Magnetic Susceptibility, Ultraviolet and Visible Absorption Spectra of Co-ordination Complexes of Iron (III) Phthalimide with Primary and Secondary Aliphatic Amines

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Abstract

The co-ordination compounds of tripositive iron with nitrogen containing ligands have been found to be of high spin type on the basis of magnetism. The ultraviolet and visible absorption measurements show three bands in the vicinity of $21\,400$ cm^{-1}, $17\,480$ cm^{-1} and $10\,650$ cm^{-1}.

Introduction

The preparation, preliminary investigations and infrared spectra of the iron (III) phthalimide complexes with primary and secondary aliphatic amines have been reported[1][2]. In the present short communication, the magnetism, ultraviolet and visible absorption spectra of the same series of complexes have been characterised.

Experimental

The susceptibilities were determined by Gouy method at room temperature. The solid complexes were finely powdered and filled in a Gouy tube carefully by tapping. The tube was calibrated with A.R.tetraquocopper (II) sulphate monohydrate. The data are recorded in table 1. The absorption spectra were recorded on a Unicam S.P. 500 spectrophotometer using nitrobenzene solutions (conc. 10^{-2} M). The bands obtained are listed in table 2.

Results and Discussion

Magnetically, all the complexes are high spin with five unpaired spins. In the high spin complexes, the magnetic moments are always very close to the spin only value of 5.9 B.M. because the ground state has no orbital angular momentum and there is no effective mechanism for introducing any by coupling with excited states[3].

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[1]) G. Narain, Z. anorg. allg. Chem. **343**, 109 (1966).

[2]) G. Narain, Cand. J. Chem., in press.

[3]) F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry (Interscience publishers) 1962, p. 718.

Table 1

Magnetic susceptibility data

Compound	$\chi g \times 10^{-6}$	$\chi M \times 10^{-6}$	Pascal's constant	$\chi M \times 10^{-6}$	Compound state	Temperature °K	μ_{eff}
1. Triphthalimido-trisammine-iron (III)	25.46	13870.05	79.95	13950.00	Solid	300.0	5.9 B.M.
2. Triphthalimido-trismethylamino-iron (III)	23.57	13829.47	115.53	13945.00	Solid	300.5	5.87 B.M.
3. Triphthalimido-trisethylamino-iron (III)	21.93	13786.89	151.11	13938.00	Solid	300.2	5.82 B.M
4. Triphthalimido-tris-n-propyl-amino-iron (III)	20.52	13773.31	186.69	13960.00	Solid	300.1	5.91 B.M
5. Triphthalimido-tris-iso-propyl-amino-iron (III)	20.51	13771.11	186.69	13957.80	Solid	300.0	5.9 B.M.
6. Triphthalimido-tris-n-butyl-amino-iron (III)	19.238	13736.93	222.27	13959.20	Solid	300.0	5.89 B.M.
7. Triphthalimido-tris-iso-butyl-amino-iron (III)	19.26	13735.73	222.27	13958.00	Solid	300.1	5.9 B.M.
8. Triphthalimido-trisdimethyl-amino-iron (III)	21.94	13799.89	151.11	13951.00	Solid	300.3	5.9 B.M.
9. Triphthalimido-trisdiethyl-amino-iron (III)	19.25	13727.70	222.27	13950.00	Solid	300.2	5.9 B.M.

The absorption spectra of the complexes have a broad charge transfer band in the vicinity of 21400 cm^{-1}. Two weak bands have also been found in the vicinity of 10650 cm^{-1} and 17480 cm^{-1}. The latter band appears as a shoulder on the side of the charge transfer band. These two bands are probably due to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}$ (G) and $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) respectively.

