ comb})$	= -0.0037
	$G_E(\pi^b_{v\ comb}, \pi^*_x(5))$	= 0.0419
	$G_E(\pi^b_{v\ comb}, \pi^*_x(6))$	= 0.0759
	$G_E(\pi^b_x(5), \pi^b_{h\ comb})$	= -0.0130
	$G_E(\pi^b_x(5), \pi^*_x(6))$	= -0.0018
	$G_E(\pi^b_x(5), \pi^*_{v\ comb})$	= 0.0568
	$G_E(\pi^b_x(5), \pi^*_{h\ comb})$	= -0.0223
	$G_E(\pi^b_{h\ comb}, \pi^*_x(6))$	= 0.0252
	$G_E(\pi^b_{h\ comb}, \pi^*_x(5))$	= -0.0301
	$G_E(\pi^b_{h\ comb}, \pi^*_{h\ comb})$	= 0.0037
	$G_E(\pi^*_x(6), \pi^*_{v\ comb})$	= -0.0931
	$G_E(\pi^*_x(6), \pi^*_x(5))$	= -0.0026
	$G_E(\pi^*_x(6), \pi^*_{h\ comb})$	= 0.0485
	$G_E(\pi^*_{v\ comb}, \pi^*_x(5))$	= 0.0682
	$G_E(\pi^*_x(5), \pi^*_{h\ comb})$	= -0.0293

[a] "comb" refers to the various linear combinations of orbitals given in Table II. [b] For group overlaps in E representation, the values are given for the first row in the orbital transformation scheme. They are the same for row 2.

Table IV. Uncorrected Coulomb Integrals (H_{ii})

Orbital	Energy, 10^3 cm.$^{-1}$
3d	-96.48
4s	-76.91
4p	-42.66
σNO	-118.74
π^bNO	-120.05
π^*NO	-74.61
σCN	-112.90
π^bCN	-122.00
π^*CN	-30.00[a]

[a] Value taken from results on metal hexacyanide complexes; J. Alexander and H. B. Gray, to be published.

Table V. MO Eigenvectors for Fe(CN)₅NO²⁻

MO	3d	4s	4p	σNO	Axial σCN	Eq. σCN	π^bNO
1a₁	0.0457	0.3004	0.0013	0.3192	0.2842	0.5972	
2a₁	0.5675	−0.0372	−0.0363	0.5807	0.1054	−0.4226	
3a₁	−0.0533	0.0001	0.0741	−0.0497	−0.0105	0.0325	
4a₁	0.1985	−0.0038	−0.0050	−0.5112	0.8316	−0.1871	
5a₁	0.7368	−0.0246	−0.4590	−0.4228	−0.3805	0.4184	
6a₁	−0.2916	0.0763	−0.2186	0.2117	0.1599	−0.2363	
7a₁	0.2556	−0.6036	−0.8268	−0.1503	−0.0499	0.5593	
8a₁	0.1906	0.9870	0.6275	−0.4618	−0.4078	−0.4646	
1a₂							
2a₂							
1b₁	0.6412					0.6264	
2b₁							
3b₁	−0.8078					0.8194	
4b₁							
1b₂	0.3133						
2b₂	−0.9513						
3b₂	0.2862						
1e	0.3155		−0.0084			−0.0007	0.4027
2e	−0.0443		−0.0721			−0.0154	−0.4140
3e	0.0111		0.0069			0.0041	−0.5384
4e	−0.0011		0.0768			0.9867	−0.0251
5e	0.0258		−0.0005			0.0144	0.5661
6e	−0.7820		−0.0111			0.0050	0.2105
7e	0.5537		−0.0480			0.0129	−0.1350
8e	−0.0615		−0.4791			0.0128	0.1068
9e	0.0379		0.1204			−0.0251	0.0107
10e	−0.2610		−0.2118			0.0427	0.0219
11e	0.0931		−0.9739			0.1887	0.1005

MO	Axial π^bCN	π^b_v	π^b_h	π*NO	Axial π*CN	π*$_v$	π*$_h$
1a₁		−0.0001				−0.0003	
2a₁		0.0644				−0.0067	
3a₁		0.9681				−0.0160	
4a₁		0.0040				0.0008	
5a₁		0.2153				−0.1079	
6a₁		0.1376				−0.8594	
7a₁		−0.3251				−0.5286	
8a₁		−0.2454				−0.2803	
1a₂			0.9979				−0.0158
2a₂			−0.1417				−1.0078
1b₁							
2b₁		0.9999				−0.0017	
3b₁							
4b₁		−0.0500				−1.0012	
1b₂			0.9035				−0.0334
2b₂			0.4646				−0.0638
3b₂			−0.0010				−1.0289
1e	0.4394	0.6131	0.0676	0.0452	−0.0203	−0.0261	−0.0012
2e	0.4749	−0.1113	0.7080	−0.0375	−0.0054	0.0016	−0.0110
3e	0.5416	0.0325	−0.6675	0.0373	−0.0002	−0.0001	+0.0023
4e	0.0188	0.0074	0.0468	−0.0022	0.0057	0.0004	0.0081
5e	0.4866	−0.7223	−0.1084	−0.0593	−0.0083	0.0104	0.0011
6e	0.1866	0.3265	−0.0657	−0.4511	−0.0182	−0.0297	0.0021
7e	−0.1321	−0.0523	−0.0707	−0.8909	0.0780	0.0418	0.0182
8e	−0.0929	−0.0324	−0.1551	0.1431	0.4405	−0.2076	0.5838
9e	0.0974	−0.0695	−0.0218	0.0170	0.5469	−0.6032	−0.5425
10e	−0.0450	0.0216	−0.0765	0.0360	0.5908	0.7873	−0.3742
11e	−0.1831	0.0180	−0.2790	0.0598	−0.4630	−0.1621	−0.5289

