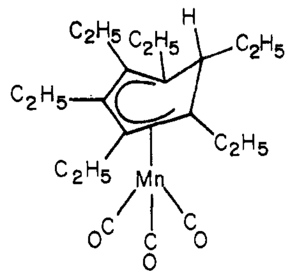
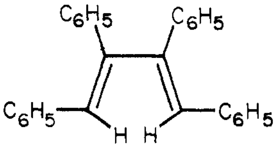


XIV



XV

process which diphenylacetylene undergoes upon its reaction with $[HMn(CO)_4]_3$ is linear dimerization accompanied by hydrogen addition; this reaction resembles the dimerization of diphenylacetylene with alkali metals.[43] The formation of the cis,cis isomer of 1,2,3,4-tetraphenylbutadiene upon reaction of diphenylacetylene with $[HMn(CO)_4]_3$ is consistent with an unstable manganacyclopentadiene or 1,2-dimanganacyclohexadiene derivative as an intermediate.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant GP-31347X, to Oberlin College for a research status appointment to Dr. M. N. Ackermann during his sabbatical leave, to Professor Bruce R. Kowalski of the Colorado State University, Fort Collins, Colo., for help with some of the mass spectra of the bimetallic manganese carbonyl derivatives, and to the Badische Anilin-und Sodafabrik, Ludwigshafen, Germany, for generous research samples of cyclooctatetraene.

Registry No. I, 32798-86-0; II, 49626-33-7; III, 49626-34-8; IV, 12108-14-4; V, 49626-35-9; VI, 49626-36-0; VII, 49626-37-1; VIII, 49626-38-2; XI, 49626-39-3; XII, 49664-76-8; XIV, 49784-17-0; XV, 1608-10-2; $C_7H_8Mn_2(CO)_7$, 50270-79-6; $[HMn(CO)_4]_3$, 18444-56-9; 1,3-cyclohexadiene, 592-57-4; cycloheptatriene, 544-25-2; 1,3-cycloheptadiene, 4054-38-0; cyclooctatetraene, 629-20-9; 1,3,5-cyclooctatriene, 1871-52-9; 1,3,6-cyclooctatriene, 3725-30-2; 6-(dimethylamino)fulvene, 4477-03-6; azulene, 275-51-4; norbornadiene, 121-46-0; 3-hexyne, 928-49-4; diphenylacetylene, 501-65-5.

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Relative Energies of the Cubic $t_{2g}(\pi^*)$ Orbitals in Some Mixed-Ligand Complexes of Iron(II)

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The temperature dependence of the quadrupole splitting of $Fe(isoq)_4X_2$ ($X^- = I^-, Br^-, Cl^-$), $Fe(py)_4X_2$ ($X^- = Br^-, OCN^-, N_3^-$), and $Fe(1,10\text{-phen})_2X_2$ ($X^- = Br^-, Cl^-, SCN^-$) was obtained in the range 77–300°. These data and those obtained earlier on $Fe(py)_4X_2$ ($X^- = I^-, Cl^-, SCN^-$) were analyzed in order to determine the splitting of the cubic $t_{2g}(\pi^*)$ orbitals. The axial splitting in these compounds was found to be less than 800 cm^{-1}. The relative energy of the $e_g(\pi^*)$ orbital in the series FeL_4X_2 (L = pyridine, isoquinoline) follows the order $I^- \leqslant Br^- \leqslant Cl^-$. Analysis of the $Fe(1,10\text{-phen})_2X_2$ ($X^- = Br^-, Cl^-, SCN^-$) data suggests a trigonal distortion from octahedral symmetry.

The relative energies of the cubic $t_{2g}(\pi^*)$ orbitals in mixed-ligand complexes have been previously investigated by Mossbauer spectroscopy.[1,2] In these treatments of the quadrupole splitting data, assumptions were made regarding the sign and the magnitude of the temperature-independent or "lattice" contributions to the quadrupole splitting. Burbridge, *et al.*,[1] assumed that the "lattice" contributions could be calculated from a crystal field model. The large quadrupole splittings observed for some iron(II) low-spin compounds[3] suggest that this is generally not a good assumption. Merrithew, *et al.*,[2] assumed that the "lattice" contributions were relatively small and that the signs of the electric field gradient tensor components could be predicted on the basis of the formal charge on the ligands. The latter assumption has been shown to be unjustified.[4] We have undertaken a more rigorous investigation of the quadrupole splitting of a series of mixed-ligand complexes to define more accurately the effect of the halogens and pseudohalogens on the energy of the cubic $t_{2g}(\pi^*)$ orbitals.

Experimental Section

Preparation of Complexes. $Fe(py)_4Br_2$ (py = pyridine) and $Fe(py)_4(OCN)_2$ were prepared by the methods of Golding, *et al.*[5] $Fe(isoq)_4Cl_2$ (isoq = isoquinoline), $Fe(isoq)_4Br_2$, and $Fe(isoq)_4I_2$ were prepared by the methods of Goodgame, *et al.*[6] $Fe(phen)_2Cl_2$ (phen = 1,10-phenanthroline), $Fe(phen)_2Br_2$, and $Fe(phen)_2(SCN)_2$ were prepared by the methods of Madeja and Konig.[7]

$Fe(py)_4(N_3)_2$ was prepared in a manner similar to the cyanate and recrystallized from pyridine. The compound decomposes slowly with the evolution of pyridine. *Anal.* Calcd for $Fe(py)_4(N_3)_2$: C, 52.63; H, 4.39; N, 30.70. Found: C, 50.42; H, 4.27; N, 29.59.

