

Registry No. (π -C₅H₅)Fe(CO)₂(CNBF₃), 40199-93-7; (π -C₅H₅)Fe(CO)₂(CNBCl₃), 40199-94-8; (π -C₅H₅)Fe(CO)₂(CNBBR₃), 40199-95-9; (π -C₅H₅)Fe(CO)₂(CNBH₃), 40199-96-0; (π -C₅H₅)Fe(CO)₂(CNAlCl₃), 40199-97-1; (π -C₅H₅)Fe(CO)₂(CNGaCl₃), 40330-51-6; (π -C₅H₅)Fe(CO)₂(CNAl(CH₃)₃), 40199-98-2; (π -C₅H₅)Fe(CO)₂(CNB(CH₃)₃), 40199-99-3; (π -C₅H₅)Fe(CO)₂(CO)₂(CNGa(CH₃)₃), 40200-00-8; (π -C₅H₅)Fe(CO)₂CN, 12152-37-3; BF₃, 7637-07-2;

BCl₃, 10294-34-5; BBr₃, 10294-33-4; B₂H₆, 19287-45-7; AlCl₃, 7446-70-0; GaCl₃, 13450-90-3; Al(CH₃)₃, 75-24-1; B(CH₃)₃, 593-90-8; Ga(CH₃)₃, 1445-79-0.

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Electronic Ground States of Dicyanobis(diimine)iron(III) Compounds

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Epr, nmr, and magnetically perturbed Mossbauer spectral data for Fe(phenanthroline)₂(CN)₂⁺ and Fe(bipyridine)₂(CN)₂⁺ are compared to similar data for the corresponding tris(diimine) systems. The principal component of the electric field gradient (V_{zz}) is positive for all of these compounds and consistent with an orbital ground state corresponding to a hole in d_{z^2} . Fits to epr spectra in various media are discussed and an axial (trigonal) model with splittings of ~ 1000 cm⁻¹ in the ground ²T₂ term is favored; *i.e.*, the basic trigonal field of the tris(diimine) systems appears to persist in the bis analogs. This is also supported by proton nmr data. Perturbed Mossbauer results for the low-spin ferrous systems [Fe(bipyridine)₂]₂(ClO₄)₂ (V_{zz} negative) and [Fe(bipyridine)₂(CN)₂]₂ (V_{zz} positive) are considered in relation to the magnitude of the quadrupole splittings of the corresponding ferric systems.

Introduction

The electronic structure of low-spin iron(III) complexes has been the subject of several recent investigations. Much of the effort expended toward the understanding of these complexes has focused on the more symmetric molecules of the type M(chelate)₃ⁿ⁺. In particular, studies of the Fe-(NN)₃³⁺ complexes² have been most fruitful while investigations of sulfur-donor compounds such as Fe(dithioacetylacetonate)₃,³⁻⁵ though providing equally interesting results, have proven much more difficult to interpret in terms of a unified model of bonding. In this paper we present the results of an nmr, epr, and magnetically perturbed Mossbauer study of the low-symmetry ferric complexes [Fe(diimine)₂(CN)₂]₂X [diimine = 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy)] as well as the perturbed Mossbauer data for the low-spin ferrous analogs.

The reduction in symmetry resulting from substitution of two CN⁻ ligands for a chelating diimine of a tris(diimine) complex is expected to lower the symmetry to less than threefold, the highest remaining symmetry axis being the C₂ which bisects the CN-M-CN angle. What is not apparent is whether this has a significant effect on the dominant trigonal distortion imposed by the chelate rings and, if so, to what factors the distortion is most sensitive. It is with these problems that the present study is concerned.

Experimental Section

The Mossbauer apparatus has been described previously.⁶ Magnetically perturbed Mossbauer spectra were determined at ambient temperature using a Varian Associates Model 4500 magnet (transverse geometry) and accompanying power supply. The applied

fields for cylindrical, tapered pole faces at 0.5-in. gap were nominally of the order of 20 kG, while the γ -ray source (50 mCi ⁵⁷Co in Cu) was maintained in a fringing field of less than 300 G.

Nmr spectra were recorded on a Jeolco C-60H nmr spectrometer at 30° in DMSO-*d*₆.⁷ No evidence for coordination of DMSO was indicated. Spectra were calibrated relative to tetramethylsilane as internal standard.