energy. Also, the 2b₂(xy) orbital is less stable than the 6e(xz,yz) level. The new and most interesting result of the calculation, however, is the fact that the 7e orbital, derived mainly from π*NO, lies between the 2b₂(xy) and 3b₁($x^2 - y^2$) orbitals. This result allows an interpretation of the spectrum of Fe(CN)₅NO²⁻ which is consistent with all the electronic spectral information available.

Ground-State Configuration. There are 42 electrons to place in the molecular orbitals shown in Figure 2.

Thus the ground state is . . .(6e)⁴(2b₂)² = ¹A₁. The effective electronic configuration of iron is 3d⁶, and Fe(CN)₅NO²⁻ *formally* contains Fe(II) and NO⁺. The calculated ground state is consistent with the observed diamagnetism of the complex ion. The calculated final charge distribution in the molecule is [(Fe)⁺⁰·³¹⁶⁶(CN)₄⁻²·²⁰⁰⁰(CN)⁻⁰·⁵⁸⁰⁹(NO)⁺⁰·⁴⁶⁴³]. It is interesting to compare the compositions of the highest-filled MO's, 6e and 2b₂. Population analysis of these two levels shows that the 2b₂ level is about
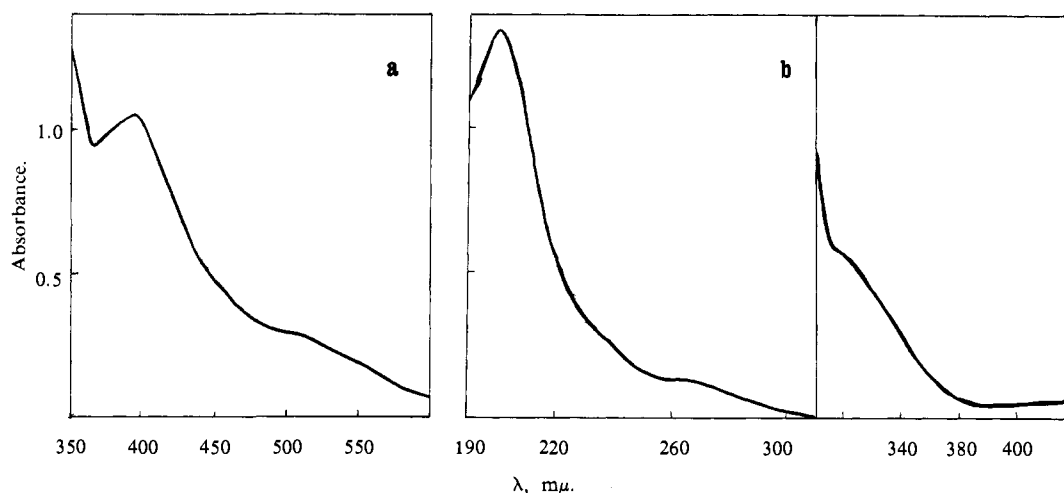
Figure 3. Electronic spectrum of $Fe(CN)_5NO^{2-}$ in aqueous solution: (a) visible spectrum of 4.2×10^{-2} M $Na_2Fe(CN)_5NO \cdot 2H_2O$; (b) ultraviolet spectrum of $Na_2Fe(CN)_5NO \cdot 2H_2O$; right curve, 4×10^{-3} M; left curve, 1.045×10^{-4} M. (1-cm. path length.)

84.5% d_{xy}, 13.9% $\pi^b CN$, and only 1.6% $\pi^* CN$. Thus the degree of Fe→CN back-bonding is relatively slight. In contrast, the 6e level is 24.8% $\pi^* NO$, indicating substantial Fe→NO back-bonding. This correlates quite well with the observed $\bar{\nu}(N-O)$ in $Fe(CN)_5NO^{2-}$ which is 1900 cm.$^{-1}$ in a $CHCl_3$ solution of $[(n\text{-}C_4H_9)_4N]_2[Fe(CN)_5NO]$ and 1944 cm.$^{-1}$ in a KBr disk or Nujol mull.[19] Although the 1900-

Table VI. Calculated One-Electron MO Energies for $Fe(CN)_5NO^{2-}$

MO	Energy, cm.$^{-1}$	MO	Energy, cm.$^{-1}$
1a$_1$	−153,450	2b$_2$	−86,100
1e	−136,700	7e	−65,560
1b$_2$	−136,260	3b$_1$	−52,530
2a$_1$	−129,520	5a$_1$	−51,050
3a$_1$	−126,890	8e	−36,000
2e	−126,150	6a$_1$	−34,200
1b$_1$	−122,160	9e	−30,110
2b$_1$	−117,880	3b$_2$	−28,050
3e	−117,420	4b$_1$	−27,760
4a$_1$	−111,200	2a$_2$	−23,480
1a$_2$	−110,250	10e	−22,020
4e	−109,850	11e	−10,030
5e	−109,200	7a$_1$	−4,260
6e	−90,670	8a$_1$	+27,730

cm.$^{-1}$ value lies *between* $\bar{\nu}(N-O)$ = 1876 cm.$^{-1}$ for gaseous NO[20] and $\bar{\nu}(N-O)$ = 2275 cm.$^{-1}$ for NO^+,[21] it is very close to the neutral $\bar{\nu}(N-O)$ value. Roughly, the calculation suggests that $\bar{\nu}(N-O)$ in $Fe(CN)_5NO^{2-}$ should be between the values for NO and NO^+, but much closer to the NO value.

