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On the Electronic Structure of Tetracyanonitrosylferrate(I)

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Single crystal EPR spectra of tetracyanonitrosylferrate(I) were measured. The EPR parameters can be sufficiently explained on the basis of simplified SCCC–MO calculations. It is suggested that the so-called "blue species" obtained from one electronic reduction of the nitroprusside ion is actually $[Fe(CN)_4NO]^{2-}$ in almost all cases.

Introduction

In 1896 K. A. Hofmann[1] studied the reaction of $[Fe(CN)_5(H_2O)]^{3-}$ with NO and proposed an intermediate complex "$NOFeCy_5Na_3$", coloured dark yellow in neutral and violet in acidified solutions, which was oxidized by excess NO to the well-known sodium nitroprusside. In the same paper the formulation "$FeCy_5NOHNa_2$" is discussed in connection with the resulting product. Again, these formulations appear in numerous publications dealing with reduction products of the nitroprusside ion[2–39]. Though several authors reported final conclusions concerning the nature and electronic structure of the reduction products, we feel that there are still enough apparently controversial facts and interpretations to justify further studies.

In a previous work[40] we could show that one of the products generated by one electron reduction of the pentacyanonitrosylferrate(II) ion is essentially tetracyanonitrosylferrate(I), the molecular structure of which is an almost regular tetragonal pyramid with apical NO. In accordance with several authors[10, 17, 21] who previously pointed out that EPR parameters required drastic structural modifications of the blue compared with the brown product of reduction, we suggested that a substantial part of the experimental data from the blue species, formerly thought to be $[Fe(CN)_5NOH]^{2-}$ [29,30] or $[Fe(CN)_5NO]^{3-}$ [14, 16, 24] has to be reinterpreted in terms of the formulation $[Fe(CN)_4NO]^{2-}$. Particularly, there has been no doubt that the blue species is a d^7 complex possessing one electron in an $a_1(d_{z^2})$ orbital. This is exactly the electronic structure expected for $[Fe(CN)_4NO]^{2-}$.

Our aim is to demonstrate that the EPR parameters of the blue species,[21, 30, 40], which we were able to verify by single crystal spectra of $[Fe(CN)_4NO]^{2-}$ doped crystals of $[Ph_4P]_2[Fe(CN)_5NO]$, can be easily interpreted on the basis of simplified SCCC–MO calculations with the proposed structure.

Experimental

$[Ph_4P]_2[Fe(CN)_5NO]$ was obtained by reaction of equivalent amounts of $[Ph_4P]Cl$ and sodium nitroprusside in ethanol, precipitation and washing with ice water, and drying in vacuum. The complex was dissolved in absolute acetonitrile together with 5% of $[Ph_4P]_2[Fe(CN)_4NO]$ prepared by previously published methods[39,40]. The solution was superposed by ether. Sufficiently large crystals (about 1.5 mm) grew during several weeks in a refrigerator. All operations with solutions or crystals containing Fe(I) were carried out in a nitrogen atmosphere.

The crystals were pasted into a bore hole centred in a small (5 mm) cube of plexiglass. This cube was mounted to a quartz rod carrying a square plate of suitable cross-section at its bottom. Since the crystal structure of $[Ph_4P]_2[Fe(CN)_5NO]$ was unknown, EPR spectra were measured relative to a coordinate system given by 3 faces of the cube. Spectra were run on a Varian V 4500 X band spectrometer with AEG NMR field accessory and Hewlett Packard frequency counters.

Data were collected from spectra taken every 20° for rotations about the three orthogonal axes. The tensors were diagonalized according to Schonland's method[41].

Principal values of the tensors resulting from two distinct sites (possibly due to twinning) of the $[Fe(CN)_4NO]^{2-}$ ion are

$[g] = [2.0076; 2.0318; 2.0340]$, $g_{av} = 2.0245$ and
$[A(^{14}N)] = [17.6; 15.0; 14.0]$, $A_{av} = 15.5$ G.

