

Cyclic Voltammetric & Spectral Investigations of Some Iron(III) Complexes

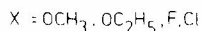
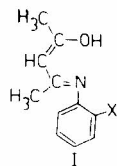
P S ZACHARIAS* & D V V RAO

School of Chemistry, University of Hyderabad, Hyderabad 500 134

Received 3 October 1981; revised and accepted 9 December 1981

Some β -ketoamine iron(III) complexes have been prepared and characterised. Magnetic and Mössbauer data show that they are high spin complexes. Cyclic voltammetric data indicate that the system is quasi-reversible.

Many inorganic complexes, particularly transition metal complexes in various stable oxidation states undergo electron transfer (oxidation-reduction) reactions, similar to those occurring in biosystems involving transition metals. While such reactions in biosystems are reversible, model systems can be reversible, quasi-reversible, irreversible or coupled chemical reactions. This prompted us to synthesise some iron(III) complexes of β -ketoamines as model systems and to study their electron transfer properties by cyclic voltammetry and other spectral methods. Although β -ketoamine complexes of various metal ions are known for a long time¹, very little information is available about their electron transfer properties. In addition, there is considerable similarity in the ligand frame-work of these to the well studied triazene 1-oxide systems^{2,3}.



The β -ketoamines (schiff bases), referred to hereafter as AcAX (see structure I) were prepared by the method described earlier⁴. It involved the direct addition of the appropriate primary amine in 50% excess to the β -diketone (acetylacetone) in benzene containing a few drops of hydrochloric acid. The mixture was refluxed at 100° for several hours under a Dean-Stark water separator. After the separation of an appropriate amount of water the reaction mixture was cooled, concentrated on a rotary evaporator, and the liquid residue cooled to afford a solid. In some cases distillation under reduced pressure was necessary to get the products which were characterized by elemental analyses.

The iron(III) complexes were synthesized as follows: To an ethanolic solution of ligand (3 mmol) was added an aqueous solution of ferric chloride (1 mmol). The mixture was stirred for sometime and cooled when red crystals were deposited. In the case of fluoro and chloro β -ketoamine complexes a few drops of 16% ammonia solution were added to the ligand solution before the addition of ferric chloride solution. The complexes were recrystallized from 1:1 benzene-hexane. The analytical data for the complexes are given below:

(AcAOCH₃)₃Fe (Found: C, 64.02; H, 6.18; N, 6.20 requires C, 64.69; H, 6.29; N, 6.29%); (AcAOC₂H₅)₃Fe (Found: C, 65.46; H, 6.71; N, 5.84 requires C, 65.93; H, 6.76; N, 5.92%). (AcAF)₃Fe (Found: C, 62.05; H, 5.20; N, 6.60 requires C, 62.70; H, 5.23; N, 6.65%); (AcACl)₃Fe (Found: C, 58.51; H, 4.79; N, 6.09 requires C, 58.12; H, 4.84; N, 6.16%).

Room temperature magnetic moments were measured in benzene using a Gouy balance. Electronic spectra were recorded on a Cary-17D spectrophotometer in chloroform. Mössbauer spectra were recorded on an Elscint model constant acceleration spectrometer using 2 mCi Co⁵⁷/Pd source. The absorbers contained 10 mg natural iron/cm². Not less than 10⁵ counts were accumulated in all the cases. Sodium nitroprusside was used as the calibrant. Cyclic voltammograms were recorded using EG and G PARC electrochemistry 370 system. HMDE (hanging mercury drop electrode) and/or platinum electrodes were used as working electrode with SCE (saturated calomel electrode) as reference electrode. Purified acetonitrile was the solvent with TEAP (tetraethylammonium perchlorate) as the supporting electrolyte. Oxygen-free nitrogen was passed through the solution for 20 min before recording the voltammograms.

The analytical data of the iron(III) complexes show that they have the general formula (AcAX)₃Fe. The magnetic moment values are in the range 5.7-5.9 B.M. expected for high spin iron(III) complexes. These complexes exhibit in their electronic spectra in chloroform high intensity bands ~23,000 and ~28,000 cm⁻¹ (Table 1). Though *d-d* transitions are forbidden in high spin iron(III) complexes, the high intensity bands ~23,000 cm⁻¹ may be ascribed to borrowing from the low lying charge transfer bands of the ligand⁵. Thus the band at 23,000 cm⁻¹ is of ⁴A_{1g}, ⁴E_g ← ⁶A_{1g} origin in an octahedral field masked by the intensity of the nearby charge transfer band.