The low-lying excited states that would be obtained on exciting an electron from the 2b$_2$ and 6e levels are listed in Table VII.

Electronic Spectrum of Fe(CN)$_5$NO^{2-}. The spectrum of $Fe(CN)_5NO^{2-}$ in aqueous solution is shown in

(19) F. A. Cotton, R. R. Monchamp, R. J. M. Henry, and R. C. Young, *J. Inorg. Nucl. Chem.*, **10**, 28 (1959).
(20) E. L. Saier and A. Pozefsky, *Anal. Chem.*, **26**, 1079 (1954).
(21) D. J. Millen and D. Watson, *J. Chem. Soc.*, 1369 (1957).

Figure 3. There are two weak bands in the visible region of the spectrum, at 20,080 (ϵ ~8) and 25,380 cm.$^{-1}$ (ϵ 25), and one intense band in the ultraviolet region, at 50,000 cm.$^{-1}$ (ϵ 24,000). In addition there are three shoulders on the low-energy side of the intense band, at 30,300 (ϵ ~40), 37,800 (ϵ 900), and 42,000 cm.$^{-1}$ (ϵ 700). All six bands are too intense to be spin-forbidden; thus in discussing the possible assignments of the $Fe(CN)_5NO^{2-}$ spectrum we shall only consider spin-allowed transitions. Further, we shall make use of the fact that, in C_{4v} symmetry with an A$_1$ ground state, only transitions to A$_1$ and E states are orbitally allowed.

Table VII. Electronic Spectrum of $Fe(CN)_5NO^{2-}$

Obsd.,[a] cm.$^{-1}$	ϵ_{max}	Calcd.,[b] cm.$^{-1}$	Band assignments
20,080($\perp$)	~8	20,540 ($\perp$)	$^1A_1 \rightarrow {}^1E$ (2b$_2 \rightarrow$ 7e)
25,380($\parallel$)	25	25,090 ($\parallel$)	$^1A_1 \rightarrow {}^1A_1$ (6e $\rightarrow$ 7e)
(30,300)[c]	(40)[c]	30,770[d]	$^1A_1 \rightarrow {}^1A_2$ (2b$_2 \rightarrow$ 3b$_1$)
(37,800)[c]	(900)[c]	37,750[d] ($\perp$)	$^1A_1 \rightarrow {}^1E$ (6e $\rightarrow$ 5a$_1$)
(42,000)[c]	(700)[c]	40,900[d] ($\perp$)	$^1A_1 \rightarrow {}^1E$ (6e $\rightarrow$ 3b$_1$)
50,000	24,000	49,900 ($\perp$)	$^1A_1 \rightarrow {}^1E$ (2b$_2 \rightarrow$ 8e)

[a] Observed maxima (for an aqueous solution spectrum of $Na_2Fe(CN)_5NO \cdot 2H_2O$) and polarizations (from the single crystal spectra). [b] Calculated energies and polarizations. [c] Shoulder, ϵ_{max} values are estimated. [d] Corrected for interelectronic-repulsion energy, assuming $F_2 = 10F_4$. The Slater–Condon parameters are from ref. 7a. The value of $(F_2 - 5F_4)$ = 400 cm.$^{-1}$ from the $Fe(CN)_6^{4-}$ spectrum was assumed for $Fe(CN)_5NO^{2-}$. Configuration interaction between the two closely-spaced ^1E states was included.

From the metal-based MO's 6e and 2b$_2$, relatively low-energy transitions are possible to the 7e($\pi^* NO$) level and to the 3b$_1(x^2 - y^2)$ and 5a$_1(z^2)$ orbitals. A ^1E state is obtained from the excitation of an electron from 2b$_2$ to the 7e($\pi^* NO$) level. From the one-electron transition 6e(xz, yz) → 7e($\pi^* NO$) are obtained the excited singlet states $^1A_1$, $^1A_2$, $^1B_1$, and $^1B_2$. Since only a transition to the $^1A_1$ state is orbitally allowed, the other states will not be considered.

Thus, using the level scheme shown in Figure 2, we assign the first shoulder at 20,080 cm.$^{-1}$ and the band at 25,380 cm.$^{-1}$ as the transitions $^1A_1 \rightarrow {}^1E$ ($2b_2 \rightarrow 7e$) and $^1A_1 \rightarrow {}^1A_1$ ($6e \rightarrow 7e$), respectively. The predicted one-electron energies, uncorrected for interelectronic repulsion energies, are 20,540 and 25,090 cm.$^{-1}$. These calculated values are very close to the observed values.

