

Orbital Ground States of Low-Spin Iron(III) Compounds. A Study of Bis(2,2',2''-terpyridine)iron(III) Perchlorate

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Abstract: The nature of the orbital ground state and unusually large quadrupole splitting of $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ are studied using magnetically perturbed Mössbauer spectra, esr, and power susceptibility measurements. The perturbed spectra show V_{zz} negative for $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ and its diamagnetic ferrous analog. For the ferric complex the Mössbauer results correlate with esr data that indicate an orbital singlet (${}^2\text{B}$) ground term corresponding to a hole primarily in d_{xy} and a large axial field (-1700 cm^{-1}). The quadrupole splitting ($\sim 3.3 \text{ mm/sec}$) is attributed to additive valence and covalence anisotropy contributions. From this and several recent studies it appears that nondegenerate orbital ground terms are favored for low-spin ferric complexes thus avoiding Jahn-Teller distortion and allowing maximum π bonding.

The planar tridentate ligand 2,2',2''-terpyridine is known^{1,2} to form a series of pseudooctahedral "bis-terpy" complexes with most of the first transition series divalent ions including iron(II) in $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_2$. Terpyridine has also recently³ been shown to form the low-spin iron(III) complex, $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$. For both of the preceding iron complexes the distortion of the octahedron is believed approximately axial in nature.⁴ Previous X-ray work⁵ shows that the central nitrogen of terpyridine bonds much more strongly than the outer nitrogens and thus one would expect a unique axis of relatively strong bonding determined by two such central nitrogens in a bis complex (Figure 1). The symmetry is approximately D_{2d} in which the triply degenerate t_{2g} of O_h splits resulting in b_2 and e levels. Evidence of distortion from O_h in this bonding situation comes from the large^{6,7} quadrupole splitting (ΔE) observed in the unperturbed Mössbauer spectra.

It is interesting to consider the magnitude of ΔE for $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ (~ 3.3 at 4.2 K) along with those of other six-coordinate low-spin ferric systems such as $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_3$ ($\Delta E = 1.90 \text{ mm/sec}$, at 4.2 K)⁸ or $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_3$ ($\Delta E = 1.84$ at 4.2 K).⁹ Esr spectra indicate the latter two systems to have axial (trigonal) symmetry and orbital singlet ground terms corresponding to a hole in the d_{z^2} orbital.¹⁰ It is worthwhile to recall that in a crystal field approach for an orbital singlet ground term one expects the maximum value of the principal component of the electric field gradient tensor (V_{zz}) for a hole in the t_{2g} manifold and half as much when a doublet term is lowest. A ${}^2\text{E}$ ground term is actually further split by spin-orbit coupling and its components mixed to some extent with those of the higher ${}^2\text{B}$ or ${}^2\text{A}$ to give three, often relatively well separated, Kramers doublets. The usual effect of this

spin-orbit interaction as well as covalency is to give a reduced electric field gradient although cause no change of sign. Table I correlates the symmetry, ground term, sign of V_{zz} , and axial field component.

Table I

	Ground term	Sign of V_{zz}
Trigonal axial field (Δ)		
+	${}^2\text{E}$	-
-	${}^2\text{A}$	+
Tetragonal axial field (Δ)		
+	${}^2\text{E}$	+
-	${}^2\text{B}$	-

A maximum value of the valence contribution to ΔE for low-spin ferric systems is predicted¹¹ to be $\sim 2.5 \text{ mm/sec}$ using current best estimates of $\langle r^{-3} \rangle_{3d}$. The "saturation" (low temperature) splittings of "octahedral" low-spin iron(III) complexes with singlet ground terms seem typically of the order 1.7–2 mm/sec with values as large as the preceding maximum seldom observed. This may be attributed to so called "lattice" or covalence anisotropy contributions to V_{zz} of opposite sign to the valence electron contribution. On the other hand, values of $\Delta E \approx 2 \text{ mm/sec}$ might also be observed with an orbital doublet ground term when there is additional augmentation of V_{zz} by covalence anisotropy. In relation to this, it has recently¹² been shown that valence and "lattice" contribution to V_{zz} need not necessarily be of opposite sign. In any event quadrupole splittings of the order 1.5–2 mm/sec as well as the study of their temperature dependence can lead to ambiguity in the determination of the type or orbital ground level using ordinary Mössbauer spectroscopy.

