Bonding Studies from Charge-transfer Absorption and Magnetic Circular Dichroism Spectra. Part II.† The Complex Hexacyanoferrate(III) and Pentacyanoferrate(III) Complexes of C_{4v} Symmetry

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Magnetic circular dichroism (m.c.d.) and absorption spectra of the hexacyanoferrate(III) ion have been measured in two host lattices at room and liquid-helium temperatures. Previous interpretations of the charge-transfer (c.t.) bands have been confirmed and new assignments of the *d–d* transitions have been made. With the complexes $[Fe(CN)_5L]^{n-}$ (L = NH_3, H_2O, PPh_3, SCN^-, or N_3^-) a new band has been detected, the energy of which is very sensitive to the nature of the ligand L. This band is assigned as L → Fe charge transfer and band energies follow the pattern previously observed in substituted halogeno-complexes of Ir^{IV}; namely, a particular high-energy filled molecular orbital with PPh_3 moves to lower energy with the ligands H_2O and NH_3. The aquopentacyanoferrate(III) complex shows indications of dimer formation in solution.

RECENT studies [1-3] of charge-transfer (c.t.) transitions in metal complexes have emphasised the importance of the low-spin d^5 configuration as the fundamental system for determining the sequence of filled molecular orbitals. As we have pointed out,[3] the advantages of this configuration arise from the simplicity of the spectra. Transitions take place successively into the vacancy in the t_{2g} shell and thus the absorption bands reveal the energies of the filled bonding orbitals relative to that of the metal t_{2g} orbital. Since there is only ever one unpaired electron, there are no electron-repulsion splittings and, further, differences between the electron-repulsion energies of the different excited states are minimised, so we can infer the relative energies of the filled bonding orbitals from the energies of the electronic transitions.

An essential part of this process is the identification of the transitions. In this, magnetic circular dichroism (m.c.d.) spectroscopy has proved an invaluable aid. Thus the main c.t. bands of the complexes $[IrCl_6]^{2-}$ (ref. 1) and $[IrBr_6]^{2-}$ (ref. 4) have been unambiguously assigned and, using these as a basis, c.t. bands in the complexes *trans*-$[IrCl_4L_2]$ (L = PR_3, AsR_3, pyridine, or SEt_2) have been identified.[3] In this work we report a study of substituted hexacyanoferrate(III) complexes, $[Fe(CN)_5L]^{n-}$ (L = H_2O, NH_3, PPh_3, N_3^-, or SCN^-), and, since this relies heavily on an understanding of the energy levels of the parent hexacyano-complex we devote the first part of this paper to a discussion of the m.c.d. and absorption spectra of $[Fe(CN)_6]^{3-}$. There have been a number of attempts to explain the absorption spectra of the hexacyanoferrate(III) ion [5-7] and its monosubstituted derivatives.[8-10] Here we use our new experimental information to clarify some of these assignments and comment on the bonding patterns in the series of derivatives.

EXPERIMENTAL

$K_3[Fe(CN)_6],2H_2O$ (AnalaR) was used without further purification. It was incorporated into KCl by slow evaporation of a solution containing the complex $[Fe(CN)_6]^{3-}$ (*ca.* 1%) where it substitutes for the entity KCl_6^{5-}, and the cubic crystals obtained were used without further treatment. The butylammonium salt was prepared by the method of Manoharan and Gray.[11] For optical examination the complex was dissolved in a chloroform solution of poly(methyl methacrylate), which was used to make a thin film. The complex $Na_2[Fe(CN)_5H_2O],H_2O$ was made by the method of Hofman,[12] $Na_2[Fe(CN)_5PPh_3],2H_2O$ using Nast and Kruger's method,[13] and $Na_2[Fe(CN)_5NH_3],$-$2H_2O$ according to the recipe of Kenney *et al.*[14] Both the azido- and thiocyanato-complexes were made by the method of Jasleskis.[10]

Absorption spectra were measured on a Cary 14 spectrometer and the magnetic circular dichroism (m.c.d.) spectra

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† Part I, ref. 3.

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on a circular dichroism (c.d.) machine built originally at the N.P.L. and modified by the authors. Magnetic fields were provided by Thor Cryogenics and Oxford Instruments superconducting magnets. Both the plastic film and the KCl crystal containing hexacyanoferrate(III) ion showed no baseline birefringence effects or linear dichroism [15] throughout the spectral range of this study and they were thus ideal hosts for m.c.d. work. Spectra were analysed using a moments [16] program. Room-temperature parameters for the complex $K_3[Fe(CN)_6]$ in solution, calculated by this method, agreed well with previous results from Gaussian analysis.[17]