The absorption bands are very weak (molar absorbance 0.01 to 0.03). The ground state of the d^5 system in a weak octahedral field has one electron in each d orbital, and their spins are parallel, making it a spin sextuplet. This same state is the ^6S state of the free ion, and it is not split by the ligand field. This, however, is the only sextuplet state possible, for every concei-

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Table 2

Ultraviolet and visible absorption spectra

Compound	$^6A_{1g}\rightarrow{}^4E_g, {}^4A_{1g}$	$^6A_{1g}\rightarrow{}^4T_{2g}$ br.sh	$^6A_{1g}\rightarrow{}^4T_{1g}$ sh
1. Triphthalimidotrisamine-iron (III)	Insoluble in	nitrobenzene	
2. Triphthalimidotrismethylamino-iron (III)	21 400 cm^{-1}	17 480 cm^{-1}	10 650 cm^{-1}
3. Triphthalimidotrisethylamino-iron (III)	21 500 cm^{-1}	17 500 cm^{-1}	10 640 cm^{-1}
4. Triphthalimidotris-n-propylamino-iron (III)	21 500 cm^{-1}	17 480 cm^{-1}	10 640 cm^{-1}
5. Triphthalimidotris-iso-propylamino-iron (III)	21 480 cm^{-1}	17 490 cm^{-1}	10 680 cm^{-1}
6. Triphthalimidotris-n-butylamino-iron (III)	21 390 cm^{-1}	17 500 cm^{-1}	10 680 cm^{-1}
7. Triphthalimidotris-iso-butylamino-iron (III)	21 400 cm^{-1}	17 500 cm^{-1}	10 620 cm^{-1}
8. Triphthalimidotrisdimethylamino-iron (III)	21 400 cm^{-1}	17 520 cm^{-1}	10 640 cm^{-1}
9. Triphthalimidotrisdiethylamino-iron (III)	21 410 cm^{-1}	17 500 cm^{-1}	10 640 cm^{-1}

br. = broad; sh. = shoulder.

Table 3

Comparison of the absorption spectra with other octahedral complexes of iron (III)

Assignments of the d−d transitions	Fe^{+3} in beryl	Fe^{+3} in [Me$_4$N]$_3$[Fe(NCS)$_6$]	Fe^{+3} in complexes (this work)
$^6A_{1g}\rightarrow{}^4T_{1g}$ $(t_{2g})^4$ (eg)	12 300 cm^{-1} 14 200 cm^{-1}	10 640 cm^{-1}	10 650 cm^{-1}
$^6A_{1g}\rightarrow{}^4T_{2g}$ $(t_{2g})^4$ (eg)	17 500 cm^{-1} 20 000 cm^{-1}	17 500 cm^{-1}	17 480 cm^{-1}
$^6A_{1g}\rightarrow{}^4E_g$ $(t_{2g})^3$ (eg)^2 $^6A_{1g}\rightarrow{}^4A_{1g}$ $(t_{2g})^3$ (eg)^2	23 000 cm^{-1}	21 400 cm^{-1}	21 400 cm^{-1}
$^6A_{1g}\rightarrow{}^4T_{1g}$ $(t_{2g})^3$ (eg)^2	26 500 cm^{-1}	---	---

vable alteration of the electron distribution t_{2g}^3 eg^2 with all spins parallel, results in the pairing of two or four spins thus making quartet or doublet states. Hence, all excited states of the d^5 system have different spin multiplicity from the ground state, and transitions to them are spin forbidden. Because of weak spin-orbit interactions, such transitions are not totally absent, but they give rise only to very weak absorption bands[4]).

[4]) F. A. COTTON and G. WILKINSON. ibid., p. 701.

Further, the spectra of the above complexes can be compared with other well known octahedral complexes of iron (III)[5][6][7]). The absorption spectra of iron (III) in beryl [where Fe(III) is co-ordinated to six oxygens] and in tetramethylammoniumhexaisothiocyanatoferrate (III) [where Fe(III) is co-ordinated to six nitrogens] have been investigated by Dvir and Low[8]) and Forster and Goodgame[9]) respectively. These spectra seem to be the most reliable so far reported and the author gives the numbers together with their likely assignments in the table 3.

[5]) C. K. Jorgensen, Acta. Chem. Scand. 8, 1502 (1954).

[6]) H. L. Schlafer, Z. physik. Chem. (Frankfurt) 4, 116 (1955).

[7]) R. Pappalardo, Nuovo Cimento 8, 954 (1958).

[8]) M. Dvir and W. Low, Phys. Rev. 119, 1587 (1960).

[9]) D. Forster and D. M. L. Goodgame, J. chem. Soc. London, 1965, 268.

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