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The Temperature Dependence of the Quadrupole Splitting of Several High-Spin Iron(II) Compounds

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Mössbauer spectra were obtained for the compounds $Fe(py)_4(SCN)_2$ (py = pyridine), $Fe(py)_4Cl_2$, $Fe(py)_4I_2$, and $Fe(py)_4I_2 \cdot 2py$ between 100 and 300°K. A theoretical expression was derived which describes the temperature dependence of the quadrupole splitting. The splittings among the d_{xy}, d_{xz}, and d_{yz} orbitals were determined approximately. It was also found that $Fe(py)_4I_2 \cdot 2py$ has a trans configuration and that $Fe(py)_4Cl_2$ has the cis configuration.

Introduction

In Mössbauer spectroscopy experiments high-spin ($S = 2$) ferrous compounds normally show relatively large, temperature-dependent electric quadrupole splittings. The magnitude of the quadrupole splitting is a function of the temperature, orbital splittings, ligand symmetry, and nature of the ligand–metal bonds. Because of the many variables involved, measurement of the quadrupole splitting at a single temperature is often not very informative.

This work was undertaken to determine if more information might be obtained from an investigation of the temperature dependence of the quadrupole splitting. The compounds $Fe(py)_4(SCN)_2$ (py = pyridine), $Fe(py)_4Cl_2$, $Fe(py)_4I_2$, and $Fe(py)_4I_2 \cdot 2py$ were chosen for investigation because this series exhibits an unusually large variation in the room-temperature quadrupole splitting.[1]

Theory

For ^{57m}Fe the quadrupole splitting is given by

$$\Delta E = \frac{1}{2}e^2qQ[1 + \frac{1}{3}\eta^2]^{1/2} \qquad (1)$$

where Q is the quadrupole moment of ^{57m}Fe. The field gradient $q = V_{zz}/e$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ are expressed in terms of the components of the electric field gradient tensor (EFG) at the nucleus. Assuming an ionic model, the quantities

$$\begin{aligned} q &= (1 - R)q_{\text{val}} + (1 - \gamma_\infty)q_{\text{lat}} \\ \eta q &= (1 - R)\eta_{\text{val}}q_{\text{val}} + (1 - \gamma_\infty)\eta_{\text{lat}}q_{\text{lat}} \end{aligned} \qquad (2)$$

can be written, where the subscript "val" refers to the charge distribution of the uncompensated 3d "valence" electron of the metal ion and the subscript "lat" refers to the charge distribution of the neighboring ions in the lattice. The Sternheimer factors[2,3] are included to account for the polarization of the electron core.

If the effects of spin–orbit coupling are neglected, the "valence" contributions to the EFG can be calculated for the ferrous ion in a distorted octahedral field,[4,5] as shown by

$$\begin{aligned} q_{\text{val}} &= \frac{4}{7}\langle r^{-3}\rangle Z^{-1}[1 - e^{-\Delta_1/kT} - e^{-\Delta_2/kT}] \\ \eta_{\text{val}}q_{\text{val}} &= \frac{4}{7}\langle r^{-3}\rangle Z^{-1}[\frac{3}{2}e^{-\Delta_1/kT} - \frac{3}{2}e^{-\Delta_2/kT}] \end{aligned} \qquad (3)$$

where $Z = 1 + e^{-\Delta_1/kT} + e^{-\Delta_2/kT}$. The displacements of the d_{yz} and d_{xz} orbitals from the ground orbital, d_{xy}, are given by Δ_1 and Δ_2, respectively. For ionic compounds the "lattice" contributions to the EFG can be calculated by performing a lattice summation. Nozik and Kaplan[6] made these calculations for several ionic compounds and found the "lattice" contributions to be relatively minor in respect to the "valence" effects but still significant.

Covalent compounds present a more difficult problem. In a covalent compound the approximations that the 3d orbitals are like those of the free ion and that the ligands are point charges are not valid. It is also likely that covalency will affect the Sternheimer factors.[6] A rigorous appraisal of covalency effects must involve a full molecular orbital treatment.[6-8]

The effects of spin–orbit coupling on the quadrupole splitting have been described by Ingalls.[4] The spin degeneracy of each orbital state is partially or completely lifted and its orbital character is altered by mixing. These effects are a complex function of Δ_1, Δ_2, and λ, the spin–orbit coupling constant. It is quite impractical to obtain an explicit expression describing the effects of spin–orbit coupling.[4]

In view of the difficulties in treating covalency and spin–orbit coupling effects in a rigorous manner, we have developed the following approximate treatment.

The contributions to the EFG are separated according to their temperature dependence

$$\begin{aligned} q &= q_{\text{i}} + q_{\text{d}} \\ \eta q &= \eta_{\text{i}}q_{\text{i}} + \eta_{\text{d}}q_{\text{d}} \end{aligned} \qquad (4)$$

The terms with subscript d represent the temperature-dependent contributions to the EFG from the electrons in the three molecular orbitals which have substantial d_{xy}, d_{xz}, and d_{yz} character. Those with subscript i represent the temperature-independent part which includes contributions from electrons which are formally assigned to the ligands and those which occupy molecular orbitals with substantial $d_{x^2-y^2}$ and d_{z^2} character.

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* Department of Chemistry, Worcester Polytechnic Institute, Worcester, Mass. 01609. Partially completed at the Chemistry Department, University of Michigan.

(1) R. M. Golding, K. F. Mok, and J. F. Duncan, *Inorg. Chem.*, **5**, 774 (1966).

(2) R. M. Sternheimer, *Phys. Rev.*, **130**, 1423 (1963).

(3) A. J. Freeman and R. E. Watson, *ibid.*, **131**, 2566 (1963).