The very large splitting of $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ is difficult to compare in a direct way to those observed for the tris-diimine systems. It does not seem reasonable that V_{zz} is reduced to a much smaller extent by spin-orbit and covalency effects relative to the foregoing diimines. On the other hand, the splitting for $[\text{Fe}(\text{terpy})_3](\text{ClO}_4)_3$ is probably due to extensive covalence anisotropy peculiar to the system and its unusual

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- (8) W. M. Reiff, *Chem. Phys. Lett.*, **8**, 297 (1971).
- (9) R. L. Collins, unpublished results.
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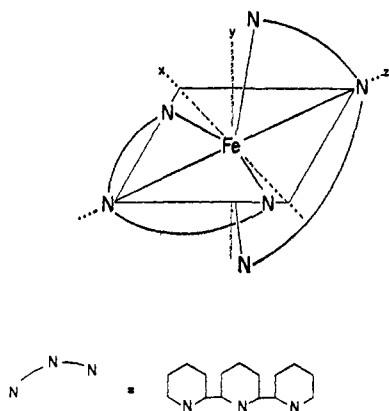
(11) R. M. Golding, *Mol. Phys.*, **12**, 13 (1967).

(12) A. J. Nozik and M. Kaplan, *Phys. Rev.*, **159**, 273 (1967).

Table II. Mössbauer Parameters^a

Compound	<i>T</i> (°K)	δ	ΔE	Γ_-	Γ_+	Γ_-/Γ_+	H_-/H_+	A_-/A_+
[Fe(terpy) ₂](ClO ₄) ₂	300	0.21	1.06	0.27	0.25	1.07	1.20	1.28
	4.2	0.29	1.06	0.31	0.30	1.05	1.17	1.22
[Fe(terpy) ₂](ClO ₄) ₃	300	0.005	3.05	0.29	0.29	1.00	0.87	0.86
	4.2	0.076	3.32	0.40	0.35	1.07	0.83	0.88

^a mm/sec relative to National Bureau of Standards iron foil; δ = isomer shift, ΔE = quadrupole splitting, Γ = width at half maximum absorption, H = peak height, A = peak area. The reproducibility of δ and ΔE is 0.01 mm/sec. The reproducibility of Γ 's is ± 0.03 , while that of the ratios is less than ± 0.08 .

Figure 1. Schematic representation of [Fe(terpy)₂]²⁺.

direct additive contribution to the valence distribution part of V_{zz} . In the present study these problems are approached using esr and the magnetic perturbation technique. The diamagnetic [Fe(terpy)₂](ClO₄)₂ is studied to see the effects of so called "lattice" or anisotropic covalent bonding *alone*. The results for this system should be helpful in interpretation of those for [Fe(terpy)₂](ClO₄)₃ for which both lattice and valence contributions to the quadrupole effect are possible.

Experimental Section

The Mössbauer spectra in longitudinal fields were determined at ambient temperature and 4.2 K, using superconductive solenoids previously¹³ described. Transverse measurements at ambient temperature were made with a Varian Associates Model 4500 magnet and accompanying power supply. Applied fields for 1-in. cylindrical tapered pole faces at 0.5 in. gap were nominally of the order 20 kG while the γ -ray source (50 mCi ⁵⁷Co in Cu) was maintained in a fringing field of less than 300 G. Unperturbed Mössbauer spectra were fitted using a modified NBS program.¹⁴

Epr spectra were obtained on a Varian E-4 spectrometer at X-band frequency and calibrated relative to diphenylpicryl-hydrazyl. Magnetic susceptibility measurements were made using the Faraday method on an apparatus whose cryogenics have been previously described.¹⁵ The compounds studied were prepared as outlined in the literature and gave satisfactory analyses.

