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Magnetic Circular Dichroism of $[Fe(CN)_6]^{3-}$

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Magnetic circular dichroism (MCD) of $[Fe(CN)_6]^{3-}$ was measured in aqueous solution and in a polyvinylalcohol film. The use of the polyvinylalcohol (PVA) film made it possible to measure the MCD and the absorption spectrum of an electrolyte such as $K_3[Fe(CN)_6]$ at dry ice - methanol and liquid nitrogen temperatures, since the film was still optically transparent at lower temperatures. From a comparison between the observations at 300°K, 195°K and 77°K, the magnitude of an angular momentum due to the orbital motion of a hole in the ground state $^2T_{2g}$ $(t_{2g}{}^5)$ was calculated to be 0.04—0.07 Bohr magneton (β). The observed reduction of the angular momentum was interpreted to be due to partial quenching of the orbital motion by the Jahn-Teller distortion, and also to the delocalization effect between the iron $d\pi$ orbital and the antibonding π molecular orbitals of the coordinating CN^- ions. The B term in $[Fe(CN)_6]^{3-}$, which had been ignored, was predicted to be non-zero and was estimated as -2.4×10^{-3} β/cm^{-1} at the band I and 0.97×10^{-3} β/cm^{-1} at the band II.

The majority of magnetic circular dichroism (MCD) measurements have been carried out with liquid solutions. However the use of the technique at low temperature makes it possible to get much more information about the electronic structure of an open-shell species such as inorganic complexes, free radicals, solvated electrons, or organic negative or positive ions. We present in this paper an MCD measurement of $[Fe(CN)_6]^{3-}$ ion which was carried out at dry ice - methanol and liquid nitrogen temperatures with a film of polyvinylalcohol (PVA) dispersing $[Fe(CN)_6]^{3-}$.

$[Fe(CN)_6]^{3-}$ has an iron(III) ion with a low spin d^5 system. A hole exists in a π molecular orbital which is delocalized over the iron $d\pi$ orbital and the antibonding orbitals of the coordinating CN^- ions. The angular momentum produced by an orbital motion of the hole in the ground state plays an important role in the temperature dependent magnetic circular dichroism. According to Buckingham and Stephens, and Schatz *et al.*,[1,2] the magnitude of molar circular dichroism observed at a transition $a\rightarrow j$ is given by

$$[\theta(a\rightarrow j)]_{\mathrm{M}} = -\frac{24\boldsymbol{N}}{\hbar c}\{f_1A+f_2(B+C/\boldsymbol{k}T)\} \tag{1}$$

where the term $C/\boldsymbol{k}T$ is only a temperature-dependent term,

$$A=\frac{3}{d_a}\sum[\langle j|\hat{\mu}_z|j\rangle-\langle a|\hat{\mu}_z|a\rangle]\cdot\boldsymbol{I}_m[\langle a|\hat{m}_x|j\rangle\langle j|\hat{m}_y|a\rangle] \tag{2}$$

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[1] A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, **17**, 399 (1966).

[2] P. N. Schatz, A. J. McCaffery, W. Suëtaka, G. N. Henning, A. B. Ritchie and P. J. Stephens, *J. Chem. Phys.*, **45**, 722 (1966).

$$
\begin{aligned}
B = \frac{3}{d_a}\sum \boldsymbol{I}_m\Big\{ & \sum_{k\neq a}\frac{\langle k|\hat{\mu}_z|a\rangle}{W_k-W_a}[\langle a|\hat{m}_x|j\rangle\langle j|\hat{m}_y|k\rangle \\
& -\langle a|\hat{m}_y|j\rangle\langle j|\hat{m}_x|k\rangle] \\
& +\sum_{k\neq j}\frac{\langle j|\hat{\mu}_z|k\rangle}{W_k-W_j}[\langle a|\hat{m}_x|j\rangle\langle k|\hat{m}_y|a\rangle \\
& -\langle a|\hat{m}_y|j\rangle\langle k|\hat{m}_x|a\rangle]\Big\}
\end{aligned} \tag{3}
$$