TABLE 1

Strong-field d-electron configurations	Terms arising (parentage)	Diagonal electrostatic energy relative to $^2T_{2g}(t_{2g}^5)$	Correction due to off-diagonal interactions	Spin–orbit splitting (1st order)		Energy relative to E_g''	
t_{2g}^5	$^2T_{2g}$	0		E_g''	$-\xi$		
				U_g'	$+\xi/2$		$3\xi/2$
$t_{2g}^4e_g^1$	$^4T_{1g}(^3T_{1g})$	$\Delta - 5B - 4C$		E_g''	$-\xi/4$	$\Delta - 5B - 4C$	$+3\xi/4$
				$3/2U_g'$	$\xi/6$		$+7\xi/6$
	$^4T_{2g}(^3T_{1g})$	$\Delta + 3B - 4C$		E_g''	$-5\xi/12$	$\Delta + 3B - 4C$	$17\xi/12$
				$3/2U_g'$	$\xi/6$		$+7\xi/6$
	$(1)^2T_{1g}(^3T_{1g})$	$\Delta - 2B - C$	$-0{\cdot}65B$	E_g'	$\xi/3$	$\Delta - 2{\cdot}65B - C$	$+4\xi/3$
				U_g'	$-\xi/6$		$+5\xi/6$
	$(1)^2T_{2g}(^1T_{2g})$	$\Delta + 2B - C$	$-B$	E_g''		$\Delta - B - C$	$+\xi$
				U_g'			
	$(1)^2E_g(^1E_g)$	$\Delta + 7B - C$	$-4B$	U_g'		$\Delta + 3B - C$	$+\xi$
	$(2)^2T_{1g}(^1T_{2g})$	$\Delta + 12B - C$	$+0{\cdot}65B$	E_g'		$\Delta + 12{\cdot}65B - C$	$+\xi$
				U_g'			
	$(2)^2T_{2g}(^3T_{1u})$	$\Delta + 12B - C$	$+B$	E_g''	$+\xi/3$	$\Delta + 13B - C$	$+4\xi/3$
				U_g'	$-\xi/6$		$+5\xi/6$
	$^2A_{1g}(^1E_g)$	$\Delta + 17B - C$		E_g'		$\Delta + 17B + C$	$+\xi$
	$(2)^2E_g(^1A_{1g})$	$\Delta + 16B + 2C$	$+4B$	U_g'		$\Delta + 16B + 2C$	$+\xi$
$t_{2g}^4e_g^1$	$^6A_{1g}(^4A_{2g},{}^3A_{2g})$	$2\Delta + 15B - 10C$		E_g'''		$2\Delta - 15B - 10C$	$+\xi$
				U_g'			

THEORY

We first discuss in detail the assignment of the hexacyanoferrate(III) spectrum in the light of our low-temperature absorption and m.c.d. spectra, and focus attention first on the d–d transitions which are interspersed among the c.t. bands. Previous treatments [5-8] of the absorption spectrum of this complex have ignored off-diagonal electrostatic interactions and spin–orbit coupling. In this work we have included both the diagonal and off-diagonal electrostatic interactions between the terms arising from $t_{2g}^4e_g^1$. Strictly we should diagonalise the interaction matrix for terms from all possible d-configurations, but the spectra, even at helium temperature, are broad banded and this complication is probably not necessary. Calculations of the off-diagonal matrix elements are simplified by the assumption that $C = 4B$. Results are found to be quite insensitive to the numerical factor and this fairly common simplification [18] was used here. Diagonal spin–orbit energies have been included and were calculated by the method of Griffith.[19] Off-diagonal spin–orbit interactions were calculated to be an order of magnitude smaller and have not been included.

Table 1 summarises the results of these calculations for the lowest-energy strong-field configurations of the low-spin d^5 system. In the second column we give terms arising from these configurations together with the t_{2g}^n parentage in parentheses. The third column shows the diagonal electrostatic energies referred to $^2T_{2g}(t_{2g}^5)$ as origin with the off-diagonal corrections in the fourth column. The next column lists O_h^* representations arising from the allowed strong-field terms, together with the first-order spin–orbit energies referred to the corresponding single group term as zero. The final column gives the energies of the excited d–d states relative to the E_g'' component of the ground state. Figure 1 shows these states on an energy scale together with

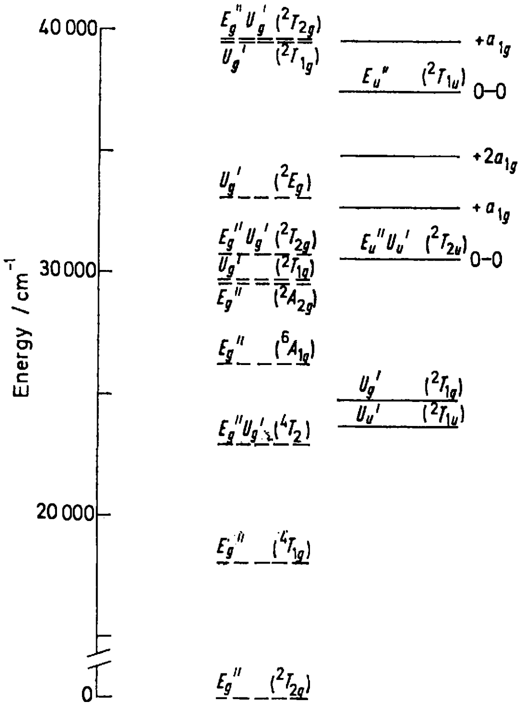

FIGURE 1 Energy-level diagram for the complex $[Fe(CN)_6]^{3-}$

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[15] R. Gale, A. J. McCaffery, and R. A. Shatwell, *Chem. Phys. Letters*, 1972, **17**, 416.

[16] P. J. Stephens, *J. Chem. Phys.*, 1970, **52**, 3489.

