given ionic strength, and this fact strongly suggests that eq 2 is in fact the equation governing the equilibrium. Subtraction of log $(1/[H_2O]^{1/2})$, the equivalent correction factor for reaction scheme 1, does not give similar agreement.

That eq 2 correctly represents the equilibrium in turn implies that the structure proposed by Griffith[5] for the violet perchromate, $HCrO_6^-$, is correct. Any of the other possible structures which have been proposed (*e.g.*, $M^IOCrO_4 \cdot H_2O$, $M^IH_2CrO_7$, and the binuclear $Cr_2O_{12}^{2-}$)[5] would have resulted in different overall proton, water, peroxide, and, in the case of the binuclear complex, chromium stoichiometries.[9] A recent report[10] has claimed that a product isolated from neutral chromium peroxide systems has the formula $K_2HCrO_6$, although it was too unstable for accurate analysis. The results reported here are inconsistent with the possibility that this formula correctly represents the species existing in neutral chromium peroxide solutions. The same paper has also reported an additional chromium peroxide, $K_3CrO_7$, isolated from peroxide solutions of intermediate basicity. The present spectrophotometric study, indicating that $CrO_8^{3-}$ and $HCrO_6^-$ are the only chromium peroxy species present in any appreciable concentration in basic aqueous hydrogen peroxide solutions, casts doubt on the possibility of isolating a triperoxy compound. Other work in this laboratory[11] has failed to obtain any product other than tetraperoxychromate under the conditions reported in ref 10.

The p*K*'s listed in Table I are still not thermodynamic equilibrium constants, as they include the term log $\gamma_{CrO_8^{3-}}/\gamma_{HCrO_6^-}$. There are various expressions allowing, at least, an approximate calculation of the values for activity coefficients. One of the most accurate is the semiempirical relationship of Davies.[12] This law states that for any ionic species, *i*, present in a solution of ionic strength $\mu$, the activity coefficient is given by the following equation

$$\log \gamma_i = -\left(\frac{e^2}{\epsilon kT}\right)^{3/2} \sqrt{\frac{2\pi N}{1000}}\, Z_i^2 \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.2\,\mu\right) \qquad (8)$$

where $T$ is the absolute temperature, $\epsilon$ is the dielectric constant of the solvent, e is the electronic charge, $k$ is the Boltzmann constant, and $N$ is Avogadro's number. This law is valid to within 1% in solutions of ionic strength below 0.01 *M* and thus can readily be applied to those solutions which have thus far been referred to as of uncontrolled ionic strength. The actual ionic strength of these solutions lies between $10^{-2}$ and $10^{-3}$ *M*. Since the values of the dielectric constants of water and hydrogen peroxide are so close ($\epsilon$ = 88 for $H_2O$, $\epsilon$ = 84 for $H_2O_2$ at 0°),[13] it was assumed that for all solutions concerned, $\epsilon = 87$. Upon substitution of the appropriate values for the ionic strength ($10^{-3} < \mu < 10^{-2}$), the additional correction term for the $pK_{cor}$ is found to be bounded by $0.12 \leqslant$ correction term $< 0.35$. Thus, it may be concluded that the thermodynamic p*K* lies between 14.0 and 14.2 for the uncontrolled ionic strength studies.

Furthermore, the variation in the corrected p*K*'s of Table I as a function of total ionic strength can be understood in terms of eq 8. Calculations of the correction term for those solutions of 0.200 *M* ionic strength yield a value of approximately 1.1. If this value is added to the $pK_{cor}$'s of Table I for such solutions, it gives an approximate value of 13.9 for the thermodynamic constant, which is in good agreement with the values calculated for the solutions of uncontrolled ionic strength. Inherent inaccuracy of the Davies law in solutions above 0.5 *M* total ionic strength[12] prevents a similar application to the data for the 1 *M* solutions; however, it is a logical assumption that the deviation of these p*K*'s from about 14.0 is accounted for by the variation in the activity coefficients of tetraperoxychromate and diperoxychromate.

**Registry No.** $CrO_8^{3-}$, 12526-97-5; $HCrO_6^-$, 40330-52-7.

**Acknowledgments.** This research was supported by a grant from the Robert A. Welch Foundation. The Cary Model 15 spectrophotometer used was obtained, in part, through a grant from the Organized Research Fund of East Texas State University.