Epr spectra were obtained on a Varian E-4 spectrometer system at X-band frequency. Samples of the bis complexes were prepared as dilute solutions in *N,N*-dimethylacetamide-H₂O and frozen rapidly in liquid nitrogen before reduction to the ferrous complexes could occur. Spectra were run in helium-cooled liquid N₂ at $\sim 73^\circ$ K in a standard low-temperature dewar. Calibration was relative to diphenylpicrylhydrazyl (DPPH), $g = 2.0036$. All complexes were prepared as outlined in the literature.⁸

Results and Discussion

Nmr. Nmr spectra of [Fe(phen)₂(CN)₂]⁺ and [Fe(bipy)₂(CN)₂]⁺ in DMSO-*d*₆ clearly show two sets of nonequivalent protons due to the inequality of the chelate rings and unambiguously identify the compounds as the cis isomers (Figure 1). In the bipyridine complex, only the 6,6' resonance remains degenerate, while in the phenanthroline complex, both the 2,9 and 5,6 proton resonances remain degenerate as in the tris complex (Table I).⁷ Interestingly, if one averages the two inequivalent resonances in the bis complexes and compares the result to the value found in the tris complexes, the difference is generally quite small. This would indicate that there is no great change in the net amount of spin density reaching the protons as one goes from tris to bis complexes. One has a situation where due to the CN⁻ ligands, less spin density is placed on one half of the diimine and more on the other half. While the situation involving spin delocalization is complicated by several unknown factors, and is undoubtedly exceedingly complex, it seems reasonable to conclude that lowering of the symmetry in these bis complexes takes place without gross distortion of the basic symmetry of the tris complexes. Were this not

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(2) (a) R. E. DeSimone and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 2343 (1970); (b) W. M. Reiff, *Chem. Phys. Lett.*, **8**, 297 (1971).

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Table I. Nmr Data.^{a,b,e,f} Isotropic Shift ν in Hz

Compound	3	3'	4	4'	5	5'	6	6'	4-CH ₃	4'-CH ₃
Fe(bipy) ₂ (CN) ₂ ⁺ ^c	-744	-123	-378	+152	-336	+474	+2965	+2965	-1410	-264
Fe(bipy) ₂ (CN) ₂ ⁺ (AVE)	-433		-140		+49		+2965		-838	
Fe(bipy) ₃ ³⁺ ^d	-426		-82		+4		+2656		-963	
Compound	5	6	4	7	3	8	2	9	4-CH ₃	7-CH ₃
Fe(phen) ₂ (CN) ₂ ⁺ ^c	-408	-408	-359	+170	-303	+591	+2885	+2885	-1265	-236
Fe(bipy) ₂ (CN) ₂ ⁺ (AVE)	-408		-95		+144		+2885		-740	
Fe(phen) ₃ ³⁺ ^d	-372		-60		+175		+2849		-1014	

^a At 60 MHz. ^b Assignments based on line widths and methyl substitution where possible. ^c In DMSO-d₆ at 30°. ^d In D₂SO₄ at 30°; see ref 2a. ^e Numbering system explained in ref 2a. ^f For the purposes of this work, the diamagnetic bis and tris complexes do not differ sufficiently to warrant use of $\Delta\nu$ values. AVE refers to an average of the resonances in the bis complexes which are identical by symmetry in the tris complexes.

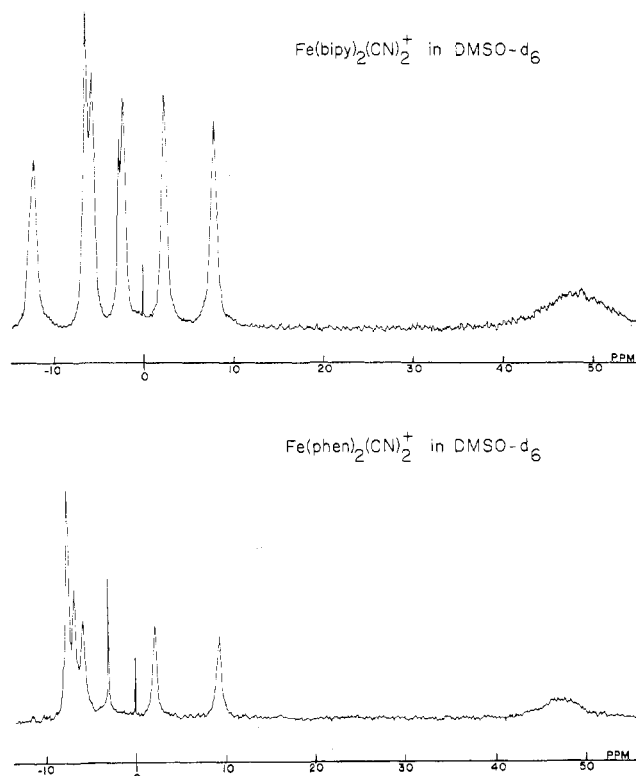


Figure 1. 60-MHz proton nmr spectra of Fe(Phen)₂(CN)₂⁺ and Fe(bipy)₂(CN)₂⁺ in DMSO-d₆ at 30°.