[17] P. N. Schatz, A. J. McCaffery, W. Suetaka, G. N. Henning, A. B. Ritchie, and P. J. Stephens, *J. Chem. Phys.*, 1966, **45**, 722.

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the odd-parity c.t. states. The theory for the latter transitions has been well developed in previous work on d^5 systems (see refs. 1—4 and 17).

In the O_h^* group, electric-dipole transitions are allowed from the ground state E_g'' to U' and E'' excited states, and we could therefore expect to observe the *d–d* transitions listed in Table 2 at energies less than 40 000 cm^{-1}, the limit of our experimental data. The values of Δ, B, and C used are referred to later in the text.

TABLE 2

Predicted transition energies

Transition	Energy of transition*/kK
$E_g''(^2T_{2g}) \longrightarrow E_g'', 3/2U'_g(^4T_{1g})$	18·23, 18·34
$\longrightarrow E_g'', 3/2U'_g(^4T_{2g})$	23·05, 23·15
$\longrightarrow E_g'', 3/2U'_g(^6A_{1g})$	26·57
$\longrightarrow E_g''(^2A_{2g})$	29·59
$\longrightarrow U_g'[(1)^2T_{1g}]$	29·75
$\longrightarrow E_g'', 3/2U_g'[(1)^2T_{2g}]$	30·79
$\longrightarrow U_g'[(1)^2E_g]$	33·20
$\longrightarrow E_g'', 3/2U_g'[(2)^2T_{2g}]$	39·12, 39·2

* $B = 602$, $C = 3\,361$, and $\Delta = 34\,455$ cm^{-1}.

In addition to the above transitions we should also see the three c.t. transitions which are the major features of the spectrum and have been assigned as transitions to $^2T_{1u}(\pi)$, $^2T_{2u}(\pi)$, and $^2T_{1u}(\sigma)$ respectively.[17]

RESULTS AND DISCUSSION

Absorption and m.c.d. spectra of the complex $[Fe(CN)_6]^{3-}$ in the poly(methyl methacrylate) and KCl host lattices are shown in Figures 2 and 3 respectively. Calculated and observed C/D values for the main bands of this complex in the two host lattices have been published elsewhere.[20] In Table 3 we list the theoretical C, D, and C/D parameters calculated by the irreducible-tensor method[19] with an orbital-reduction factor of 0·87.[21] Also listed are experimental parameters obtained by the method of moments.[16] The observed and calculated values are in good agreement at both temperatures used in this work and give strong support to the assignment of the c.t. spectrum as outlined in ref. 19. To summarise, transitions take place successively from the filled bonding orbitals (mainly ligand in character) to the hole in the *d* shell. The main observed bands have been assigned as $^2T_{2g} \longrightarrow {}^2T_{1u}(\pi)$, $\longrightarrow {}^2T_{2u}(\pi)$, and $\longrightarrow {}^2T_{1u}(\sigma)$ at 25 500, 32 700, and 40 000 cm^{-1} respectively. In this work we consider spin–orbit coupling to be important in states where there are open *d* shells and thus the ground state is actually the E_g'' component of $^2T_{2g}$. Note however that the excited c.t. states involve open ligand shells and here spin–orbit effects are not too important, partly for the reasons given in ref. 3 and partly because the spin–orbit constant for CN$^-$ is very small.

We now turn to a detailed assignment of the structure developed at helium temperatures which is due in part to the *d–d* transitions. For this purpose we divide the spectrum into three main regions.

(*a*) 28 000—36 000 cm^{-1}. In his treatment of the *d–d* transitions, Naiman[5] chose the two shoulders at 30 200 and 35 600 cm^{-1} in the absorption spectrum as the spin-allowed transitions $^2T_{2g} \longrightarrow {}^2A_{2g}$ and $^2T_{1g} \longrightarrow {}^2E_g$ respectively. He assumed that these two transitions were enhanced by borrowing intensity from the 33 500 cm^{-1} c.t. band and were ' drawn closer ' to the allowed band as a result of the resonance process. This assumption is hard to justify since the forbidden vibronic state must have the same symmetry as the allowed state in order for resonance to take place. Simple perturbation theory predicts a repulsive effect for two interacting states of the same symmetry and, whereas the situation for three interacting states is more complex, there seems no reason for assuming that the states will end up drawn closer as a result of the mixing. The intensity ' stolen ' in this assignment implies some 23% c.t. character in the *d–d* bands and we might expect to see similar enhancement in some of the substituted complexes discussed later.