Mossbauer Spectra. The Mossbauer spectrometer and associated cryostat have been described previously.[8] The temperature was measured with a copper-constantan thermocouple and controlled to within 2° of the indicated temperature. The spectra were fitted with

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a least-squares program and the accuracy determined statistically.[9]

Theory

The quadrupole splitting ΔE for ^{57}Fe is

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

where Q is the quadrupole moment of the nucleus and q and η are functions of the components of the EFG tensor.[10] The quantities q and ηq may be conveniently expressed[2]

$$q = q_d + q_i$$

$$\eta q = \eta_d q_d + \eta_i q_i$$

where the subscript d refers to temperature-dependent contributions and i to temperature independent contributions. For high-spin ($S = 2$) ferrous ions in a (pseudo)octahedral environment, asymmetries in the $t_{2g}(\pi^*)$ electron distribution produce contributions to q_d and η_d. Charge asymmetries in the $e_g(\sigma^*)$ orbitals and the bonding orbitals produce contributions to q_i and η_i.

The wave functions which describe the $^5T_{2g}$ term under simultaneous perturbation by spin-orbit coupling and a rhombic field may be obtained by solving a 15 × 15 matrix similar to the one given by Figgis, *et al.*[11] The quantities q_d and η_d are calculated in the usual manner.[10] The results obtained are found to be in agreement with those of Ingalls.[10] The distortion parameters are defined in the following manner. The axial splitting of the $^5T_{2g}$ term is Δ. A positive Δ indicates an orbitally nondegenerate ground term. (For a tetragonal distortion this corresponds to an xy ground orbital.) The ^5E_g term which arises from the axial splitting of the ground $^5T_{2g}$ term may be split by low-symmetry components. This splitting is taken as ϵ. In order to account for anisotropies in the radial parts of the $t_{2g}(\pi^*)$ orbitals, the radial factor for the basis function, xy, was taken as $\beta^2\langle r^{-3}\rangle_0$ and that for xz, yz as $\alpha^2\langle r^{-3}\rangle_0$. The appropriate changes were made to account for the accompanying anisotropy in the spin-orbit coupling constant, λ. As in previous treatments of ferrous ions, the magnitude of $(2/7)e^2Q(1-R)\langle r^{-3}\rangle_0$ was taken as 4.0 mm/sec.[12]

Results

The quadrupole splitting results are given in Table I. The temperature dependence of the quadrupole splitting of $Fe(isoq)_4X_2$ ($X^- = Cl^-, Br^-, I^-$) agrees within experimental error with that of $Fe(py)_4X_2$.[2] These results are compared in Figures 1-3.

Table I. Quadrupole Splitting Data[a]

Temp, °K	Quadrupole splitting, mm/sec	Temp, °K	Quadrupole splitting, mm/sec
	$Fe(isoq)_4I_2$		
88 ± 2	0.56 ± 0.02	150	0.54 ± 0.05
116	0.55 ± 0.02	159	0.52 ± 0.02
121	0.54 ± 0.03	178	0.49 ± 0.03
146	0.52 ± 0.04	298	0.41 ± 0.02
	$Fe(py)_4Br_2$		
80	2.89 ± 0.05	210	2.53 ± 0.03
112	2.80 ± 0.03	298	2.06 ± 0.05
155	2.64 ± 0.04		
	$Fe(isoq)_4Br_2$		
87	2.87 ± 0.03	160	2.66 ± 0.04
119	2.86 ± 0.04	178	2.54 ± 0.08
149	2.76 ± 0.04	298	2.19 ± 0.04
	$Fe(isoq)_4Cl_2$		
78	3.47 ± 0.04	140	3.45 ± 0.02
88	3.53 ± 0.02	164	3.46 ± 0.02
89	3.50 ± 0.02	186	3.41 ± 0.02
107	3.47 ± 0.02	232	3.31 ± 0.03
114	3.44 ± 0.02	298	3.20 ± 0.02
	$Fe(py)_4(N_3)_2$		
84	3.04 ± 0.02	191	2.96 ± 0.02
107	3.03 ± 0.01	210	2.93 ± 0.02
121	3.01 ± 0.01	227	2.88 ± 0.02
133	2.99 ± 0.01	252	2.85 ± 0.02
152	2.99 ± 0.01	298	2.74 ± 0.02
166	2.98 ± 0.02		
	$Fe(py)_4(OCN)_2$		
81	2.59 ± 0.01	147	2.56 ± 0.02
88	2.59 ± 0.02	198	2.52 ± 0.02
102	2.59 ± 0.02	250	2.47 ± 0.02
103	2.58 ± 0.02	298	2.44 ± 0.03
118	2.58 ± 0.02	300	2.40 ± 0.04
136	2.57 ± 0.02		
	$Fe(1,10\text{-}phen)_2(SCN)_2$		
179	3.01 ± 0.01	223	2.92 ± 0.01
185	2.99 ± 0.01	298	2.61 ± 0.01
203	2.97 ± 0.01		
	$Fe(1,10\text{-}phen)_2Cl_2$		
83	3.33 ± 0.01	199	3.20 ± 0.01
95	3.31 ± 0.01	247	3.10 ± 0.01
103	3.30 ± 0.01	296	3.01 ± 0.01
153	3.26 ± 0.01		
	$Fe(1,10\text{-}phen)_2Br_2$		
88	3.31 ± 0.03	163	3.15 ± 0.03
109	3.29 ± 0.03	299	2.85 ± 0.02

[a] The isomer shift of these compounds is 1.40 ± 0.04 mm/sec *vs.* $Na_2Fe(CN)_5NO \cdot 2H_2O$ at 100°.

