Magnetic Properties of some Low-spin Iron(III) Compounds

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The magnetic susceptibility of $K_3[Fe(CN)_6]$, $[Fe(phen)_3][ClO_4]_3,3H_2O$, $[Fe(phen)_3][PF_6]_3$, $[Fe(bipy)_3][ClO_4]_3,3H_2O$, and $[Fe(bipy)_3][PF_6]_3$ have been measured between 4 and 300 K. The e.s.r. *g*-values of the compounds, other than the first, were measured at *ca.* 85 K. The results are interpreted in terms of a three-parameter model for the splitting of the $^2T_{2g}$ ground term of the $t_{2g}{}^5$ configuration. The spin–orbit coupling constant is *ca.* 270 cm^{-1} in each compound. The t_{2g} orbital angular-momentum reduction factor is 0·75 in $K_3[Fe(CN)_6]$ and *ca.* 0·89 in the other compounds. The splitting of the t_{2g} orbital set by an axial ligand-field component is small for $K_3[Fe(CN)_6]$ (130 cm^{-1}) and may not reflect details of the ligand positions. The splitting is larger in the other compounds (*ca.* 850 cm^{-1}) and appears to be an intrinsic property of the ion, not much affected by the nature of the anion or by the presence of solvent molecules.

THE average magnetic susceptibility of the compounds potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$, tris(*o*-phenanthroline)iron(III) perchlorate trihydrate, $[Fe(phen)_3][ClO_4]_3,3H_2O$, and tris(2,2′-bipyridyl)iron(III) perchlorate trihydrate, $[Fe(bipy)_3][ClO_4]_3,3H_2O$, have been studied[1] and the magnetic anisotropy of the first compound subsequently examined[2] over the temperature range 80—300 K. The results were interpreted by means of a three-parameter model for the perturbation of the $^2T_{2g}$ ground term of the low-spin t_{2g}^5 configuration.[3] The parameters are k, the coefficient of the orbital angular-momentum operator in the form $\mu_i = kL_i + 2S_i$ ($i = x, y$, or z), λ, the effective spin-orbit coupling constant for the $^2T_{2g}$ term of t_{2g}^5, and Δ, the splitting of the orbital degeneracy of that term by a ligand-field component of axial symmetry. More extensive models have been developed for the splitting of the term, in which k and λ are allowed to be anisotropic and a rhombic component in the ligand field is included. These models introduce more parameters into the theory than can be evaluated from the experimental data and are not pursued here.

This paper presents the results of studies of the average magnetic susceptibility of those compounds down to 4·2 K, and also of the hexafluorophosphate salts of the cations, *viz.* $[Fe(phen)_3][PF_6]_3$ and $[Fe(bipy)_3][PF_6]_3$. The results are interpreted in the same framework as before, but with the aid of the e.s.r. g-values, and account is taken of the presence of the $^2T_{2g}$ terms from an excited configuration in influencing the meaning of the parameter k.[4-7]

Data exist in the literature for the magnetic susceptibility of $K_3[Fe(CN)_6]$ over various temperature intervals, which span the range 1—400 K.[3,8-10] However, there is not good agreement between the results reported. Since the magnetic moment is close to the spin-only value at low temperatures, and varies little with temperature there, the interpretation is quite sensitive to the accuracy of the experimental data for $\bar{\chi}$. The magnetic anisotropy has also been reported at various sections of the same temperature range.[2,11-13] Where the ranges overlap, there is reasonable agreement between the results. The present treatment is to employ our newly measured average susceptibility data to deduce the magnetic moments $\mu_{\text{eff}_\parallel}$ and $\mu_{\text{eff}_\perp}$ from the anisotropy measurements of the literature.

RESULTS

The magnetic susceptibilities and moments of the compounds studied are given in the Table at a series of temperatures. They are smoothed values from the data taken at *ca.* 35 temperatures over the range 4—300 K, and of which the scatter was less than 2%. The absolute accuracy of the susceptibility data was estimated to be *ca.* ±2%. The experimental points were taken at approximately equal increments of log T.