$$
C = \frac{3}{d_a}\sum\langle a|\hat{\mu}_z|a\rangle \boldsymbol{I}_m[\langle a|\hat{m}_x|j\rangle\langle j|\hat{m}_y|a\rangle] \tag{4}
$$

d_a is the degeneracy of the state a, and $\hat{m}$ and $\hat{\mu}$ are the electric and magnetic dipole operators, respectively. The summations are over all transitions degenerate with $a \rightarrow j$, and the state a and j are diagonal in $\hat{\mu}_z$. W_a is the energy of the state a. A correction for condensed medium effects has been avoided by expressing $[\theta(a\rightarrow j)]_M$ in terms of ratios of A, B, or C to D, the dipole strength ($D \equiv 3\sum|<a|\hat{m}_x|j>|^2/d_a$) obtained from the observed absorption intensity.

Recently McCaffery, *et al.*[3] observed a temperature-dependent MCD of $[IrCl_6]^{2-}$ doped in a crystalline $(CH_3NH_3)_2SnCl_6$. The temperature-dependence was assumed to arise primarily from the term C/kT. The term C/kT is ascribed to the orientation effect of a temperature-independent magnetic moment of the ground state in a magnetic field. However, another possibility is a temperature-dependent magnetic moment,[4] which arises from a population of the higher sublevels ($J=3/2$) other than the lowest sublevels ($J=1/2$) of the ground state $^2T_{2g}$. Since the spin-orbit coupling in $[IrCl_6]^{2-}$ is so strong that a sufficient gap exists between the sublevels $J=1/2$ and $J=3/2$, the higher sublevels are not populated.[4d] In the case of $[Fe(CN)_6]^{3-}$, however has been observed a temperature-dependent orbital contribution to the magnetic susceptibility due to a population of the higher sublevels.[4c] In this paper, a temperature-dependent MCD of $[Fe(CN)_6]^{3-}$ in a PVA matrix will be presented.

Experimental

The aqueous solution of polyvinylalcohol was added with an aqueous solution of $K_3[Fe(CN)_6]$ and the mixture was allowed to evaporate to dryness on a glass plate. When it was dried, it gave a yellow transparent film.[*1] The concentrations and their mixing ratio of the solutions were adjusted to give a film with an optical density of 1.0—2.0.

Our measurement techniques of magnetic circular dichroism will be described elsewhere.[5] All measurements were carried out by a JASCO model ORD/UV-5 instrument with a drastically modified optical path for an electromagnet which produced a magnetic field up to 12000 gauss. When the current in the magnet is reversed, the signal coming out is also reversed. The deviation between two curves thus obtained (Figs. 1—3) gives an effective signal corresponding to that observed in a magnetic field of twofold strength.

The instrument was also furnished with a special Dewar system for the low temperature measurement.

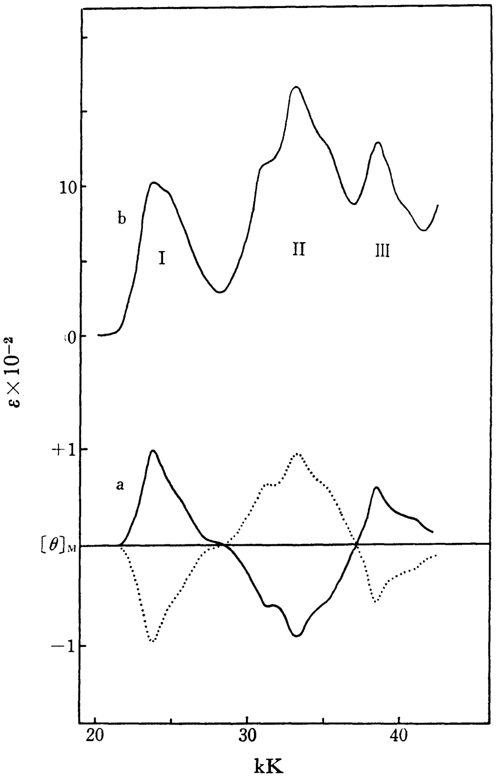

Fig. 1. (a) Molar ellipticity per unit magnetic field of $[Fe(CN)_6]^{3-}$ in aqueous solution at room temperature (300°K).