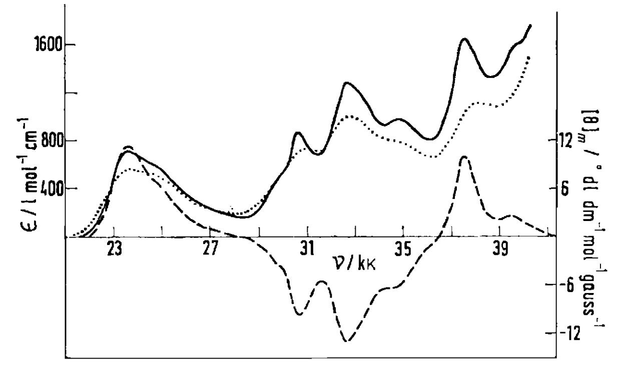

FIGURE 2 Absorption and m.c.d. spectra of the complex $[Fe(CN)_6]^{3-}$ in polymethyl methacrylate: (· · · ·), absorption at 290 K; (——), absorption at 12 K; (– – – –), m.c.d. at 12 K

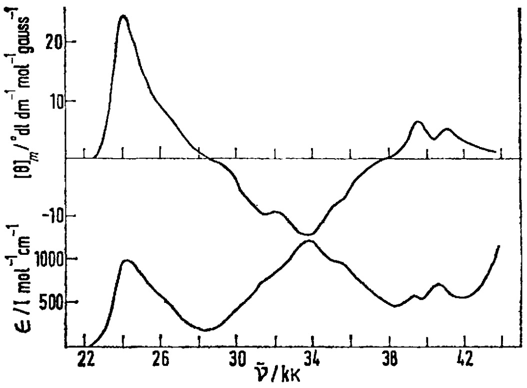

FIGURE 3 Absorption and m.c.d. spectra of the complex $[Fe(CN)_6]^{3-}$ doped into KCl at 12 K

Alexander and Gray[6] found that these two shoulders decreased in oscillator strength on cooling to liquid-nitrogen temperature in EPA and thus supported Naiman's analysis. Our results for the two host lattices

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[20] R. Gale and A. J. McCaffery, *J.C.S. Chem. Comm.*, 1972, 832.

[21] B. Bleaney and M. C. M. O'Brien, *Proc. Phys. Soc.*, 1956, **69**, 1216.

do not support this observation. The reduction in oscillator strength was not observed and we prefer to assign as *d–d* transitions the small shoulders at 29 800 cm^{-1} (Figure 3) and 30 200 cm^{-1} (Figure 2), and the slight shoulder at 33 200 cm^{-1} (Figure 2) which was not resolved in the KCl sample. We, therefore, assign these bands as $E_g''(^2T_{2g}) \longrightarrow U_g'(^2T_{1g})$, $E_g''(^2A_{2g})$ and $E_g''(^2T_{2g}) \longrightarrow U_g'(^2E_g)$ respectively; using the calculated energies from Table 1 (fourth column), this leads to a value of $B = 602$ cm^{-1}. The intensity of these transitions implies only about 5% c.t. mixing into the forbidden state and could explain why no *d–d* transitions are identifiable in the spectra of the complexes of C_{4v} symmetry.

The three central peaks at 31 600, 33 700, and 35 800 cm^{-1} (Figure 3) are assigned as the 0—0, 0—1, and 0—2 components of a vibrational progression in the totally symmetric mode of the $^2T_{2u}$ excited state. The excited-state vibrational frequency is 2100 cm^{-1}, a value somewhat lower than the ground-state frequency [22] of 2125 cm^{-1}, and it reflects lowered σ-bonding due to reduced nuclear charge and, further, π-bonding is diminished by the transfer of an electron from a non-bonding to an antibonding orbital.[23] As expected the m.c.d. of all these components has the same sign.

The m.c.d. spectrum also provides evidence for some form of resonance overlap giving intensity to the parity-forbidden bands, since all the shoulders and maxima in the m.c.d. spectra coincide with shoulders and peaks in the absorption. Thus they all have the same sign m.c.d., as expected if the overall vibronic symmetry is the same as that of the major peak.

(*b*) 25 000 cm^{-1}. Again the m.c.d. provides some evidence for intensity borrowing from the allowed band, as the peaks and shoulders lined up in m.c.d. and absorption spectra. The band at 23 600 cm^{-1} is the L ⟶ M c.t. transition $E_g''(^2T_{2g}) \longrightarrow U_u'[^2T_{1u}(\pi)]$.[17] The experimental C/D value for this transition is in good agreement with the theory. We first consider the broad featureless absorption centred around 18 000 cm^{-1}. We assign this to the transitions $E_g''(^2T_{2g}) \longrightarrow E_g''$, $3/2U_g'(^4T_{1g})$ leading to values of $C = 3361$ cm^{-1} and $\Delta = 34\,455$ cm^{-1}. The energies of the allowed transitions are then as given in Table 2. For the purpose of calculation, ξ_d has been set equal to 300 cm^{-1}, about 70% of the free-ion value. The Racah B parameter was also reduced by roughly the same amount. Using these energies we assign the weak absorption at 26 900 cm^{-1} to $E_g''(^2T_{2g}) \longrightarrow E_g''$, $3/2U_g'(^6A_1)$. This is assumed to have gained intensity from the allowed band at 23 600 cm^{-1}. The remaining band in this region is at 24 800 cm^{-1}. This we assign as a parity-forbidden ligand (π)⟶metal c.t. transition $E_g''(^2T_{2g}) \longrightarrow E_g''(^2T_{1g})$ which has also gained intensity from the allowed band. Dickinson *et al.*, in a recent high-resolution study of Ir^{4+} in Cs$_2$[ZrBr$_6$],[4] found this transition at a slightly higher energy than that of the ligand (π)-to-metal allowed charge transfer, and our interpretation is consistent with this finding.