FeL_4X_2. The compound $Fe(py)_4(SCN)_2$ is known to be trans.[13] X-Ray powder photographs and electronic spectra suggest that $Fe(py)_4X_2$ ($X^- = Cl^-, Br^-$) and $Fe(isoq)_4X_2$ ($X^- = Cl^-, Br^-, I^-$) have the trans configuration.[6,14] In this analysis we will assume that the compounds FeL_4X_2 have the trans configuration.

The local symmetry in *trans*-FeL_4X_2 is formally D_{4h}. The z axis is taken along the major symmetry axis (X-Fe-X). Because of the formally high symmetry we have assumed initially that $\epsilon \cong 0$ and $\eta_i \cong 0$. The latter assumption is consistent with the magnetic perturbation spectra of a series of low-spin iron(II) complexes of the form FeA_4B_2 which show η_i as small.[15] The quadrupole splitting cannot be fitted uniquely in terms of the remaining parameters, λ, Δ, α^2, β^2, and q_i. For this reason the data have been fitted for two extreme cases, $q_i = 0$ and $\beta^2/\alpha^2 = 1$. The case $q_i = 0$ assumes that the observed anisotropy is due totally to differences in the radii of the t_{2g} orbitals. The other case $\beta^2/\alpha^2 = 1$ assumes that the t_{2g} orbital radii are equal and that the anisotropies are due to differences in the radii of the e_g orbitals or to anisotropic σ bonding. Since the magnitude of the spin-orbit coupling constant, λ, is not known, the data were fitted for $\lambda = -100$, -80, -60, and -40 cm^{-1}. (The free-ion value, λ_0, is -100 cm^{-1}.[16])

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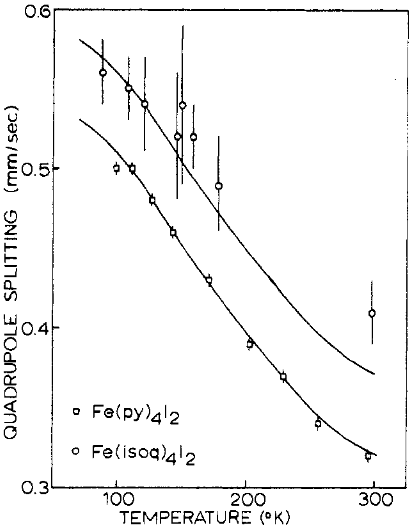

Figure 1. The temperature dependence of the quadrupole splitting of $Fe(py)_4I_2$ and $Fe(isoq)_4I_2$. The top line gives a fitting with $\Delta = 60$ cm^{-1}, $\lambda = -60$ cm^{-1}, $\beta^2 = 0.54$, $\beta^2/\alpha^2 = 1.0$, and $(1/2)e^2Qq_1 = 0.17$ mm/sec. The bottom line is a fitting with the same parameters but with $(1/2)e^2Qq_1 = 0.12$ mm/sec. The $Fe(py)_4I_2$ data are from ref 2.

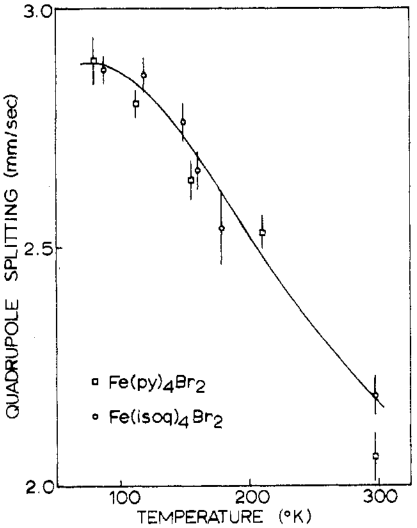

Figure 2. The temperature dependence of the quadrupole splitting of $Fe(py)_4Br_2$ and $Fe(isoq)_4Br_2$. The continuous line gives a fitting with $\Delta = 300$ cm^{-1}, $\lambda = -60$ cm^{-1}, $\beta^2 = 0.61$, $\beta^2/\alpha^2 = 1.0$, and $(1/2)e^2Qq_1 = 1.0$ mm/sec.

A least-squares program was employed to fit the data in terms of Δ and q_1 or β^2/α^2. Since the $Fe(py)_4X_2$ data are similar to those of $Fe(isoq)_4X_2$, only the better quality data have been fitted when both sets are available. Those fittings for which the reduced χ^2 value, x_v, are less than 3 have been considered. At $\lambda = -100$ cm^{-1}, only the FeL_4Cl_2, $Fe(py)_4(OCN)_2$, and $Fe(py)_4(N_3)_2$ data can be fitted. The resulting α^2, β^2 values (<0.7) are considerably smaller than those which would be expected where $\lambda = -100$ cm^{-1}. The solutions found at $\lambda = -80$, -60, and -40 cm^{-1} are given in Tables II and III. Solutions with $\alpha^2, \beta^2 > 0.3$ and $\alpha^2, \beta^2 < 0.9$ are included in the tables. Examination of these tables reveals that the Δ values obtained with $q_1 = 0$ are not significantly different from those with $\beta^2/\alpha^2 = 1.0$. In addition, except for FeL_4I_2 and FeL_4Br_2, the Δ values are seen to be relatively insensitive to the magnitude of λ. Typical solutions are compared with the experimental results in Figures 1-5.

