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A Study of Fe (II) and Fe(III) Complexes of Fluorescein-Part III.

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Complexes of fluorescein with Fe(II) and Fe(III) show anomalous magnetic properties suggesting intermolecular interactions. The Mössbauer spectrum of the Fe(III) complex gives proof to the Fe-Fe interaction.

Fe(III) having a d^5 configuration possesses $^6A_{1g}$ and $^2T_{2g}$ ground terms in octahedral ligand fields. The magnetic moments of the high-spin complexes with $^6A_{1g}$ ground terms are found to be very close to the spin-only value 5.92 B.M. independent of temperature. The spin-paired complexes with $^2T_{2g}$ ground terms show reduction in magnetic moments with decrease in temperature. In certain dithiocarbamate complexes of iron[1] it has been observed that the ligand field makes the ground terms $^6A_{1g}$ and $^2T_{2g}$ of almost equal energy and the magnetic behaviour in relation to temperature is quite complicated. Similarly, effective magnetic moments of some polynuclear iron complexes range from 0.70 to 4.74 B.M. with intermediate values of 1.81, 3.25 and 3.39 B.M. [2]

Fe(II) with d^6 configuration gives spin-free and spin-paired complexes. In octahedral spin-paired complexes, the first order Zeeman effect is absent but the second order Zeeman effect contribution T.I.P. of about 50×10^{-6} c.g.s. per mole.

Experimental

Preparation of metal complexes

The Fe(II) complex was precipitated as a dull red compound by adding an alcoholic solution of fluorescein in an atmosphere of nitrogen to an aqueous solution of Fe(II) SO_4, the *p*H of the resulting solution being around 7. The precipitate was washed several times with distilled water and dried at 70° under partial vacuum.

The Fe(III) complex was obtained as a dark brown precipitate by mixing an aqueous solution of Fe(III) nitrate with an alcoholic solution of fluorescein, the *p*H being near about 7. The precipitate was washed several times with ethanol water mixture and dried at 120°.

Analysis

Found : C, 60.58; H, 4.72; Fe, 5.43%. Calculated for $Fe_2C_{100}H_{80}O_{37}$: C, 60.47; H, 4.03; Fe, 5.64%.

Found : C, 61.16; H, 3.16; Fe, 9.88%. Calculated for $Fe_4C_{120}H_{180}O_{38}$: C, 61.17; H, 3.40; Fe, 9.52%.

Magnetic, thermomagnetic and spectral measurements were recorded as given in the previous communication[3]. Mössbauer spectrum of Fe(III) complex was recorded at T.I.F.R., Bombay.

All chemicals including solvents used in the present investigation for the preparation of the two complexes and for the measurement of their physical properties were of extra pure quality and they were further purified by standard methods, wherever necessary.

Results and Discussion

From the magnetic data (Fig. 1) for Fe(II) complex it is seen that it possesses a small moment of the order of 1.0 B.M. and is independent of temperature which shows that second order Zeeman effect may

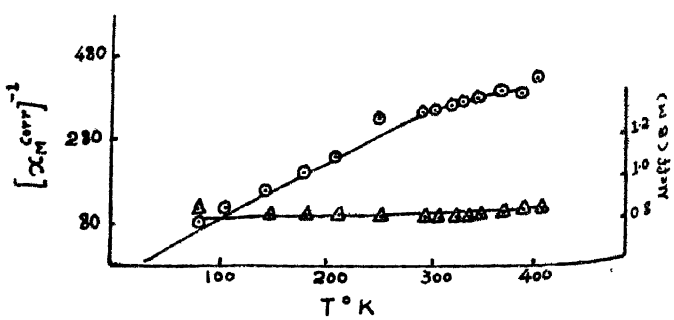


Fig. 1. Fe (II)-fluorescein Complex

be playing its part. Sugden[4] has attributed the low magnetic moments for the complex $[Fe(Phen_3)]^{2+}$ to a deeper interaction or more intimate bonding.

The spectral data are presented in Table 1. The fluorescein complex of Fe(II) gives one diffuse reflectance band at 19050 cm^{-1}, one at 18,980 cm^{-1} in nitromethane and three bands at 19,050 cm^{-1}, 23,200 cm^{-1} and 39,840 cm^{-1} in acetonitrile. The last two bands appear to be charge-transfer bands. If the

band observed at 19,050 cm^{-1} is due to d–d transition and the paramagnetic state $^5T_{1g}$ lies close to the spin-paired $^1A_{1g}$ state, it may be possible to estimate the Dq and B parameters with the help of Tanabe-Sugano diagrams. The estimated values of Dq and B are $\sim$ 2,199 cm^{-1} and $\sim$ 1,000 cm^{-1} respectively, the nephelauxetic ratio β being 0.94 [B_{ion} = 1,058 cm^{-1}].