The $^1A_1 \rightarrow {}^1A_2$ ($2b_2 \rightarrow 3b_1$) orbitally forbidden transition logically accounts for the weak shoulder at 30,300 cm.$^{-1}$. This is essentially a d–d transition from the $2b_2(xy)$ orbital to the $3b_1(x^2 - y^2)$ orbital. Support for this assignment is derived from the fact that a similar d–d band at 31,000 cm.$^{-1}$ is observed in Fe(CN)$_6{}^{4-}$ ion.[22] One expects the $xy \rightarrow x^2 - y^2$ separation to be about the same in Fe(CN)$_6{}^{4-}$ and Fe(CN)$_5$NO^{2-}, because the ligand interactions are about the same in the xy plane. The predicted transition energy, after correcting for interelectronic repulsions, is 30,770 cm.$^{-1}$, in close agreement with the observed value.

The broad shoulder at 37,800 cm.$^{-1}$ may be assigned as the electronic transition from the $6e(xz,yz)$ level to the $5a_1(z^2)$ level. The predicted energy of this $^1A_1 \rightarrow {}^1E$ ($6e \rightarrow 5a_1$) transition, corrected for interelectronic repulsion, is 37,750 cm.$^{-1}$ and is very close to the observed value. The shoulder at 42,000 cm.$^{-1}$ may be assigned to the orbitally allowed transition from $6e(xz,yz)$ to $3b_1(x^2 - y^2)$. The predicted energy, corrected for interelectronic repulsion, is 40,900 cm.$^{-1}$, in reasonable agreement with the observed energy.

The intense band at 50,000 cm.$^{-1}$ is most likely the M $\rightarrow$ L charge-transfer band involving the transfer of an electron from the $2b_2(xy)$ orbital to the $8e(\pi^*CN)$ level. The predicted orbital energy of 49,900 cm.$^{-1}$ compares quite well with the observed energy of 50,000 cm.$^{-1}$. A similar M $\rightarrow$ L band is found in Fe(CN)$_6{}^{4-}$ at 45,000 cm.$^{-1}$.

In summary, the electronic absorption spectrum of Fe(CN)$_5$NO^{2-} consists of two relatively low-energy bands of metal(d) $\rightarrow \pi^*$NO character, three shoulders in the 30,000–45,000-cm.$^{-1}$ range assigned to d–d transitions, and an intense metal(d) $\rightarrow \pi^*$CN band at 50,000 cm.$^{-1}$. Strong support for this assignment scheme comes from the fact that the spectrum of Fe(CN)$_5$NO^{2-} can be directly derived from the spectrum of Fe(CN)$_6{}^{4-}$. The metal(d) $\rightarrow \pi^*$CN band is at 45,000 cm.$^{-1}$ in Fe(CN)$_6{}^{4-}$ and at 50,000 cm.$^{-1}$ in Fe(CN)$_5$NO^{2-}. Since the difference in the energies of π^*NO and π^*CN can be closely estimated at ca. 44,000 cm.$^{-1}$ (with π^*NO more stable) from ionization potential and spectroscopic data, the metal(d) $\rightarrow \pi^*$NO bands in Fe(CN)$_5$NO^{2-} are expected to be found at relatively low energies, the exact positions depending on the degree of antibondedness of the 7e level derived from π^*NO. Thus the lowest electronic bands, at 20,080 and 25,380 cm.$^{-1}$, are logically the metal(d) $\rightarrow \pi^*$NO bands. Finally, the two d–d bands in Fe(CN)$_6{}^{4-}$ are at 31,000 ($^1A_{1g} \rightarrow {}^1T_{1g}$) and 37,000 cm.$^{-1}$ ($^1A_{1g} \rightarrow {}^1T_{2g}$). With the level ordering $xz,yz < xy < x^2 - y^2 < z^2$, the three bands in the 30,000–45,000-cm.$^{-1}$ range in Fe(CN)$_5$NO^{2-} may be consistently assigned as d–d transitions. The 31,000-cm.$^{-1}$ band in Fe(CN)$_6{}^{4-}$ and the 30,300-cm.$^{-1}$ band in

(22) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

Fe(CN)$_5$NO^{2-} both represent the in-plane transition $xy \rightarrow x^2 - y^2$. The fact that their transition energies are so similar is strong evidence in favor of the assignment in the case of Fe(CN)$_5$NO^{2-}.

Low-Temperature Spectrum of Fe(CN)$_5$NO^{2-}. The electronic absorption spectrum of Fe(CN)$_5$NO^{2-} at liquid nitrogen temperature was studied by freezing [$(n$-C$_4$H$_9)_4$N]$_2$[Fe(CN)$_5$NO] in an EPA glass. The EPA solution absorption spectrum of [$(n$-C$_4$H$_9)_4$-N]$_2$[Fe(CN)$_5$NO] at room temperature and the glass spectrum at liquid nitrogen temperature are shown in Figure 4. The first band, at 20,080 cm.$^{-1}$ in an aqueous
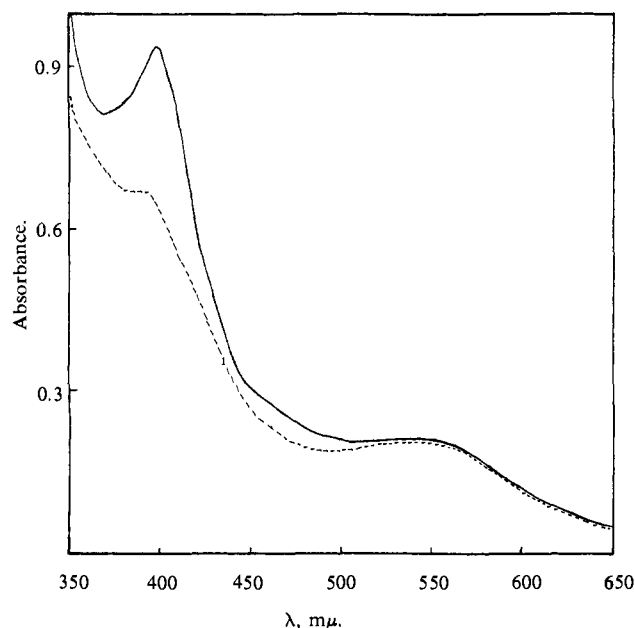