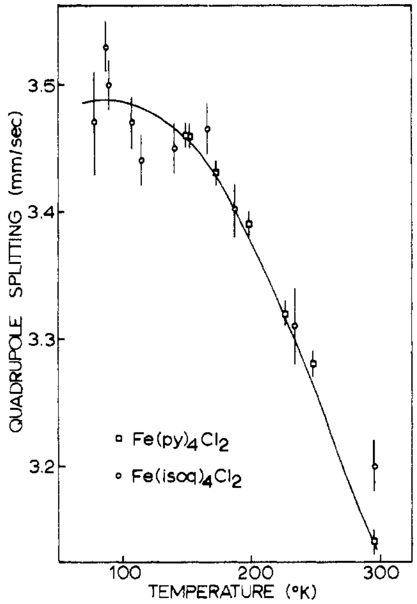

Figure 3. The temperature dependence of the quadrupole splitting of $Fe(py)_4Cl_2$ and $Fe(isoq)_4Cl_2$. The continuous line gives a fitting with $\Delta = 500$ cm^{-1}, $\lambda = -60$ cm^{-1}, $\beta^2 = 0.50$, $\beta^2/\alpha^2 = 1.0$, and $(1/2)e^2Qq_1 = 1.67$ mm/sec. The $Fe(py)_4Cl_2$ data are from ref 2.

Table II. Quadrupole Splitting Fitted with the Assumption of an Axial Perturbation ($\epsilon = 0$) and $q_1 = 0$

Compd	Δ, cm^{-1}	β^2	β^2/α^2
	$\lambda_{\parallel} = -80$ cm^{-1}, $\lambda_{\perp} = (\beta/\alpha)\lambda_{\parallel}$		
$Fe(py)_4I_2$[a]	80-200	0.70-0.30	0.99-0.97
$(Fe(isoq)_4I_2)$[b]			
$Fe(py)_4I_2 \cdot 2py$[a]	300-400	0.52-0.53	0.86-0.76
$Fe(py)_4Br_2$	250-350	0.89-0.88	1.14-1.05
$(Fe(isoq)_4Br_2)$[c]			
$Fe(py)_4(SCN)_2$[a]	250-300	0.73-0.67	1.13-1.07
$Fe(py)_4Cl_2$[a]	350-600	0.76-0.87	1.79-1.11
$(Fe(isoq)_4Cl_2)$[c]			
$Fe(py)_4(N_3)_2$	450-650	0.65-0.80	1.58-1.02
$Fe(py)_4(OCN)_2$	500-750	0.53-0.80	1.68-0.95
	$\lambda_{\parallel} = -60$, $\lambda_{\perp} = (\beta/\alpha)\lambda_{\parallel}$		
$Fe(py)_4I_2$[a]	50-100	0.75-0.31	1.03-1.07
$(Fe(isoq)_4I_2)$[b]	−100 to −130	0.59-0.44	1.00-0.99
$Fe(py)_4I_2 \cdot 2py$[a]	350-450	0.39-0.45	0.84-0.72
$Fe(py)_4Br_2$	150-400	0.56-0.70	1.38-1.09
$(Fe(isoq)_4Br_2)$[c]			
$Fe(py)_4(SCN)_2$[a]	350-400	0.53-0.55	1.16-1.06
$Fe(py)_4Cl_2$[a]	400-650	0.64-0.88	2.20-1.05
$(Fe(isoq)_4Cl_2)$[c]			
$Fe(py)_4(N_3)_2$	500-700	0.54-0.82	1.79-1.00
$Fe(py)_4(OCN)_2$	600-800	0.50-0.76	1.63-0.89
	$\lambda_{\parallel} = -40$, $\lambda_{\perp} = (\beta/\alpha)\lambda_{\parallel}$		
$Fe(py)_4I_2$[a]	−170 to −200	0.35-0.31	1.00-0.99
$(Fe(isoq)_4I_2)$[b]			
$Fe(py)_4I_2 \cdot 2py$[a]	400-450	0.37-0.44	0.80-0.73
$Fe(py)_4Br_2$	300-450	0.38-0.67	1.56-1.06
$(Fe(isoq)_4Br_2)$[c]			
$Fe(py)_4(SCN)_2$[a]	400	0.47	1.17
$Fe(py)_4Cl_2$[a]	550-650	0.65-0.81	1.70-1.10
$(Fe(isoq)_4Cl_2)$[c]			
$Fe(py)_4(N_3)_2$	550-700	0.53-0.76	1.9-1.0
$Fe(py)_4(OCN)_2$	650-800	0.48-0.73	1.60-0.92

[a] The quadrupole splitting data are from ref 2. [b] The $Fe(isoq)_4I_2$ data can be fitted with parameters similar to those for $Fe(py)_4I_2$ with small changes in β^2 and β^2/α^2. [c] The $Fe(isoq)_4Br_2$ and $Fe(isoq)_4Cl_2$ data can be fitted with parameters the same as those for $Fe(py)_4Br_2$ and $Fe(py)_4Cl_2$, respectively.