(b) Molar extinction coefficient of $[Fe(CN)_6]^{3-}$ in aqueous solution at room temperature (300°K).

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[3] A. J. McCaffery, P. N. Schatz and T. E. Lester, *J. Chem. Phys.*, **50**, 379 (1969).

[4] a) M. Kotani, *J. Phys. Soc. Jap.*, **4**, 293 (1949); *Progr. Theor. Phys., Suppl.*, **14**, 1 (1960). b) B.N. Figgis, J. Lewis, R. S. Nyholm and R. D. Peacock, *Discuss. Faraday Soc.*, **26**, 103 (1952); B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York (1966), Chap. 10. c) $[Fe(CN)_6]^{3-}$: J.B. Howard, *J. Chem. Phys.*, **3**, 813 (1935); B. Bleaney and M. C. M. O'Brien, *Proc. Phys. Soc.*, **B69**, 1205 (1956); F. R. McKim and W. P. Wolf, *ibid.*, **B69**, 1231 (1956). d) $[IrCl_6]^{4-}$: V. Norman and J. C. Morrow, *J. Chem. Phys.*, **31**, 455 (1959); A. H. Cooke, R. Lazenby, F. R. McKim, J. Owen and W. P. Wolf, *Proc. Roy. Soc.*, **A250**, 97 (1959).

[*1] The authors are indebted to Dr. T. Hoshi, Department of Chemistry, Aoyama Gakuin University, who kindly showed them how to prepare a PVA film for optical measurement.

[5] H. Kobayashi, M. Shimizu and I. Fujita, This Bulletin, **43**, 2335 (1970).

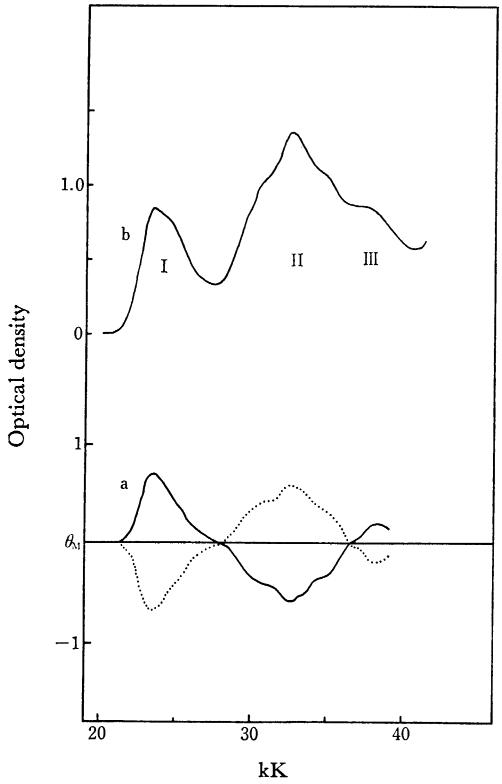

Fig. 2. (a) Ellipticity per unit magnetic field of $[Fe(CN)_6]^{3-}$ in PVA at room temperature (300°K). (b) Absorption spectrum of $[Fe(CN)_6]^{3-}$ in PVA at room temperature (300°K).