(*c*) 36 500—40 000 cm^{-1}. In this region, quantitative measurements were impossible because of a steeply rising background absorption, particularly in the plastic matrix. The qualitative features are quite valuable however and two bands were resolved in the absorption and m.c.d. spectra in both lattices. The temperature dependence of the absorption spectra yielded no information of value in identifying the bands. The intense band at 37 500 cm^{-1} (Figure 3) we assign as the origin of the c.t. transition $E_g'' \longrightarrow U_u'(^2T_{1u})$.[14] The band at 39 500 cm^{-1} could then be either the 0—1 vibrational component of this transition or one of the *d–d* bands which has borrowed intensity from it. Alexander and Gray [6] found a sharp decrease in intensity with temperature for the band at 39 500 cm^{-1} and as a result assign it as a *d–d* transition. Our results are difficult to analyse in this region but we did not detect the large temperature change found by these authors. We prefer to assign the 39 500 cm^{-1} band as the vibrational overtone of the 37 500 cm^{-1} charge transfer. This gives a value of 2000 cm^{-1} for the excited-state vibrational frequency, which is consistent with decreased σ-bonding in this state due to charge transfer and increased bond length together with decreased π-bonding due to population of a π-antibonding level.

We now have a fully assigned hexacyanoferrate(III) spectrum which necessitated some changes of previous identifications in the light of the liquid-helium temperature spectra. The interpretation of the c.t. spectrum is confirmed and, with this understanding of the parent hexacyano-complex, we move on to discuss the optical properties of the substituted pentacyanoferrate(III) complexes.

Pentacyanoferrate(III) *Complexes of* C_{4v} *Symmetry*.—In this section we discuss m.c.d. and absorption spectral details of the complexes [Fe(CN)$_5$L]$^{2-}$ (L = H$_2$O, PPh$_3$, or NH$_3$). The m.c.d. spectra of the thiocyanato- and azido-complexes were also recorded and are discussed at the end of this section.

We first deal with the complex Na$_2$[Fe(CN)$_5$NH$_3$]. Its m.c.d. and absorption spectra, in aqueous solution at room temperature, are shown in Figure 4; the qualitative similarity to the hexacyanoferrate(III) complex is very striking. The bands have the same sign as, and similar energy to, the first two bands of the hexacyanoferrate(III) solution. The 21 K e.s.r. spectra also indicate that the ground state of this ion is very nearly octahedral. E.s.r. results for the complexes of C_{4v} symmetry are summarised in Table 4. g Values of d^5 ions are known to be very sensitive to small changes in environment [24] and the deviations from the expected value, $g = 2/3(2k + 1)$ where k is the orbital reduction factor, are small enough that the ground state of the ions can be taken as octahedral to a good approximation. Values of C, D, and C/D were calculated for the complexes

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[22] V. Caglioti, G. Sartori, and M. Scrocco, 'Chemistry of the Co-ordination Compounds,' Pergamon Press, London, 1958.

[23] L. H. Jones, *Inorg. Chem.*, 1963, **2**, 777.

[24] A. Hudson and M. J. Kennedy, *J. Chem. Soc.* (*A*), 1969, 1116.

of C_{4v} symmetry using the method of Griffith. For this purpose, complex functions were used which were *simultaneously* bases for O_h and C_{4v}. Faraday parameters were then evaluated using operators and coupling coefficients of the octahedral group (Table 3). The labelling of the bands is shown in Figures 4—7. For band (I) of the ammine and aquo-complexes, C was calculated by summing the whole dispersion under the double-humped band.

TABLE 3

(*a*) Experimental C, D, and C/D values

Sample	Band position cm^{-1}	T K	$(B + C/kT)$	C *	D	C/D
$[Fe(CN)_6]$–KCl	24 500	290	$-3{\cdot}9$	$-0{\cdot}78$	$1{\cdot}57$	$-0{\cdot}50$
		12	$-77{\cdot}3$	$-0{\cdot}64$	$1{\cdot}45$	$-0{\cdot}44$
	32 500	290	$4{\cdot}75$	$0{\cdot}95$	$2{\cdot}86$	$0{\cdot}32$
		12	$72{\cdot}5$	$0{\cdot}60$	$2{\cdot}98$	$0{\cdot}20$
$[Fe(CN)_6]$–poly(methyl methacrylate)	24 500	290	$-1{\cdot}85$	$-0{\cdot}37$	$0{\cdot}85$	$-0{\cdot}44$
		12	$-37{\cdot}4$	$-0{\cdot}31$	$0{\cdot}89$	$-0{\cdot}35$
	32 500	290	$1{\cdot}95$	$0{\cdot}39$	$3{\cdot}28$	$0{\cdot}12$
		12	$38{\cdot}6$	$0{\cdot}32$	$3{\cdot}04$	$0{\cdot}11$

(*b*) Calculated

Electronic transition	C $(D^2\beta)$	D (D^2)	C/D (β)	$k = 0{\cdot}87$
$^2T_{2g} \longrightarrow {}^2T_{1u}(\pi)$	$-km^2/6$	$m^2/3$	$-k/2$	$-0{\cdot}435$
$^2T_{2g} \longrightarrow {}^2T_{2u}(\pi)$	$+km^2/6$	$m^2/3$	$+k/2$	$+0{\cdot}435$
$^2T_{2g} \longrightarrow {}^2T_{1u}(\sigma)$	$-km^2/6$	$m^2/3$	$-k/2$	$-0{\cdot}435$

$m = \langle t_2 \| t_1 \| t_1 \rangle$ or $\langle t_2 \| t_1 \| t_2 \rangle$.