The main axes of these tensors are nearly coincident; the angle between them can be estimated from the

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transformation matrices to about 5 to 10 degrees. However, since g_{xx} is very similar to g_{yy} and the error in A is comparably large, direction cosines could deviate considerably.

The above tensors closely resemble those given in the literature for the blue species.[11,21,30]

Molecular Orbital Calculations

In order to interprete the spectroscopic results with respect to molecular and electronic structure we have performed simplified SCCC–MO calculations. Thus, following the procedure of Ballhausen and Gray[42,43] we applied several modifications: π bonding MOs of the ligands CN^- and NO^+ were completely neglected. Non-diagonal elements of the H matrix were determined by Cusachs' method[44]. A basis set of metal radial and ligand functions similar to those used by other authors[43] was assumed. An alternative calculation was performed with extremely simplified single ζ functions[45]. The two basis sets are given in Table I.

Structural parameters of $[Fe(CN)_4NO]^{2-}$ were taken as determined before[40], with the exception of assuming a linear Fe–N–O direction to preserve C_{4v} symmetry. Overlap integrals were calculated[46] from these functions and the coordinates of the ligand atoms with respect to the central atom according to well known procedures[47,48]. To avoid tedious group overlap corrections[42,43] we dropped collecting overlaps according to irreducible representations and solved the full characteristic equation of rank 24[46].

The above approach was tested for the nitroprusside ion affording values comparable with those from Manoharan and Gray[43], as far as the orbitals near the highest occupied MO are concerned. It may be worth mentioning that calculations using the single ζ basis and assuming the geometry of $[Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_4NO]^{2-}$ lead to realistic predictions[45] of the ligand stretching force constants for the complete set of ions in the reduction scheme[39,45,61]

$$\begin{tikzcd}
{[Fe(CN)_5NO]^{2-}} \arrow[r, "e"] & {[Fe(CN)_5NO]^{3-}\ (\text{brown})} \arrow[d, shift left, "-CN^-"] & \\
& {[Fe(CN)_4NO]^{2-}\ (\text{blue})} \arrow[u, shift left] \arrow[r, "e"] & {[Fe(CN)_4NO]^{3-}.}
\end{tikzcd}$$

Overlap integrals for the complete basis are presented in Table II, eigenvalues, eigenvectors, and Mulliken populations of the molecular orbitals of $[Fe(CN)_4NO]^{2-}$ in Table III.

We wish to stress, however, that the purpose of our calculation was exclusively to provide a heuristic tool for the interpretation of observables. Thus, the severe approximations[49] included in this calculation can be legitimated only empirically.

TABLE I. Basis Functions and H_{ii} Matrix Elements Used in the SCCC–MO Approach[43,45].