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[9] A referee has suggested, correctly, that this conclusion assumes that the tetraperoxychromate ion, in solution, has the same composition as in the solid state, namely $CrO_8^{3-}$. If this is not the case then the conclusion as to the structure of the diperoxy species must be changed. It is clear, however, that (1) the two species are related by a reaction involving two protons and (2) *both* must be mononuclear or *both* binuclear (otherwise straight line plots would not be obtained).

[10] B. Rodriguez Rios and P. Gili Trujillo, *An. Quim.*, 64, 55 (1968).

[11] R. Brown, J. Duke, B. Bartlett, and D. Quane, Abstracts, 27th Southwest Regional Meeting of the American Chemical Society, San Antonio, Texas, Dec 1971, No. 404; and subsequent unpublished work by R. Brown, B. Bartlett, G. Reimondo, and D. Quane.

[12] J. N. Butler, "Ionic Equilibria," Addison-Wesley, Reading, Mass., 1964, p 437.

[13] "Handbook of Chemistry and Physics," 51st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970, pp E 61, E 67.

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## Mossbauer Spectroscopy and Electron Paramagnetic Resonance Study of Some Iron(III)-Tris(diimine) Complexes

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A recent interpretation of the electron paramagnetic resonance (epr) and Mossbauer spectral data of potassium ferricyanide reveals that $\langle r^{-3}\rangle_{t_{2g}}$ and the spin-orbit coupling constant are reduced to about 15% of their free ion values.[1] We have examined the electronic structure of some tris(1,10-phenanthroline) (phen) and tris(2,2′-bipyridyl) (bipy) complexes of iron(III) in order to determine if extensive delocalization is typical of low-spin iron(III) complexes.

### Experimental Section

**Preparation of Complexes.** The complexes $Fe(phen)_3(PF_6)_3$ and $Fe(bipy)_3(PF_6)_3$ were prepared by the methods of DeSimone and Drago.[2] $Fe(phen)_3(ClO_4)_3$ and $Fe(bipy)_3(ClO_4)_3$ were prepared by the methods of Burstall and Nyholm.[3]

**Physical Measurements.** The Mossbauer spectrometer and associated cryostat have been described previously.[1] The spectra were fit with a least-squares fitting program and the accuracy was determined statistically.[4] Epr spectra were measured at X-band frequencies at 77°K. The magnetic field was measured with a gaussmeter and checked with DPPH.

### Results

**Epr.** Spectra were obtained with pure powdered samples of $Fe(phen)_3(PF_6)_3$, $Fe(bipy)_3(PF_6)_3$, $Fe(phen)_3(ClO_4)_3$, and

[1] P. B. Merrithew and A. J. Modestino, *J. Amer. Chem. Soc.*, 94, 3361 (1972).

[2] R. E. DeSimone and R. S. Drago, *J. Amer. Chem. Soc.*, 92, 2343 (1970).

[3] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

[4] J. F. Ullrich, Ph.D. Thesis, University of Michigan, 1967.

$Fe(bipy)_3(ClO_4)_3$ at 77°K. The *g* values were determined by employing the methods of Kneubuhl.[5] These results are given in Table I. The $Fe(bipy)_3(PF_6)_3$ results are identical with those obtained by DeSimone and Drago with the sample diluted in a diamagnetic host.[2] The spectrum of pure $Fe(phen)_3(PF_6)_3$, however, is not the same as the spectrum of the diluted material.

The epr data were interpreted in a manner similar to that described by Hill[6] with the basis wave functions changed to be consistent with trigonal symmetry. The six five-electron states may be taken as

$$|{}^2T_2\ {}^1/_2\ 1\rangle = -|t_a t_b{}^2 t_0{}^2\rangle \qquad |{}^2T_2\ -{}^1/_2\ 1\rangle = |\overline{t}_a t_b{}^2 t_0{}^2\rangle$$

$$|{}^2T_2\ {}^1/_2\ 0\rangle = |t_a{}^2 t_b{}^2 t_0\rangle \qquad |{}^2T_2\ -{}^1/_2\ 0\rangle = -|t_a{}^2 t_b{}^2 \overline{t}_0\rangle$$

$$|{}^2T_2\ {}^1/_2\ -1\rangle = |t_a{}^2 t_b t_0{}^2\rangle \qquad |{}^2T_2\ -{}^1/_2\ -1\rangle = -|t_a{}^2 \overline{t}_b t_0{}^2\rangle$$

where $t_0 = |0\rangle$, $t_a = \sqrt{2/3}|2\rangle - \sqrt{1/3}|-1\rangle$, and $t_b = \sqrt{2/3}|-2\rangle + \sqrt{1/3}|1\rangle$.