(4) R. Ingalls, *ibid.*, *A*, **133**, 787 (1964).

(5) M. Weissbluth, *Struct. Bonding (Berlin)*, **2**, 1 (1967).

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

(7) R. Bersohn and R. G. Shulman, *J. Chem. Phys.*, **45**, 2298 (1966).

(8) M. Weissbluth and J. E. Maling, *ibid.*, **47**, 4166 (1967).

The temperature dependence of the quadrupole splitting is given by the difference $\Delta E^0 - \Delta E$, where ΔE^0 is the low-temperature maximum quadrupole splitting. When q_i and η_i are small relative to q_d and η_d, the temperature-independent contributions to the EFG will have a small effect on the orientation of the major axis of the EFG. The temperature-independent contributions will also have little effect on the major axis when the sum $\eta_i q_i + \eta_d q_d$ is small relative to $q_i + q_d$. Under these conditions the temperature dependence of the quadrupole splitting can be expressed approximately as a function of q_d and η_d only

$$\Delta E^0 - \Delta E \simeq \Delta E_d{}^0 - \Delta E_d \tag{5}$$

where $\Delta E_d{}^0 = {}^1/_2 e^2 q_d{}^0 Q[1 + {}^1/_3(\eta_d{}^0)^2]^{1/2}$ and $\Delta E_d = {}^1/_2 e^2 q_d Q[1 + {}^1/_3(\eta_d)^2]^{1/2}$. The quantities $q_d{}^0$ and $\eta_d{}^0$ refer to q_d and η_d when $T = 0$.

The quadrupole splitting exhibited by low-spin ($S = 0$) ferrous compounds is temperature independent[9,10] and seldom exceeds 0.8 mm/sec.[9-13] The temperature-independent contributions to the EFG in high-spin ferrous compounds must, in general, be smaller than those in low-spin compounds for two reasons. Low-spin compounds show stronger ligand metal interactions. In low-spin compounds anisotropic bonding to the d_{xy}, d_{xz}, and d_{yz} orbitals produces temperature-independent contributions to the EFG. These contributions are temperature dependent in high-spin ferrous compounds. For high-spin compounds temperature-independent contributions to the EFG are usually small in comparison to the large temperature-dependent field gradient, q_d, which produces a quadrupole splitting of 3.67 mm/sec in one ionic ferrous compound.[14] Equation 5 is a satisfactory approximation for at least some of the data treated here.

When Δ_1 and Δ_2 (eq 3) are large in comparison to the orbital splittings caused by spin–orbit coupling and when the analysis is confined to temperatures high in comparison to those splittings, q_d and η_d can be described in terms of three states. If the orbital mixing and covalent bonding are isotropic, these factors can be described in terms of a single parameter. Under these conditions (3) can be modified to account for spin–orbit coupling mixing and covalency

$$\begin{aligned} q_d &= aY^{-1}[1 - {}^1/_2 e^{-\Delta_1'/kT} - {}^1/_2 e^{-\Delta_2'/kT}] \\ \eta_d q_d &= aY^{-1}[{}^3/_2 e^{-\Delta_1'/kT} - {}^3/_2 e^{-\Delta_2'/kT}] \end{aligned} \tag{6}$$

where $Y^{-1} = 1 + e^{-\Delta_1'/kT} + e^{-\Delta_2'/kT}$. The splitting parameters Δ_1' and Δ_2' represent the average separation between the lowest energy states and the first and second excited groups of states, respectively. The parameter a is related to the degree of covalency and spin–orbit coupling mixing. In the ionic extreme and in the limit of negligible spin–orbit coupling $a = (1 - R)\cdot{}^4/_7\langle r^{-3}\rangle_0$, where $\langle r^{-3}\rangle_0$ represents the free-ion value of $\langle r^{-3}\rangle$. Under those conditions ${}^1/_2 e^2 Qa \simeq 4.0$ mm/sec.[6,15] The assumption of isotropic mixing of the orbitals is reasonable when $\Delta_1 \simeq \Delta_2$ or when $\Delta_1 \simeq 0$.[4] Covalent bonding is isotropic when the ligands have similar π-bond properties.

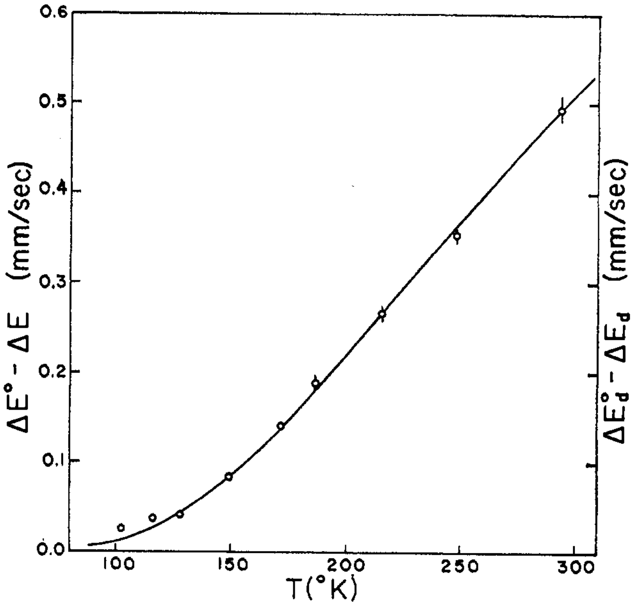

Figure 1.—Quadrupole splitting data for $Fe(py)_4I_2\cdot 2py$ plotted as $\Delta E^0 - \Delta E$, shown as circles. The calculated function plotted as $\Delta E_d{}^0 - \Delta E_d$, shown as a line. $\Delta E_d{}^0$ and ΔE_d are calculated according to (6) with $\Delta_1' = \Delta_2' = 410$ cm^{-1} and ${}^1/_2 e^2 Qa = 1.55$ mm/sec; $\Delta E^0 = 1.042$ mm/sec.