The crystal structure of $Fe(py)_4(SCN)_2$[12] indicates that the bond angles in the plane of the four (pyridine) nitrogens

Table III. Quadrupole Splitting Fitted with the Assumption of an Axial Perturbation ($\epsilon = 0$) and $\alpha^2 = \beta^2$

Compd	Δ, cm^{-1}	β^2	$(1/2)e^2Qq_i$, mm/sec
	$\lambda_\parallel = \lambda_\perp = -80$ cm^{-1}		
$Fe(py)_4I_2$[a] $(Fe(isoq)_4I_2)$[b]	60-180	0.90-0.31	−0.02 to −0.04
$Fe(py)_4I_2 \cdot 2py$[a]	250-350	0.60-0.62	−0.36 to −0.78
$Fe(py)_4Br_2$ $(Fe(isoq)_4Br_2)$[c]	300-350	0.86-0.87	0.59-0.33
$Fe(py)_4(SCN)_2$[a]	250-350	0.66-0.65	0.53-0.14
$Fe(py)_4Cl_2$[a] $(Fe(isoq)_4Cl_2)$[c]	400-600	0.48-0.83	2.00-0.52
$Fe(py)_4(N_3)_2$	350-650	0.33-0.74	2.10-0.40
$Fe(py)_4(OCN)_2$	500-750	0.30-0.74	1.58 to −0.15
	$\lambda_\parallel = \lambda_\perp = -60$ cm^{-1}		
$Fe(py)_4I_2$[a]	40-100	0.85-0.32	0.11-0.12
$(Fe(isoq)_4I_2)$[b]	−80 to −120	0.69-0.49	0.01 to −0.01
$Fe(py)_4I_2 \cdot 2py$[a]	350-400	0.45-0.50	−0.43 to −0.74
$Fe(py)_4Br_2$ $(Fe(isoq)_4Br_2)$[c]	200-450	0.61-0.80	1.20 to −0.10
$Fe(py)_4(SCN)_2$[a]	350-400	0.45-0.54	0.46-0.18
$Fe(py)_4Cl_2$[a] $(Fe(isoq)_4Cl_2)$[c]	450-600	0.42-0.84	1.99-0.30
$Fe(py)_4(N_3)_2$	450-700	0.32-0.32	1.89 to −0.11
$Fe(py)_4(OCN)_2$	600-800	0.35-0.85	1.50 to −0.68
	$\lambda_\parallel = \lambda_\perp = -40$ cm^{-1}		
$Fe(py)_4I_2$[a] $(Fe(isoq)_4I_2)$[b]	−160 to −200	0.36-0.31	0.01 to −0.01
$Fe(py)_4I_2 \cdot 2py$[a]	400-450	0.42-0.51	−0.53 to −0.91
$Fe(py)_4Br_2$ $(Fe(isoq)_4Br_2)$[c]	250-450	0.44-0.70	1.46-0.22
$Fe(py)_4(SCN)_2$[a]	400	0.45	0.37
$Fe(py)_4Cl_2$[a] $(Fe(isoq)_4Cl_2)$[c]	450-650	0.37-0.78	2.11-0.40
$Fe(py)_4(N_3)_2$	500-700	0.32-0.75	1.76-0.08
$Fe(py)_4(OCN)_2$	600-800	0.31-0.81	1.36 to −0.59

[a] The quadrupole splitting data are from ref 2. [b] The $Fe(isoq)_4I_2$ data can be fitted with parameters the same as those for $Fe(py)_4I_2$ but with $(1/2)e^2Qq_i$ increased by 0.05 mm/sec. [c] The $Fe(isoq)_4Br_2$ and $Fe(isoq)_4Cl_2$ data can be fitted with parameters the same as those for $Fe(py)_4Br_2$ and $Fe(py)_4Cl_2$, respectively.

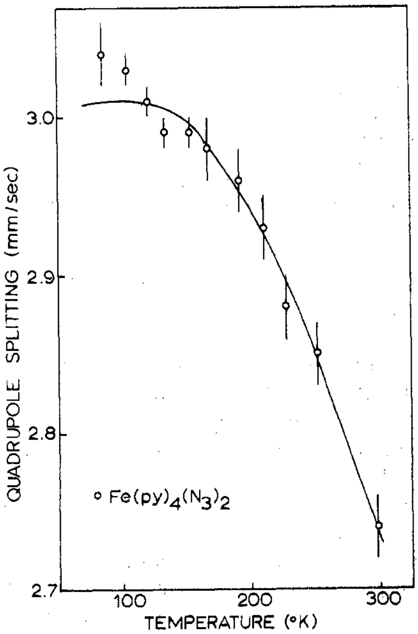

Figure 4. The temperature dependence of the quadrupole splitting of $Fe(py)_4(N_3)_2$. The continuous line gives a fitting with $\Delta = 600$ cm^{-1}, $\lambda = -60$ cm^{-1}, $\beta^2 = 0.55$, $\beta^2/\alpha^2 = 1.0$, and $(1/2)e^2Qq_i = 0.95$ mm/sec.