The lowest Kamers doublet has the form

$$\psi = A_1|{}^2T_2\ {}^1/_2\ -1\rangle + B_1|{}^2T_2\ -{}^1/_2\ 0\rangle + C_1|{}^2T_2\ {}^1/_2\ 1\rangle$$

$$\psi^* = A_1|{}^2T_2\ -{}^1/_2\ 1\rangle + B_1|{}^2T_2\ {}^1/_2\ 0\rangle + C_1|{}^2T_2\ -{}^1/_2\ -1\rangle$$

The energies $E_n$ and coefficients $A_n$, $B_n$, and $C_n$ may be obtained by solving the spin-orbit distortion matrix.[6,7] The *g* values are

$$g_z = 2[A_1{}^2 - B_1{}^2 + C_1{}^2 + k(A_1{}^2 - C_1{}^2)]$$

$$g_x = 2[-2A_1C_1 - B_1{}^2 - \sqrt{2}kB_1(A_1 + C_1)]$$

$$g_y = 2[-2A_1C_1 + B_1{}^2 + \sqrt{2}kB_1(A_1 - C_1)]$$

There are two mechanisms which give rise to configuration interaction, interelectronic electrostatic repulsion and spin-orbit coupling. The existence of electrostatic repulsion is reflected in the *g* tensor only by replacement of the parameter, $k$, by $K = (1 + 12B/E)k$.[6] $B$ is the Racah parameter and $E$ is the excitation energy. The corrections necessary to account for the spin-orbit interaction were calculated in the manner of Hill.[6] For simplicity pure trigonal symmetry was assumed ($C_n = 0$). The appropriate corrections are

$$\Delta g_z = 2\zeta k/E\,(-2A_1{}^2 + 2\sqrt{2}A_1B_1)$$

$$\Delta g_x = 2\zeta k/E\,(2B_1{}^2 - \sqrt{2}B_1A_1)$$

$$\Delta g_y = 2\zeta k/E\,(-2B_1{}^2 + \sqrt{2}B_1A_1)$$

The single electron spin-orbit coupling constant, $\zeta$, is inherently positive. The parameter $E$ is taken as 20,000 $cm^{-1}$ and $B$ as 500 $cm^{-1}$.[8]

The epr data were fitted in terms of $\zeta$, $\Delta$, $\epsilon$, and the parameter, $k$. The splitting between the ${}^2A$ and ${}^2E$ terms is $\Delta$. A positive value of $\Delta$ designates a ${}^2A$ ground term. The splitting of the ${}^2E$ term due to low symmetry components is $\epsilon$. The results are shown in Table II. The series of solutions could be extended to include both higher and lower values for the spin-orbit coupling constant but it will be shown that these additional solutions are inconsistent with the quadrupole splitting results.

Table I

| Sample | $g_1, g_2$ | $g_3$ | Half-width $g_1$, G |
|---|---|---|---|
| $Fe(phen)_3(PF_6)_3$ | 2.69 ± 0.03 | 1.51 ± 0.02 | 85 |
| $Fe(bipy)_3(PF_6)_3$ | 2.64 ± 0.03 | 1.63 ± 0.02 | 80 |
| $Fe(phen)_3(ClO_4)_3$ | 2.65 ± 0.03 | 1.49 ± 0.02 | 160 |
| $Fe(bipy)_3(ClO_4)_3$ | 2.72 ± 0.02,<br>2.57 ± 0.02 | 1.46 ± 0.02 | 50 |