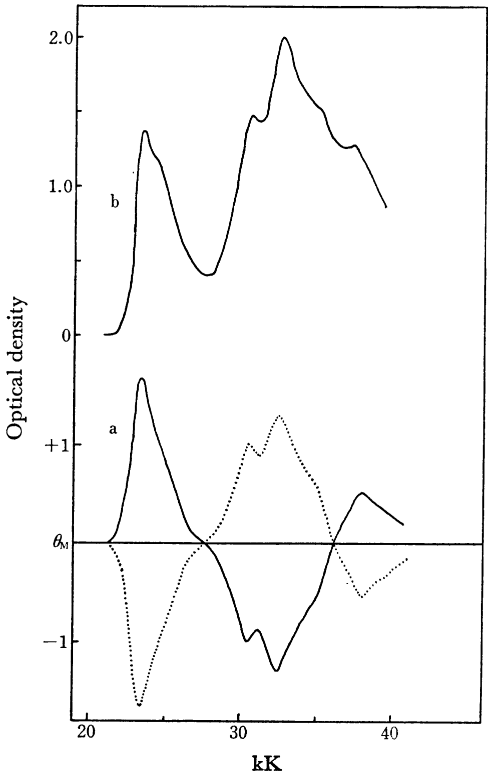

Fig. 3. (a) Ellipticity per unit magnetic field of $[Fe(CN)_6]^{3-}$ in PVA at liquid nitrogen temperature (77°K). (b) Absorption spectrum of $[Fe(CN)_6]^{3-}$ in PVA at liquid nitrogen temperature (77°K).

Results and Discussion

The magnetic circular dichroism (MCD) and the absorption spectrum of $[Fe(CN)_6]^{3-}$ were measured with an aqueous solution and a polyvinylalcohol (PVA) matrix at room temperature. They are shown in Figs. 1 and 2. There seems to be only a little solvent effect. The magnitude of MCD was given in molar ellipticity per unit external magnetic field $[\theta]_M$. Since the concentration of $[Fe(CN)_6]^{3-}$ in PVA was unknown, the MCD was given in experimentally observed ellipticity per unit external magnetic field θ_M. The film was actually 0.25 mm thick and had an optical density corresponding to that observed for 0.82×10^{-3} mol/l aqueous solution of $[Fe(CN)_6]^{3-}$ in a 1 cm path. If it is necessary, $[\theta]_M=\theta_M/C\cdot l$, where C is the concentration, l is the path length and the product $C\cdot l$, is given by optical density measurement as 0.82×10^{-3} mol l^{-1} cm.

The observed $[\theta]_M$ of $[Fe(CN)_6]^{3-}$ arises predominantly from the term $(B+C/\boldsymbol{k}T)$, since the MCD spectrum shows its maximum at the position of an absorption maximum. If the A term plays an important role, however, the observed MCD should give a sigmoid dispersion curve at the position of the absorption maximum. The function f_1 in (1) is approximately given by a function such as

$$\{\pi^{1/2}\tilde{\nu}(\tilde{\nu}_{ja}-\tilde{\nu})\exp[-(\tilde{\nu}-\tilde{\nu}_{ja})^2/\Delta_{ja}^2]\}/\boldsymbol{h}\Delta_{ja}^3$$

which shows a sigmoid dispersion curve at the position of the absorption maximum $(\tilde{\nu}_{ja})$ and the area obtained by integration of $f_1/\tilde{\nu}$ over whole range of an absorption band should be zero. The function f_2 is approximately given by a function such as Gaussian

$$\{\pi^{1/2}\tilde{\nu}\exp[-(\tilde{\nu}-\tilde{\nu}_{ja})^2/\Delta_{ja}^2]\}/2\Delta_{ja}$$

which shows a maximum at the position of the absorption maximum $(\tilde{\nu}_{ja})$ and the area obtained by integration of $f_2/\tilde{\nu}$ over whole range of an absorption band should be $\pi/2$. The A term makes no contribution to the integrated MCD and

$$\int\frac{[\theta(a\rightarrow j)]_M}{\tilde{\nu}}d\tilde{\nu}=-\frac{24\boldsymbol{N}}{\hbar c}\frac{\pi}{2}(B+C/\boldsymbol{k}T). \qquad (5)$$

We avoided troublesome correction for condensed medium effect by expressing our results in terms of a ratio of $\int[\theta]_M/\tilde{\nu}d\tilde{\nu}$ to the dipole strength D. Assuming the best fit Gaussian $\varepsilon(\tilde{\nu})$ to the molar