In order to examine the effects of anisotropic orbital mixing (6) can be modified, as in

$$\begin{aligned} q_d &= aY^{-1}[1 - {}^3/_2\alpha - {}^3/_2\beta - \\ &\qquad ({}^1/_2 - {}^3/_2\alpha)e^{-\Delta_1'/kT} - ({}^1/_2 - {}^3/_2\beta)e^{-\Delta_2'/kT}] \\ \eta_d q_d &= aY^{-1}[{}^3/_2(\alpha - \beta) + {}^3/_2(1 - \alpha - 2\gamma)e^{-\Delta_1'/kT} - \\ &\qquad {}^3/_2(1 - \beta - 2\gamma)e^{-\Delta_2'/kT}] \end{aligned} \tag{7}$$

where $(\alpha + \beta + \gamma) \leq 1$. The parameters α, β, and γ represent the extent of orbital mixing between the d_{xy} and d_{yz}, the d_{xy} and d_{xz}, and the d_{xz} and d_{yz} orbitals, respectively.[16]

To account for anisotropic covalent bonding (6) is modified as

$$\begin{aligned} q_d &= aY^{-1}[A - {}^1/_2 Be^{-\Delta_1'/kT} - {}^1/_2 Ce^{-\Delta_2'/kT}] \\ \eta_d q_d &= aY^{-1}[{}^3/_2 Be^{-\Delta_1'/kT} - {}^3/_2 Ce^{-\Delta_1'/kT}] \end{aligned} \tag{8}$$

The parameters A, B, and C approach unity in the limit of no covalent interactions.

Experimental Section

Preparation of Complexes.—The complexes were prepared according to the methods of Golding, *et al.*,[1] with the following exceptions. The compounds were dried in a stream of nitrogen since vacuum drying produced some decomposition presumably through the loss of pyridine. The Mössbauer spectra for the complex $Fe(py)_4I_2\cdot 2py$ were obtained with wet samples since it was found to be impossible to obtain this compound dry without some contamination with the complex $Fe(py)_4I_2$.

Mössbauer Spectra.—The spectra were obtained using a

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[9] W. Kerler, W. Newwirth, E. Fluck, P. Kuhn, and B. Zimmermann, *Z. Phys.*, **173**, 321 (1963).

[10] E. Fluck, W. Kerler, and W. Newwirth, *Angew. Chem., Int. Ed. Engl.*, **2**, 227 (1963).

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[12] P. R. Brady, J. F. Duncan, and K. F. Mok, *Proc. Roy. Soc., Ser. A*, **287**, 343 (1965).

[13] R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, **28**, 1001 (1966).

[14] C. E. Johnson, W. Marshall, and G. J. Perlow, *Phys. Rev.*, **126**, 1503 (1962).

[15] R. Ingalls, K. Ôno, and L. Chandler, *ibid.*, **172**, 295 (1968).

[16] We have assumed that the system can be treated in terms of three states. The orbitally mixed states have the following wave functions: $\psi_0 = (1 - \alpha - \beta)^{1/2}|xy\rangle + \alpha^{1/2}|yz\rangle + \beta^{1/2}|zx\rangle$, $\psi_1 = \alpha^{1/2}|xy\rangle + (1 - \alpha - \gamma)^{1/2}|yz\rangle + \gamma^{1/2}|zx\rangle$, and $\psi_2 = \beta^{1/2}|xy\rangle + \gamma^{1/2}|yz\rangle + (1 - \beta - \gamma)^{1/2}|zx\rangle$. To obtain (7) see ref 5.

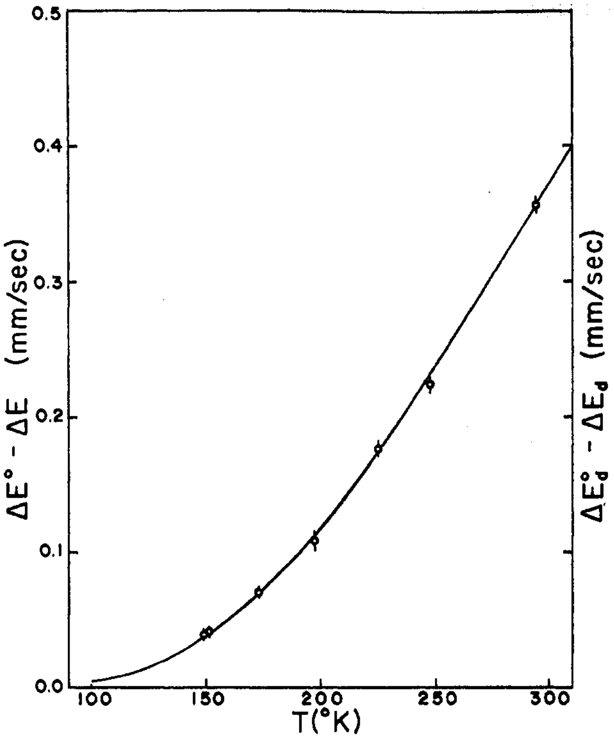

Figure 2.—Quadrupole splitting data for Fe(py)$_4$Cl$_2$, plotted as $\Delta E^0 - \Delta E$, shown as circles. The calculated function, plotted as $\Delta E_d{}^0 - \Delta E_d$, shown as a line. $\Delta E_d{}^0$ and ΔE_d are calculated according to (7) with $\Delta_1' = 480$, $\Delta_2' = 900$, $\alpha = 0.113$, $\beta = 0.057$, $\gamma = 0.0$, and $^1/_2e^2Qa = 3.60$ mm/sec; $\Delta E^0 = 3.500$ mm/sec.