Results

Mössbauer. The unperturbed Mössbauer spectrum of [Fe(terpy)₂](ClO₄)₂ at 4.2 K is given in Figure 3a while its spectra as a function of increasing applied field (at 4.2 K) are shown in Figures 3b, c, and d as well as at room temperature in Figure 2a. In relation to the unperturbed spectrum it is noteworthy that the quadrupole splitting is large and temperature independent. This is indicative of a rather large static distortion relative to other diamagnetic six-coordinate polyimine sys-

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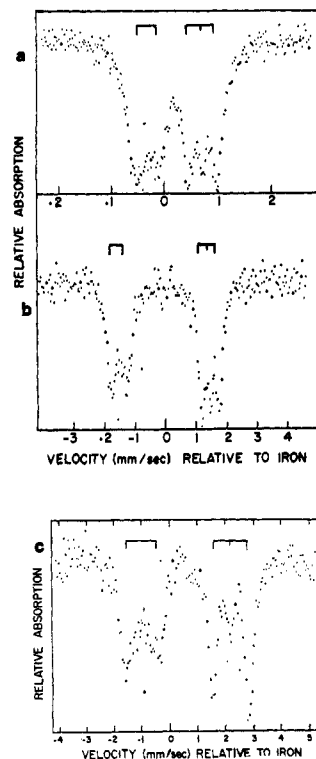


Figure 2. (a) Mössbauer spectrum of [Fe(terpy)₂](ClO₄)₂, 300 K, H (perpendicular) = 20 kG. (b) Mössbauer spectrum of [Fe(terpy)₂](ClO₄)₃, 300 K, H (perpendicular) = 20 kG. (c) Mössbauer spectrum of [Fe(terpy)₂](ClO₄)₃, 300 K, H (longitudinal) = 45 kG.

tems, *e.g.*, [Fe(phen)₃](ClO₄)₂ and [Fe(bipy)₃](ClO₄)₂, whose splittings are of the order 0.2–0.4 mm/sec, respectively.¹⁶ The other parameters (Table II) are normal for low-spin iron(II) except for the measurable and nearly temperature-independent, nonunity, peak height and area ratios. The iron(III) complex also exhibits height and area ratio asymmetry. It is not likely that this is due to Goldanski-Karyagin distortion¹⁷ in view of the lack of temperature dependence. On the other hand, owing to the general instability of perchlorates and the fact that the ferric compound reduces readily on pulverization, each sample was gently and only partially ground. This most probably results in residual orientation of sample microcrystals leading to the observed line intensity asymmetry.

It is evident from the perturbed spectra of [Fe(terpy)₂](ClO₄)₂, especially Figures 2a and 3d, that there is an apparent triplet at positive velocity and a broadened doublet at negative. In the case of iron-57 this implies both V_{zz} (the principal component of the electric

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(17) S. V. Karyagin, *Dokl. Phys. Chem.*, **148**, 110 (1964).

field gradient tensor) and ΔE negative.^{18,19} In addition the overall shape of the spectra, *i.e.*, broadened doublet and resolved triplet, suggests a small or near zero asymmetry²⁰ parameter (η) or therefore axial symmetry. The doublet-triplet splittings are nearly equal as is usually the case for the perturbed powder spectrum of an isotropic diamagnetic iron(II) complex or rapidly relaxing paramagnet at high temperatures. The effective field at the iron nucleus may be estimated from the observed triplet splitting.²⁰ Fields calculated in this manner are given in Table III. It is seen that for the

Table III. Effective Fields (4.2 K)

Compound	H_{applied}	$H_{\text{effective}}$
$[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_2$	26.0	25.3
$[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$	9.0	33.8
	18.2	66.0
	26.0	96.4

ferrous complex the effective field is nearly equal to the applied, reflecting the diamagnetic nature of this compound.

$[\text{Fe}(\text{terpy})_3](\text{ClO}_4)_3$. Several comments concerning the unperturbed spectra of $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ are in order. First of all the near zero value of isomer shift is typical of low-spin iron(III) bound to strong field ligands of the polyimine type under discussion. The quadrupole effect is very large. It is greater by a factor of nearly 2 than those reported for other low-spin ferric-polyimine systems and to this author's knowledge the largest yet observed for six-coordinate iron(III). The nature of the splitting in this and some other systems will be discussed subsequently. Finally it should be pointed out that the line width ratios are near unity and indicate little if any relaxation broadening. This is not unexpected for low-spin ferric where rapid spin-lattice relaxation is possible owing to incomplete quenching of the orbital angular momentum of the 2T ground term.