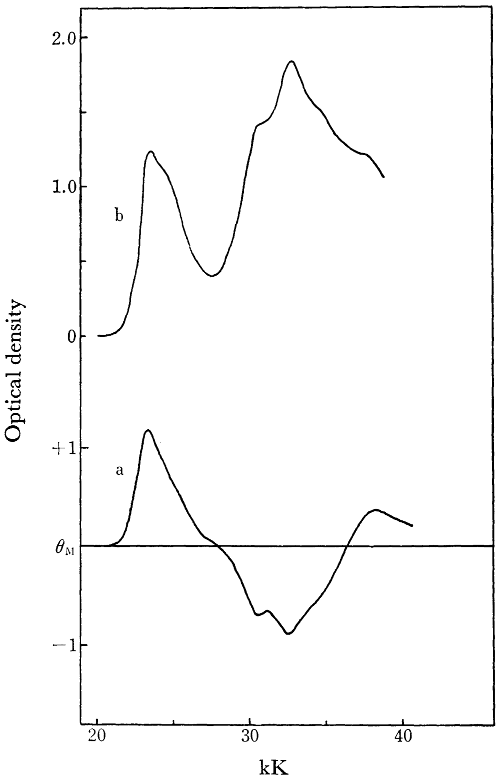

Fig. 4. (a) Ellipticity per unit magnetic field of $[Fe(CN)_6]^{3-}$ in PVA at dry ice-methanol temperature (195°K).
(b) Absorption spectrum of $[Fe(CN)_6]^{3-}$ in PVA at dry ice-methanol temperature (195°K).

absorption curve, the dipole strength D was evaluated from the area obtained by the integration of $\varepsilon(\bar{\nu})/\bar{\nu}$ over whole range of an absorption band. The value of $\int[\theta]_M/\bar{\nu}d\bar{\nu}$ was also obtained by the integration of a Gaussian which best reproduced the observed magnetic molar ellipticity curve. B and C/kT were given in units of square Debye·Bohr magneton per cm^{-1}. Our observation at room temperature and the value of C obtained by an assumption that the B term is negligibly small, are given in Fig. 1 and Table 1, respectively, and are in good agreement with the data published by Schatz, *et al.*2) Measurements of MCD at various temperatures are expected to give a criterion to the validity of the assumption.

Table 1. Parameter values for $[Fe(CN)_6]^{3-}$ in aqueous solution at room temperature (300°K)

	$C(D^2\cdot\beta)$	$D(D^2)$	$C/D(\beta)$
Band I	−0.824	1.34	−0.615
Band II	0.961	3.03	0.317
Band III	−0.153	1.35	−0.113

D: Debye unit; β: Bohr magneton.

Three bands of moderate intensity (ε_{max} ~1000—2000) at 24000, 33000 and 38500 cm^{-1} have been observed.6) These bands have been assigned to the allowed "ligand to metal" charge transfer transitions. Of these, two are $^2T_{2g}\rightarrow{}^2T_{1u}$ and one is $^2T_{2g}\rightarrow{}^2T_{2u}$. After some different assignments had been given,7,8) the first band was assigned to $^2T_{2g}\rightarrow{}^2T_{1u}$ transition and the second to $^2T_{2g}\rightarrow{}^2T_{2u}$ transition based on magneto-optical rotatory dispersion (MORD) measurements9) which had been carried out by Shashoua10) and Briat.11) Since C/D is a measure of the angular momentum of an orbital motion in the ground state, the magnitude of $|C/D|$ should not be changed from one band to another and the sign of C/D should be opposite that for the transitions to T_{1u} and T_{2u} states. Actually the MCD observed at the second band shows an opposite sign to the MCD observed at the first band and at the third band. From existing MCD data2) including a semiquantitative measurement by Foss and McCarville12) and also MORD data, it follows that the first band and the third band corresponding to $^2T_{1u}$ excited states show a negative C, and the second band corresponds to $^2T_{2u}$ excited state and shows a positive C.