The magnetic moment of $K_3[Fe(CN)_6]$ quoted here is distinctly higher at ambient temperature than was reported earlier[1] (2·25 B.M.), although it agrees with the values given by some other authors.[14,15] The data at low temperatures are in reasonable agreement with that of some other authors.[11,12] The magnetic moments of $[Fe(phen)_3][ClO_4]_3,3H_2O$ and $[Fe(bipy)_3][ClO_4]_3,3H_2O$ are slightly above and below the earlier values respectively (2·40 B.M. in each case).[1] The magnetic moments of $[Fe(phen)_3][PF_6]_3$ and $[Fe(bipy)_3][PF_6]_3$ agree fairly well with the values from the literature (2·37 B.M.).[16]

It has been shown[4] that the presence of $^2T_{2g}$ terms from the configuration $t_{2g}^4 . e_g^1$, lying above the ground $^2T_{2g}(t_{2g}^5)$ term affects this by increasing the effective value of the orbital angular-momentum reduction parameter, k. If k_t is the value for that factor within the t_{2g} orbital set, and k_e that for the e_g orbital set, the observed reduction factor can be put in the form[6]

$$k = k_t + \varepsilon k_e$$

where

$$\varepsilon = 6B(a_1E_1^{-1} + a_2E_2^{-1})$$

B Is the Racah interelectronic repulsion parameter for the metal ion in the complex, a_1 and a_2 are molecular-orbital mixing coefficients, and E_1 and E_2 are the energy separations from the ground $^2T_{2g}$ term to the excited $^2T_{2g}$ terms. a_1 and a_2 Have been evaluated to be $-0{\cdot}2$ and 2·2, respectively.[6] ε Can, in principle, be obtained from a study of the absorption spectrum of the complex ion. However, in low-spin ferric compounds the ligand-field bands are confused by charge-transfer bands, and only approximate interpretations are available. The assumption $k_e = k_t$ needs to be introduced in the absence of any direct method for obtaining k_e, and usually one must approximate $E_1 \sim E_2 = E$.

In the original e.s.r. studies of $K_3[Fe(CN)_6]$ expressions which relate the three parameters for the perturbation of the $^2T_{2g}$ term were developed.[17]

$$g_\parallel = 2[\sin^2\alpha - (1 + k\cos^2\alpha)] \qquad (1a)$$

$$g_\perp = -2[\sin^2\alpha + 2^{\frac{1}{2}}k\cos\alpha\sin\alpha] \qquad (1b)$$

The angle α is related to the quantity $v = \Delta/\lambda$ by[18]

$$\tan\alpha = 2^{\frac{1}{2}}/(\tfrac{1}{2} \pm v),$$

the + sign applying to a tetragonal distortion, the − sign to a trigonal distortion, of the octahedron.

From the e.s.r. data alone it is not possible to deduce the three parameters. The most convenient procedure is to determine k and v, and even that cannot be done unambiguously since the relative signs of $g_\parallel$ and $g_\perp$ are not available from the experiment. However, the magnetic susceptibility data suffice to remove the ambiguity and

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The magnetic susceptibilities ($m^3\ mol^{-1} \times 10^9$) and moments (B.M.*) of the compounds studied at a series of temperatures. For $K_3[Fe(CN)_6]$ the magnetic moments have been corrected for the slight magnetic exchange present ($\theta_{\parallel} = -0{\cdot}255°$, $\theta_{\perp} = -0{\cdot}18°$) [11] by the relationship $\mu_{eff} = 798\ [\chi_{Fe}(T - \theta)]^{\frac{1}{2}}$. Magnetic-exchange interaction was not apparent in the other compounds