Figure 4. Electronic spectra of [$(n$-C$_4$H$_9)_4$N]$_2$[Fe(CN)$_5$NO] in EPA solution: dashed curve, 2×10^{-2} M solution at 300°K.; solid curve, 2×10^{-2} M frozen solution at 77°K. The band at 18,650 cm.$^{-1}$ has oscillator strength $f = 1.76 \times 10^{-4}$ at 300 and 77°K. The band at 25,380 cm.$^{-1}$ has $f = 6.29 \times 10^{-4}$ at 300°K. and $f = 6.57 \times 10^{-4}$ at 77°K. (1.332-cm. path length).

solution of Na$_2$Fe(CN)$_5$NO·2H$_2$O, is red-shifted to 18,650 cm.$^{-1}$ in EPA solution. The second band is located at 25,380 cm.$^{-1}$, not appreciably shifted from its aqueous solution value. The most important result is that the intensities of the first two bands are not appreciably affected in going from 300 to 77°K. The shape and oscillator strength f of the first band do not change from room to low temperature, but the 25,380-cm.$^{-1}$ band is slightly more intense at 77°K. Since there is no net decrease in intensity in either case, we conclude that the electronic transitions responsible for these two bands are orbitally allowed. This result is therefore consistent with our assignments of the two bands as orbitally allowed transitions from the $2b_2(xy)$ and the $6e(xz,yz)$ levels to the $7e(\pi^*$NO) level.

Polarized Crystal Spectra of Na$_2$Fe(CN)$_5$NO·2H$_2$O. The electronic absorption spectra of a single crystal of Na$_2$Fe(CN)$_5$NO·2H$_2$O were determined with the electric vector of light polarized both parallel ($\parallel$) and perpendicular ($\perp$) to the a axis of the crystal.

These spectra were analyzed to find the complete band polarizations of all optically equivalent molecular Fe–NO groups. The details of the analysis are found in the Experimental section. These spectra are shown in Figure 5. The positions of the shoulder and the band in the visible region found for the crystal do not
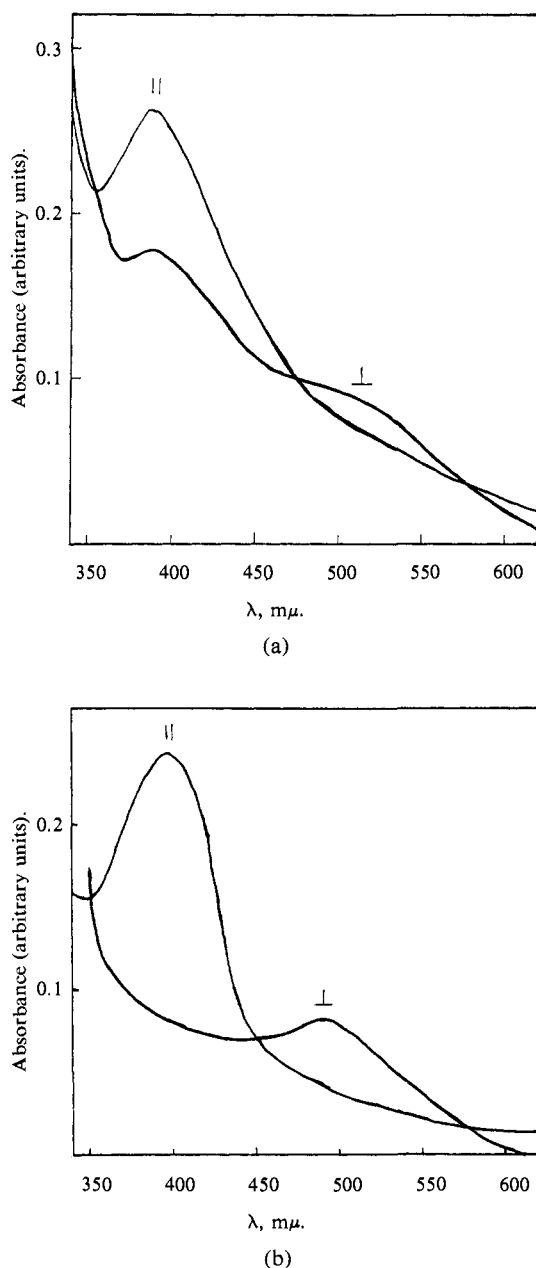

(a)

(b)

Figure 5. (a) Measured spectra of a single crystal of $Na_2Fe(CN)_5$-$NO \cdot 2H_2O$, using light with electric vector polarized parallel and perpendicular to the a axis. (b) Corrected spectra for the electric vector polarized parallel and perpendicular to optically equivalent Fe–NO axes.