The PVA film was optically transparent even at liquid nitrogen temperature (77°K). An optically transparent PVA film dispersing $[Fe(CN)_6]^{3-}$ was measured for MCD at various temperatures. The results are shown in Figs. 2—4. The PVA film technique made it possible to observe the MCD and the absorption spectrum of an electrolyte such as $K_3[Fe(CN)_6]$ at dry ice-methanol temperature and at liquid nitrogen temperature. When the measurements of the MCD and the absorption were carried out with exactly the same sample, the ratio of the observed value of the integrated MCD to the observed value of the integrated absorption is independent of the actual concentration of $[Fe(CN)_6]^{3-}$ in the film and gives the value of $(B+C/kT)/D$.

Table 2. Parameter values for $[Fe(CN)_6]^{3-}$ in PVA film

	$(B+C/kT)/D\times10^3(\beta/cm^{-1})$		
	300°K	195°K	77°K
Band I	−2.72	−3.02	−3.73
Band II	1.19	1.29	1.80

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6) For example, C. K. Jϕrgensen, *Acta Chem. Scand.*, **10**, 518 (1956).

7) C. S. Naiman, *J. Chem. Phys.*, **35**, 323 (1961); *ibid.*, **39**, 1900 (1963).

8) G. Basu and R. L. Belford, *ibid.*, **37**, 1933 (1962).

9) P. J. Stephens, *Inorg. Chem.*, **4**, 1690 (1965).

10) V. E. Shashoua, *J. Amer. Chem. Soc.*, **86**, 2109 (1964).

11) B. Briat, *Compt. Rend.*, **259**, 2408 (1964).

12) J. G. Foss and M. E. McCarville, *J. Amer. Chem. Soc.*, **87**, 228 (1965).

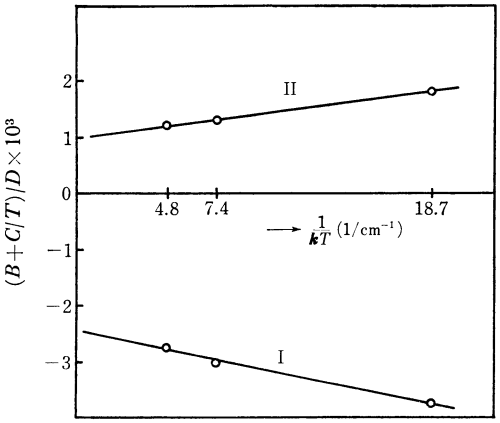

Fig. 5. Temperature dependence of $(B+C/kT)/D$.

Table 2 shows our observed values of $(B+C/kT)/D$.

As shown in Fig. 5, a plot of the observed values of $(B+C/kT)/D$ *versus* $1/kT$ gave a straight line. It gave non-zero B/D from its intercept and fairly small C/D from its slope. The value of B/D was found to be $-2.44\times10^{-3}\,\beta/\text{cm}^{-1}$ for the first band, while the value was obtained to be $0.97\times10^{-3}\,\beta/\text{cm}^{-1}$ for the second band. The ignored angular momentum induced by magnetic field is not zero. A difference of the magnitudes of B/D between the two bands seems to be appreciable. The value of C/D was $-0.070\,\beta$ for the first band and $+0.044\,\beta$ for the second band. These values of C/D in the absolute value are fairly smaller than $0.5\,\beta$ theoretically expected for an orbital motion of a hole at the central iron.[2] Delocalization of the hole over whole complex will reduce the absolute value of C/D. However, another important mechanism expected to reduce the value is a quenching of the orbital motion by trapping the hole in the lowest component of t_{2g} molecular orbitals split by a dynamical or static Jahn-Teller distortion of the open shell $d\pi^5$ system. As far as the MCD measurements are concerned, a population of the higher sublevels ($J=3/2$) in $[Fe(CN)_6]^{3-}$ does not seem to change the values of B and C since the plot shown in Fig. 5 gives a nice straight line. However, a theoretical approach to the problem is required. Theoretical interpretations including molecular orbital calculation will be given elsewhere.