Electronic Structure of Potassium Ferricyanide

P. B. Merrithew* and A. J. Modestino

Contribution from the Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609. *Received March 25, 1971*

Abstract: An electronic model for potassium ferricyanide has been developed which is consistent with the low-temperature electron spin resonance data, the temperature dependence of the quadrupole splitting, the components of the electric field gradient tensor as measured from area-ratio experiments, and the "lattice" contributions to the electric field gradient tensor as determined from nmr experiments. This model requires a low value for the spin–orbit coupling constant, -80 ± 5 cm^{-1}. The magnitudes of the spin–orbit coupling constant and the orbital reduction factor indicate that $\langle r^{-3}\rangle_{t_{2g}}$ is about 15% of the free ion value.

The electronic structure of potassium ferricyanide has been studied extensively. In 1956, Baker, Bleaney, and Bowers[1] measured the electron spin resonance (esr) spectrum of potassium ferricyanide diluted in the isomorphous cobalt salt. Bleaney and O'Brien,[2] by comparison of these esr data with the susceptibility data of Jackson[3] and Masson,[4] concluded that the effective spin-orbit coupling constant $\zeta' = -278$ cm^{-1}. Oosterhuis and Lang[5] fit the low-temperature Mössbauer spectroscopy quadrupole splitting and some of the paramagnetic hyperfine spectra in terms of a model similar to that of Bleaney and O'Brien. However, they were unable to account for the temperature dependence of the quadrupole splitting or the components of the electric field gradient tensor (EFG). Oosterhuis and Lang[5] suggested that the lack of agreement of their model and the temperature dependence of the quadrupole splitting was due to a temperature-dependent crystal field. Figgis, Gerloch, and Mason[6] investigated the paramagnetic anisotropy and developed a model which was in reasonable agreement with that of Bleaney and O'Brien.

It should be possible for a model of the electronic structure of potassium ferricyanide to account for the low-temperature esr data of the dilute salt, the temperature dependence of the magnetic susceptibility of the concentrated and dilute salts, and the temperature dependence of the Mössbauer spectroscopy data of the concentrated and dilute salts if the following conditions are satisfied: (a) the structure of the ferricyanide ion is the same in the dilute salt as in the concentrated salt and (b) the crystal structure of potassium ferricyanide does not change with temperature.

Guha[7] and Ristau, Ruckpaul, and Schoffa[8] reported unusual behavior in the magnetic susceptibility at about 130°. Stephanson and Morrow[9] reported an anomaly in the specific heat at the same temperature. Figgis, *et al.*,[6] performed a detailed investigation of this unusual behavior. The bulk susceptibility has no discontinuity. In the concentrated salt, one of the principal crystal anisotropies shows a maximum at 130°. This maximum is absent in the dilute crystals. The crystal structures obtained by these authors at 95 and 300° show no change in the structure of the ferricyanide octahedra. Figgis, *et al.*, concluded that the maximum "probably represents only a small effect due to a slight change or reorientation of the ligand field. . . ."

The quadrupole splitting results obtained for the dilute salt[5] are in substantial agreement with the results obtained for the concentrated salt.[10,11] None of the quadrupole splitting data, including that herein, shows any discontinuity.

In view of these results, it appears that (a) and (b) are reasonably well satisfied and that a model for potassium ferricyanide should account for the temperature dependence of quadrupole splitting. In particular, the failure of the model proposed by Bleaney and O'Brien to account for the temperature dependence of the quadrupole splitting cannot be attributed to a temperature-dependent crystal field. According to this model, the excited states cease to be populated at temperatures lower than about 125°. The change in the quadrupole splitting which occurs between this temperature and 20° (a change of about 30%) must then be due to a change in the "lattice" contributions. Such a large change is contrary to that which is normally observed[11,12] and would require a fundamental alteration in the structure. A change of this magnitude is especially unreasonable in view of the fact that the crystal structure shows no substantial changes between 95 and 300°.[6]

Experimental Section

Mössbauer spectra were obtained with powdered samples of $K_3Fe(CN)_6$. The spectrometer consists of a constant acceleration type of drive synchronized with a 512 channel analyzer run in time mode. The reproducibility is better than 0.1%, and the integral nonlinearity is less than 1%. Low-temperature spectra were obtained by employing a vacuum-insulated cryostat. The temperature was varied by altering the rate of flow of liquid nitrogen to the sample chamber. Temperature measurement was by a copper–constantan thermocouple. The accuracy is ±2°. The spectra were fit with a least-squares fitting program.[13] The accuracy of the quadrupole splitting data was determined statistically.[14] The quadrupole splitting results are given in Table I (see also Figure 1).

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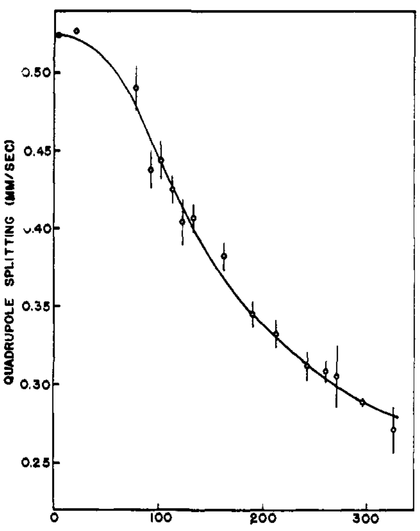

Figure 1. The temperature dependence of the quadrupole splitting fitted to model II. The data points at 20 and 4.2° are from ref 10.