The doublet-triplet perturbed spectra (Figures 2b and 2c) of $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ at room temperature clearly show the principal component of the electric field gradient tensor *negative* for this system; *i.e.*, the doublet is at lower energy than the triplet. For these spectra the observed internal and applied fields are essentially equal. This is expected for a rapidly relaxing paramagnet at high temperatures where the Curie susceptibility is small. In D_{2d} symmetry using the basis set d_{xy} , d_{zz} , d_{yz} , the foregoing V_{zz} negative corresponds to a hole in d_{xy} and an orbital singlet ground term. These results will be seen to correlate with the esr data.

At 4.2 K (Figure 4a-d), the central component of the triplet is apparently much weaker perhaps reflecting the effects of magnetic anisotropy. The spread of the g values for the esr spectrum certainly suggests such anisotropy. Significant magnetic anisotropy is also implied by the large deviation of the triplet to doublet splitting ratio from unity and the broadness of the transitions. The value of this ratio is ~ 2 and slightly field dependent

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(19) W. M. Reiff, *Coord. Chem. Rev.*, **10**, 37 (1972).

(20) R. L. Collins and J. C. Travis, "Mössbauer Effect Methodology," Vol. 3, Plenum Press, New York, N. Y., 1967, p 123.

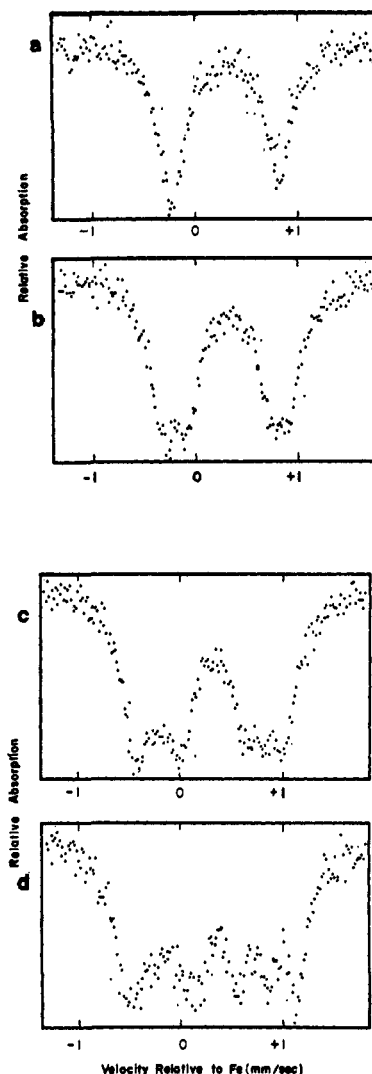


Figure 3. (a) Mössbauer spectrum of $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_2$, 4.2 K; $H(\text{longitudinal}) = (a) 0, (b) 9, (c) 18, (d) 26$ kG.

indicating that the material is not completely magnetically saturated for the values of H_{app}/T involved. An approximate value of the angle θ between V_{zz} and the internal field can be calculated from the triplet to doublet splitting ratio and θ is of the order $\sim 90^\circ$ for the present case.

Slower spin-lattice relaxation in conjunction with a larger Curie susceptibility and its anisotropy can also significantly affect the low temperature perturbed spectra.²¹ In particular a large internal field may result from the application of relatively small external fields. This appears to be the case as seen in Table III.

Esr and Susceptibility Data. The X-band esr spectrum of $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ as the undiluted powder at 78 K is shown in Figure 5. An inset spectrum corresponds to the $g = 2.54$ signal for the material diluted in frozen H_2SO_4 solution at 78 K. The spread of the g values is large and indicates considerable magnetic anisotropy. Although there is some asymmetry to the $g = 2.54$ signal of the polycrystalline powder, it is evident that the system is axial and certainly so when diluted. From the g values, it is often possible to obtain the axial (Δ) and rhombic (ϵ) components of the