Table II

| Compound | $\zeta$, $cm^{-1}$ | $\Delta$, $cm^{-1}$ | $\epsilon$, $cm^{-1}$ | $k$ | $K$ | $N^2$ | $\Delta E_i$, mm/sec | $\chi_\nu$ |
|---|---|---|---|---|---|---|---|---|
| $Fe(phen)_3(PF_6)_3$ | 200 | 560 | 0 | 0.92 | 1.19 | 0.27 | 0.80 | 1.0 |
| | 225 | 630 | 0 | 0.91 | 1.18 | 0.35 | 0.51 | 1.1 |
| | 250 | 702 | 0 | 0.91 | 1.19 | 0.49 | 0.01 | 1.6 |
| $Fe(bipy)_3(PF_6)_3$ | 200 | 650 | 0 | 0.94 | 1.22 | 0.34 | 0.60 | 1.0 |
| | 225 | 740 | 0 | 0.96 | 1.25 | 0.56 | −0.20 | 1.2 |
| | 250 | 825 | 0 | 0.96 | 1.25 | 0.78 | −1.00 | 1.4 |
| $Fe(phen)_3(ClO_4)_3$ | 175 | 470 | 0 | 0.83 | 1.08 | 0.28 | 0.86 | 1.0 |
| | 200 | 540 | 0 | 0.85 | 1.10 | 0.37 | 0.52 | 1.3 |
| | 225 | 610 | 0 | 0.85 | 1.11 | 0.63 | −0.42 | 2.1 |
| $Fe(bipy)_3(ClO_4)_3$ | 175 | 455 | 78 | 0.82 | 1.07 | 0.25 | 1.00 | 1.0 |
| | 200 | 525 | 90 | 0.83 | 1.08 | 0.32 | 0.76 | 1.2 |
| | 225 | 585 | 90 | 0.83 | 1.08 | 0.42 | 0.40 | 1.9 |

Table III

| Temp, °K | Quadrupole splitting, mm/sec |
|---|---|
| | $Fe(phen)_3(PF_6)_3$ |
| 298 ± 2 | 1.643 ± 0.011 |
| 245 | 1.689 ± 0.013 |
| 242 | 1.679 ± 0.011 |
| 206 | 1.722 ± 0.008 |
| 105 | 1.767 ± 0.009 |
| 95 | 1.770 ± 0.019 |
| 84 | 1.751 ± 0.011 |
| | $Fe(bipy)_3(PF_6)_3$ |
| 298 | 1.725 ± 0.009 |
| 272 | 1.767 ± 0.020 |
| 221 | 1.803 ± 0.010 |
| 172 | 1.845 ± 0.010 |
| 122 | 1.874 ± 0.010 |
| 105 | 1.847 ± 0.009 |
| 96 | 1.847 ± 0.015 |
| 85 | 1.853 ± 0.016 |
| | $Fe(phen)_3(ClO_4)_3$ |
| 298 | 1.590 ± 0.021 |
| 271 | 1.645 ± 0.038 |
| 247 | 1.664 ± 0.011 |
| 241 | 1.679 ± 0.037 |
| 222 | 1.692 ± 0.009 |
| 211 | 1.718 ± 0.008 |
| 183 | 1.749 ± 0.025 |
| 152 | 1.774 ± 0.018 |
| 127 | 1.810 ± 0.016 |
| 102 | 1.826 ± 0.018 |
| 81 | 1.844 ± 0.018 |
| | $Fe(bipy)_3(ClO_4)_3$ |
| 298 | 1.699 ± 0.011 |
| 271 | 1.718 ± 0.011 |
| 242 | 1.757 ± 0.010 |
| 218 | 1.780 ± 0.009 |
| 189 | 1.812 ± 0.010 |
| 142 | 1.838 ± 0.013 |
| 124 | 1.858 ± 0.011 |
| 115 | 1.854 ± 0.011 |
| 105 | 1.874 ± 0.011 |
| 96 | 1.874 ± 0.014 |
| 81 | 1.883 ± 0.011 |

**Mossbauer Spectra.** The quadrupole splitting data are given in Table III. The quadrupole splitting, $\Delta E$, can be expressed as

$$\Delta E \cong \Delta E_d + \Delta E_i$$

if the temperature-independent contributions to the quad-

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[5] F. K. Kneubuhl, *J. Chem. Phys.*, 33, 1074 (1960).