Discussion

The spin-orbit distortion matrix for the low-spin d^5 ion[2] was solved in terms of ζ', the effective spin-orbit coupling constant, and δ' and ϵ', the effective values of the distortion parameters as defined by Golding.[15]

Table I. Quadrupole Splitting Results for $K_3Fe(CN)_6$

Temp, °K	Quadrupole splitting, mm/sec
326	0.271 ± 0.015
296	0.289 ± 0.002
271	0.306 ± 0.020
260	0.309 ± 0.007
242	0.312 ± 0.009
212	0.333 ± 0.009
190	0.345 ± 0.008
163	0.382 ± 0.009
133	0.407 ± 0.009
123	0.404 ± 0.015
113	0.425 ± 0.009
103	0.444 ± 0.011
93	0.438 ± 0.011
89	0.470 ± 0.010
81	0.452 ± 0.010
78	0.490 ± 0.014

The g values and the temperature-dependent or "valence" contributions to the EFG were calculated by employing the equations of Oosterhuis and Lang[5] (after making the appropriate changes to account for the difference in basis wave functions).

When the temperature-independent or "lattice" contributions to the EFG are small in comparison to the temperature-dependent or valence contributions, the temperature dependence of the quadrupole splitting can be expressed as a function of the temperature-dependent contributions only[16]

$$\Delta E^0 - \Delta E \simeq \Delta E_d{}^0 - \Delta E_d$$

The superscript zero refers to the quadrupole splitting at $T = 0$ and the subscript d refers to the quadrupole splitting calculated from the temperature-dependent contributions. ΔE^0 was taken as 0.524 mm/sec,[10] and the temperature dependence of the quadrupole splitting was fitted in terms of ζ', δ', ϵ', and the orbital reduction factor, N^2. A unique fit is not obtained, but no solution is found with the absolute value of ζ' greater than 100 cm^{-1}.

In the original work, Bleaney and O'Brien[2] found that there were two solutions consistent with the esr g values. One of these solutions required that the factor $k = 0.875$, the other $k = 0.56$. By comparison with the susceptibility data, they found that the former solution was consistent with $\zeta' = -278$ cm^{-1}. The latter solution was ruled out because "even an approximate fit requires an excessively low value of the spin-orbit coupling."

Taking $k = 0.56$, a solution is found which is consistent with the temperature dependence of the quadrupole splitting and the esr data. This solution (model I) gives $\zeta' = -80$ cm^{-1}, $\delta' = 40.3$ cm^{-1}, $\epsilon' = -5.0$ cm^{-1}, and $N^2 = 0.124$. The susceptibility data of Jackson[3] and Masson[4] indicate a reversal in the magnetic anisotropy in the ab plane of the concentrated salt below 70°. This observation was confirmed by Bleaney and O'Brien.[2] Such a reversal corresponds to an interchange in the $g = 2.10$ and $g = 2.35$ directions. The reversal causes ϵ' to change sign (model II) and interchanges the V_{zz} and V_{xx} components of the electric field gradient tensor. The interchange, however, does not affect the temperature dependence of the quadrupole splitting. The experimental and calculated g values are compared in Table II.

Table II

	g_{xx}	g_{yy}	g_{zz}
Measured at 20° dilute crystal	0.915 ± 0.01	2.35 ± 0.02	2.10 ± 0.02
Model I ($k = 0.56$)	0.912	2.337	2.102
Model II ($k = 0.56$)	0.912	2.102	2.337

The "lattice" contributions to the EFG can be estimated from the ^{59}Co nmr measurements of the isomorphic cobaltic salt.[17] Column 3 of Table III gives the lattice contributions as calculated by Oosterhuis and Lang.[5] The sign of the V_{zz} and V_{yy} components were assigned to be consistent with the positions of the potassium ions in the lattice. The sign of V_{xx} was assigned to give the best fit to the Mössbauer spectroscopy data. Columns 6 and 7 give the EFG components as determined from area-ratio experiments on the concentrated salt.[5] The results at 300° are suspect, since a 5° rotation of the EFG tensor was required to fit the experimental data. There are no experimental data to confirm such a change. Such a rotation may not be real, but the result of resolution difficulties encountered at room temperature.