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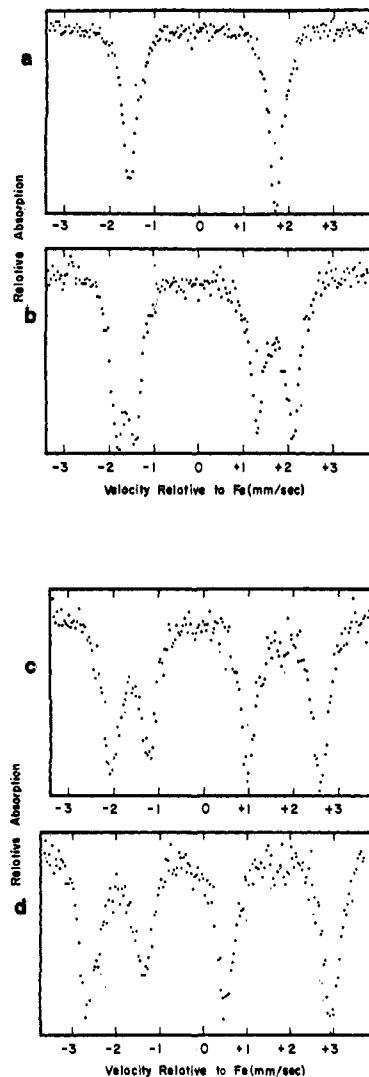


Figure 4. Mössbauer spectrum of $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$, 4.2 K; $H(\text{longitudinal}) = (\text{a}) 0, (\text{b}) 9, (\text{c}) 18, (\text{d}) 26 \text{ kG}$.

crystal field as well as the coefficients of the ground Kramers doublet using theoretical methods outlined by Stevens²² and Griffith.²³ The other important parameter is k , the orbital angular momentum reduction factor of Stevens. The ground Kramers doublet is then given by

$$\begin{aligned}\psi &= A_1|1^+\rangle + B_1|\zeta^-\rangle + C_1|-1^+\rangle \\ \psi &= A_1|1^-\rangle - B_1|\zeta^+\rangle + C_1|-1^-\rangle \\ \zeta &= \frac{1}{\sqrt{2}}\{|2\rangle - |-2\rangle\}\end{aligned}$$

with

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

The matrix of the combined action of spin-orbit coupling and a low-symmetry ligand field for a single hole in the t_{2g} manifold was solved by computer with the best

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(23) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961, p 364.

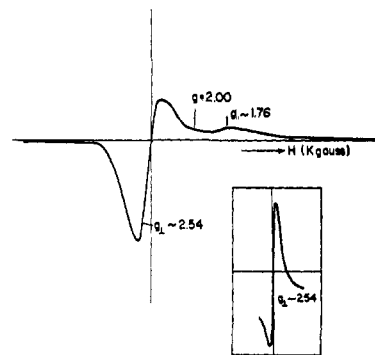


Figure 5. X-Band esr spectrum of $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ at 78 K for the undiluted polycrystalline powder; inset is for solution in H_2SO_4 at 78 K.

fit found for $g_x, g_y = -2.54, g_z = +1.76$, and $k = 1.13$. The coefficients of the ground Kramers doublet are $A_1 = 0.19, B_1 = 0.98$, and $C_1 = 0.00$ while those of the excited doublets are $A_2 = 0.98, B_2 = 0.19$, and $C_2 = 0.00$ and $A_3 = 0, B_3 = 0.00$, and $C_3 = 1.00$. The ground doublet is therefore primarily a d_{xy} "hole." Energies of the three Kramer doublets in multiples of the absolute value of the spin-orbit coupling constant (λ) are $E_1 = -2.74, E_2 = 0.94, E_3 = 1.80$, or therefore three well-separated doublets. Finally the low-symmetry splitting parameters are such that $\epsilon/\lambda \approx 0$ and $\Delta/\lambda = +3.90$. Since λ for low-spin iron(III) is negative, Δ is therefore *negative*. Thus the esr data correlate with a 2B ground term (d_{xy} hole) in the absence of spin-orbit splitting and are consistent with the Mössbauer results. The magnitude of Δ can be assessed after an appropriate choice of λ is made. Since k is greater than unity, it is not unreasonable to choose λ at least equal to λ_0 , the free ion value. Thus using²⁴ $\lambda_0 = -435 \text{ cm}^{-1}$, $\Delta \approx -1700 \text{ cm}^{-1}$, a rather large axial field component. This is not surprising in view of the ease with which the esr spectrum can be determined, *i.e.*, cooling to only 78 K. Cooling to even lower temperatures is required for relatively undistorted systems having formally 2T ground terms owing to broadening by rapid spin-lattice relaxation. Spin-lattice relaxation times, however, become longer with distortion and significant splitting of the 2T ground term as in the present case.