differ significantly from the positions found for an aqueous solution containing $Fe(CN)_5NO^{2-}$. This, of course, is compelling evidence that the structure of $Fe(CN)_5NO^{2-}$ is essentially the same in solution and in the crystal. The first two bands are found at 20,400 and 25,640 cm.$^{-1}$ in the unpolarized single crystal

spectrum. Although the first two bands mutually overlap and also are both overlapped by higher energy bands, the single crystal spectra clearly show that the 20,400-cm.$^{-1}$ band appears in $\perp$ or x,y polarization, while the 25,640-cm.$^{-1}$ band is definitely $\parallel$ or z polarized. The observed polarizations are thus consistent with the transition assignments given above, as follows: 20,400 cm.$^{-1}$, $^1A_1 \rightarrow {}^1E$ ($2b_2 \rightarrow 7e$); 25,640 cm.$^{-1}$, $^1A_1 \rightarrow {}^1A_1$ ($6e \rightarrow 7e$).

Electronic Structure of $Fe(CN)_5NO^{3-}$. The complex ion $Fe(CN)_5NO^{3-}$ has been generated electrolytically and photochemically and its properties have been studied.[2c,9,11b,23,24] E.s.r. results are consistent with a nonlinear Fe–N–O grouping in $Fe(CN)_5NO^{3-}$. There is also X-ray evidence that Co–N–O in $Co[S_2-CN(C_2H_5)_2]_2NO$ is nonlinear.[3a] From interelectronic-repulsion considerations we suggest that all metal nitrosyls with one or more electrons in molecular orbitals derived *mainly* from π^*NO will have a bent M–N–O system. Since the exact symmetry will vary from case to case, the two resulting nondegenerate orbitals in the metal nitrosyl complex will be called π^*_1NO and π^*_2NO, with the energy order $\pi^*_1NO < \pi^*_2NO$.

Retaining the C_{4v} symmetry symbols for convenience for the other levels, the ground-state electronic configuration of $Fe(CN)_5NO^{3-}$ is $(6e)^4(2b_2)^2(\pi^*_1NO)^1$. This configuration indicates that $Fe(CN)_5NO^{3-}$ formally consists of Fe(II) and NO, *i.e.*, the odd electron is mainly localized on the NO. Griffith had concluded earlier that the $Fe(CN)_5NO^{3-}$ complex contains a neutral NO ligand.[1c] It should be emphasized, however, that although the 7e level is principally π^*NO (population analysis gives 72.53% π^*NO), it contains some d_π, σCN, πCN, and π^*CN contributions. Experimental evidence for the delocalized nature of the 7e level is the equatorial ^{13}C splitting of 4.5 gauss observed[25] in $Fe(CN)_5NO^{3-}$.

Strong evidence in support of this ground-state assignment comes from the fact that $\langle A \rangle_N = 14.8$ gauss for $Fe(CN)_5NO^{3-}$. The ^{14}N hyperfine splitting of 14.8 gauss in $Fe(CN)_5NO^{3-}$ is substantially larger than the isotropic ^{14}N splitting observed in $Cr(CN)_5NO^{3-}$ ($\langle A \rangle_N = 5.32$ gauss).[10] The ground-state electronic structure of the latter complex is $(6e)^4(2b_2)^1$, according to our energy levels for $Fe(CN)_5NO^{2-}$. Thus the unpaired electron in this electronic structure is *mainly* d in character and is confined to π-interaction with the four CN^- ligands in the x,y plane. Further support for the assignment of $Fe(CN)_5NO^{3-}$ as Fe(II) and NO is derived from the fact that –NO and –NO$_2$ containing organic radicals and radical ions, in which the unpaired electron has a high probability of being on the N, have similar $\langle A \rangle_N$ values. For example, nitrobenzene radical anion has $\langle A \rangle_N = 13.87$ gauss,[26a] p-nitrophenol radical anion has $\langle A \rangle_N = 14.60$ gauss,[26a] and di(t-butyl) nitroxide has $\langle A \rangle_N = 15.18$ gauss.[26b] It is also interesting that isolated NO has $\langle A \rangle_N = 14.2 \pm 0.2$ gauss.[27] The striking similarity

(23) I. Bernal and E. F. Hockings, *Proc. Chem. Soc.*, 361 (1962).
(24) J. B. Raynor, *Nature*, 201, 1216 (1964).
(25) E. F. Hockings and I. Bernal, *J. Chem. Soc.*, 5029 (1964).
(26) (a) L. H. Piette, P. Ludwig, and R. N. Adams, *J. Am. Chem. Soc.*, 84, 4212 (1962); (b) H. Lemaire, A. Rassat, and P. Servoz-Gavin, *J. chim. phys.*, 59, 1247 (1962).
(27) C. Jaccard, *Phys. Rev.*, 124, 60 (1961).

of the isotropic N splittings in $Fe(CN)_5NO^{3-}$ and NO is suggestive of our assigned electronic structure of $Fe(CN)_5NO^{3-}$. However, many factors contribute to the $\langle A \rangle_N$ and isolated NO is probably not as good a comparison molecule as the organic radicals cited above.