* Assuming $B = 0$.

TABLE 4

g Values for the complexes $[Fe(CN)_5L]^{n-}$ ($T = 21$ K)

L	g_1	g_2	g_3
PPh_3	$2{\cdot}19$	$2{\cdot}48$	
NH_3	$1{\cdot}99$		
H_2O	$1{\cdot}92$	$2{\cdot}14$	$2{\cdot}35$
N_3^-	$1{\cdot}88$	$2{\cdot}19$	$2{\cdot}38$
SCN^-	$1{\cdot}87$	$2{\cdot}28$	$2{\cdot}40$

In the aquo-, triphenylphosphine, and ammine complexes there are bands at *ca.* 25 500 and 34 000 cm^{-1} which appear to be direct analogues of the 24 500 and 32 700 cm^{-1} bands of the hexacyanoferrate(III) complex. Thus the bands at 25 400, 24 600, and 25 300 cm^{-1} in the complexes for which L = NH_3, H_2O, and PPh_3 respectively can be confidently assigned as the equivalent of the transition $^2T_{2g} \longrightarrow {}^2T_{1u}(\pi)$. Similarly those at 34 600, 34 800, and 34 200 cm^{-1} respectively are the $^2T_{2g} \longrightarrow {}^2T_{2u}$ transition equivalents. Experimental C, D, and C/D values are summarised in Table 5.

The lack of m.c.d. under the intense absorption band at 17 500 cm^{-1} in the aquo-complex in solution has been the subject of a prior communication.[25] The absence of m.c.d. in this region is confirmation of the presence of a diamagnetic dimer in equilibrium with the paramagnetic aquo-monomer. There remains one band unassigned in each of the absorption spectra of the pentacyano-complexes: the transitions at 26 900, 27 700, and 16 000 cm^{-1}. There are several possible assignments for these bands and we discuss these in turn. One possible interpretation is that the bands are the components of a low-symmetry splitting of the orbital triplets. However, if this low symmetry was effective in splitting the excited states, we might reasonably expect a substantial splitting of both T_{1u} and T_{2u} terms. Further, a low-symmetry perturbation, which can produce excited-state splitting of up to 7000 cm^{-1}, would surely have been detected in the e.s.r. experiment. Yet another piece of evidence against this interpretation is the sign of the m.c.d. under this extra band. It can be easily shown that the component bands of an orbital triplet split by low-symmetry distortions have opposite sign m.c.d.[4] Thus the extra band cannot be a C_{4v} split component of the $^2T_{1u}$ state. It could of course be a component of the $^2T_{2u}$ state, but this requires an even larger low-symmetry distortion and can reasonably be ruled out. A Jahn–Teller interaction can be shown to give bands of the

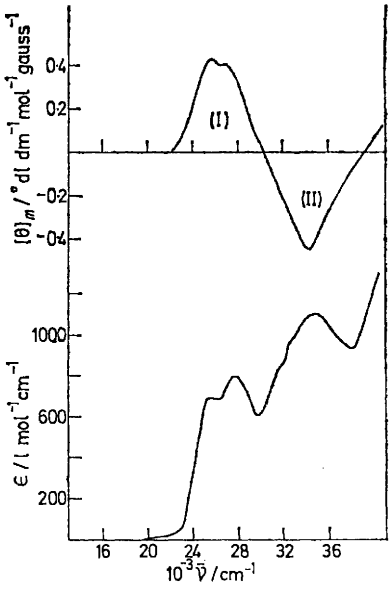

FIGURE 4 Absorption and m.c.d. spectra of the complex $[Fe(CN)_5NH_3]^{2-}$ in aqueous solution at room temperature

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[25] R. Gale, A. J. McCaffery, and C. K. Jorgensen, *Chem. Phys. Letters*, 1972, **15**, 512.

TABLE 5

Experimental Faraday parameters for the complexes $[Fe(CN)_5L]^{n-}$

L	Band (I)			Band (II)		
	C * ($D^2\beta$)	D (D^2)	C/D (β)	C ($D^2\beta$)	D (D^2)	C/D (β)
PPh_3	−0·116	0·47	−0·25	−0·25	0·85	−0·3
NH_3	−0·47	1·36	−0·34	0·44	1·83	+0·24
H_2O	−1·32	6·72	−0·2	2·56	5·96	+0·43
SCN^- at 290 K	−0·079	4·87	−0·016	−0·074	0·65	−0·114
at 10 K	−0·008	6·0	−0·0014	−0·14	1·2	−0·004

* C Values are in fact $kT[B + (C/kT)]$.