In passing, it should be mentioned that while values of k greater than unity are not expected for π delocalizing polyimine ligands such as terpyridine, similar results have been obtained in other investigations. For instance k values of unity have been found for $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_3$ and $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_3$ in studies of powder susceptibility²⁴ while $k = 1.07$ was found for the latter complex using esr.¹⁰

To conclude this section it is worthwhile to present some susceptibility data for $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ that serves as an independent measure of the axial splitting (Δ). The temperature dependence of the molar susceptibility of this system has been carefully determined from 300 to 22 K for the powder using the Faraday method (Table IV). The effective magnetic moment varies smoothly from 2.17 to 1.95 BM over this range and this variation was fitted according to the method of Figgis.²⁵ The most reasonable, although by no means

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Table IV. Magnetic Data for $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$

T (°K)	χ_g ($\times 10^6$ cgs)	χ'_M ($\times 10^6$ cgs)	μ_{eff} (BM)
290.0	1.98	2,030	2.17
248.0	2.39	2,370	2.17
201.0	2.88	2,770	2.11
166.0	3.55	3,320	2.10
116.0	5.03	4,530	2.05
80.0	7.18	6,300	2.01
44.5	13.07	11,130	1.99
30.5	18.89	15,910	1.97
22.0	25.84	21,610	1.95

unique, fit (Figure 5) to these data corresponds to $\Delta \approx +820 \text{ cm}^{-1}$. Thus while there is still a relatively large axial field component it is now of positive sign indicating a doubly degenerate (2E) ground term. The fact that the sign is opposite to that found here spectroscopically is not surprising. Several recent investigations^{26,27} have shown that the temperature dependence of the mean magnetic moment of powders is not nearly as sensitive to the variation of sign and magnitude of Δ as the principal moments obtained from single-crystal susceptibility anisotropy measurements. Even though fits to such powder susceptibility data are unreliable for the determination of the sign of Δ and type of ground term (especially in the limit of very large distortion), it is still worthwhile to present the temperature dependence of μ_{eff} . The rather low value of μ_{eff} at room temperature and its approach to the spin-only value with decreasing temperature clearly suggest a very large distortion for the system consistent with the Mössbauer and esr results.

Discussion

Sign of V_{zz} . In the systems under consideration, distorted, strong-field complexes, σ and π bonding effects are not readily separable. However, we give the following analysis in view of the approximate planar geometry of the coordinated ligand and the fact that its central nitrogen bonds most strongly. For the diamagnet, $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_2$, the buildup of charge concomitant to strong σ bonding along a unique axis should result in V_{zz} negative as observed. The σ MO corresponding to strong axial bonding and V_{zz} negative will have considerable metal d_{z^2} character. At the same time π bonding by the " t_{2g} " orbitals cannot be ignored. π bonding of importance to stabilization of low-spin ferrous complexes is delocalization of metal electrons (in the present case those in d_{z^2} , d_{yz}) to empty π^* molecular orbitals of the ligand. This is evidenced in the relatively low energy ($540 \text{ m}\mu$), high intensity charge transfer band for the visible spectrum⁴ of the $[\text{Fe}(\text{terpy})_2]^{2+}$ cation. However, such π bonding does not appear to be of primary importance in relation to the electric field gradient tensor for then the quadrupole splitting might well be smaller and even positive.

In relation to the ferric complex, the following considerations are important. The planarity of the coordinated ligand requires that the π network of each pyridine no longer be independent but conjugated. It is then reasonable to assume that the lowest energy filled ligand MO is antisymmetric with respect to the

(26) A. K. Gregson and S. Mitra, *Chem. Phys. Lett.*, **3**, 528 (1969).

(27) M. Gerloch, J. Lewis, G. G. Phillips, and P. N. Quedest, *J. Chem. Soc. A*, 194 (1970).