the case it seems difficult to believe that relative energies of metal and ligand orbitals would be so unchanged as to affect the total spin delocalization as little as is observed. Previous experience dictates considerable caution, however, on matters of this sort.^{2a,7}

Mossbauer. The magnetically perturbed Mossbauer spectra of [Fe(phen)₃](ClO₄)₃ and [Fe(phen)₂(CN)₂]NO₃ are shown in Figures 2a and 2b. It is clear that for both systems there is a reasonably well-defined triplet at lower velocity than a doublet. For iron-57 this implies that the principal component of the electric field gradient tensor, V_{zz} , as well as the quadrupole interaction, is *positive*. Similar spectra ($V_{zz} > 0$) have been obtained for the corresponding bipyridine compounds at ambient temperature and at 4.2°K.^{2b} All of the systems exhibit spectra indicating a small asymmetry parameter η and thus near-axial symmetry.

The fact that V_{zz} has the same sign for both the tris- and bis(diimine) systems as well as similar magnitude (Table II) is consistent with essentially the same electronic ground state (a ²A term or a hole in d_{z^2}) and symmetry (approximately trigonal) for both types of compound. This possibility, although not the symmetry involved, was first sug-

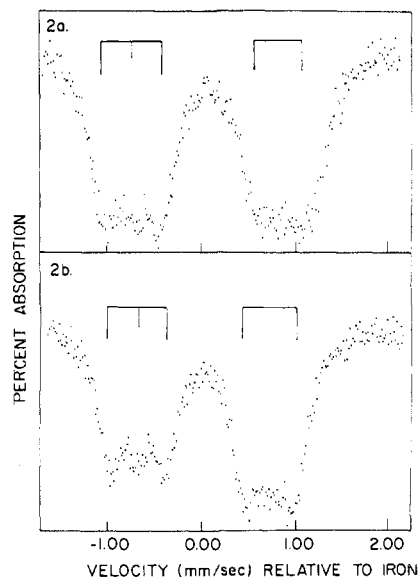


Figure 2. Magnetically perturbed Mossbauer spectra of (a) [Fe(phen)₃](ClO₄)₃ and (b) [Fe(phen)₂(CN)₂](NO₃) at room temperature. $H \sim 18$ kG.

Table II. Mossbauer Data (300°K)

Compound	ΔE_q	Sign of V_{zz}
Ferric Compounds		
[Fe(phen) ₃](ClO ₄) ₃	1.60	+
[Fe(bipy) ₃](ClO ₄) ₃	1.73	+
[Fe(bipy) ₃ (CN) ₂](NO ₃)	1.49	+
[Fe(phen) ₂ (CN) ₂](NO ₃)	1.38	+
Ferrous Compounds		
[Fe(phen) ₃](ClO ₄) ₂	0.29	-
[Fe(bipy) ₃](ClO ₄) ₂	0.39	-
[Fe(bipy) ₂ (CN) ₂]	0.60	+

gested by Figgis, *et al.*,⁹ in a study of the temperature dependence of powder susceptibilities for these systems. In particular from fits to powder data, they found the bis-(diimine) systems to show axial fields (Δ) of the same sign and similar magnitude, +500 → 600 cm⁻¹, as the analogous tris complexes.^{10,11} It has since been shown^{12,13} that the temperature dependence of mean powder susceptibilities often constitutes a relatively unreliable technique for determination of the sign or magnitude of Δ . Thus, for ex-

(9) B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. A*, 422 (1966).

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ample, fits to epr data appear to favor a negative axial field (2A ground term) of $\sim 1000 \text{ cm}^{-1}$ for the tris systems,^{2a} *i.e.*, opposite in sign and somewhat larger than found from susceptibility data.¹⁰ The magnetically perturbed Mossbauer spectra data correlate with the epr results and not the susceptibility.¹¹ Specifically, assuming D_3 symmetry for the tris complexes, $V_{zz} > 0$ corresponds to a hole in the d_{z^2} orbital implying $\Delta < 0$ which translates to an orbital singlet ground term for d^5 systems.