Complete Set			H_{ii} (kK)
Fe	$3d$	$0.5366\ (3d; 5.35) + 0.6678\ (3d; 1.80)$	
	$4s$	$0.0705\ (2s; 9.75) - 0.1744\ (3s; 4.48) + 1.0125\ (4s; 1.40)$	
	$4p$	$0.0118\ (2p; 10.6) - 0.0383\ (3p; 4.17) + 1.0007\ (4p; 0.80)$	
NO	σ	$0.4727\ (2s_N; 1.95) + 0.2368\ (2s_O; 2.275) + 0.6149\ (2p_N; 1.95) - 0.5794\ (2p_O; 2.275)$	–118.7
	π^*	$0.8781\ (2p_N; 1.95) - 0.6936\ (2p_O; 2.275)$	–74.6
CN	σ	$0.0950\ (2s_C; 1.1678) + 0.2738\ (2s_C; 1.8203) + 0.0547\ (2s_N; 1.3933) + 0.1354\ (2s_N; 2.2216) + 0.5613\ (2p_C; 1.2557) + 0.1824\ (2p_C; 2.7262) - 0.5192\ (2p_N; 1.5058) - 0.1879\ (2p_N; 3.2674)$	–112.9
	π^*	$0.7535\ (2p_C; 1.2557) + 0.2448\ (2p_C; 2.7262) - 0.6505\ (2p_N; 1.5058) - 0.2354\ (2p_N; 3.2674)$	–30.0
Simplified, Single ζ Basis			
Fe	$3d$	$(3d; 2.1)$	
	$4s$	$(4s; 1.0)$	
	$4p$	$(4p; 1.0)$	
NO	σ	$0.473\ (2s_N; 1.95) + 0.615\ (2p_N; 1.95) + 0.237\ (2s_O; 2.3) - 0.579\ (2p_O; 2.3)$	–118.7
	π^*	$0.878\ (2p_N; 1.95) - 0.694\ (2p_O; 2.3)$	–74.6
CN	σ	$0.407\ (2s_C; 1.6) + 0.820\ (2p_C; 1.6) + 0.209\ (2s_N; 2.0) - 0.780\ (2p_N; 2.0)$	–112.9
	π^*	$0.892\ (2p_C; 1.6) - 0.792\ (2p_N; 2.0)$	

TABLE II. Overlap Integrals (σ, π_h^*, and π_v^* refer to CN^-).

$d_{z2}; \sigma_{NO}$	0.1964	$\sigma_{NO}; \sigma$	0.0457
$s; \sigma_{NO}$	0.2508	$\sigma_{NO}; \pi_v^*$	0.0270
$p_z; \sigma_{NO}$	0.1836	$\pi_{NO}^*; \sigma$	±0.0236
$d_{x,yz}; \sigma$	±0.0515	$\pi_{NO}^*; \pi_h^*$	±0.0108
$d_{X2-y2}; \sigma$	±0.1174	$\pi_{NO}^*; \pi_v^*$	±0.0252
$d_{z2}; \sigma$	–0.0613	$\sigma; \sigma_{cis}$	0.0801
$s; \sigma$	0.2748	$\sigma; \sigma_{trans}$	0.0284
$p_{x,y}; \sigma$	±0.1322	$\sigma; \pi_{h,cis}^*$	±0.0476
$P_z; \sigma$	–0.0289	$\sigma; \pi_{v,cis}^*$	–0.0103
$d_{x,yz}; \pi_{NO}^*$	0.1345	$\sigma; \pi_{v,trans}^*$	–0.0055
$p_{x,y}; \pi_{NO}^*$	0.0947	$\pi_h^*; \pi_{h,cis}^*$	–0.0646
$d_{xy}; \pi_h^*$	±0.1144	$\pi_h^*; \pi_{h,trans}^*$	–0.0057
$d_{x,yz}; \pi_h^*$	±0.0251	$\pi_h^*; \pi_{v,cis}^*$	±0.0068
$p_{x,y}; \pi_h^*$	±0.1654	$\pi_v^*; \pi_{v,cis}^*$	0.0347
$d_{x,yz}; \pi_v^*$	±0.1064	$\pi_v^*; \pi_{v,trans}^*$	0.0069
$d_{x2-y2}; \pi_v^*$	±0.0245		
$d_{z2}; \pi_v^*$	–0.0425		
$p_{x,y}; \pi_v^*$	±0.0355		
$P_z; \pi_v^*$	0.1615		

TABLE III. Eigenvectors and Mulliken Populations (in brackets) of the Resulting Molecular Orbitals (σ, $\pi_v{}^*$, and $\pi_h{}^*$ refer to CN ligand functions).