TABLE 1—SPECTRAL DATA FOR Fe(II) FLUORESCEIN COMPLEX

	cm^{-1}	ϵ(molar)	Assignment
Solid, diffuse reflectance	19,050	—	$^1A_{1g} \rightarrow {}^1T_{1g}$
Solution $1.3 \times 10^{-3}M$	39.840	1464	Charge transfer
in Acetonitrile	23,200	940	Charge transfer
	19,050	734	$^1A_{1g} \rightarrow {}^1T_{1g}$
$1.1 \times 10^{-3}M$ in Nitromethane.	18,980	643	$^1A_{1g} \rightarrow {}^1T_{1g}$

The conductivity data for the Fe(II) complex of iron in Table 2 favour a neutral electrolyte.

TABLE 2—CONDUCTIVITY DATA FOR Fe(II)-FLUORESCEIN COMPLEX

Solvent	Concentration	Λ_M $cm^2\ mole^{-1}\ ohm^{-1}$
Acetonitrile	$1.8 \times 10^{-3}M$	11.41
	$1.1 \times 10^{-3}M$	13.62
	$0.7 \times 10^{-3}M$	20.46
Nitromethane	$0.8 \times 10^{-3}M$	20.66
	$0.66 \times 10^{-3}M$	11.92

Fe(III)-fluorescein complex

The $1/\chi$—T curve shown in Fig. 2 for the magnetic behaviour of the Fe(III) complex indicates that the complex follows the Curie-Weiss low from 82.6°K to 302°K beyond which its magnetic behaviour tends to become complex. Table 3 gives the μ_{eff} (B.M.) values of the complex between 82.6 and 391.2°K.

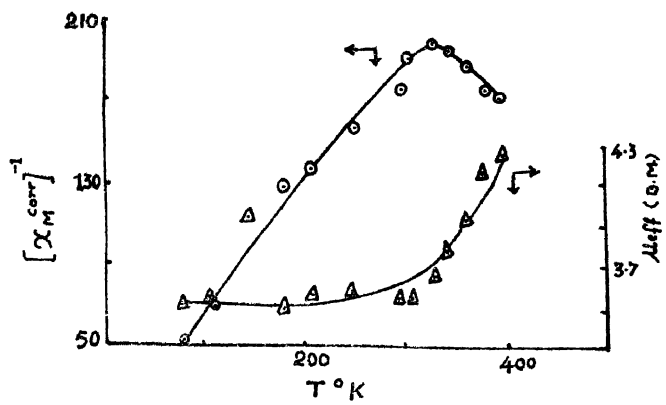


Fig. 2. Fe (III)-fluorescein complex

TABLE 3—Fe(III)-FLUORESCEIN COMPLEX, MAGNETIC DATA

Molecular weight 2351.40

T°K	$\chi_M^{Corr} \times 10^6$	μ_{eff}(B.M.)
82.6	18490.0	3.51
110.4	13855.0	3.54
148.2	13080.0	3.94
181.2	8302.5	3.48
217.2	7220.0	3.55
254.6	6340.0	3.59
289.0	5395.0	3.54
302.6	5122.5	3.53
324.5	5052.5	3.64
342.8	5107.5	3.79
360.6	5277.0	3.91
378.2	5677.5	4.17
391.2	5800.0	4.27

The room temperature magnetic moment value of 3.5 B.M. of the ferric complex is slightly lower than the spin only value expected for a square planar symmetry (μ_{eff} = 3.87 B.M.). The value of the magnetic moment of the complex is intermediate between those expected for spin-free (5.9 B.M.) and spin-paired (2.5 B.M.) configurations which may suggest the possibility of spin-free spin-paired equilibrium in the Ferric complex. The polynuclear nature of the complex in the octahedral symmetry, as seen from the elemental analysis, however, rules out such possibility.

The assignment to different transitions observed in the reflectance spectra of the ferric complexes have been made by getting the best fit in the Tanabe-Sugano diagram for d^5 configuration (Dq/B = 3.0) Table 4.

TABLE 4—SPECTRAL DATA FOR Fe(III)-FLUORESCEIN COMPLEX

	cm^{-1}	ϵ(molar)	Assignment
Solid	29,850	—	$^2T_{2g} \rightarrow {}^4E_g(0)$
	28,180	—	$^2T_{2g} \rightarrow {}^4T_{2g}(F)$
	26,300	—	$^2T_{2g} \rightarrow {}^4E_{(a)},({}^4A_{1g})$
	11,630	—	$^2T_{1g} \rightarrow {}^4T_{2g}$
	11,110	—	
Solution $0.88 \times 10^{-3}M$ in Acetonitrile	29,240	21.8	
	27,620	18.4	
	25,380	10.2	
	11,440	6.4	
$1.08 \times 10^{-3}M$ in D.M.F.	29,500	46.4	
	27,860	41.2	
	25,640	36.2	
	11,740	21.2	

The values of extinction coefficients which are somewhat higher than those expected for spin forbiddend d–d transitions may be due to departure of the complex from the octahedral symmetry.

The infrared spectra were obtained as described in the previous communication[3]. The frequencies 1235, 1255 and 1375 cm^{-1} corresponding to CO and OH groups in the ligand fluorescein appear to have shifted to 1245, 1266 and 1390 cm^{-1} in the Fe(III) complex. These shifts are not as marked as those observed in the complexes of fluorescein with Cu(II) or lanthanides (III)[3].