The choice of orbital ground term and sign of the axial field solely on the basis of perturbed Mossbauer and epr results is less clear-cut for the dicyano systems where there is the added possibility of a rhombic component to the ligand field. This problem is considered in more detail below. At this point, however, we would like to discuss some pertinent observations on the Mossbauer spectra of some low-spin ferrous complexes related to the ferric systems under consideration.

Figure 3a illustrates the perturbed spectrum of $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$. The quadrupole splitting (0.60 mm/sec at 300°K) is smaller than that found in the ferric systems, thus resulting in partial overlap of the inner components of its magnetically perturbed spectrum. However, it is evident that there is a triplet at lower velocity than a doublet; therefore V_{zz} is also positive for this system. $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_2$ has an even smaller quadrupole splitting (0.39 mm/sec at 300°K) and determination of the sign of this small splitting by magnetic perturbation is pushing this technique to its limit.¹⁴ In any event we have attempted this and the result is shown in Figure 3b for which there are greater than 2×10^6 counts in the spectrum base line. We tentatively assign V_{zz} negative for this system as indicated by the stick diagram above the spectrum showing the sharper triplet now at higher velocity than the broader doublet. The spectrum appears to be essentially the reverse of that obtained from $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$ as must be the case if the signs of V_{zz} are opposite. The spectrum of $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_2$ is very similar to $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_2$, implying V_{zz} negative.

These results indicate the possibility that the signs of any covalence anisotropy contribution to the quadrupole splitting may be opposite in the corresponding low-spin ferric bis complexes. That this does not seem to be the case, however, is indicated by the results of a calculation of the valence contribution to the quadrupole splittings. This may be done as outlined by Golding¹⁵ using the eigenvalues and eigenvectors of the Kramers' doublets obtained from fits of the epr data. Such a calculation for $[\text{Fe}(\text{phen})_2(\text{CN})_2]^+$ yields a valence contribution to the quadrupole splitting of 2.17 mm/sec. The smaller observed value suggests a negative covalence contribution; thus, the sign of this contribution changes on going from the bis ferrous to ferric systems. In any event, studies and comparisons of the electronic structures of these systems based on the magnitude and detailed temperature dependence of quadrupole splittings may not be straightforward. The sign as well as magnitude of covalence anisotropy contributions will have to be carefully considered.

Epr. The epr spectra of $\text{Fe}(\text{phen})_2(\text{CN})_2^+$ and $\text{Fe}(\text{bipy})_2(\text{CN})_2^+$ are shown in Figures 4a and 4b, respectively. Note that $\text{Fe}(\text{phen})_2(\text{CN})_2^+$ is apparently axial while the rhombic component of $\text{Fe}(\text{bipy})_2(\text{CN})_2^+$ is much more apparent. It should be borne in mind that in these bis(diimine) complexes the role of the solvent is likely to be more important

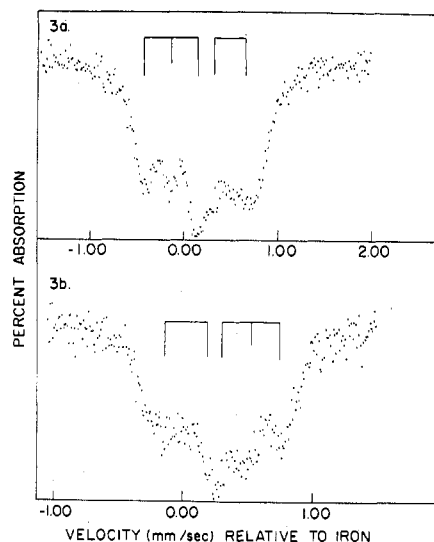


Figure 3. Magnetically perturbed Mossbauer spectra of (a) $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$ and (b) $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_2$ at room temperature. $H \sim 18 \text{ kG}$.