Representation a_1			Eigenvector Components		
d_{z^2}	s	p_z	σ_{NO}	$(\sigma_1+\sigma_2+\sigma_3+\sigma_4)$	$(\pi_1{}^*+\pi_2{}^*+\pi_3{}^*+\pi_4{}^*)_v$
$a_1(1)$	−136.9 kK				
−0.026	+0.202	+0.000	+0.385	+0.346	+0.000
(0.001)	(0.137)	(0.0)	(0.190)	(0.168)	(0.0)
$a_1(2)$	−122.0 kK				
0.422	+0.013	+0.047	+0.732	−0.183	+0.002
(0.257)	(0.0)	(0.010)	(0.581)	(0.038)	(0.0)
$a_1(3)$[a]	−74.9 kK				
−0.885	−0.066	+0.216	+0.492	−0.122	+0.054
(0.680)	(0.005)	(0.077)	(0.160)	(0.012)	(0.008)
$a_1(4)$	−36.3 kK				
0.319	−0.036	+0.722	−0.351	+0.095	+0.227
(0.060)	(0.001)	(0.573)	(0.043)	(0.004)	(0.077)
$a_1(5)$	−22.9 kK				
−0.006	+0.808	−0.515	−0.139	−0.241	+0.332
(0.0)	(0.411)	(0.154)	(0.006)	(0.015)	(0.092)
$a_1(6)$	−19.2 kK				
0.074	−0.852	−0.559	+0.298	+0.230	+0.306
(0.002)	(0.446)	(0.187)	(0.021)	(0.013)	(0.073)

Representation a_2 $(\pi_1{}^*+\pi_2{}^*+\pi_3{}^*+\pi_4{}^*)_h$	
$a_2(1)$	−25.6 kK
0.538	
(0.250)	

Representation b_1 $d_{x^2-y^2}$	$(\sigma_1-\sigma_2+\sigma_3-\sigma_4)$	$(\pi_1{}^*-\pi_2{}^*+\pi_3{}^*-\pi_4{}^*)_v$
$b_1(1)$	−114.1 kK	
0.581	+0.365	+0.003
(0.437)	(0.141)	(0.0)
$b_1(2)$	−61.1 kK	
−0.851	+0.417	−0.023
(0.560)	(0.109)	(0.001)
$b_1(3)$	−27.7 kK	
0.091	−0.014	−0.517
(0.003)	(0.0)	(0.249)

Representation b_2 d_{xy}	$(\pi_1{}^*-\pi_2{}^*+\pi_3{}^*-\pi_4{}^*)_h$
$b_2(1)$	−91.5 kK
0.979	−0.039
(0.976)	(0.006)
$b_2(2)$	−27.6 kK
0.300	+0.482
(0.024)	(0.244)

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[a] Highest occupied molecular orbital. Input configuration: d 7.1726, s 0.2793, p 0.2137; resulting configuration: d 7.1729, s 0.2794, p 0.2140, q(Fe) 0.334.

TABLE III (Cont.)

Representation e, y projection d_{yz}	p_y	π_{yNO}	$(\sigma_2–\sigma_4)$	$(\pi_2{}^*–\pi_4{}^*)_v$	$(\pi_1{}^*–\pi_3{}^*)_h$
$e(1)_y$	–112.2 kK				
–0.274	+0.077	+0.019	+0.661	–0.001	–0.001
(0.093)	(0.020)	(0.0)	(0.425)	(0.0)	(0.0)
$e(2)_y$	–93.0 kK				
–0.812	–0.063	–0.418	–0.189	–0.032	–0.001
(0.695)	(0.010)	(0.227)	(0.030)	(0.004)	(0.0)
$e(3)_y$	–67.1 kK				
0.513	–0.026	–0.913	+0.150	+0.049	+0.000
(0.197)	(0.002)	(0.764)	(0.015)	(0.004)	(0.0)
$e(4)_y$	–37.1 kK				
–0.022	+0.843	–0.125	–0.205	+0.056	+0.279
(0.0)	(0.736)	(0.006)	(0.013)	(0.004)	(0.112)
$e(5)_y$	–27.1 kK				
–0.222	+0.118	+0.019	–0.019	+0.661	+0.260
(0.014)	(0.009)	(0.001)	(0.0)	(0.424)	(0.064)
$e(6)_y$	–23.9 kK				
–0.045	–0.605	+0.068	+0.024	+0.271	–0.618
(0.001)	(0.223)	(0.002)	(0.0)	(0.064)	(0.323)