[6] N. J. Hill, *J. Chem. Soc., Faraday Trans. 2*, 68, 427 (1972).

[7] B. Bleaney and M. C. M. O'Brien, *Proc. Phys. Soc., London, Sect. B*, 69, 1216 (1956).

[8] R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, 9, 1207 (1970).

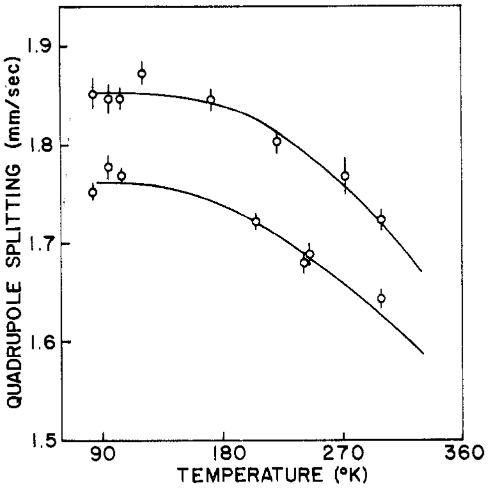

**Figure 1.** Top curve: $Fe(bipy)_3(PF_6)_3$ fitted with $\zeta = 225$ cm$^{-1}$, $\Delta = 740$ cm$^{-1}$, $\epsilon = 0$, $N^2 = 0.56$, and $\Delta E_i = -0.20$ mm/sec. Bottom curve: $Fe(phen)_3(PF_6)_3$ fitted with $\zeta = 225$ cm$^{-1}$, $\Delta = 630$ cm$^{-1}$, $\epsilon = 0$, $N^2 = 0.35$, and $\Delta E_i = 0.51$ mm/sec.

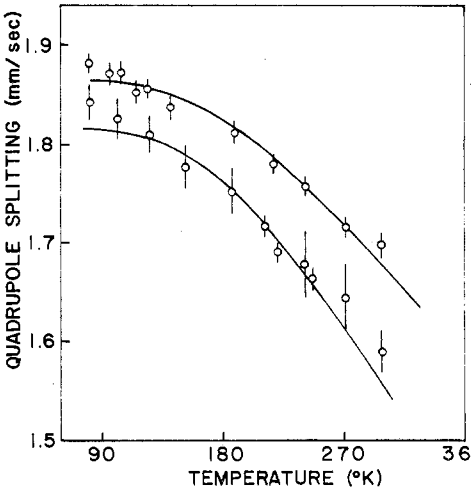

**Figure 2.** Top curve: $Fe(bipy)_3(ClO_4)_3$ fitted with $\zeta = 200$ cm$^{-1}$, $\Delta = 525$ cm$^{-1}$, $\epsilon = 75$ cm$^{-1}$, $N^2 = 0.32$, and $\Delta E_i = 0.76$ mm/sec. Bottom curve: $Fe(phen)_3(ClO_4)_3$ with $\zeta = 200$ cm$^{-1}$, $\Delta = 540$ cm$^{-1}$, $\epsilon = 0$, $N^2 = 0.47$, and $\Delta E_i = 0.16$ mm/sec.

**Table IV.** Results Obtained When Configuration Interactions Are Neglected

| Compound | $\zeta$, cm$^{-1}$ | $N^2$ | $\Delta E_i$, mm/sec | $\chi_\nu$ |
|---|---|---|---|---|
| $Fe(phen)_3(PF_6)_3$ | 200 | 0.25 | 0.85 | 1.1 |
| $\Delta/\zeta = 2.70$ | 225 | 0.33 | 0.60 | 1.0 |
| $k = 1.12$ | 250 | 0.44 | 0.18 | 1.4 |
| $Fe(bipy)_3(PF_6)_3$ | 200 | 0.32 | 0.72 | 1.0 |
| $\Delta/\zeta = 3.03$ | 225 | 0.40 | 0.39 | 1.1 |
| $k = 1.07$ | 250 | 0.64 | −0.47 | 1.3 |
| $Fe(phen)_3(ClO_4)_3$ | 175 | 0.35 | 0.60 | 1.0 |
| $\Delta/\zeta = 2.64$ | 200 | 0.40 | 0.40 | 1.3 |
| $k = 1.04$ | 225 | 0.52 | −0.03 | 2.3 |
| $Fe(bipy)_3(ClO_4)_3$ | 175 | 0.24 | 1.04 | 1.0 |
| $\Delta/\zeta = 2.55$ | 200 | 0.30 | 0.81 | 1.1 |
| $\epsilon/\zeta = 0.42$ | 225 | 0.47 | 0.22 | 1.7 |
| $k = 1.02$ | | | | |