TABLE I

Temp, °K	Quadrupole splitting, mm/sec	Line widths, mm/sec Γ_1	Line widths, mm/sec Γ_2
	Fe(py)$_4$I$_2$·2py		
293.5	0.548 ± 0.013	0.29 ± 0.02	0.29 ± 0.02
248.2	0.689 ± 0.008	0.27 ± 0.01	0.27 ± 0.01
216.2	0.775 ± 0.008	0.26 ± 0.01	0.26 ± 0.01
187.4	0.853 ± 0.006	0.27 ± 0.01	0.27 ± 0.01
172.2	0.901 ± 0.005	0.31 ± 0.01	0.31 ± 0.01
149.2	0.957 ± 0.004	0.31 ± 0.01	0.31 ± 0.01
128.2	1.000 ± 0.004	0.32 ± 0.01	0.32 ± 0.01
116.2	1.005 ± 0.005	0.31 ± 0.01	0.31 ± 0.01
103.2	1.015 ± 0.005	0.31 ± 0.01	0.31 ± 0.01
	Fe(py)$_4$Cl$_2$		
294.0	3.144 ± 0.006	0.26 ± 0.02	0.26 ± 0.02
248.2	3.275 ± 0.006	0.28 ± 0.02	0.28 ± 0.02
225.2	3.323 ± 0.006	0.28 ± 0.02	0.28 ± 0.02
197.4	3.392 ± 0.006	0.29 ± 0.02	0.29 ± 0.02
172.8	3.430 ± 0.005	0.29 ± 0.01	0.28 ± 0.01
150.8	3.458 ± 0.005	0.30 ± 0.01	0.30 ± 0.01
149.4	3.460 ± 0.005	0.30 ± 0.01	0.30 ± 0.01
	Fe(py)$_4$(SCN)$_2$		
294.2	1.538 ± 0.005	0.32 ± 0.01	0.30 ± 0.01
261.7	1.625 ± 0.005	0.29 ± 0.01	0.28 ± 0.01
227.7	1.730 ± 0.005	0.30 ± 0.01	0.27 ± 0.01
196.7	1.829 ± 0.005	0.31 ± 0.01	0.28 ± 0.01
140.2	1.987 ± 0.005	0.33 ± 0.01	0.33 ± 0.01
120.2	2.011 ± 0.005	0.34 ± 0.01	0.32 ± 0.01
98.7	2.033 ± 0.005	0.33 ± 0.01	0.32 ± 0.01
	Fe(py)$_4$I$_2$		
295.0	0.317 ± 0.007	0.32 ± 0.01	0.32 ± 0.01
255.6	0.337 ± 0.006	0.29 ± 0.01	0.29 ± 0.01
228.5	0.368 ± 0.006	0.30 ± 0.01	0.30 ± 0.01
201.5	0.388 ± 0.006	0.31 ± 0.01	0.31 ± 0.01
171.5	0.434 ± 0.005	0.31 ± 0.01	0.31 ± 0.01
142.5	0.462 ± 0.005	0.31 ± 0.01	0.31 ± 0.01
126.1	0.480 ± 0.005	0.33 ± 0.01	0.33 ± 0.01
110.5	0.498 ± 0.005	0.33 ± 0.01	0.33 ± 0.01
99.4	0.503 ± 0.005	0.31 ± 0.01	0.31 ± 0.01

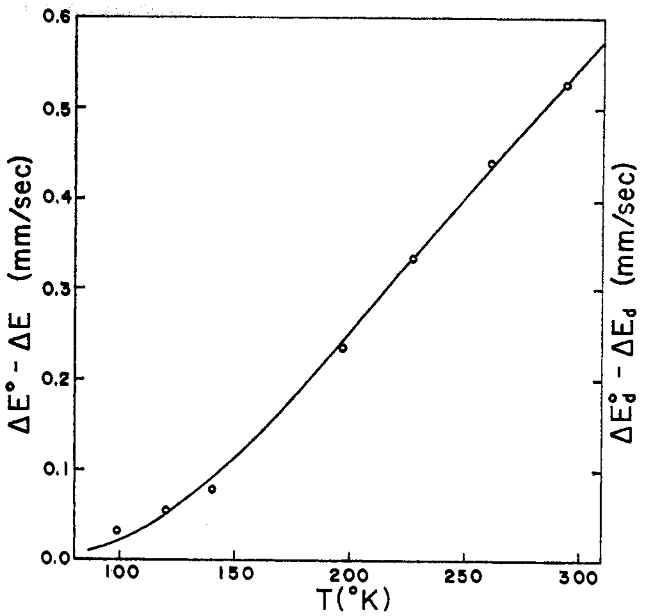

Figure 3.—Quadrupole splitting data for Fe(py)$_4$(SCN)$_2$, plotted as $\Delta E^0 - \Delta E$, shown as circles. The calculated function, plotted as $\Delta E_d{}^0 - \Delta E_d$, shown as a line. $\Delta E_d{}^0$ and ΔE_d are calculated according to (7) with $\Delta_1' = 340$ cm^{-1}, $\Delta_2' = 780$ cm^{-1}, $\alpha = 0.135$, $\beta = 0.067$, $\gamma = 0.0$, and $^1/_2e^2Qa = 3.43$ mm/sec; $\Delta E^0 = 2.065$ mm/sec.