Discussion

The calculations with alternative basis functions agree in the order of MOs near the ground state and predict the same ground state $^2A_1$ with strong d_{z^2} character. Moreover, eigenvectors and populations are predominantly very similar. Major displacements occur between $3d_{z^2}$, $4s$, and $4p_z$ populations. As a result it seems that drastic simplifications of the basis functions do not add too severe changes to the relative energies of the orbitals near the highest occupied orbital and, with some restrictions discussed below, even to their eigenvectors – as far as the aim of offering an easily tractable interpretational tool to "normal" chemists is envisaged.

We wish to show that the predicted $^2A_1$ ground state seems to be compatible with the EPR parameters observed from $[Fe(CN)_4NO]^{2-}$.

g Values

Retaining C_{4v} symmetry for the ion $[Fe(CN)_4NO]^{2-}$ leads to spin orbit coupling of the ground state solely with E (via L_x, L_y) and A_2 (via L_z) excited states. Since the only a_2 orbital is a pure ligand orbital under these conditions, g_{zz} is expected to be near 2.0023.

To explain the observed g_{xx}, g_{yy} the application of simple crystal field models will be inadequate because of the essentially covalent character of the metal–ligand bonding system in this complex. Thus, we applied the approach of Maki and McGarvey[50] together with the usual modifications[51–54]. Formulae are then of the type

$$\Delta g_{\nu\nu} = \sum_k \frac{m\lambda}{E_o - E_k} \alpha^2 \alpha_k{}^{*2} [1 - \sum_i \frac{\beta_i \beta_i{}^*}{\alpha \alpha_k{}^*} T(n)_i + \sum_j \frac{\beta_j}{\alpha_j} S_j].$$

To simplify the calculations, we have considered only substantial contributions from the $a_1(3)$ ground state and e(1), e(2), e(3), and e(5) orbitals. Small contributions within the eigenvectors (below 0.05 for metal and 0.1 for ligand functions), as well as all contributions from ligand atoms not bonded directly to the metal atom, were neglected[54].

With the spin orbit coupling constant of Fe^+, $\lambda = 356$ (cm^{-1})[55], the approximation yields $g_\perp = 2.066$ (or $g_\perp = 2.042$, respectively, from the single ζ basis). Regarding the sign and order of magnitude of $\Delta g_\perp$ these values are in a reasonable agreement with the measured g tensors. Since W–H type calculations tend to overemphasize covalent character and the various contributions to $\Delta g_\perp$ are governed by terms due to electron delocalization onto the ligands, it is not surprising to find a $\Delta g_\perp$ larger than observed. In addition, the energy separation between e(3) and the ground state orbital is obviously too low compared with the observed band (16.5 kK)[10,30,37,40] in the electronic spectrum. This may be an effect of the exclusion of bonding π orbitals of the ligands.

If the slight bending of the Fe–N–O bond is taken into account, g_{zz} is expected to increase via mixing of, say, d_{xz} into the ground state according to

$$\Psi_g{}^* = \cos\varepsilon \cdot \Psi_g + \sin\varepsilon \cdot (d_{xz})$$

and coupling with d_{yz}. One of the components of $g_\perp$ will then decrease by similar amounts.

Metal Hyperfine Interactions

Van Voorst and Hemmerich[30] have found the ^{57}Fe hyperfine coupling tensor elements of $A_{\parallel} \cong 9$ G,

$A_\perp = -14.3$ G, and $|A_{iso}| = 7.21$ G for their blue species "$[Fe(CN)_5NOH]^{2-}$". We assign the same tensor to $[Fe(CN)_4NO]^{2-}$ (see discussion below), a suggestion which is supported by our own result of $|A_{iso}| = 8.4$ G from $[Ph_4As]_2[Fe(CN)_4NO]$ in acetonitrile solution. Since A_{iso} will be lowered by interaction of solvent donor molecules with the central atom at a position *trans* to the nitrosyl ligand, the lower value of 7.21 G possibly reflects the higher donor abilities of the DMF/water system used by Van Voorst.