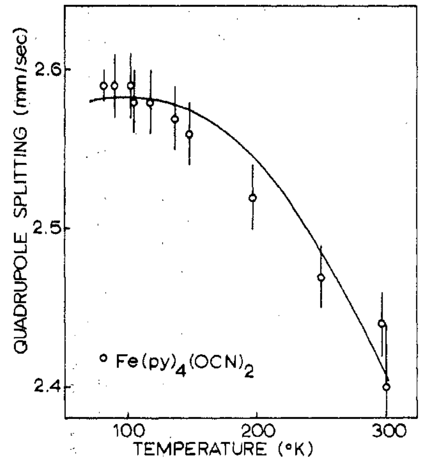

Figure 5. The temperature dependence of the quadrupole splitting of $Fe(py)_4(OCN)_2$. The continuous line gives a fitting with $\Delta = 650$ cm^{-1}, $\lambda = -60$ cm^{-1}, $\beta^2 = 0.42$, $\beta^2/\alpha^2 = 1.0$, and $(1/2)e^2Qq_i = 1.00$ mm/sec.

about the iron deviate from 90°. It is therefore possible that ϵ and η_i have magnitudes different from zero. For this reason the data have also been fitted with ϵ large and $\eta_i = 1.0$.

Typical results obtained with $\epsilon \neq 0$ are shown in Table IV. In general, with Δ positive, inclusion of a large rhombic distortion allows the magnitude of Δ to be increased by as much as 200 cm^{-1}. When the $Fe(L)_4I_2$ data are fitted with a rhombic distortion, $|\Delta|$ can be increased by less than 75 cm^{-1} and solutions between the positive and negative extremes can be obtained.

The solutions obtained with $\eta_i = 1.0$ and $\epsilon \neq 0$ are not significantly different from those obtained with $\eta_i = 0$. Fitting the data with $\eta_i = 1$ changes the required magnitude of q_i but does not significantly change the range of Δ and ϵ. The magnitude of β^2 is changed by less than 0.10.

Because of the many variables involved, it is impossible to define the magnitude of Δ precisely. The major difficulty arises from the fact that a decrease in the temperature dependence of the quadrupole splitting can be interpreted as either an increase in Δ or a decrease in α^2. The possibility of a rhombic distortion also increases the uncertainty in Δ. These results indicate a broader range of possible solutions than were considered in the earlier works.[1,2] In spite of the ambiguities in the results, it is possible to draw some conclusions.

The compounds $Fe(L)_4I_2$ show smaller axial splittings than the other compounds except possibly the bromides. The axial splittings in these compounds are all relatively small, less than 800 cm^{-1}. The relative energies of the $e_g(\pi^*)$ orbitals in FeL_4X_2 are found to follow the order $Cl^- \geqslant Br^- \geqslant I^-$. The effect is small, with $e_g(\pi^*, Cl^-)$ less than 800 cm^{-1} higher than $e_g(\pi^*, I^-)$. Near-infrared studies[6] indicate that the $a_{1g}(\sigma^*)$ orbitals follow a similar trend: $Cl^- > Br^- > I^-$. The $a_{1g}(\sigma^*, Cl^-)$ orbital lies ~3000 cm^{-1} higher than $a_{1g}(\sigma^*, I^-)$. The d orbitals bonded to L behave differently. With the possible exception of FeL_4I_2, the $b_{2g}(\pi^*, L)$ (or $b_{2g}(\pi, L)$ if L is considered as a back-bonding ligand) orbital lies lower than $e_g(\pi^*, X^-)$. The near-infrared investigation[6] shows that $b_{1g}(\sigma^*, L)$ lies close to or higher than $a_{1g}(\sigma^*, X^-)$. These results do not necessarily indicate that L functions as a π acceptor but only that the σ- and π-bonding properties of L are significantly different.

The wide range of possible solutions makes it difficult to determine the magnitude of β^2 and α^2. The $b_{2g}(\pi^*)$ orbital, xy, does not interact directly with X^-. For this reason, the magnitude of β^2 should be reasonably constant among the

Table IV. Effect of a Low-Symmetry Component on the Magnitude of the Fitting Parameters. The Data Were Fitted with the Assumptions $\beta^2 = \alpha^2$ and $\lambda = -60$ cm^{-1}

Compd	Δ, cm^{-1}	ϵ, cm^{-1}	β^2	$(1/2)e^2Qq_i$, mm/sec
Fe(py)$_4$(SCN)$_2$	400	100	0.54	0.20
		250	0.55	0.24
	500	350	0.66	−0.26
		450	0.63	−0.09
	600	500	0.77	−0.74
		600	0.72	−0.45
Fe(py)$_4$Cl$_2$	400	50	0.38	2.21
	500	100	0.50	1.69
		200	0.48	1.77
		300	0.46	1.87
	600	100	0.73	0.73
		200	0.69	0.92
		300	0.64	1.13
		400	0.59	1.37
	700	400	0.81	0.41
		500	0.73	0.77
	800	600	0.87	0.18

compounds *trans*-FeL$_4$X$_2$. Assuming ϵ to be relatively small, it is possible to refer to Tables II and III to determine β^2. Reasonably consistent values are found with β^2 in the range of 0.40 to 0.70 with the values becoming somewhat more consistent as $|\lambda|$ is reduced. A relatively low value for λ is consistent with the conclusions of some recent work. Johnson and Ingalls[17] have shown $|\lambda|$ to be less than 70 cm^{-1} in FeF$_2$.