	$K_3[Fe(CN)_6]$			$[Fe(phen)_3][ClO_4]_3,3H_2O$		$[Fe(phen)_3][PF_6]_3$		$[Fe(bipy)_3][ClO_4]_3,3H_2O$		$[Fe(bipy)_3][PF_6]_3$	
T/K	χ_{Fe}	$\mu_{eff\parallel}$	$\mu_{eff\perp}$	χ_{Fe}	μ_{eff}	χ_{Fe}	μ_{eff}	χ_{Fe}	μ_{eff}	χ_{Fe}	μ_{eff}
4	1052	0·863	1·957	1625	2·044	1662	2·057	1654	2·052	1588	2·011
5	856	0·876	1·963	1307	2·048	1332	2·059	1324	2·053	1273	2·013
10	454	0·938	1·994	667	2·064	672	2·069	667	2·061	643	2·024
15	317	0·990	2·022	449	2·077	453	2·080	448	2·068	434	2·035
20	244·9	1·041	2·052	343	2·090	343	2·089	338	2·074	328	2·045
30	176·0	1·149	2·101	232·7	2·108	232·0	2·105	227·8	2·086	223·0	2·062
40	140·0	1·266	2·138	177·0	2·123	176·3	2·119	172·7	2·097	169·6	2·078
50	117·4	1·360	2·168	143·6	2·138	142·9	2·133	139·7	2·109	137·5	2·092
60	101·7	1·443	2·191	121·2	2·152	120·6	2·146	117·7	2·120	116·1	2·106
70	90·4	1·528	2·211	105·3	2·166	104·6	2·159	102·0	2·132	100·5	2·116
80	82·1	1·604	2·236	92·8	2·179	92·6	2·172	90·2	2·143	88·9	2·128
100	69·7	1·725	2·275	76·7	2·209	83·3	2·200	73·7	2·166	72·6	2·149
120	61·3	1·840	2·315	65·5	2·237	76·0	2·224	62·8	2·190	61·5	2·168
140	55·3	1·938	2·349	57·7	2·267	64·7	2·250	55·0	2·215	53·7	2·188
160	49·9	1·998	2·378	51·8	2·297	50·6	2·271	49·2	2·238	47·7	2·205
180	56·1	2·068	2·405	47·1	2·324	45·8	2·290	44·5	2·259	43·1	2·221
200	42·5	2·120	2·425	43·3	2·347	41·8	2·308	40·7	2·276	39·3	2·236
220	39·4	2·159	2·438	40·1	2·369	38·6	2·325	37·5	2·291	36·1	2·250
260	34·2	2·218	2·457	34·9	2·404	33·6	2·358	32·6	2·321	34·1	2·278
280	32·0	2·238	2·462	32·9	2·420	31·6	2·374	30·6	2·337	29·4	2·290
300	30·0	2·255	2·463	30·6	2·437	29·9	2·390	29·0	2·353	27·7	2·300

* 1 B.M. $9{\cdot}274 \times 10^{-24}$ A m^2.

permit the evaluation of the parameter λ and hence of Δ_1, λ_1, and k_1, say, since allowance has not been made for the configurational interaction. Improvement of the values of λ_1 and Δ_1 to allow for configurational interaction follows by using them in the corrected formulae.

$$g_{\parallel} = -2[\sin^2\alpha^1 - (1 + k_t)\cos^2\alpha^1] + \frac{2k_t\lambda}{E}[4\sin^2\alpha^1 - 8^{\frac{1}{2}}\sin\alpha^1\cos\alpha^1]$$

$$g_{\perp} = 2[2^{\frac{1}{2}}k_t\cos\alpha^1\sin\alpha^1 + \sin^2\alpha^1] + \frac{2k_t\lambda}{E}[\cos^2\alpha^1 - 2^{\frac{1}{2}}\sin\alpha^1\cos\alpha^1]$$

where $\tan\alpha^1 = 2^{\frac{1}{2}}/(\frac{1}{2} \pm v^1)$

$$v^1 = \Delta/\left(1 + \frac{\lambda}{E}\right)\lambda$$

From this treatment, a final set of the parameters k_t, λ, and Δ is obtained.