Finally, we turn to the level scheme proposed recently for $M(CN)_5NO^{n-}$ complexes by McNeil, Raynor, and Symons.[9] These authors proposed the ordering $xz,yz < xy < z^2 < x^2 - y^2$, which gives the ground state $(xz,yz)^4(xy)^2(z^2)^1$ for $Fe(CN)_5NO^{3-}$. Now that we have shown that the π^*NO level is almost certainly more stable than either $x^2 - y^2$ or z^2, there appears to be no justification for the assignment of the unpaired electron to the z^2 orbital. In fact, the measured $\langle A \rangle_{13C}$ value for the axial CN^- in $Fe(CN)_5NO^{3-}$ is much smaller than the equatorial $\langle A \rangle_{13C}$ value (equatorial = 4.5 gauss; axial $\leqslant$ 1.5 gauss).[23] This is strong evidence against a $(z^2)^1$ assignment. Indeed, the comparison of $\langle A \rangle_{13C}$ values in $Cr(CN)_5NO^{3-}$ and $Fe(CN)_5NO^{3-}$ is strong evidence for our scheme. For $Cr(CN)_5NO^{3-}$, $\langle A \rangle_{13C}$ = 12.49 gauss for the equatorial CN^- ligands.[10] The smaller equatorial ^{13}C splitting in $Fe(CN)_5NO^{3-}$ is consistent with the $(2b_2)^1$ assignment for $Cr(CN)_5NO^{3-}$ and the $(\pi_1^*NO)^1$ assignment for $Fe(CN)_5NO^{3-}$, since population analysis of the $2b_2$ and $7e$ levels of $Fe(CN)_5NO^{2-}$ gives $2b_2$ = 13.89% π^bCN; 1.58% π^*CN and $7e$ = 0.40% π^bCN (equatorial); 0.33% π^*CN (equatorial); 0.008% σCN (equatorial). Finally, the electronic spectral results for $Fe(CN)_5NO^{2-}$ cannot be accommodated using a scheme with $z^2 < x^2 - y^2$.

We admit that the g_{xx} = 1.9730, g_{yy} = 2.0051, and g_{zz} = 2.0051 values reported[9] by McNeil, Raynor, and Symons for $Cr(CN)_5NO^{3-}$ are certainly not compatible with our assignment of its electronic structure as $(6e)^4(2b_2)^1$. However, we believe the suggested $(xz)^2-(z^2)^2(yz)^1$ structure is unreasonable, particularly in view of the established spectroscopic levels of $Fe(CN)_5NO^{2-}$. There are insufficient experimental details reported for a critical evaluation, but we can only hope that further work will show that $g_{xx} = g_{yy} > g_{zz}$, which is expected for the $(6e)^4(2b_2)^1$ assignment and with the excited states available from energy levels similar to those derived for $Fe(CN)_5NO^{2-}$.[28]

Experimental

Preparation of $[(n\text{-}C_4H_9)_4N]_2[Fe(CN)_5NO]$. The $[(n\text{-}C_4H_9)_4N]_2[Fe(CN)_5NO]$ complex was needed for the spectral measurements in transparent glasses at low temperatures. The $[(n\text{-}C_4H_9)_4N]_2[Fe(CN)_5NO]$ complex was prepared by thoroughly shaking a 0.03 *M* aqueous solution of $Na_2Fe(CN)_5NO \cdot 2H_2O$ with a 0.03 *M* chloroform solution of $(n\text{-}C_4H_9)_4NBr$. The chloroform layer was separated and the solvent was stripped. The residue was repeatedly extracted with water-free chloroform and the solvent completely removed. The resulting red compound was dried over anhydrous $CaCl_2$ in a desiccator.

(28) Very recently Kuska and Rogers have measured the e.s.r. spectra of $Cr(CN)_5NO^{3-}$ in alkali halide lattices. Their assignment of internal axes disagrees with that in ref. 9 and is compatible with our ground-state assignment of electronic structure. Kuska and Rogers find $g_{xx} = g_{yy}$ = 2.0045 and g_{zz} = 1.9722 for $Cr(CN)_5NO^{3-}$ in KCl: H. A. Kuska and M. T. Rogers, to be published.

Other Chemicals. EPA solvent, a mixture of ethyl alcohol, isopentane, and ethyl ether in 2:5:5 volume proportion, was obtained from Hartman–Leddon. Reagent grade $Na_2Fe(CN)_5NO \cdot 2H_2O$ was crystallized from water solution before use. For the single crystal absorption spectra of $Na_2Fe(CN)_5NO \cdot 2H_2O$, crystals a few microns in thickness were used. A very dilute solution of recrystallized sodium nitroprusside in water was made and was evaporated quickly by pouring on a flat dish. The crystals formed were collected and dried with filter paper.

Physical Measurements. Solution spectra were obtained using a Cary Model 14 spectrophotometer. The low-temperature spectrum was measured using an EPA solution of $[(n\text{-}C_4H_9)_4N]_2[Fe(CN)_5NO]$, which forms a perfectly transparent glass at liquid nitrogen temperature. The spectrum was obtained with the Cary Model 14 spectrophotometer, using a cold cell contained in a quartz dewar with optical windows. Liquid nitrogen was used as the coolant and the temperature was measured by an iron–constantan thermocouple. The observed low-temperature spectrum was corrected for solvent contraction, using the data of Passerani and Ross.[29]

Single crystal absorption spectra were obtained with a microspectrophotometer based on a modified Leitz polarizing microscope, designed at the Yale University Chemistry Department. The light was rendered plane polarized by a Glan prism and the polarization of the incident beam was fixed and the crystal was rotated on a mount.

