

## Spectral and Mössbauer studies of some iron(III) high spin complexes

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**Abstract.** Some new iron(III) complexes of triazene 1-oxides are synthesised and characterised by analysis, magnetic, electronic and Mössbauer spectra. They are found to be high spin  $Fe^{3+}$  systems.

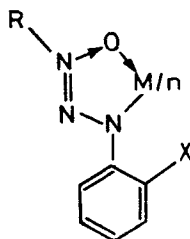
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### 1. Introduction

In recent years the synthesis and study of new iron(II) and iron(III) complexes have gained considerable interest (Baldwin and Huff 1973; Collman *et al* 1975; Cotton 1972). As part of our studies on transition metal complexes of triazene 1-oxide system shown in structure I, we report in this paper the synthesis and studies on some new iron(III) complexes. The ligand in structure I, with  $X =$  halogens, can be bidentate (Tucker *et al* 1979) or tridentate (Zacharias and Chakravorty 1971) forming complexes of the type  $(R-C_6H_4X)_3M$  and  $(R-C_6H_4X)_2M$ . In subsequent discussion the complexes in I will be abbreviated as  $(R-C_6H_4X)_n M$ .

### 2. Experimental

The different ligands for the preparation of iron(III) complexes were synthesised by the known procedure (Zacharias and Chakravorty 1971). The iron(III)



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complexes were prepared as follows. To an ethanolic solution of triazene 1-oxide (3 moles) was added, a slightly acidic solution of ferric acetate (1 mole) prepared by dissolving freshly precipitated ferric hydroxide in acetic acid. The mixture was stirred vigorously when dark blue iron complexes separated. It was filtered and recrystallised from acetone. Analysis of the complexes was done by C, H, N analysis. Electronic spectral measurements were done on Cary 17D spectrophotometer using quartz cells. Magnetic susceptibility values were obtained by using Gouy balance with  $\text{NiCl}_2$  (30%) solution as calibrant. Mössbauer spectra were recorded on Elscint model constant acceleration spectrometer using 2 m Ci  $\text{Co}^{57}/\text{Pd}$  source. The absorbers contained 10 mg natural iron/cm<sup>2</sup>. Not less than  $10^5$  counts were accumulated in all the cases. Sodium nitropruside was used as the calibrant.

### 3. Results and discussion

Analytical data for the iron(III) complexes presented in table 1 show that they are of the general formula  $(\text{R}-\text{C}_6\text{H}_4\text{X})_3\text{Fe}$ . Their magnetic moment values are tabulated in table 2. They fall in the range of 5.70–5.92 B.M. as is expected for the high spin iron(III) complexes. The electronic spectral data for these iron(III) complexes are presented in table 2. All the compounds except  $(\text{CH}_3-p\text{-CH}_3\text{C}_6\text{H}_3\text{Cl})_3\text{Fe}$  show two intense bands at  $\sim 16500\text{ cm}^{-1}$  and  $21000\text{ cm}^{-1}$ . A comparison of the spectra of the present complexes with some of the other well-studied octahedral complexes (Barnum 1961; Piper and Carlin 1963) shows that transition  ${}^4\text{T}_{2g} \leftarrow {}^6\text{A}_{1g}$  lies near the intense band at  $16000\text{ cm}^{-1}$  and  ${}^4\text{A}_{1g}$ ,  ${}^4\text{E}_g \leftarrow {}^6\text{A}_{1g}$  transition around  $21,000\text{ cm}^{-1}$ . Obviously these weak transitions are masked by the charge transfer bands of the system.

The Mössbauer spectra are characterised by isomer shift values (table 2) typical of high spin  $\text{Fe}^{3+}$  complexes (Greenwood and Gibb 1971) and these agree with the spectral and magnetic data reported earlier. They all give rise to asymmetric absorption lines with considerable line broadening ( $\sim 1.8\text{ mm/sec}$ ). Cooling down to liquid nitrogen temperature showed no change in the spectral pattern except that they improve the percentage absorption. The large line broadening

Table 1. Analytical data for iron(III) complexes.

Compound	%C		%H		%N	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$(\text{CH}_3-\text{C}_6\text{H}_4\text{F})_3\text{Fe}$	44.76	44.20	4.26	5.00	22.38	22.00
$(\text{CH}_3-\text{C}_6\text{H}_4\text{Cl})_3\text{Fe}$	41.10	41.51	3.91	4.25	20.55	20.12
$(\text{CH}_3-\text{C}_6\text{H}_4\text{Br})_3\text{Fe}$	33.78	34.12	3.21	3.50	16.89	17.20
$(\text{CH}_3-p\text{-CH}_3\text{C}_6\text{H}_3\text{Cl})_3\text{Fe}$	43.96	44.28	4.58	5.21	19.23	19.61
$(\text{CH}_3-m\text{-CH}_3\text{C}_6\text{H}_3\text{Cl})_3\text{Fe}$	43.96	44.25	4.58	5.11	19.23	20.05
$(\text{C}_2\text{H}_5-\text{C}_6\text{H}_4\text{F})_3\text{Fe}$	47.60	48.00	4.95	4.25	20.82	21.25

Table 2. Spectral, magnetic and isomer shift data for iron(III) compounds.

Compound	$\nu$ ( $\epsilon$ ) <sup>a</sup>	$\mu_{\text{eff}}$ (B.M.)	Isomer shift ( $\delta$ /Fe/mm <sup>-1</sup> )
(CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> F) <sub>3</sub> Fe	16530 (1760); 20625 (2170)	5.90	0.3825
(CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> Cl) <sub>3</sub> Fe	16810 (1600); 21510 (1680)	5.75	0.4080
(CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> Br) <sub>3</sub> Fe	17090 (1170); 21275 (1180)	5.80	0.4155
(CH <sub>3</sub> - <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cl) <sub>3</sub> Fe	16950 (2490)	5.74	0.4352
(CH <sub>3</sub> - <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cl) <sub>3</sub> Fe	16900 (1750); 21510 (2280)	5.72	0.4371
(C <sub>2</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> F) <sub>3</sub> Fe	16810 (2290); 21275 (2380)	5.90	0.3920

<sup>a</sup>  $\nu$  in cm<sup>-1</sup> and  $\epsilon$  in 1 mol<sup>-1</sup> cm<sup>-1</sup>.

in these complexes may be due to the relaxation processes (Bancroft *et al* 1967; Edwards and Johnson 1968).

#### 4. Conclusion

From the experimental evidence it can be said that these iron(III) complexes are octahedral high spin where the ligands act as bidentates.

#### References

- Baldwin J E and Huff J 1973 *J. Am. Chem. Soc.* **95** 5757  
 Bancroft G M, Maddock A G, Ong W K, Prince R H and Stone A J 1967 *J. Chem. Soc. (A)* 1966  
 Barnum D W 1961 *J. Inorg. Nucl. Chem.* **21** 221  
 Collman J P, Gagne R P, Reed C A, Halbert T R, Long G and Robinson W T 1975 *J. Am. Chem. Soc.* **97** 1427  
 Colton F A 1972 *Coord. Chem. Rev.* **8** 185  
 Edwards P R and Johnson C E 1968 *J. Chem. Phys.* **49** 211  
 Greenwood N N and Gibb T C 1971 *Mössbauer spectroscopy* (London : Chapman and Hall) p. 159.  
 Piper T S and Carlin R L *Inorg. Chem.* **2** 260  
 Tucker I, Singh R P and Zacharias P S 1979 *Indian J. Chem.* **A17** 368  
 Zacharias P S and Chakravorty A 1971 *Inorg. Chem.* **10** 1961