$K_3[Fe(CN)_6]$.—The e.s.r. signals for $K_3[Fe(CN)_6]$ have been reported to be difficult to interpret,[19,20] and the g-values were not at all consistent. The values $g_{\parallel} = 0{\cdot}95 \pm 0{\cdot}02$ and $g_{\perp} = 2{\cdot}25 \pm 0{\cdot}06$ seem to be the best compromise. The original authors chose to use the more accurate g-values for the salt diluted in the isomorphous cobalt(III) compound, and to compare them with the magnetic susceptibility data for the pure compound. However, the g-values vary rapidly with v in the region of interest, and v can be fixed fairly well by using the e.s.r. data for the concentrated salt. This seems to us to be a more satisfactory procedure.

The only solution to the equations (1) which is likely to be compatible with the magnetic susceptibility data is $k = 0{\cdot}92 \pm 0{\cdot}03$, $v = -0{\cdot}49 \pm 0{\cdot}03$ (assuming the distortion from octahedral stereochemistry to be tetragonal in character). With this information as the starting point, we obtained the value of the parameter λ which reproduces the experimental variation of $\mu_{eff_{\parallel}}$ and $\mu_{eff_{\perp}}$ as a function of temperature by a computer-operated least-squares fitting procedure. Up to 16 temperature points were employed. This procedure gives the *optimum* value of the parameter, but does not give a clear indication of what ranges give an *acceptable* fit of the experimental data. Such an indication was obtained by using the extremes of the e.s.r. g-values range to fit with the magnetic anisotropy data. It was deduced that $k_1 = 0{\cdot}897 \pm 0{\cdot}008$, $\lambda_1 = -273 \pm 10\ cm^{-1}$ and, hence, $\Delta_1 = 131 \pm 10\ cm^{-1}$. For these ranges of the parameters the magnetic moment and anisotropy data are reproduced within the experimental error over the entire temperature range. There was no need to invoke the change in the value of Δ at *ca.* 130 K which has been suggested.[21,22] After correction for the higher lying $^2T_{2g}$ terms, using spectral information from other studies,[23,24] the set of parameters $k_t = 0{\cdot}75$ ($\pm$ 0·01), $\lambda = -271 \pm 10\ cm^{-1}$, $\Delta = 130 \pm 10\ cm^{-1}$ was obtained.

$[Fe(phen)_3]^{3+}$ *Salts*.—At *ca.* 85 K the values of $g_{\parallel}$ and $g_{\perp}$ for $[Fe(phen)_3][ClO_4]_3,3H_2O$ and $[Fe(phen)_3][PF_6]_3$ were found to be $1{\cdot}46 \pm 0{\cdot}02$ and $2{\cdot}71 \pm 0{\cdot}05$, and $1{\cdot}52 \pm 0{\cdot}02$ and $2{\cdot}69 \pm 0{\cdot}05$ respectively. It may be noted that the experimental value for $\bar{g}$ for the $[Fe(phen)_3]^{3+}$ ion in solution [25] (as the hexafluoro-salt in sulphuric acid) is 2·30, with $g_{\perp} = 2{\cdot}69 \pm 0{\cdot}02$ and $g_{\parallel} = 1{\cdot}19 \pm 0{\cdot}02$. The observation that $\bar{g}$ differs very little between solid and solution is expected.

The magnetic susceptibility data were analysed in the fashion outlined under $K_3[Fe(CN)_6]$, using constraints set by the g-values. The parameter sets obtained are set out below, where the values in parentheses held before allowance was made for configurational interaction.

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	k_t	λ	Δ
$[ClO_4]^-$ salt:			
	0·86 ± 0·03	−270 ± 30	790 ± 80
	(1·06)	(−273) cm^{-1}	(690) cm^{-1}
$[PF_6]^-$ salt:			
	0·92 ± 0·01	−271 ± 30	880 ± 80
	(1·13)	(−175) cm^{-1}	(710) cm^{-1}