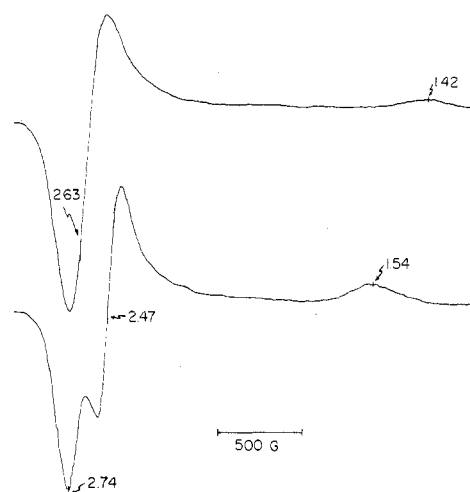


Figure 4. Epr spectra of $[\text{Fe}(\text{bipy})_2(\text{CN})_2]^+$ (top) and $[\text{Fe}(\text{phen})_2(\text{CN})_2]^+$ in dimethylacetamide- H_2O (frozen solution) at 77°K (bottom).

than in the tris complexes in producing small structural changes, since some of the rigidity imposed by the chelate rings is lost upon substitution by CN^- . Thus, the apparent axiality of $\text{Fe}(\text{phen})_2(\text{CN})_2^+$ should not be too surprising; in a different solvent the spectrum might in fact appear rhombic.¹⁶ The choice of DMA- H_2O as solvent was based on its good solvent properties and the fact that it is likely to be very weakly coordinating, if at all. No evidence of decomposition was evidenced in solution from which epr spectra were obtained.

Analysis of the epr spectra by the method of Bleaney and O'Brien¹⁷ leads to much the same results for both the bis and tris complexes. Results are presented in Table III. Since some of the parameters are defined slightly differ-

(16) The complex $\text{Fe}(\text{phen})_3^{3+}$ is in fact also quite sensitive to the medium in which spectra are obtained. Previously reported g values^{2a} in Co(III) host lattice indicate considerably different distortion compared to the pure powder. Spectra in H_2SO_4 glass indicate still different distortion. The bipyridine complex, $\text{Fe}(\text{bipy})_3^{3+}$, gives identical spectra in all three media.⁷ This behavior is likely due to the greater rigidity of the phen rings which does not allow it to flex and relieve distortions imposed by the environment.

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Table III. Epr Data^{a,b}

Compound	g_x	g_y	g_z	k	Δ/ξ	ϵ/ξ	A	B	C	Model
Fe(bipy) ₂ (CN) ₂ ⁺ ^c	-2.74	-2.47	+1.54	1.01	2.82	-0.15	0.275	0.961	-0.035	Trigonal
	-2.74	+1.54	-2.47	1.01	-0.74	-0.54	0.800	0.219	-0.559	Rhombic
Fe(phen) ₂ (CN) ₂ ⁺ ^c	-2.74	-2.47	-1.54	1.21	0.36	-0.02	0.742	0.670	-0.026	Trigonal
	-2.63	-2.63	+1.42	0.98	2.42	0.0	0.312	0.950	0.0	Trigonal
	-2.63	+1.42	-2.63	0.98	-1.21	-0.40	0.828	0.220	-0.516	Rhombic
Fe(bipy) ₃ ³⁺ ^d	-2.63	-2.63	+1.42	1.20	0.40	0.0	0.730	0.683	0.0	Trigonal
Fe(phen) ₃ ³⁺ ^d A	-2.61	-2.61	+1.61	1.07	3.03	0.0	0.252	0.968	0.0	Trigonal
Fe(phen) ₃ ³⁺ ^d B	-2.69	-2.69	1.19	0.99	2.01	0.0	0.368	0.930	0.0	Trigonal
Fe(phen) ₃ ³⁺ ^d C	-2.67	-2.67	1.32	1.00	2.23	0.0	0.337	0.942	0.0	Trigonal
Fe(phen) ₃ ³⁺ ^d C	-2.60	-2.60	1.47	0.97	2.54	0.0	0.299	0.954	0.0	Trigonal

^a At 73-77°K. ^b At X-band frequencies. ^c In frozen dimethylacetamide (DMA)-H₂O solution. ^d Fe(phen)₃³⁺ is very sensitive to medium, Fe(bipy)₃³⁺ is not. Values quoted for Fe(phen)₃³⁺ are (A) in Co(III) host, (B) in H₂SO₄ glass, (C) pure powder.

ently¹⁸ than previously,^{2a} we present the necessary equations here

$$\begin{aligned} g_z &= -2[A^2 - B^2 + C^2 + k(A^2 - C^2)] \\ g_x &= 2[2AC - B^2 + kB\sqrt{2}(C - A)] \\ g_y &= 2[2AC + B^2 + kB\sqrt{2}(C + A)] \end{aligned} \quad (1)$$

where A , B , and C are the eigenvector coefficients of the lowest Kramers' doublet.