rupole splitting, $\Delta E_i$, are small in comparison to the temperature-dependent contributions, $\Delta E_d$, or if the symmetry of the molecule is close to axial.[9] The temperature dependence of the quadrupole splitting was calculated in a manner described previously.[1]

The effect of spin-orbit mixing of the $e_g$ orbitals into the ground state may be estimated by following the methods of Hill.[6] If $\psi_0$ is the five-electron basis function, the first-order perturbation correction to $\psi_0$ gives

$$\psi = \psi_0 + \sum_n a_n \psi_n$$

$$a_n = \langle \psi_n | \zeta l \cdot s | \psi_0 \rangle / E$$

where $\psi_n$ are the excited configurations. With $\zeta < 400$ cm$^{-1}$ and $E \cong 20{,}000$ cm$^{-1}$, $\Sigma_n a_n^2$ is less than 0.01. Since the quadrupole splitting is proportional to $a_n^2$,[1] these interactions have a negligible effect on the quadrupole splitting.

When fitting the experimental data, the magnitudes of $\Delta$ and $\epsilon$ were taken as those given by the epr experiment. A least-squares fitting program was employed to fit the data in terms of the "orbital reduction factor," $N^2$, and $\Delta E_i$ for various values of $\zeta$. These results are shown in Table II. The magnitude of the reduced $\chi$-squared value, $\chi_v$, provides a measure of the quality of the fit. $\chi_v$ approaches 1.0 for a satisfactory fit. It is possible to find solutions with lower values of $\zeta$ than are shown in Table II. These solutions, however, may be ruled out since they result in unreasonably large values for $\Delta E_i$. The analogous iron(II) compounds, $Fe(phen)_3(ClO_4)_2$ and $Fe(bipy)_3(ClO_4)_2$, which have no "valence" or temperature-dependent contributions to the quadrupole splitting show quadrupole splittings of 0.23 and 0.39 mm/sec, respectively.[10]

## Discussion

Before attributing any validity to the results given in Table II, it is necessary to discuss some of the difficulties with this experiment and the assumptions involved in the data analysis. It is possible that the $g$ values are inaccurate due to line-broadening effects.[11] Line broadening may also obscure a small splitting of the $g_\perp$ ($g_1$,$g_2$) line. In the analysis of the epr data it was assumed that the coupling constant which applied to the spin-orbit interaction of the $e_g$ with the $t_{2g}$ orbitals is the same as that which describes the spin-orbit interaction among the $t_{2g}$ orbitals. This assumption is not necessarily valid since the radial parts of the $t_{2g}$ and $e_g$ orbitals are likely to be different. This assumption will have a marked effect on only the magnitude of $k$. Complete neglect of configuration interactions decreases the ratio, $\Delta/\zeta$, by less than 10% but results in $k$ values greater than 1.0. The results obtained when configuration interactions are neglected are given in Table IV.

In the analysis of the quadrupole splitting it was assumed that the "lattice" contributions to the quadrupole splitting are temperature independent and that the parameters $\Delta$ and $\epsilon$ are temperature independent. High-spin iron(III) and low-spin iron(II) compounds have no "valence" contributions to the quadrupole splitting. Therefore, these compounds provide a direct means to investigate "lattice" contributions. A very precise investigation of many of these compounds by Kerler and coworkers[12] shows no significant temperature dependence to the quadrupole splitting. Investigations of some low-spin mixed ligand complexes of

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

(11) J. A. Ibers and J. D. Swalen, *Phys. Rev.*, **127**, 1914 (1962).