$[Fe(bipy)_3]^{3+}$ *Salts.*—At *ca.* 85 K the values of $g_\parallel$ and $g_\perp$ for $[Fe(bipy)_3][ClO_4)_3],3H_2O$ were found to be 1·48 ± 0·02 and 2·68 ± 0·02 (g_1 = 2·76, g_2 = 2·60) respectively, with $\bar{g}$ = 2·34. For $[Fe(bipy)_3][PF_6]_3$ they were 1·61 ± 0·02 and 2·62 ± 0·02 respectively, with $\bar{g}$ = 2·32. These e.s.r. data were used to obtain values of k and v and their limits, and the magnetic susceptibility data was fitted with those constraints. The parameter sets which resulted for the two salts were:

	k_t	λ	Δ
$[ClO_4]^-$ salt:			
	0·88 ± 0·03	−262 ± 30	790 ± 80
	(1·08)	(265) cm^{-1}	(690) cm^{-1}
$[PF_6]^-$ salt:			
	0·89 ± 0·03	−257 ± 30	950 ± 80
	(1·09)	(260) cm^{-1}	(800) cm^{-1}

The solution values for the e.s.r. of the $[Fe(bipy)_3]^{3+}$ ion as the hexafluorophosphate salt in sulphuric acid were reported to be $g_\parallel$ = 1·71, $g_\perp$ = 2·61, with $\bar{g}$ = 2·32.[23] We found that the $g_\perp$ signals of the perchlorate salt showed a very small splitting due to the presence of a rhombic component in the ligand field acting on the iron atom. No account was taken of this rhombic component. Within the approximations of the present study it does not affect the interpretation of the results upon the basis of the axial ligand-field model. The rhombic splitting could be taken into account as perturbation of the axial ligand-field model to obtain the separation between the components of the higher-lying orbital doublet of the split $^2T_{2g}$ term.[3] Such a result would be useful if a detailed study and interpretation of the Mössbauer spectrum, or a more satisfactory set of e.s.r. data on the undiluted solid, were available.

DISCUSSION

The value of Δ for $K_3[Fe(CN)_6]$ is deduced with much greater certainty from the present studies. Previously it was deduced that Δ lay between 150 and 300 cm^{-1}. However the increased certainty does not remove the difficulty in relating the details of the molecular geometry about the iron atom with the sign of the low-symmetry ligand-field component effective at that atom.[2] It was pointed out in the earlier studies that the first co-ordination sphere geometry around the iron atom is almost precisely that of a regular octahedron, being distorted if anything so as to make Δ negative on a simple crystal-field model. Either the low-symmetry ligand-field component arises from a perturbation by the rather distant potassium cations, as suggested earlier,[2] or it is not directly and simply related to the crystallographic positions of the ligand atoms through crystal-field theory. This latter alternative is more probably the interpretation to be put upon the result.

Studies of the Mössbauer spectrum of $K_3[Fe(CN)_6]$ have been carried out over the same temperature range as the magnetic susceptibility data. The temperature dependence of the quadrupole-splitting parameter has been interpreted in the same model of the perturbed $^2T_{2g}$ term. Basically, the procedure is the same with the two types of data: given values of k and v determined from the e.s.r. data, the parameters λ and Δ are chosen so as to give a set of energy levels, occupation of which gives a temperature dependence matching that of the experimental quantity. With the magnetic susceptibility data, the absolute magnitude is also of importance but that is not the case for the Mössbauer quadrupole splitting to nearly the same extent.

The choice from the e.s.r. data which was used above, k = 0·92, v = −0·49, is incompatible with the most recent interpretation of the Mössbauer data.[26] An alternative choice, k = 0·56, v = −1·50 is acceptable from that point of view. It leads to the result, λ = −80 cm^{-1} and Δ = 120 cm^{-1}. Although the $^2T_{2g}$ term splitting is very similar from the interpretations of the two types of data, the low values of k and λ mean that the interpretation of the Mössbauer data is incompatible with that of the magnetic susceptibility and anisotropy data. The interpretation of the Mössbauer quadrupole-splitting data depends upon assumptions about the size and temperature dependence of the various contributions to the effective electric-field gradient at the nucleus of the iron atom. The interpretation of the magnetic susceptibility data is essentially free of such assumptions, magnetic exchange effects, and the configurational interaction with excited $^2T_{2g}$ terms having been taken into account.