The EFG components as calculated according to models I and II are given in the first two columns of Table III. The total EFG components are obtained by summing the valence and lattice contributions. Since the quadrupole splitting does not change between 20 and 0°,[10] a comparison can be made between

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Table III

	"Valence" EFG[a] Model I (II) 0°	"Valence" EFG[a] Model I (II) 300°	"Lattice" EFG[b]	Total EFG[b] Model I (II) 0°	Total EFG[a] Model I (II) 300°	Exptl EFG[b] (from area ratios) 20°	300°
			Preliminary Results, $N^2 = 0.124$				
V_{xx}/e	0.680 (0.586)	0.240 (0.135)	−0.08	0.600 (0.506)	0.160 (0.055)	0.47	0.396
V_{yy}/e	−1.266 (−1.266)	−0.377 (−0.377)	−0.57	−1.836 (−1.836)	−0.947 (−0.947)	−1.89	−1.03
V_{zz}/e	0.586 (0.680)	0.135 (0.240)	0.65	1.236 (1.330)	0.785 (0.890)	1.42	0.65
			Final Results, $N^2 = 0.127\ (0.131)$				
V_{xx}/e	0.697 (0.620)	0.246 (0.143)	−0.08	0.617 (0.540)	0.166 (0.063)	0.47	0.396
V_{yy}/e	−1.296 (−1.337)	−0.384 (−0.401)	−0.57	−1.866 (−1.907)	−0.954 (−0.971)	−1.89	−1.03
V_{zz}/e	0.600 (0.719)	0.139 (0.254)	0.65	1.250 (1.369)	0.789 (0.904)	1.42	0.65
	Includes factor of $(1 - R) = 0.68$		Includes factor $(1 - \gamma_\infty) = 10.0$				

[a] 10^{24} cm^{-3}. [b] See ref 5; 10^{24} cm^{-3}.

the 0° predictions and the data obtained at 20°. Model II is in excellent agreement with the nmr and area-ratio data at 20°. The agreement between the data and model I at room temperature is not as good. The difference between the Model I predictions and the room-temperature data is possibly due to experimental difficulties or a small change in structure with temperature. However, model I agrees with the data much better than model II, in agreement with the anisotropy reversal.

Since the lattice contributions have a small effect on the temperature dependence of the quadrupole splitting, these contributions were included in the calculation of the temperature dependence. In order to obtain a fit, the magnitude of N^2 was increased to 0.127 and 0.131 for models I and II, respectively. This change slightly improves the agreement between the models and the EFG component data.

This model (model II at low temperatures, model I above 70°) cannot be reconciled with the magnetic susceptibility data. The susceptibility may be estimated from the tables listed by Figgis.[18] A comparison of the observed[18] and calculated values is given in Table IV. The treatment of Figgis assumes an axial distortion. It does not appear possible that the small rhombic distortion indicated by this model can account for the differences between the observed and calculated values. We cannot account for the susceptibility results.

Table IV

Temp, °K	μ_{eff}(calcd)	μ_{eff}(obsd)[a]
300	~2.00	2.24
200	~2.05	2.18
100	~2.05	1.95
80	~1.99	1.90

[a] See ref 18.

The esr data and the temperature dependence of the quadrupole splitting suffice to determine a unique model. Since this model agrees with the EFG component data obtained from area-ratio and nmr experiments, the model is not the result of fortuitous agreement. The earlier model based on the magnetic susceptibility[2,6] is not confirmed by such additional experiments. The fact that the model proposed here is internally consistent and in accord with the structural data provides further evidence that the model is real.

The relative orbital energies predicted by this model are the same as those deduced by Figgis, *et al.*[6] The $1/\sqrt{2}(xz - yz)$ orbital (as defined in the cubic axis system) lies 121 ± 15 cm^{-1} ($3\delta'$) higher than the $1/\sqrt{2}\cdot(xz + yz)$ and xy orbitals.

The separation between the $1/\sqrt{2}(xz + yz)$ and xy orbitals varies with temperature from −30 to +30 cm^{-1} ($6\epsilon'$). The potassium ions, which lie along the crystalline c axis approximately midway between the x and y axes, evidently stabilize the $1/\sqrt{2}(xz + yz)$ and xy orbitals by approximately the same amount.

The magnitude of the spin–orbit coupling constant, −80 ± 5 cm^{-1}, is very small in comparison to the free-ion value, 460 cm^{-1}.[19] The orbital reduction factor, N^2, is reduced from the free-ion value by approximately the same factor. Ballhausen[20] derives a formula $k = 1 - 1/2N^2A_\pi^2$, where $\psi = N(\psi_{\text{Fe}} + A_\pi\psi_{\text{lig}})$. With $k = 0.56$, neglecting overlap, this leads to $N^2 = 0.12$. This value of N^2 is in agreement with that found from the Mössbauer data. This model indicates that $\langle r^{-3}\rangle_{t_{2g}}$ is about 15% of the free ion value.

The substantial reduction from the free-ion value of both the spin–orbit coupling constant and the orbital reduction factor observed for potassium ferricyanide may be typical of low-spin iron compounds. It has been shown from the quadrupole splitting data[21] that the *N*,*N*-dialkyldithiocarbamate complexes of Fe(III) (those which exhibit typical low-spin behavior) also show low values for the spin–orbit coupling constant and the orbital reduction factor. Data have been obtained in this laboratory on numerous low-spin Fe(III) complexes. Most of these data show that the quadrupole splitting is temperature dependent at 77°. As mentioned in the introduction, this result is inconsistent with a spin–orbit coupling constant with absolute magnitude greater than 200 cm^{-1}.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Professor Hobey of this department for helpful discussions.

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