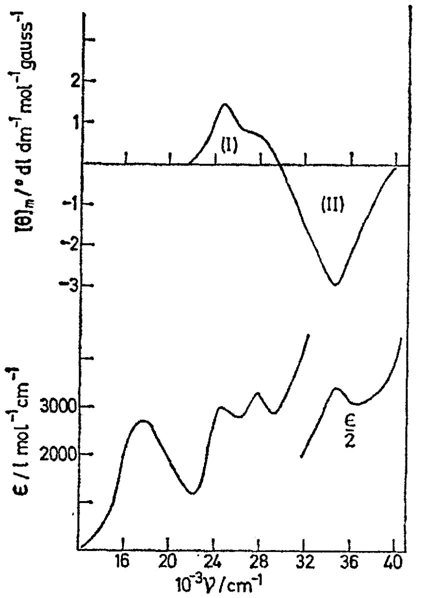

FIGURE 5 Absorption and m.c.d. spectra of the complex $[Fe(CN)_5H_2O]^{2-}$ in aqueous solution at room temperature

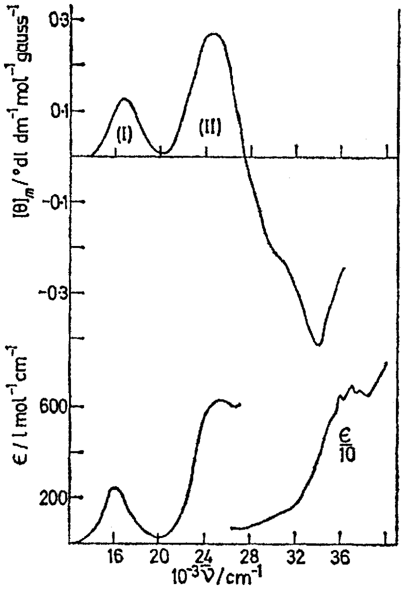

FIGURE 6 Absorption and m.c.d. spectra of the complex $[Fe(CN)_5PPh_3]^{2-}$ in solution at room temperature

same sign, but it seems unreasonable to invoke this particular phenomenon in the absence of any other supporting evidence.

A more probable explanation is that the extra band is due to charge transfer from the ligand L σ (or π) orbitals to the metal t_{2g} shell. This transition would be expected to shift tremendously with the nature of ligand L. This phenomenon has been observed in Ir^{IV} complexes of D_{4h} symmetry[3] where charge transfer from phosphine

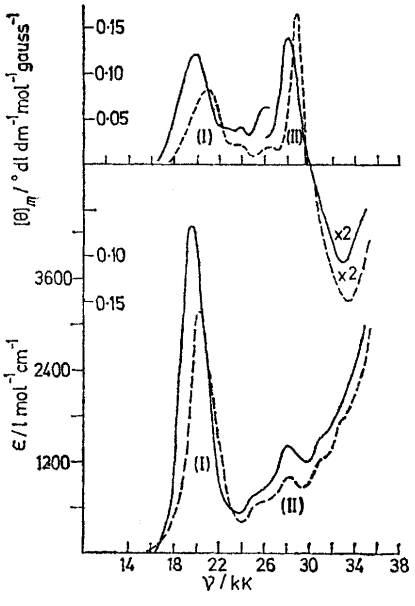

FIGURE 7 Absorption and m.c.d. spectra of the butylammonium salt of the complex $[Fe(CN)_5NCS]^{3-}$ in chloroform solution at room temperature (- - -) and in poly(methyl methacrylate) at 10 K (——)

and arsine ligands has been found to occur at exceptionally low energies, sulphides at higher energies, and amines well into the u.v. In this work[3] the reactivity of the co-ordinated ligand L was related to the energy of the filled σ-bonding orbital provided by L. The sign of the m.c.d. under this band supports this assignment. The value of C/D for this transition was calculated in the C_{4v} double group. Under this lower symmetry the T_{2g} ground state splits into B_2 and E components. These mix together under first-order spin–orbit coupling to give a 'pseudo-octahedral' ground state. The excited state can then either be pseudo-octahedral or pure C_{4v}. The calculation of C/D is given in detail elsewhere[26] for the isomorphous D_4 group, and the sign and magnitude of the calculated C/D value are the same

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[26] M. D. Rowe, D. Phil. Thesis, University of Sussex, 1972.

as those for C_{4v}. The magnitude is in reasonable agreement with experiment and we can have considerable confidence in this assignment, paralleling as it does the L $\longrightarrow$ M c.t. energies in *trans*-$[IrCl_4L_2]$ complexes.

As mentioned earlier, there is little or no evidence of *d–d* transitions of the same order of magnitude as those postulated by Naiman to occur in the hexacyanoferrate(III) ion. The substitution of one cyano-ligand would not be expected to change the energies of these forbidden bands by very much and this view is supported by the e.s.r. and m.c.d. evidence. We therefore take this as support for our new assignment of the *d–d* bands in hexacyanoferrate(III) ion.

One of the most striking features of the spectra is the mobility of the extra band as a function of the nature of ligand L. In the case of phosphine and amine ligands this represents transitions from filled ligand σ-donor molecular orbitals to the metal. For the water ligand it is probably ligand $\pi \longrightarrow t_{2g}$ though in fact may be $\sigma \longrightarrow t_{2g}$; the sign of the m.c.d. supports the latter interpretation. What this means is that, in the case $L = PPh_3$, there is a high-energy filled σ-bonding molecular orbital which is lower in energy for $L = NH_3$ and H_2O. This was also found in the $[IrCl_4L_2]$ series [4] where the filled bonding orbital in $L = PR_3$ and AsR_3 is only *ca.* 1 eV below that of t_{2g} and in $L = SR_2$ and pyridine, becomes progressively more stable. Our pentacyanoferrate(*III*) results provide confirmation of this work. The transitions have moved to higher energies as expected for ligand to metal charge transfer on going from metal oxidation state IV to III.