The splittings of the $^2T_{2g}$ term orbital degeneracy introduced in the $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$ ions are several times larger than in the $[Fe(CN)_6]^{3-}$ ion. Although an *X*-ray crystallographic structure determination on an $[Fe(phen)_3]^{3+}$, $[Fe(bipy)_3]^{3+}$, or similar ion salt does not seem to be available,* it does not seem likely that a close approach to strict octahedral stereochemistry about the iron atom could result: a trigonal ligand-field component, if not one of lower symmetry, is certainly to be anticipated on account of the way in which three bidentate ligand groups of more or less fixed 'bite' tend to arrange themselves around a central metal atom.[27] The splitting parameter in each case is positive, so that the orbital singlet lies lowest. The parameter is the same, within experimental error, for the perchlorate and hexafluorophosphate salts of a given cation. It does not differ appreciably between the two ions. Studies by Mössbauer spectroscopy [28,29] on the same compounds also indicate that the term-splitting

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* The structures of the perchlorate salts of these ions are being determined in these laboratories.

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parameter Δ is of about the same magnitude as deduced here. Again, the spin–orbit coupling constant and the value of k_t are deduced to be smaller (*ca.* 200 cm^{-1} and 0·85) although the discrepancy is not as large as for $K_3[Fe(CN)_6]$. *X*-Ray absorption edge spectroscopic techniques also indicate a moderately large value for Δ in the compounds.[30]

The low-symmetry ligand-field component seems to be an inherent property of the cation in these compounds, rather than arising from, say, crystal-packing forces, as the e.s.r. $g_\parallel$ and $g_\perp$ values for each of the two salts and in solution are almost identical.

The value of the spin–orbit coupling constant, λ, is the same, within the experimental error of *ca.* 10%, for the $[Fe(CN)_6]^{3-}$, $[Fe(phen)_3]^{3+}$, and $[Fe(bipy)_3]^{3+}$ ions. This is a satisfactory result, and encourages confidence in the present parameter sets for the $^2T_{2g}$ term splitting in $K_3[Fe(CN)_6]$, as opposed to the set suggested by interpretation of the Mössbauer data.[24,28]

With the same approximations as for the ferricyanide case, and employing spectral data available from the literature,[25,26] the orbital angular-momentum reduction parameter for the t_{2g} orbital set in the $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$ ions may be evaluated from the new values of k deduced. k_t For the four compounds involved does not differ by more than the experimental error of 0·03, and may be averaged over them to give a mean value of 0·89. The position with regard to the orbital angular-momentum reduction factor for the t_{2g} orbital set is, then, also improved relative to earlier appraisals.[1,2] The value for the *o*-phenanthroline and 2,2′-bipyridyl compounds is distinctly less than unity, and that for the ferricyanide ion more than 25% less. Previously, without the allowance for the effects of the higher $^2T_{2g}$ terms, it had been remarked that the values of the parameters were unexpectedly high, especially for the cations. For them no reduction in effective orbital-angular momentum seemed to take place in what were believed to be ligands of fairly polarisable nature. Similarly, for the ferricyanide ion, where the ligands are very polarisable, only a very moderate reduction had been proposed.

EXPERIMENTAL

Magnetic susceptibility was measured on equipment which has been described previously.[31,32] The performance of the variable-temperature equipment at the low end of the range was improved by reducing the heat loss across the leak vacuum space. This removed the need for automatic temperature control below 20 K and made control by means of the platinum resistance thermometer above that temperature satisfactory. It also improved the attainment of thermal equilibrium between the walls of the sample chamber and the sample. The temperature scale was calibrated by reference to the magnetic susceptibility of $K_2Cu[SO_4]_2,6H_2O$ ($\theta = 0{\cdot}016°$) [33] below *ca.* 20 K and by reference to the susceptibility of $[NH_4]_2Mn[SO_4]_2,6H_2O$ above that temperature, where the temperature-independent contribution to the paramagnetic susceptibility of the previous salt presents a complication. The temperature scale was estimated to be accurate to ±1%. It agreed well with the platinum-resistance thermometer temperature scale where that applied.