Fe(phen)$_2$X$_2$. The compounds Fe(phen)$_2$X$_2$ are thought to have the cis configuration. Powder X-ray data suggest the cis structure for some of these compounds.[18] No trans complexes of the form [M(phen)$_2$X$_2$]Y have been substantiated.[19,20]

Initially it was assumed that these cis complexes exhibit a (pseudo)tetragonal distortion such as that described by Ballhausen.[21] For this symmetry $\eta_i = 0$. The data were fitted in the same manner as that of FeL$_4$X$_2$. Typical solutions are shown in Table V. Some of these fittings are compared with the experimental data in Figure 6. Because of the limited quantity of Fe(phen)$_2$Br$_2$ data, no fitting was attempted. However, a comparison of the bromide data to those of the chloride and thiocyanate reveals no significant difference among the compounds. The results suggest a positive axial distortion. No solutions are found with Δ negative and $\epsilon < 400$ cm^{-1}. Magnetic perturbation experiments on Fe(phen)$_2$Cl$_2$ and Fe(phen)$_2$(SCN)$_2$[22] as well as on Fe(phen)$_2$(N$_3$)$_2$[23] show q to be negative. For a positive tetragonal distortion (xy ground orbital) or for a negative distortion with ϵ large, a positive q is expected. The results are therefore not consistent with this type of distortion.

It has recently been shown that the low-spin iron(III) complex Fe(phen)$_2$(CN)$_2^+$ exhibits a trigonal distortion.[24] It has also been suggested that the compounds Fe(phen)$_2$X$_2$ may exhibit trigonal distortions.[25] The observed positive Δ and negative q are consistent with a trigonal distortion (z^2 ground orbital).

Table V. Quadrupole Splitting of Fe(phen)$_2$(SCN)$_2$ and Fe(phen)$_2$Cl$_2$ Fitted with the Assumptions $\beta^2 = \alpha^2$ and $\lambda = -60$ cm^{-1}

Compd	Δ, cm^{-1}	ϵ, cm^{-1}	β^2	$(1/2)e^2Qq_i$, mm/sec
Fe(phen)$_2$(SCN)$_2$	500	0	0.71	0.55
		100	0.71	0.56
		200	0.70	0.61
	600	200	0.90	−0.26
		300	0.87	−0.09
		400	0.84	0.08
Fe(phen)$_2$Cl$_2$	400	0	0.31	2.24
		100	0.31	2.26
		200	0.30	2.30
	500	0	0.44	1.75
		100	0.42	1.78
		200	0.40	1.86
		300	0.38	1.98
	600	300	0.53	1.34
		400	0.47	1.57
		500	0.42	1.80
	700	500	0.61	1.04
		600	0.52	1.41
		700	0.44	1.72
	800	700	0.64	0.90
		800	0.53	1.33

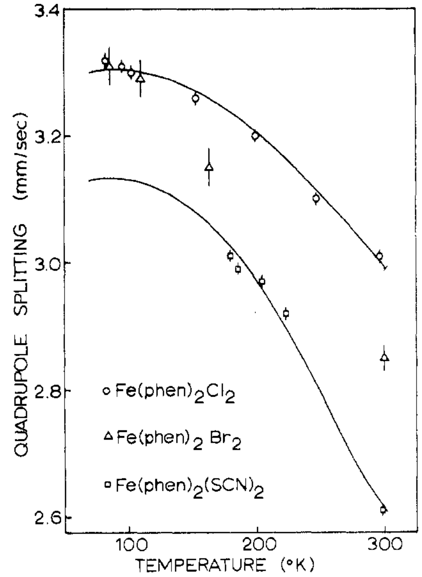

Figure 6. The temperature dependence of the quadrupole splitting of Fe(phen)$_2$X$_2$ (X$^-$ = Br$^-$, Cl$^-$, SCN$^-$). The top line shows the Fe(phen)$_2$Cl$_2$ data fitted with $\Delta = 500$ cm^{-1}, $\epsilon = 100$ cm^{-1}, $\lambda = -60$ cm^{-1}, $\beta^2 = 0.42$, $\beta^2/\alpha^2 = 1.0$, and $(1/2)e^2Qq_i = 1.78$ mm/sec. The bottom line shows the Fe(phen)$_2$(SCN)$_2$ data fitted with $\Delta = 500$ cm^{-1}, $\epsilon = 100$ cm^{-1}, $\lambda = -60$ cm^{-1}, $\beta^2 = 0.71$, $\beta^2/\alpha^2 = 1.0$, and $(1/2)e^2Qq_i = 0.56$ mm/sec.

For a trigonal distortion from octahedral symmetry the approximation $\eta_i = 0$ no longer holds. The data should therefore be refitted with an appropriate value for η_i. However, it is impossible to estimate η_i in this symmetry since the effect of the trigonal distortion from octahedral symmetry on the temperature-independent or "lattice" components cannot be predicted. The data were refitted for various values of η_i and also for the case $q_i = 0$ with the product $\eta_i q_i$ large. The chosen value for η_i is found not to have a significant effect on the magnitudes of Δ and ϵ which will give a reasonable fit. The chosen value for η_i does have a significant effect on the magnitude of β^2. In particular, the Fe(phen)$_2$Cl$_2$ data can be

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fitted with β^2 values as large as 0.85. The results presented in Table V represent reasonably well the range of possible Δ and ϵ but give a misleading view of the magnitude of β^2.