The implications of the relative energies of these filled σ-donor orbitals to the lability of the co-ordinated ligands were made in Part I of this series. The higher lying the orbital, the more labile will be the ligand, since the energy of M–L bond formation contributes to the change in thermodynamic stability and may make a significant contribution to the activation energy.[27] One might expect the energy of the highest-lying filled bonding orbital to play an important part in the rate of redox reactions. The finding of a similar pattern of orbital ordering in the present iron(III) complexes is important in that it indicates that this can be expected to be a general phenomenon. Of some significance is the observation that the ' soft ' ligands AsR_3 and PR_3 can be expected to have particularly high-lying filled σ-bonding molecular orbitals. This situation is shown in Figure 8 where the experimental energies of the filled ligand bonding molecular orbitals are shown for Fe^{III} relative to the metal t_{2g} energy (arbitrarily set at zero) and the significance of this and related results will be discussed elsewhere.[27]

One other feature of some interest is the evidence of dimer formation in the aquo-complex. This was discussed in a previous paper [25] and is briefly summarised here. An equilibrium can be shown to exist between a paramagnetic monomer $[Fe(CN)_5H_2O]^{2-}$ and a diamagnetic dimer, shown by Emschwiller [28] to be $[Fe_2(CN)_{10}]^{4-}$. The absence of m.c.d. under the characteristic band in the red region at 17 500 cm^{-1} is confirmation of the presence of a diamagnetic species in solution, since it is clear from the foregoing theory that no bands of the monomer can be expected to have zero m.c.d. Furthermore, it is very improbable that charge transfer from a water ligand would take place as low in energy as 17 500 cm^{-1}. The dimer has been formulated as involving two cyano-bridges. Other cyano-bridged dimer structures are known, for example the Fe^{II}–Co^{III} dimer of Haim and Wilmarth,[29] $[(NC)_5FeCNCo(CN)_5]^{6-}$, and Adamson's [30] purple dimer $[Co_2(CN)_{10}]^{6-}$ both of which involve a single cyano-bridge. That suggested by Emschwiller is formulated as $[(NC)_4Fe(NC,CN)Fe(CN)_4]$.

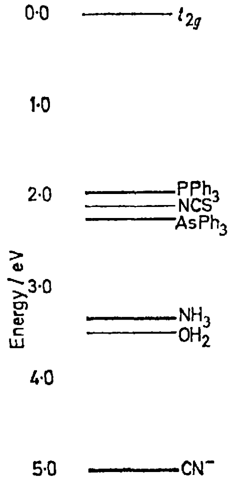

FIGURE 8 Energies of the filled ligand molecular orbitals relative to that of the t_{2g} (3*d*) orbital of Fe^{III}. The energy of t_{2g} orbital is arbitrarily set at zero. It is to be noted that the position of $L = NCS^-$ is rather tentative and that for $L = CN^-$ the energy of the ligand σ orbital is shown; that of the lowest ligand π orbital is about 2 eV lower in energy

We also have results on the complexes $[Fe(CN)_5N_3]^{3-}$ and $[Fe(CN)_5(NCS)]^{3-}$ which show new absorption bands in the red region of the spectrum. These have recently been the subject of a thorough study by Gutterman and Gray.[31] Our m.c.d. results on these two systems in solution are not clear-cut for, although the absorption spectra agree well with published data, the m.c.d. is not explicable on the basis of the previously outlined theory. The thiocyanato-complex is reasonably in line with our general interpretation since the two bands at 28 600 and 33 400 cm^{-1} show negative and positive *C* terms which are clearly part of the cyano-group transitions. However the band in the red shows only a very small m.c.d. (*C*/*D* *ca.* 0·01) and this does not increase markedly at 10 K. The azido-complex is more puzzling since there is very little m.c.d. under any of the absorption bands,

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[27] R. Gale, A. J. McCaffery, and M. D. Rowe, unpublished work.

[28] G. Emschwiller, *Compt. rend.*, 1967, **265C**, 281.

[29] A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 509.

[30] A. W. Adamson, *J. Amer. Chem. Soc.*, 1951, **73**, 5710.

[31] D. Gutterman and H. B. Gray, *Inorg. Chem.*, 1972, **8**, 1727.

with no sign of the basic cyanide to metal charge transfer. Other synthetic methods were tried for the azido- and thiocyanato-complexes but there was no change in the absorption and m.c.d. spectra. Both these results suggest that the solution spectra of the azido- and thiocyanato-complexes should be approached with caution. Work is continuing on these systems and we hope to report further on them in due course.*

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[2/2673 *Received, 27th November*, 1972]

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* *Note added in proof:* S. C. Jain, A. V. Warrier, and H. K. Sehgal (*J. Phys. Chem.*, 1973, **6**, 193) have measured the absorption spectra of the complex $[Fe(CN)_6]^{3-}$ in KCl at 4 K. The results are in agreement with those presented above.