In sodium nitroprusside crystal, the linear Fe–NO groups are found in two different orientations A and B. These A and B molecular groups lie in two parallel planes perpendicular to the crystal c axis; the angle between A and B groups is 112° 10'. The A and B planes make an angle of ±33° 55' with the a axis. Keep in mind that the Fe–NO axis is the fourfold axis of the nitroprusside ion.

The spectra were obtained with the electric vector of light vibrating in a plane parallel and perpendicular to the a axis of the sodium nitroprusside crystal. The light was incident on the ab plane. Since the two molecular Fe–NO axes make an angle with the a axis of ±33° 55' (θ) and an angle of 112° 10' (ϕ) with each other, the measured crystal spectra were analyzed to obtain the spectra for equivalently oriented molecular groups. With the electric vector of polarized light parallel ($\parallel$) and perpendicular ($\perp$) to the a axis of the crystal, the fraction of light transmitted may be resolved parallel and perpendicular to the A and B axes of Fe–NO molecular groups. Following an analysis by Piper and Carlin[30] we arrived at the equations

$$A_\parallel = a_\parallel \cos^2 \theta + a_\perp \sin^2 \theta + b_\parallel \cos^2 (\theta + \phi) + b_\perp \cos^2 (\theta + \phi)$$

and

$$A_\perp = a_\parallel \cos^2 (90 + \theta) + a_\perp \sin^2 (90 + \theta) + b_\parallel \cos^2 (90 + \theta + \phi) + b_\perp \cos^2 (90 + \theta + \phi)$$

(29) R. Passerani and I. G. Ross, *J. Sci. Instr.*, **30**, 274 (1953).
(30) T. S. Piper and R. L. Carlin, *Inorg. Chem.*, **2**, 260 (1963).

where $A_{\parallel}$ and $A_{\perp}$ are the experimental values for absorbance when the electric vector of the light is parallel and perpendicular to the axis. The $a_{\parallel}$, $b_{\parallel}$, $a_{\perp}$, and $b_{\perp}$ are, respectively, the actual values for absorbance for the A and B molecular axes when these axes are parallel and perpendicular to the electric vector of the light. Since A and B are optically equivalent molecules, $a_{\parallel} = b_{\parallel}$ and $a_{\perp} = b_{\perp}$. So the calculated spectra correspond to the equations

$$a_{\parallel} = 1.8252A_{\parallel} - 0.8252A_{\perp}$$

$$a_{\perp} = -0.8252A_{\parallel} + 1.8252A_{\perp}$$

where $a_{\parallel}$ and $a_{\perp}$ are the values for the total absorbance of the Fe–NO molecular groups, calculated as if they *all* were oriented unidirectionally parallel and perpendicular to the electric vector of the light. Both the uncorrected and corrected spectra are shown in Figure 5.

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Appendix

In the MO calculation of CN we have taken $1\sigma = 1s_N$ and $2\sigma = 1s_C$. The molecular orbitals $3\sigma \ldots 6\sigma$ are constructed as linear combinations of $2s_C$, $2s_N$, $2p\sigma_C$, and $2p\sigma_N$ atomic functions. Similarly π^b- and π^*-orbitals are linear combinations of $2p\pi_C$ and $2p\pi_N$ atomic functions. The atomic functions which we used to construct the MO's of CN are Clementi's double ζ-functions.[31] The secular equations $H_{ij} - S_{ij}E = 0$ were solved, where the Coulomb integrals were taken as valence orbital ionization potentials of carbon and nitrogen and the resonance integrals were estimated as $H_{ij} = -2.00S_{ij}(H_{ii} \cdot H_{jj})^{1/2}$. The calculation was performed to obtain self-consistent charge and configuration on both atoms, using Mulliken's[16] population analysis. Calculated one-electron energies are very close to the observed spectroscopic energies.

Table I summarizes the radial functions for Fe, CN, and NO used in the calculation. Tables II–V give orbital transformations, ligand–ligand corrections, group overlap integrals, coulomb integrals, and MO eigenvectors.

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Photoreduction of Cobalt(III) Complexes at 2537 Å.[1]

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Irradiation of ligand–metal charge-transfer bands of several Co(III) complexes at 2537 Å. has been found to lead only to photoreduction of the Co center. The quantum yield of Co(II) has been found to decrease markedly as the number of amine groups per ligand increases, to depend in a complicated way on pH, and to increase with [I⁻]. Species resulting from oxidation of the ligands have been identified in some cases. A few studies of the 2537-Å. irradiation of ion-pair charge-transfer bands have been performed. Much of the photochemistry seems best understood if photoreduction proceeds through a relatively long-lived ($\geq 10^{-8}$ sec.) metastable excited

state of the Co(III) complex. Mechanisms are proposed and discussed.

When aqueous solutions of Co(III) complexes are irradiated with visible light, both photoreduction and photoaquation take place.[2a] The ratio of the quantum yields for these processes is dependent, to some extent, upon the wave length of the light and the temperature of the solution. In the near-ultraviolet, photoreduction is increasingly favored over photoaquation as the

(1) Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) (a) A. W. Adamson, *Discussions Faraday Soc.*, **29**, 163 (1960); (b) A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958).