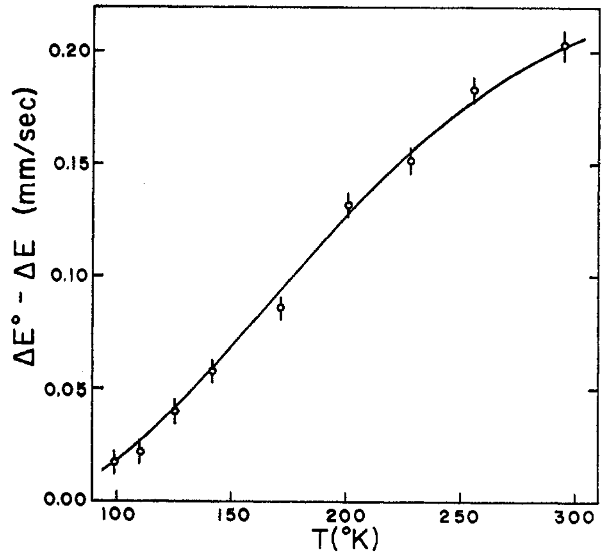

Figure 4.—Quadrupole splitting data for Fe(py)$_4$I$_2$, plotted as $\Delta E^0 = \Delta E$, shown as circles. The calculated function shown as a line. ΔE^0 and ΔE are calculated from q_d, η_d, q_i, and η_i according to (1) and (4). $\eta_i = 0.0$ and $^1/_2e^2Qq_i = -0.74$ mm/sec. q_d and η_d are calculated from (7) with $\Delta_1' = 300$ cm^{-1}, $\Delta_2' = 700$ cm^{-1}, $\alpha = 0.170$, $\beta = 0.07$, $\gamma = 0.1$, and $^1/_2e^2Qa = 1.93$ mm/sec; $\Delta E^0 = 0.520$ mm/sec.

constant-acceleration drive with a 256-channel analyzer operated in the time mode.[17] The peak positions were located by employing a least-squares fitting program.[18] Sample temperatures in the region 100–300° were obtained using a Styrofoam-insulated cryostat described elsewhere.[18] Sample temperatures could be maintained to ±0.5° for indefinite periods. A computer was employed to fit the temperature dependence of the quadrupole splitting to theory.

Results and Discussion

The Mössbauer spectral results are shown in Table I.

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(17) J. F. Ullrich, Ph.D. Thesis, University of Michigan, 1967.

(18) P. B. Merrithew, Ph.D. Thesis, University of Michigan, 1969.

The quadrupole splitting results obviously cannot be fit uniquely in terms of eight independent parameters. However, the number of possible results can be reduced since limits can be placed on the magnitude of A, B, and C and the difference between ΔE^0 and ΔE_d^0. The extent of orbital mixing can be related to the magnitude of Δ_1' and Δ_2'.[4]

Since the change in ΔE at 100° is very small, it is possible to estimate ΔE^0. In order to account for the uncertainty in ΔE^0 the data were fit for the maximum and minimum of the possible values. Initial results were obtained by fitting the data to (6). The results are given in Table II. If the ground state is assumed to be degenerate (case 1), an unambiguous solution is found. If the ground state is not degenerate (case 2), the magnitude of Δ_2' is dependent on the assumed magnitude of a.

TABLE II
PRELIMINARY RESULTS

Compd	ΔE^0, mm/sec	Δ_1', cm^{-1}	Δ_2', cm^{-1}	ΔE_d^0, mm/sec
$Fe(py)_4I_2 \cdot 2py$				
Case 1	1.030	0	400	2.4
	1.055	0	380	>2.4
Case 2	1.030	430–400	430–∞	1.6–2.5
	1.055	400–380	400–∞	1.5–2.5
$Fe(py)_4Cl_2$				
Case 1	3.485	0	~490	>2.0
	3.515	0	~425	>2.0
Case 2	3.485	525	525–∞	1.5–2.9
	3.515	475–450	475–∞	1.4–2.3
$Fe(py)_4(SCN)_2$				
Case 1	2.050	0	350	1.95
	2.080	0	340	2.03
Case 2	2.050	390–385	390–∞	1.4–2.52
	2.080	385–370	385–∞	1.5–2.62
$Fe(py)_4I_2$				
Case 1	0.520	0	270	0.787
	0.545	0	230	0.550
Case 2	0.520	310–300	310–∞	0.45–0.77
	0.545	260–250	260–∞	0.42–0.72

Equations 7 were employed to determine the effect of anisotropic orbital mixing on the validity of the results shown in Table II. The magnitudes of the mixing parameters α, β, and γ have a very significant effect on the size of a. However, if a significant change in Δ_1' is to be produced (a change larger than the uncertainty in Δ_1' due to the uncertainty in ΔE^0), it is necessary to assume that the orbital mixing is more anisotropic and that the quadrupole splitting reduction is greater than that expected on the basis of Ingalls' work.[4] For example the $Fe(py)_4(SCN)_2$ data can be fit according to (7) with $^1/_2e^2Qa = 4.0$ mm/sec, $\alpha = 0.26$, $\beta = 0.0$, $\gamma = 0.0$, $\Delta_1' = 350$ cm^{-1}, and $\Delta_2' = 620$ cm^{-1} when $\Delta E^0 = 2.050$ mm/sec. Equations 8 were employed to determine the effect of anisotropic covalent bonding. The magnitude of Δ_1' was found to be insignificantly affected for reasonable values of A, B, and C (values which differ by less than 100%). For example, the $Fe(py)_4(SCN)_2$ data can be fit according to (8) with $^1/_2e^2Qa = 4.0$ mm/sec, $A = 0.430$, $B = 0.700$, $C = 0.775$, $\Delta_1' = 385$ cm^{-1}, and $\Delta_2' = 600$ cm^{-1} when $\Delta E^0 = 2.050$ mm/sec. Since neither the assumption of very large anisotropic spin–orbit effects nor the assumption of extremely anisotropic covalent bonding appears significantly to alter the magnitude of Δ_1', it is reasonable to assume that when these effects appear in concert, but to a lesser extent, in an actual complex, they will have little effect on the magnitude of Δ_1'. The simplified eq 6 can therefore be employed to determine reasonably accurate values of Δ_1'.