Diamagnetic corrections were made according to a standard tabulation [34] and by direct measurement for *o*-phenanthroline ($1{\cdot}51 \times 10^{-9}$ m^3 mol^{-1}) and 2,2′-bipyridyl ($1{\cdot}32 \times 10^{-9}$ m^3 mol^{-1}). It was $1{\cdot}57 \times 10^{-9}$ m^3 mol^{-1} for $K_3[Fe(CN)_6]$, $6{\cdot}72 \times 10^{-9}$ m^3 mol^{-1} for $[Fe(phen)_3][ClO_4]_3,3H_2O$, $6{\cdot}57 \times 10^{-9}$ m^3 mol^{-1} for $[Fe(phen)_3][PF_6]_3$, $5{\cdot}86 \times 10^{-9}$ m^3 mol^{-1} for $[Fe(bipy)_3][ClO_4]_3,3H_2O$ and $5{\cdot}71 \times 10^{-9}$ m^3 mol^{-1} for $[Fe(bipy)_3][PF_6]_3$.

E.s.r. spectra were taken on a Varian model V-4502 spectrometer. Powder samples of the pure solids were studied at *ca.* 85 K in a liquid-nitrogen Dewar attachment. Solutions of the $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$ salts in nitric acid glasses were examined at the same temperature and the observed *g*-values were identical with those found earlier in sulphuric acid.[23]

Potassium Hexacyanoferrate(III).—The AnalaR material was employed after recrystallisation.

The remaining compounds were prepared by adaptations of the method of Burstall and Nyholm.[35]

Tris(o-*phenanthroline*)*iron*(III) *Hexafluorophosphate*.—$FeSO_4,7H_2O$ (0·92 g) was dissolved in water (25 ml) and H_2SO_4 (0·2 ml) and 1,10-phenanthroline (2·0 g) was added. The solution was cooled to 0 °C and Cl_2 gas was bubbled through it until the blood-red colour changed to blue. The mixture was warmed to room temperature and poured into a solution of $K[PF_6]$ (10 g) in water (50 ml). The dark blue powder which precipitated immediately was washed with cold water and then a little ethanol and dried. It was stored in the dark (Found: C, 41·2; H, 2·25; N, 8·10. Calc. for $C_2H_{18}F_{18}FeN_6P_3$: C, 41·92; H, 2·35; N, 8·15%).

Tris(o-*phenanthroline*)*iron*(III) *Perchlorate Trihydrate*.—The same method as for the previous compound was employed, using $Na[ClO_4]$ in place of $K[PF_6]$ (Found: C, 45·1; H, 2·7; N, 9·1; Cl, 10·9. Calc. for $C_{24}H_{18}Cl_3FeN_6O_{12}$: C, 45·56; H, 3·19; N, 8·86; Cl, 11·21%).

Tris(2,2′-*bipyridyl*)*iron*(III) *Hexafluorophosphate*.—The same method as for the first compound was employed, using 2,2′-bipyridyl (1·56 g) in place of 1,10-phenanthroline. The product also was a blue powder (Found: C, 36·8; H, 2·4; N, 8·8; P, 9·45. Calc. for $C_{30}H_{24}F_{18}FeN_6P_3$: C, 37·55; H, 2·52; N, 8·76; P, 9·6%).

Tris(2,2′-*bipyridyl*)*iron*(III) *Perchlorate Trihydrate*.—The same method as for the preceding compound was used, with $Na[ClO_4]$ replacing $K[PF_6]$. The product formed dark green crystals (Found: C, 41·1; H, 3·65; Cl, 12·1. Calc. for $C_{30}H_{24}Cl_3FeN_6O_{12}$: C, 41·06; H, 3·45; Cl, 12·12%).

The authors are grateful to the Australian Research Grants Committee for support with equipment for the measurement of magnetic susceptibility. We thank Dr. L. M. Engelhardt for assistance with the measurement of the e.s.r. spectra.

[4/1750 *Received*, 20*th August*, 1974]

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