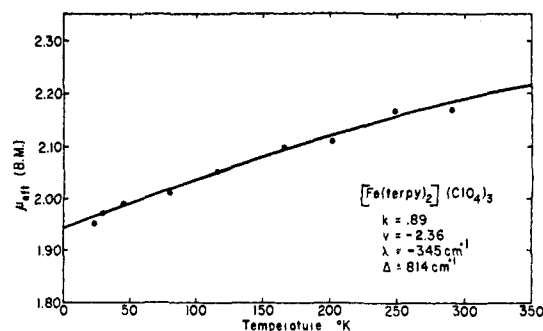


Figure 6. Effective moment vs. temperature for $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$: (· · ·) experimental data, (—) fit to experiment.

plane of the ligand. A model of $[\text{Fe}(\text{terpy})_2]^{2+}$ shows that the metal t_{2g} orbitals have appropriate symmetry for various degrees of π bonding with the foregoing ligand MO. Ligand to metal π bonding can then stabilize the system by reduction of the metal ion charge. A charge transfer band corresponding to this process is observed²⁸ at $704 \text{ m}\mu$, somewhat lower in energy than the metal to ligand band of the ferrous system. Such π bonding apparently destabilizes the metal d_{xy} since V_{zz} is negative and the coefficients of the lowest energy Kramers doublets indicate a hole in d_{xy} .

Magnitude of ΔE . The sign of V_{zz} for $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_2$ is the same as that in the ferric analog. This lends support to the explanation that the unusually large quadrupole splitting of the latter system is due to a nearly direct, additive covalency contribution similar in nature to that present in the iron(II) system, *i.e.*, strong σ bonding along a single axis. This can be better seen from the following considerations. Let it be assumed that a rough estimate of the quadrupole splitting of $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ due to the valence electron distribution *alone* (ΔE_{val}) can be obtained by subtracting the splitting for the diamagnetic ferrous system at 4.2 K from that observed for the ferric. This gives a value of 2.26 mm/sec for ΔE_{val} at 4.2 K. An independent value of ΔE_{val} for $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ can be calculated using the coefficients of the three Kramers doublets and their respective eigenvalues in the theory outlined by Golding.¹¹ This calculation gives $\Delta E_{\text{val}} = 2.39 \text{ mm/sec}$, in fair agreement with that obtained above. Similar calculations for $[\text{Fe}(\text{bipy})_3](\text{PF}_6)_3$ using published¹⁰ esr data give $\Delta E_{\text{val}}(4.2 \text{ K}) = 2.30 \text{ mm/sec}$. The observed value of $\Delta E(4.2 \text{ K})$ is 1.90 mm/sec . Thus a covalency contribution of opposite sign and 0.40 mm/sec is required to result in the observed value of ΔE . The sign of V_{zz} has recently²⁹ been shown to be positive for $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_3$ and $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_3$. Interestingly, and perhaps not coincidentally, the value¹⁶ of ΔE for $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_2$ is 0.39 mm/sec and negative.²⁹ In other words it appears that a rough estimate of the covalency contribution to ΔE for low-spin ferric complexes may be sought in the value of ΔE for the analogous low-spin ferrous complex, should the latter exist. Thus similarly, using the esr data for $[\text{Fe}(\text{phen})_3](\text{PF}_6)_3$, one calculates $\Delta E(4.2 \text{ K})_{\text{val}} = 2.02 \text{ mm/sec}$ while $\Delta E(4.2 \text{ K})$ observed is 1.84 mm/sec and that¹⁶ of the corresponding ferrous system for which there are only data to 78 K is 0.23 mm/sec . An attempt at using

(28) R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

(29) W. M. Reiff and R. DeSimone, *Inorg. Chem.*, **12**, 1793 (1973).

the method of Golding for analysis of the temperature dependence of ΔE for $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ was somewhat less successful and no discussion of this type is presented here.