Supposing that $A_\perp = -14.3$ G and $A_{iso} = -7.2$ are the most probable values, the ^{57}Fe hyperfine tensor will be

$$\begin{bmatrix} +7 \\ -14.3 \\ -14.3 \end{bmatrix} = \begin{bmatrix} +14.2 \\ -7.1 \\ -7.1 \end{bmatrix} + \begin{bmatrix} -7.2 \\ -7.2 \\ -7.2 \end{bmatrix} .$$

Since coupling of the ground state with excited states is evidently weak, the tensor elements can be deduced directly from the corresponding Fe eigenvector components to a close approximation. If we assume $P_{3d} = 33$ G for Fe^+ (d^7)[30] and tentatively suppose $P_{4p} \cong P_{3d}/3$ (in analogy to a proposal for vanadium[56]) we obtain the following values for the traceless part of the ^{57}Fe coupling tensor: $B_{zz} = 15.1$; $B_{xx} = B_{yy} = -7.5$G (or 11.8; –5.9 G, respectively, from the single ζ basis). Lowering the symmetry of the ion will result in $B_{xx} \neq B_{yy}$.

The Fe(4*s*) eigenvector component of the ground state together with $A_{iso}{}^{\circ}(^{57}Fe) \cong 160$ G[57] leads to a contribution of +0.7 G to the isotropic part of the tensor. However, the large $3d_{z^2}$ (and $4p_z$) spin densities must produce considerable spin polarization. On the basis of the theoretical contact term $\chi = -3.3$ a.u. (corresponding to A_{pol} about –14 G) for the total polarization of Fe 1*s*, 2*s*, 3*s* orbitals by one 3*d* electron[57,58], spin polarization contributions (neglecting $4p_z$) can be roughly estimated to be about –11 G.

We feel that the estimated total coupling of $A_{iso} = -10$ G as well as the calculated anisotropic coupling lend strong support to the validity of the postulated ground state eigenvector. Our $3d_{z^2}$ population agrees equally well with $n_{z^2} = 0.6$ proposed by Raynor[20]. In the case of the single basis the 4*s* component of the eigenvector seems to be unrealistic and would yield an isotropic coupling of about +1 G.

Ligand Hyperfine Coupling

Deducing ligand hyperfine coupling constants from the calculated eigenvectors encounters several difficulties. Effects like solvent donor interactions, small deviations from the linearity of Fe–N–O bonds, spin polarization, or the excessively high covalency of the calculated molecular orbitals may all reduce the ligand hyperfine coupling and cannot be accounted for in a simple manner. Merely mixing with excited states can be neglected in the case of $[Fe(CN)_4NO]^{2-}$ ligand hyperfine coupling.

If the Mulliken population of σ_{NO} is assumed to represent the total spin density on the nitrosyl ligand and if the spin density distribution upon N and O is approximately proportional to the respective squared LCAO coefficients of these atoms, we obtain an upper limit of $A_{iso}(^{14}N)$ with $A_{iso}(^{14}N) = A_{iso}{}^{\circ}(^{14}N) \cdot POP(\sigma_{NO}) \cdot c_s{}^2(N) = 19.7$ G.