Both covalency and orbital mixing will reduce ΔE_d^0 from its free-ion value. All solutions which require $^1/_2e^2Qa > 4.0$ mm/sec can therefore be eliminated. This eliminates case 1 for all compounds except $Fe(py)_4I_2$.

Some estimate of Δ_2' can be made since constraints can be placed on the magnitude of the difference $\Delta E^0 - \Delta E_d^0$. The magnitude of ΔE_d^0, as given by (6), can differ from that of ΔE^0 for several reasons. The temperature-independent contributions q_i and η_i will contribute to the magnitude of ΔE^0. The magnitude of ΔE_d^0 is found by assuming that the covalent bonding is isotropic. If the excited states are more or less delocalized than the ground state, then ΔE_d^0 will appear different from ΔE^0. Both of the above factors contribute to the quadrupole splitting exhibited by low-spin ferrous compounds but to a greater extent. It is therefore reasonable to assume that the temperature-independent contributions q_i and η_i and anisotropic covalent bonding cause ΔE^0 and ΔE_d^0 to differ by less than 0.8 mm/sec.

Anisotropic orbital mixing will also cause ΔE_d^0, as given by (6), to appear small relative to ΔE^0. Fitting the data to (7) reveals that as the degree of anisotropy is increased (α made large with respect to β and γ), ΔE_d^0 increases. In those cases where the initial results (Table II) show that ΔE_d^0 is small relative to ΔE^0, it is necessary to employ (7) to estimate Δ_2'.

Tetrakis(pyridine)diiodoiron(II) Dipyridate.—Initial results for the compound $Fe(py)_4I_2 \cdot 2py$ indicate that ΔE_d^0 is always large with respect to ΔE^0. An upper limit can be placed on Δ_2' by setting $\Delta E_d^0 = \Delta E^0 + 0.8$ mm/sec and employing (6) to obtain a fit. With $\Delta E^0 = 1.030$ mm/sec and $^1/_2e^2Qa = 1.80$ mm/sec a fit is obtained with $\Delta_1' = 380$ cm^{-1} and $\Delta_2' = 580$ cm^{-1}. With $\Delta E^0 = 1.055$ mm/sec and $^1/_2e^2Qa = 1.80$ mm/sec a fit is obtained with $\Delta_1' = 370$ cm^{-1} and $\Delta_2' = 530$ cm^{-1}.

The fact ΔE_d^0 is greater than ΔE^0 indicates that this compound has a trans configuration. Two factors can cause ΔE^0 to be less than ΔE_d^0: the temperature-independent contributions to the EFG are opposite in sign from the temperature-dependent contributions and the ground d_{xy} orbital is delocalized by covalent bonding more than the d_{xz} and d_{yz} orbitals. Both of these factors would be expected when relatively weak negatively charged ligands occupy the axial sites.[19] The relatively small separation between Δ_1' and Δ_2' is consistent with the assignment of a trans configuration.[20]

Tetrakis(pyridine)dichloroiron(II).—Initial results for this compound show that ΔE_d^0 is less than ΔE^0. A lower limit can be placed on the magnitude of Δ_2' by employing (7) to fit the data. The parameters β and γ are set to zero and α is varied to obtain the maximum spin–orbit coupling reduction consistent with Ingalls' theoretical predictions[4] and $\Delta_1 \geqslant 450$ cm^{-1}. Assuming $\lambda = 90$ cm^{-1}, ΔE_d^0 is reduced from its maximum value of 4.0 mm/sec by a factor $\leqslant 0.75$.

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(19) For a calculation of "lattice" effects see, for example, R. L. Collins and J. C. Travis in "Mössbauer Effect Methodology," Vol. 3, Plenum Press, New York, N. Y., 1966, p 23.

(20) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.

The parameter a is then reduced to allow for the maximum reduction due to covalent bonding (a reduced to obtain $\Delta E_d{}^0 = \Delta E^0 - 0.8$ mm/sec). The temperature-dependence data are fit by varying Δ_2'. The parameter Δ_2' is found to be greater than 740 cm^{-1}. With $\Delta_2' = 740$ cm^{-1} it is unreasonable to assume that no mixing occurs between the d_{xy} and d_{xz} orbitals. A more reasonable lower limit on Δ_2' is found by allowing $\beta = {}^1/_2\alpha$ and repeating the above procedure. The parameter Δ_2' is found to be greater than 820 cm^{-1}. With $\Delta E^0 = 3.485$ mm/sec, ${}^1/_2e^2Qa = 3.6$ mm/sec, $\alpha = 0.113$, $\beta = 0.0565$, and $\gamma = 0.0$ a fit is obtained with $\Delta_1' = 525$ cm^{-1} and $\Delta_2' = 820$ cm^{-1}. With $\Delta E^0 = 3.515$ and the other parameters as above, a fit is obtained with $\Delta_1' = 460$ cm^{-1} and $\Delta_2' = 1000$ cm^{-1}. Both of these solutions are consistent with $\Delta E_d{}^0 = 2.7$ mm/sec. A further refinement (and a still larger lower limit on Δ_2') could be made by allowing γ to assume a finite value. This refinement is probably not justified in view of the approximate nature of this treatment.

Since ΔE^0 is approximately equal to $\Delta E_d{}^0$ or larger, this compound must have a cis configuration.[19] An electronic structure such that Δ_2' is approximately double Δ_1' or greater is not inconsistent with a cis configuration.