(12) W. Kerler and W. Neuwirth, *Z. Phys.*, **167**, 176 (1962); W. Kerler, *ibid.*, **167**, 194 (1962); W. Kerler, W. Neuwirth, E. Fluck, P. Kuhn, and B. Zimmerman, *ibid.*, **173**, 321 (1963); E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem., Int. Ed. Engl.*, **2**, 227 (1963).

iron(II) with cyanide and aromatic diimines shows no temperature dependence.[13] A study of numerous ferrous low-spin complexes exhibiting large quadrupole splittings showed a small temperature dependence to the quadrupole splitting.[14] These results indicate that a significant temperature dependence to the "lattice" contributions is a rare occurrence. Since changes in the "lattice" contributions would be expected to accompany changes in the distortion parameters, these results imply that the distortion parameters are not normally significantly temperature dependent.

In the analysis described above, it was assumed that the radii of the three $t_{2g}$ orbitals were identical. The quadrupole splitting was also fitted allowing for as much as a 100% difference in the factor $\langle r^{-3}\rangle_{t_{2g}}$. This large anisotropy has no significant effect on the overall analysis. Inclusion of this anisotropy allows the parameter $\Delta E_i$ to be reduced and causes a small reduction in the average value of $N^2$. Allowance for an anisotropy in $k$ also has an insignificant effect on the analysis.

In this analysis of the epr and quadrupole splitting data, deviations from the crystal field model were treated in the simplest possible manner. For this reason the parameters, $k$ and $N^2$, should be treated as semiempirical parameters which reflect the ligand character of the molecular orbital and the extent of orbital delocalization, respectively.

In view of these difficulties it is probably not meaningful to discuss the results in Table II in terms of small differences among the four compounds studied. However, it does appear clear fom the results in Table II that $\langle r^{-3}\rangle_{t_{2g}}$ for all these compounds is substantially reduced from the free ion value. The spin-orbit coupling constant $\zeta$ falls in the range of 175-250 $cm^{-1}$. This represents a reduction to 40-55% of the free ion value, 460 $cm^{-1}$.[15] The "orbital reduction factor," as defined here, is 0.25-0.60, a reduction to 25-60% of the free ion value.

Ballhausen[16] derives a formula $k = 1 - {}^1/_2N^2A_\pi{}^2$, where $\psi = N(\psi_{Fe} + A_\pi\psi_{lig})$. With $k = 0.85$, neglecting overlap, this leads to $N^2 = 0.70$. This value is not in good agreement with that found from the Mossbauer spectroscopy data. No particular agreement is expected here, however, since $\pi$ bonding is not the only mechanism for orbital delocalization.

The magnitude of the spin-orbit coupling constant provides the best measure of orbital delocalization. The magnitude of $N^2$ depends on assumptions concerning the magnitudes of the quadrupole moment $Q$, the shielding factor, $(1 - R)$, and the free ion value of $\langle r^{-3}\rangle$.[17] The magnitude of $k$ is very sensitive to the manner in which configuration interactions are treated.

**Registry No.** $Fe(phen)_3(PF_6)_3$, 40192-51-6, $Fe(bipy)_3(PF_6)_3$, 40192-52-7; $Fe(phen)_3(ClO_4)_3$, 14634-90-3; $Fe(bipy)_3(ClO_4)_3$, 15388-50-8.

**Acknowledgments.** We thank J. A. Weiss and N. Family of the physics department at WPI for aid in obtaining the epr spectra. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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## Photoaquation of Some Complexes of Iridium(III)[1]

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*Received September 26, 1972*

Qualitative observations of the photochemistry of complexes of Ir(III) indicate that there is a close resemblance to the photochemistry of Rh(III).[3-8] Complexes which, like their Rh(III) analogs, undergo photoaquation of halide include *trans*-$Ir(en)_2X_2{}^+$,[3-5] *cis*-$Ir(phen)_2X_2{}^+$,[6] and *cis*-$Ir(bipy)_2X_2{}^+$,[6] where en is ethylenediamine, phen is 1,10-phenanthroline, bipy is 2,2′-bipyridyl, and X is Cl, Br, or I. Photoaquation of pyridine (py) has been observed both for the Rh(III) and Ir(III) complexes of the type *trans*-$Ir(py)_4X_2{}^+$.[7,8] It seemed of interest to obtain quantum yields for some of these Ir(III) systems for comparison with the analogous Rh(III) systems.[9]