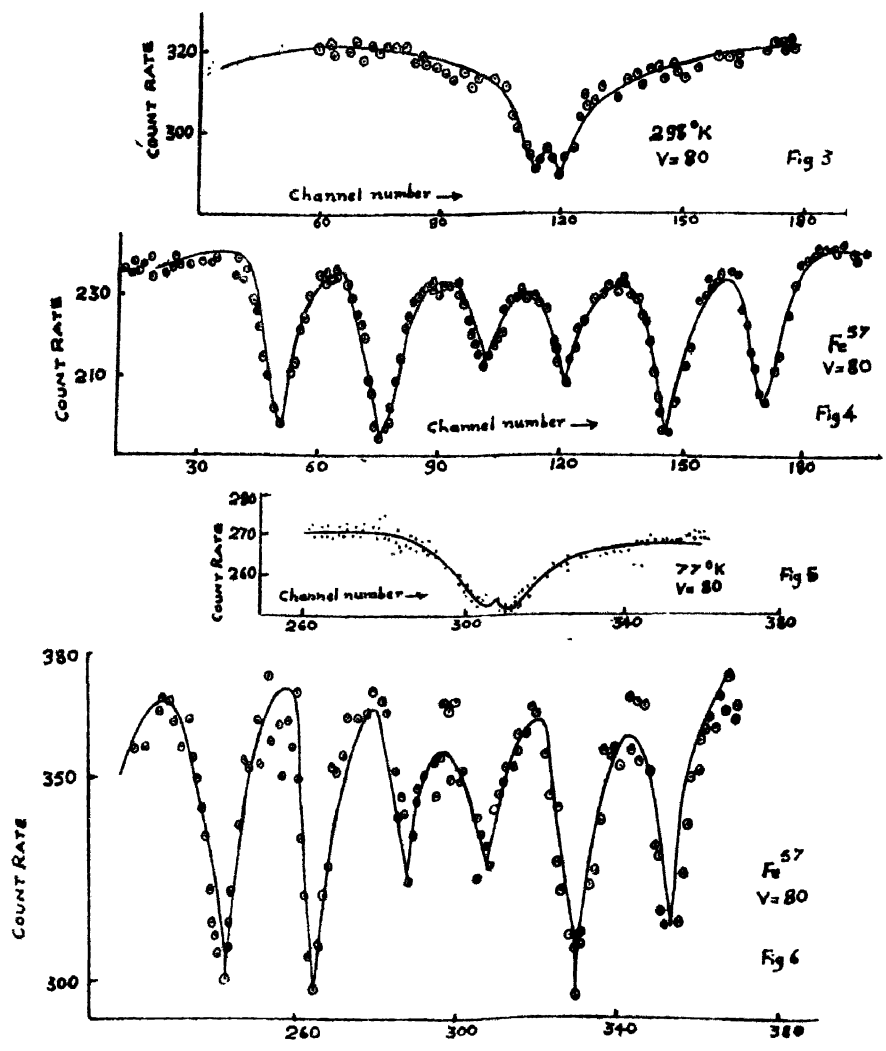
The conductivity data in D.M.F. (Table 5) are in favour of a neutral electrolyte whereas the conductivity measurements in acetonitrile and nitromethane give results which are intermediate between those expected for a neutral and 1 : 1 electrolyte.

The magnetic behaviour of Fe(III)-fluorescein complex being anamolous did not give much help in arriving at the structure of the complex except it hinted at the possible Fe-Fe interaction in the solid. The data obtained from the Mössbauer spectrum (Figs. 3–6) was of some help.

TABLE 5—CONDUCTIVITY DATA FOR Fe(III)-FLUORESCEIN COMPLEX

Solvent	Conc.	Λ_M $cm^2, mole^{-1}, ohm^{-1}$
Acetonitrile	$0.96\times10^{-3}M$	43.6
	$0.76\times10^{-3}M$	62.9
	$0.68\times10^{-3}M$	52.0
D.M.F.	$1.2\times10^{-3}M$	14.2
	$1.6\times10^{-3}M$	11.1
Nitromethane	$1.18\times10^{-3}M$	64.0
	$1.7\times10^{-3}M$	55.0

The isomer shift δ and quadrupole splitting ΔE of the 14.4 K ev transiton in ^{57}Fe were measured for the Fe(III) complex on the Mössbauer spectrometer at T.I.F.R., Bombay. The chemical shift with respect to iron metal was found as $\delta = 0.25$ mm/sec. and $\Delta E = 0.60$ mm/sec. (Figs. 3–6). This indicates a quadrupole splitting at 300°K which is unresolved but broadens at 77°K. This may be due to either (i) Fe-Fe exchange which is predicted in the present investigation or (ii) decrease in relaxation



Channel number

Figs. 3-6.

time. Mössbauer spectrum of the complex at liquid helium temperature would have unequivocally shown the Fe-Fe interaction but unfortunately there was no arrangement for taking such spectra.

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