Tetrakis(pyridine)dithiocyanatoiron(II).—A lower, limit can be placed on the magnitude of Δ_2' in $Fe(py)_4(SCN)_2$ by employing a procedure similar to that employed for $Fe(py)_4Cl_2$. However, $Fe(py)_4(SCN)_2$ is known to have the trans configuration.[21] Since the compound is trans, $\Delta E_d{}^0$ must be greater than ΔE^0. A low estimate of Δ_2' is made by setting $\Delta E_d{}^0 = \Delta E^0$. Employing a spin–orbit coupling reduction factor of 0.70, setting $\alpha = {}^1/_2\beta$, and requiring $\Delta E_d{}^0 = \Delta E^0$, Δ_2' is found to be greater than 630 cm^{-1}. By making the more realistic assumption that $\Delta E_d{}^0 = \Delta E^0 + 0.35$ mm/sec, Δ_2' is greater than 770 cm^{-1}. With $\Delta E^0 = 2.050$ mm/sec, ${}^1/_2e^2Qa = 3.43$ mm/sec, $\alpha = 0.135$, $\beta = 0.0675$, and $\gamma = 0.0$ a fit is obtained with $\Delta_1' = 360$ cm^{-1} and $\Delta_2' = 770$ cm^{-1}. With $\Delta E^0 = 2.080$ mm/sec and the other parameters as above, $\Delta_1' = 340$ cm^{-1} and $\Delta_2' = 810$ cm^{-1}. Both of these solutions are consistent with $\Delta E_d{}^0 = 2.4$ mm/sec.

The large splitting between the d_{xz} and d_{yz} orbitals apparent here is evidently a result of the fact that the triatomic thiocyanate ligands are bent toward the xy plane.[21]

In order to test the validity of (5), (7) was modified to include temperature-independent contributions to the EFG. Reasonable values for q_i and $\eta_i q_i$ do not significantly alter the temperature dependence of the quadrupole splitting for the compounds $Fe(py)_4I_2 \cdot 2py$, $Fe(py)_4Cl_2$, and $Fe(py)_4(SCN)_2$. However, the magnitude of q_i and $\eta_i q_i$ for $Fe(py)_4I_2$ will significantly affect the analysis of temperature dependence of the quadrupole splitting. Analysis of the quadrupole splitting data for this compound requires knowledge of its configuration and the magnitude of q_i and $\eta_i q_i$.

Tetrakis(pyridine)diiodoiron(II).—Because of the large size of the iodide ion it is reasonable to assume that this compound has a trans configuration. The analysis will be based on this assumption. Since a trans compound has axial symmetry, $\eta_i q_i = 0$. The case 1 solution is not affected by the magnitude of q_i since for this solution $q_d\eta_d = 0$. The case 1 solution, however, is unreasonable for two reasons. For a trans compound with a doubly degenerate ground state ΔE^0 should be greater than $\Delta E_d{}^0$. ΔE^0, however, is approximately equal to or less than $\Delta E_d{}^0$. If the pyridine molecules hold their expected orientation in the xz and yz planes, the ground state should be nondegenerate. A degenerate ground state would be expected only if the pyridine molecules lay in the xy plane.

More reasonable case 2 solutions can be found. Approximate solutions are obtained by calculating q_d and η_d according to (7) with the parameter a set to reflect approximately the same degree of covalent interaction as $Fe(py)_4I_2 \cdot 2py$ and the parameters α, β, and γ set to be consistent with the magnitudes of Δ_1' and Δ_2'. The temperature-independent contribution, q_i, is assumed to be approximately equal to that observed for $Fe(py)_4I_2 \cdot 2py$. The quadrupole splitting is calculated according to (1) and (4). With $\Delta E^0 = 0.520$ mm/sec a fit is obtained with ${}^1/_2e^2Qa = 1.93$ mm/sec, $\alpha = 0.170$, $\beta = 0.07$, $\gamma = 0.1$, $\Delta_1' = 300$ cm^{-1}, $\Delta_2' = 700$ cm^{-1}, $\eta_i = 0.0$, and ${}^1/_2e^2Qq_i = -0.74$ mm/sec. With $\Delta E^0 = 0.545$ mm/sec a fit is obtained with ${}^1/_2e^2Qa = 1.9$ mm/sec, $\alpha = 0.19$, $\beta = 0.085$, $\gamma = 0.1$, $\Delta_1' = 250$ cm^{-1}, $\Delta_2' = 600$ cm^{-1}, $\eta_i = 0.0$, and ${}^1/_2e^2Qq_i = -0.60$ mm/sec. Both of these solutions are consistent with $\Delta E^0(\text{exptl}) - \Delta E^0(\text{calcd}) < 0.003$ mm/sec.

The removal of the adducted pyridine from $Fe(py)_4I_2 \cdot 2py$ causes a lowering of the ligand symmetry and produces a greater splitting between the d_{xz} and d_{yz} orbitals in $Fe(py)_4I_2$.

Conclusion

While it must be admitted that the fittings to the quadrupole splitting data are not unique, nevertheless the results (Table III) are accurate enough to make them useful. The ordering of the sublevels within a term state is a troublesome problem in coordination chemistry. Direct spectroscopic observations are usually not possible, and other methods such as fitting magnetic susceptibilities[22,23] oridinarily require the assumption of axial symmetry and typically result in large uncertainties.