While the calculated value of A_{iso} is higher than the observed coupling (14.5 to 15.5 G)[11,21,30,40], the traceless part of the coupling tensor evaluated in an analogous way ($B_{\parallel} = A_{aniso}{}^{\circ} \cdot POP(\sigma_{NO}) \cdot c_p{}^2(N) = +2$ G; $B_\perp = -1$ G) is almost exactly that which is measured[11,21,30], namely

$$\begin{bmatrix} 17.6 \\ 15.0 \\ 14.0 \end{bmatrix} = \begin{bmatrix} 2.1 \\ -0.5 \\ -1.5 \end{bmatrix} + \begin{bmatrix} 15.5 \\ 15.5 \\ 15.5 \end{bmatrix}$$

with the exception of $B_{xx} \neq B_{yy}$ due to the nonlinearity of Fe–N–O.

Hyperfine coupling with ^{13}C ($A_{iso}(^{13}C) \cong 10$ G) has been measured in solution[11]. Danon *et al.*[25] have published a similar value from single crystal measurements. They observed however a splitting pattern according to 5 CN^- groups. So it is doubtful that their results can be attributed to $[Fe(CN)_4NO]^{2-}$.

The value of $A_{iso}(^{13}C)$ which can be derived from the C(2*s*) contribution to σ_{CN} population of the ground state is $A_{iso}(^{13}C) = A_{iso}{}^{\circ}(^{13}C) \cdot POP(\sigma_{CN}) \cdot c_s{}^2(C) = 1.7$ G.

Because it is highly improbable that more sophisticated MO calculations would increase the σ_{CN} population by nearly one order of magnitude, $A_{iso}(^{13}C)$ may be essentially due to spin polarization. Following the arguments of Symons[59], the calculated 3*d* population gives rise to an isotropic coupling of about –11 to –12 G and a comparatively small anisotropy in the order of +1 G. Hence a total coupling of $A_{iso}(^{13}C) = -9$ to –10 G results. This fits nicely with the observed value and the reported small anisotropic changes.

Nevertheless, there is still some doubt about the correct interpretation of ^{13}C hyperfine coupling of CN^- ligands. Other authors[60] discuss direct overlap of d_{z^2} with carbon *s*/*p* hybrids and, not applying the diminishing factor $c_s{}^2(C)$, arrive at even higher, positive ^{13}C coupling constants. Possibly, the influence of spin polarization is overestimated in our suggestion. On the other hand, there are uncertainties both regarding the magnitude of the ^{13}C coupling (4.6 *vs.* about 10 G, compare ref. 10, 11 and 25) and the correct attribution of the coupling to one of the postulated ions.

Conclusions

It has been shown that simplified SCCC–MO calculations may serve as a convenient tool for the interpretation of the complete set of EPR parameter of the blue reduction product of the nitroprusside ion. In addition, this product is well characterized by its X-ray structure and its infrared spectrum (ν_{NO} = 1755 cm^{-1})[39,40] as $[Fe(CN)_4NO]^{2-}$. It seems to be a reasonable assumption now to assign this formulation to all those reduction products of the nitroprusside which exhibit EPR parameters equivalent to the corresponding values of $[Fe(CN)_4NO]^{2-}$.

It is suggestive to explain a p_H dependent equilibrium of the reduction products accompanied by considerable changes in the electronic structure of the nitrosyl group by the formulation $[Fe(CN)_5NOH]^{2-}$. However, it must be pointed out that, as far as we can see, no direct proof of an H atom bonded to the nitrosyl group of the above complex (*e.g.* NMR signal, EPR coupling, specific IR absorption etc.) has ever been given. Such a proof would be impossible if CN^- is cleaved off as HCN[21] because of the relative instability of the trans CN group in $[Fe(CN)_5NO]^{3-}$ (see ref. 45). Consequently, further reduction of $[Fe(CN)_5NO]^{3-}$ by Na in liquid ammonia leads to $[Fe(CN)_4NO]^{3-}$ (ν_{NO} = 1555 cm^{-1})[39,45,61] with cleavage of the *trans* CN^- as well.

We propose to consider carefully whether the known experimental facts necessitate the assumption of an ion $[Fe(CN)_5NOH]^{2-}$ at all.

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