$$\begin{aligned} \psi &= A|+1\rangle + B|\xi_1\rangle + C|-1\rangle \\ \psi' &= A|-1\rangle - B|\xi_1\rangle + C|+1\rangle \end{aligned} \quad (2)$$

In tetragonal quantization, the complex orbitals of (2) are defined as¹⁸

$$\begin{aligned} |1\rangle &\equiv 1/\sqrt{2}(d_{xz} + id_{yz}) \\ |-1\rangle &\equiv 1/\sqrt{2}(d_{xz} - id_{yz}) \\ |\xi_1\rangle &\equiv id_{xy} \end{aligned} \quad (3)$$

In trigonal quantization, $|\xi_1\rangle$ is associated with $t_2^0 \equiv d_{z^2}$, while $|1\rangle$ and $|-1\rangle$ are combinations of the trigonal orbitals¹⁹

$$\begin{aligned} t_2^+ &\equiv \sqrt{2/3}d_{x^2-y^2} - \sqrt{1/3}d_{xz} \\ t_2^- &\equiv \sqrt{2/3}d_{xy} + \sqrt{1/3}d_{yz} \end{aligned} \quad (4)$$

The derived parameters are given by

$$\begin{aligned} \epsilon/\xi &\equiv (-A\sqrt{2} + B)/3\sqrt{2} \cdot (C/(C^2 - A^2)) \\ \Delta/\xi &\equiv -A/B\sqrt{2} - 1/2 + 3A/C(\epsilon/\xi) \\ k &\equiv \frac{\langle \psi | L | \psi \rangle}{\langle d | L | d \rangle} \end{aligned} \quad (5)$$

In (5), Δ is the axial field parameter, ϵ the rhombic field parameter, ξ the spin-orbit coupling constant defined as positive, and k the orbital reduction factor.¹⁸

Based on the trigonal model, the "hole" is calculated to be in the t_2^0 orbital ($B > A, C$) leaving the orbital doublet

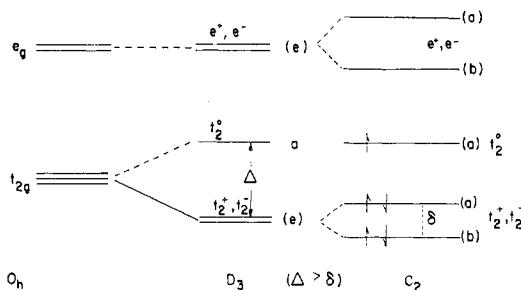


Figure 5. A simple "real" orbital arrangement for [Fe(diimine)₂(CN)₂]⁺ systems. Splittings are not drawn to scale. The splitting due to the primary crystal field (10Dq) which separates the e_g and t_{2g} orbitals is assumed large enough so that interaction of upper and lower "e orbitals" may be neglected.

t_2^{\pm} lowest, i.e., $\Delta < 0$. The ground state is thus ²A. Based on a rhombic model, with greatest anisotropy in the xy plane, the hole is predicted to be in ($d_{xz} + id_{yz}$) ($A > B, C$) resulting in $\Delta > 0$ and a ²E ground term. Both solutions produce the same values of k as well as $V_{zz} > 0$, in agreement with Mossbauer results. The rhombic solution must be considered, of course, since the axis to which a particular g value corresponds is unspecified in powder or frozen solution spectra. It seems, however, that the rhombic solution should be rejected on the basis of the small magnitude of Δ/ξ relative to the tris complex; this is inconsistent with the comparable quadrupole splittings. In conclusion, the model based on a slightly perturbed trigonal geometry seems most reasonable and is summarized in the "real" orbital arrangement of Figure 5.

Registry No. Fe(bipy)₂(CN)₂⁺, 40187-08-4; Fe(bipy)₃³⁺, 13479-48-6; Fe(phen)₂(CN)₂⁺, 40187-09-5; Fe(phen)₃³⁺, 13479-49-7; [Fe(phen)₃](ClO₄)₃, 14634-90-3; [Fe(bipy)₃](ClO₄)₃, 15388-50-8; [Fe(bipy)₂(CN)₂](NO₃), 40187-10-8; [Fe(phen)₂(CN)₂](NO₃), 40187-11-9; [Fe(phen)₃](ClO₄)₂, 14586-54-0; [Fe(bipy)₃](ClO₄)₂, 15388-48-4; [Fe(bipy)₂(CN)₂], 14841-10-2.

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