TABLE III
FINAL RESULTS

Compd	ΔE^0, mm/sec	Δ_1', cm^{-1}	Δ_2', cm^{-1}
$Fe(py)_4I_2 \cdot 2py$	1.030	430–380	430–580
	1.050	400–370	400–530
$Fe(py)_4Cl_2$	3.485	525	>820
	3.515	460	>1000
$Fe(py)_4(SCN)_2$	2.050	360	>770
	2.085	340	>810
$Fe(py)_4I_2$	0.520	~300	~700
	0.545	~250	~600

The method and results described herein provide a basis for assignment of geometry in analogous compounds or a means of interpreting geometrical effects on energy levels in compounds of known structure. The compound $Fe(py)_4(SCN)_2$ is illustrative of the latter approach and shows substantial deviation from the level

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scheme one would derive from crystal field theory in D_{4h} symmetry.

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A Study of the Electronic and Structural Properties of Bis(pyridine)dichloroiron(II)

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Bis(pyridine)dichloroiron(II), $Fe(py)_2Cl_2$, has been prepared by two different methods. The structure of the material at room temperature has been shown to be polymeric and to possess two symmetric bridging chloride ligands which are equivalently bonded between two iron atoms. On the basis of the Mössbauer spectral properties of the two preparations, it has been concluded that the crystalline material undergoes a transformation at lower temperatures to a polymeric structure containing asymmetric bridging chloride ligands. The magnetic and electronic spectral properties of these materials have been measured and the results are discussed in terms of the proposed structural change at low temperature.

Introduction

Several papers have been published[1] which deal with the electronic properties of the pyridine complexes containing iron(II) halides of stoichiometry $Fe(py)_4X_2$, but relatively little attention has been given to the detailed electronic properties of the complexes of stoichiometry $Fe(py)_2X_2$. Gill, *et al.*,[2] recorded the room-temperature magnetic moment of $Fe(py)_2Cl_2$ as 5.75 BM and concluded on the basis of its X-ray powder pattern that the complex possesses a polymeric octahedral structure. Goodgame, *et al.*,[1a] investigated the electronic spectral bands for $Fe(py)_2Cl_2$ but did not describe the method which they used for its preparation. Clark and Williams[3] measured the infrared spectrum of $Fe(py)_2Cl_2$ but were unable to assign the metal–ligand vibrational bands. The purpose of this paper is to present the experimental results of an investigation of the spectral and magnetic properties of $Fe(py)_2Cl_2$ and discuss these results in terms of a proposed temperature-dependent structural model.

Experimental Section

Synthesis of Compounds.—$Fe(py)_4Cl_2$ was prepared by following essentially the same procedure as previously reported[4] except that all manipulations were carried out under a stream of dry nitrogen gas. *Anal.* Calcd for $FeC_{20}H_{20}N_4Cl_2$: C, 54.20; H, 4.55; N, 12.64. Found: C, 53.87; H, 4.47; N, 12.48.

$Fe(py)_2Cl_2$.—(A) This compound was prepared by rapidly adding, while stirring, a concentrated solution of $FeCl_2 \cdot 4H_2O$ in deoxygenated anhydrous methanol to a deoxygenated solution of approximately 50% freshly distilled pyridine in anhydrous methanol. The addition was carried out under a stream of dry nitrogen gas to prevent oxidation of the $FeCl_2 \cdot 4H_2O$ solution. When the $FeCl_2 \cdot 4H_2O$ solution was added, a deep yellow color immediately formed, and golden yellow crystals precipitated within 3–5 min. The precipitate was filtered *via* suction under nitrogen and was washed first with a small amount of cold deoxygenated absolute ethanol and then with cold deoxygenated absolute ether. This procedure must be closely followed. If the complex does not precipitate within about 5 min, $Fe(py)_4Cl_2$ will form and precipitate over a period of several hours. No difficulty was experienced in reproducing this preparation.

A completely dry sample of $Fe(py)_2Cl_2$ is relatively stable with respect to air oxidation and can be stored for a period of several weeks without apparent decomposition in a desiccator which is filled with dry nitrogen. *Anal.* Calcd for $FeC_{10}N_{10}N_2Cl_2$: C, 42.15; H, 3.54; N, 9.83. Found: C, 41.96; H, 3.53; N, 9.73.

(B) An alternate preparation of $Fe(py)_2Cl_2$ involved decomposing $Fe(py)_4Cl_2$ in a drying pistol, which was heated to 65° and subjected to continuous evacuation for a period of approximately 1 hr. This evacuation produced a loss of 49.8–50.2% of the original pyridine, as determined by weight loss measurements. The resulting sample of $Fe(py)_2Cl_2$ was found to be stable. *Anal.* Found: C, 42.23; H, 3.67; N, 9.89.

Physical Measurements.—All electronic spectra were recorded on a Cary 14 spectrophotometer. To make the measurements, the solid samples were mulled with Kel-F No. 90 grease and placed between quartz plates.

The Mössbauer spectral results were obtained with an Austin Science Associates constant-acceleration spectrometer. The spectrometer was calibrated by using natural iron foil, and the source was maintained at room temperature for all measurements. The low-temperature results were obtained with a liquid nitrogen cryostat that has a sample holder which protects the polycrystalline sample from the cryostat vacuum. The National Bureau of Standards Parlor computer program[5] was used to evaluate the spectral results. The error limits for the results that are recorded in Table I are less than or equal to ±0.05 mm/sec, as calculated from the variance of the final computer iteration.[5] All magnetic measurements were made on a Faraday magnetic susceptibility balance described by Long.[6] The balance was calibrated by using $CoHg(NCS)_4$, and the sample temperature was measured with a platinum resistance thermometer. All magnetic moments were measured at three field strengths. In some cases (noted below) these moments exhibited a field dependence. The error limits for the magnetic moments that are recorded in Table II are ±0.05 BM at higher temperatures (above 150°K) and are ±0.10 BM at the lower temperatures.

All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

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