### Experimental Section

**Physical Measurements.** A Perkin-Elmer 202 spectrophotometer was used to obtain visible–uv absorption spectra and a Hitachi Perkin-Elmer 139 spectrophotometer was used to determine concentration from the absorbance values at selected wavelengths. The molar conductance was determined with a Beckman RC16 B2 bridge and a dip-type cell with a cell constant of 1.022 $cm^{-1}$. X-Ray powder diffraction photographs were obtained from a Philips Debye-Scherrer 5.73-cm camera with nickel-filtered Cu radiation ($\lambda$ 1.5418 Å).

**Materials.** Solvents were glacial acetic acid, reagent grade thiophene-free benzene, and water distilled from an all-glass still. Chemicals used in the preparation of complexes were reagent grade 2,2′-bipyridyl, reagent grade 1,10-phenanthroline, and ethylenediamine from Aldrich Chemical Co., $K_3IrCl_6$ from K & K Laboratories, $IrCl_3$ and $IrBr_3$ from Pfaltz and Bauer Co., and pyridine, which was refluxed 2 hr over BaO and distilled (bp 113–114°).

The complexes were prepared and purified by known methods and characterized by their X-ray powder patterns, molar conductance, and visible–uv spectra, as summarized below.

*trans*-**[Ir(py)$_4$Cl$_2$]Cl·5H$_2$O.**[10] *d* spacings (all in angstroms): 12.63 s, 7.49 s, 6.91 w, 6.43 s, 6.08 w, 5.27 m, 4.45 w, 4.13 w, 3.95 w, 3.67 s, 3.22 m, 2.99 w; $\Lambda_M$ (0.001 *M*, $H_2O$): 89 $ohm^{-1}$ $cm^2$ $mol^{-1}$. Vis–uv ($H_2O$) (nm): 410 ($\epsilon$ 24), 285 ($7.3 \times 10^3$), 272 ($1.2 \times 10^4$), 265 ($1.5 \times 10^4$), 258 ($1.6 \times 10^4$), 252 ($1.8 \times 10^4$), 246 ($1.9 \times 10^4$). [Lit.[11] vis–uv ($H_2O$) (nm): 410 ($\epsilon$ 24), 285 ($7.3 \times 10^3$), 272 ($1.18 \times 10^4$), 264 ($1.49 \times 10^4$), 258 ($1.63 \times 10^4$), 250 ($1.79 \times 10^4$), 246 ($1.8 \times 10^4$).]

*cis*-**[Ir(bipy)$_2$Cl$_2$]Cl·2H$_2$O.**[11] *d* spacings: 12.90 vs, 8.93 vs, 6.88 m, 6.53 w, 5.92 s, 5.78 s, 5.58 m, 5.25 m, 4.68 w, 4.22 m, 4.07 w, 3.93 s, 3.78 s. $\Lambda_M$ (0.001 *M*, $H_2O$): 85.5 $ohm^{-1}$ $cm^2$ $mol^{-1}$. Vis–uv ($H_2O$) (nm). 448 ($\epsilon$ 130), 420 (420), 350 ($2.4 \times 10^3$), 316 ($2.2 \times 10^4$), 306 ($2.0 \times 10^4$), 280 ($1.8 \times 10^4$), 254 ($2.4 \times 10^4$). [Lit.[11] *d* spacings: 12.9 vs, 9.02 vs, 6.96 m, 6.55 w, 5.90 s, 5.78 s, 5.32 m, 4.98 m, 4.50 w, 4.23 m, 4.11 w, 3.93 w, 3.78 s. $\Lambda_M$ (0.001 *M*, $H_2O$): 83 $ohm^{-1}$ $cm^2$ $mol^{-1}$. Vis–uv ($H_2O$) (nm): 448 ($\epsilon$ 130),

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[1] Presented in part at the regional meeting of the American Chemical Society, Metrochem 71, San Juan, Puerto Rico, 1971.

[2] Abstracted from the thesis presented by W.-L. H. to the University of Puerto Rico, in partial fulfillment of the requirements for the degree M.Sc., 1971.

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