Orbital Ground States. A study of the literature for low-spin ferric complexes shows that where detailed investigations have been performed, nondegenerate orbital ground terms seem to be generally favored. Thus for instance in addition to $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$ considered here and for which the ground term is ${}^2\text{B}$, nitrogen systems^{8,10} such as $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_3$, $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_3$, and the corresponding dicyano bisdiimine complexes²⁹ all have nondegenerate (${}^2\text{A}$) ground terms. These observations extend to sulfur compounds, e.g., $[\text{Fe}(\text{dithioacetylacetonate})_3]$,³⁰ $[(\text{phenyl})_4\text{P}]_3[\text{Fe}(\text{S}_2\text{C}_2(\text{CCN})_2)_3]$ —a tris dithiolene,³¹ and the persulfides³² $[\text{Fe}(\text{ttd})_2(\text{dtt})]$ and $[\text{Fe}(\text{ttd})(\text{dtt})_2]$ where ttd is trithioperoxy-*p*-toluate and dtt is dithio-*p*-toluate. For $[\text{Fe}(\text{dtt})_3]$, V_{zz} is positive and Hill, *et al.*,³² assign the hole in the t_{2g} manifold equally to d_{zz} and d_{yz} or thus a doubly degenerate ground term. However, the probable near D_3 symmetry of this complex suggests threefold quantization and hence $V_{zz} > 0$ corresponds to a hole in d_{zz} or once again an orbitally nondegenerate ground term. Finally it is interesting to point out that

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the trans dichloroarsenic system $[\text{Fe}(o\text{-phenylenebis}(\text{dimethylarsine}))_2\text{Cl}_2]\text{BF}_4$ also exhibits a nondegenerate ground term on the basis of perturbed Mössbauer and esr results.³³

The foregoing observations for a variety of systems may be rationalized from two points of view. The most obvious is that a nondegenerate ground term allows avoidance of Jahn-Teller distortion which although not usually large for t_{2g} configurations would still have to occur for a ${}^2\text{E}$ ground term. The second point deals with reduction of the ferric ion charge by ligand to metal π bonding. For low-spin d^5 , a nondegenerate ground term readily results when there is destabilization of a single metal orbital (d_{xy} in the present case) by strong ligand to metal π bonding and concomitant metal charge reduction.

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Preparation, Structure, and Magnetism of a Tetranuclear Basic Quinoline Adduct of Copper(II) Trifluoroacetate

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Abstract: The basic copper(II) trifluoroacetate adduct $[\text{Cu}_2\text{OH}(\text{O}_2\text{CCF}_3)_3(\text{quinoline})_2]$ has been prepared and shown by a crystal structure analysis to have a novel tetranuclear structure. This complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.401$ (16) Å, $b = 12.773$ (20) Å, $c = 15.237$ (24) Å, $\alpha = 58.07$ (5)°, $\beta = 124.22$ (4)°, $\gamma = 113.81$ (4)°. Observed and calculated densities are 1.73 (2) and 1.76 g/cm³, respectively. The structure determination was based upon 3332 data collected by counter methods; full-matrix least-squares refinement converged to a conventional R factor of 0.073. The crystal structure is comprised of centrosymmetric tetranuclear molecules in which copper atoms are linked by carboxylate bridges and by triply bridging OH^- ions. Each of the two crystallographically independent Cu^{2+} ions is coordinated to four oxygen atoms and a quinoline nitrogen atom in a distorted square pyramidal configuration. Two of the three independent carboxylate groups form bridges from an apical coordination site of one copper atom to a basal site of another; the third trifluoroacetate group is monodentate. Magnetic susceptibility measurements clearly demonstrate the presence of substantial Cu-Cu interaction. Consideration of various models for this interaction leads to the conclusion that it must involve all four metal atoms and must be transmitted, at least in part, by the triply bridging hydroxo group.

Copper(II) trifluoroacetate differs in a number of important respects from copper(II) acetate and its higher homologs. Magnetic studies have shown anhydrous $\text{Cu}(\text{O}_2\text{CCF}_3)_2$ to possess a room-temperature effective magnetic moment of ~ 1.8 BM and to exhibit molar magnetic susceptibilities in conformity with the Curie-Weiss expression over the temperature range 94-

297°K.¹ These results may be contrasted with the room-temperature μ_{eff} of 1.4 BM and the antiferromagnetic χ_M vs. T behavior exhibited by anhydrous copper(II) acetate.² It has been suggested that this

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