The results obtained for both FeL_4X_2 and $Fe(phen)_2X_2$ reflect a substantial degree of ligand-t_{2g} metal orbital interaction. Most of the fittings require $|\lambda| \leqslant 80$ cm^{-1} and $\beta^2 \leqslant 0.8$. A consistent interpretation of the results requires that both of these parameters take on lower values. The theory employed should be discussed in terms of this significant ligand-metal interaction. The model assumes that "covalency" effects on the t_{2g} metal orbitals can be treated simply as an expansion of the free-ion orbitals. In other words "covalency" effects are treated simply as a reduction in the parameters λ and β^2, α^2. The angular part of the wave function is assumed to be the same as the free-ion wave function. In view of the fact that the quadrupole splitting is sensitive only to that part of the wave function close to the nucleus (the quadrupolar interaction is proportional to $\langle r^{-3} \rangle$) this would appear to be a reasonably good approximation. However, the results presented here must be considered in view of this assumption.

Magnetic Susceptibility. The average magnetic susceptibilities of these compounds have been investigated over the range 20-300° by Long and Baker.[26] The data were fitted in terms of a model which assumed axial symmetry. The fitting parameters obtained for $Fe(isoq)_4I_2$, $Fe(isoq)_4Br_2$, $Fe(isoq)_4Cl_2$, $Fe(py)_4I_2$, and $Fe(py)_4Br_2$ are in qualitative agreement with those presented here with $\Delta(Cl^-) > \Delta(Br^-) > \Delta(I^-)$. Quantitative agreement is found only for $Fe(isoq)_4Cl_2$.

An attempt was made to find better agreement by introducing the rhombic distortion parameter, ϵ, in the analysis of the susceptibility data. The magnetic susceptibility was calculated in terms of Δ, ϵ, and the "orbital reduction factor," k, by employing methods which have been described previously.[27] Introduction of this parameter was found not to improve agreement. Employing the parameters given in Tables II and III and a consistent spin-orbit coupling constant, it was found possible to reproduce qualitatively the data of $Fe(isoq)_4I_2$, $Fe(isoq)_4Br_2$, and $Fe(isoq)_4Cl_2$. This procedure gives the higher magnitudes and greater temperature dependence expected for μ_{eff} when the trend from the chloride to the iodide is followed. Exact agreement is not found, however. In view of the problems associated with the analysis of the magnetic susceptibility data which were discussed by Long and Baker,[26] it may be that exact agreement is not expected.

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Registry No. $Fe(isoq)_4I_2$, 15245-93-9; $Fe(py)_4Br_2$, 34406-12-7; $Fe(isoq)_4Br_2$, 15245-92-8; $Fe(isoq)_4Cl_2$, 15245-91-7; $Fe(py)_4(N_3)_2$, 49567-50-2; $Fe(py)_4(OCN)_2$, 49567-51-3; $Fe(1,10\text{-phen})_2(SCN)_2$, 15131-05-2; $Fe(1,10\text{-phen})_2Cl_2$, 15553-84-1; $Fe(1,10\text{-phen})_2Br_2$, 15553-83-0; $Fe(py)_4(SCN)_2$, 18251-76-8; $Fe(py)_4Cl_2$, 15245-99-5.

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Iron-57 and Antimony-121 Mossbauer Spectroscopic Studies of $[X_nSb(Fe(CO)_2(\pi\text{-}C_5H_5))_{4-n}]^+$ Species. Nature of the Iron-Antimony Bond

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A number of cations containing Fe–Sb σ bonds of the type $[X_nSb(Fe(CO)_2(\pi\text{-}C_5H_5))_{4-n}]^+$ ($X = Cl, Br, I, CF_3, C_6H_5, n\text{-}C_4H_9$; $n = 1\text{–}3$, but not all combinations), some of which have been prepared for the first time, have been studied *via* ^{57}Fe and ^{121}Sb Mossbauer spectra. These compounds are nominally isoelectronic with the extensively investigated neutral tin derivatives $X_nSn(Fe(CO)_2(\pi\text{-}C_5H_5))_{4-n}$. The ^{121}Sb isomer shifts fall between the ranges of values typically associated with Sb(III) and Sb(V); hence assignment of a formal oxidation state for antimony in these compounds has little justification. For $[R_3SbFe(CO)_2(\pi\text{-}C_5H_5)]^+$ ($R = n\text{-}C_4H_9, C_6H_5$) the ^{121}Sb quadrupole coupling constant $(e^2qQ)_{Sb}$ is positive, whereas $(e^2qQ)_{Sn}$ is negative in $(n\text{-}C_4H_9)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$. Isomer shift data for ^{57}Fe, ^{119}Sn, and ^{121}Sb suggest that Fe–Sb π bonding is of more importance than Fe–Sn π bonding. The fact that Sn and Sb are essentially isoelectronic and that ^{57}Fe Mossbauer parameters are very similar in corresponding tin and antimony derivatives indicates that the positive charge in the latter complexes is not extensively delocalized onto the ligands.

Introduction

The nature of heteronuclear metal–metal bonds has been the subject of much recent discussion, particularly in compounds where a group IV element is bonded to a transition metal such as manganese, iron, or cobalt. Compounds containing Fe–Sn bonds have been rather extensively studied by Mossbauer spectroscopy,[1-8] where use of both ^{57}Fe and ^{119}Sn resonances has led to valuable insights concerning the nature

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