The Mössbauer spectra are characterized by isomer shift values (Table 1) typical of high spin Fe³⁺

Table 1—Electronic and Mössbauer Data for the Iron(III) Complexes

Compound	$\nu(\bar{\nu})^a$	$\delta(\text{mms}^{-1})^b$	$\Delta(\text{mms}^{-1})$
(AcAOCH ₃) ₃ Fe	22,990(4490) 28,170(9135)	0.54	0.44
(AcAOC ₂ H ₅) ₃ Fe	22,990(4470) 28,170(8070)	0.55	0.42
(AcAF) ₃ Fe	23,450(3590) 28,570(8540)	0.48	0.42
(AcACl) ₃ Fe	23,450(4540) 28,570(6310)	0.51	0.39

(a) ν in cm^{-1} and in litre $\text{mol}^{-1} \text{cm}^{-1}$.

(b) With respect to sodium nitroprusside.

Table 2—Cyclic Voltammetric Data for the Iron(III) Complexes

Scan rate (mV sec ⁻¹)	$E_{p,c}$ (V sec ⁻¹)	$E_{p,a}$ (V sec ⁻¹)	ΔE_p (mV)	$i_{p,c}$ (μA)	$i_{p,a}$ (μA)
(AcAOCH ₃) ₃ Fe					
100	-0.73	-0.645	85	9.6	8.6
200	-0.73	-0.64	90	13.0	11.0
(AcAOC ₂ H ₅) ₃ Fe					
50	-0.755	-0.64	115	3.5	2.7
200	-0.76	-0.64	120	3.8	3.0
(AcAF) ₃ Fe					
20	-0.72	-0.65	70	5.0	4.2
50	-0.73	-0.655	75	7.6	6.2
(AcACl) ₃ Fe					
20	-0.75	-0.665	85	2.4	1.8
100	-0.75	-0.665	85	5.4	4.2
200	-0.74	-0.65	90	5.8	4.8

complexes^{6,7}. This observation is in agreement with the spectral and magnetic data reported earlier. Since in an octahedral crystal field iron(III) has a closed d^5 subshell, the quadrupole splitting is expected to be zero⁸. The observed quadrupole splittings for these complexes (Table 1) suggest a distorted octahedral geometry and may be due to the non-identical coordinating groups of the ligands.

The cyclic voltammetric (CV) results are given in Table 2. The number of electrons (n) involved in the reaction has been experimentally found to be one. An examination of experimental data shows that the

reduction of iron(III) is quasi-reversible. In this type of electron transfer process the current is controlled by a mixture of diffusion and charge transfer kinetics and can be identified by the following diagnostic criteria^{9,10}.

(i) $\Delta E_p (= E_{p,c} - E_{p,a})$ may approach $60/n(\text{mV})$ value at low v but should increase with increase in v (v is the scan rate); and (ii) $i_{p,c}/i_{p,a}$ is equal to unity only for $\alpha = 0.5$ (α is the charge transfer coefficient). On the other hand reversible process (purely diffusion-controlled) is characterized by: (i) ΔE_p is $60/n(\text{mV})$ and independent of v ; and (ii) $i_{p,c}/i_{p,a}$ is unity and independent of v while for an irreversible case there is no anodic current^{10,11}. The ψ values for the present system have been found to be between 0.35 and 2 while for reversible systems it has a value > 7 . Several examples of iron(III) complexes are known where reversible electron transfer processes are reported to occur¹²⁻¹⁴. From the experimental data it is clear that the behaviour of (AcAF)₃Fe is almost reversible while it is not so with the rest of them. The $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ seems to be a more facile process than $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$.

References

- Holm R H, Everett (Jr) G W & Chakravorty A, *Progress in inorganic chemistry*, edited by F.A. Cotton (Interscience, New York), 7 (1966) 83.
- Zacharias P S & Salvapati G S, *Proc Indian Acad Sci (Chem Sci)*, **90** (1981) 121.
- Zacharias P S & Subramani C, *Indian J Chem*, **19** (1980) 71.
- Collman J P & Kittleman E T, *Inorg Chem*, **1** (1962) 499.
- Bertrand J A & Eller P G, *Inorg Chem*, **13** (1974) 927.
- Greenwood N N & Gibb T C, *Mössbauer spectroscopy* (Chapman & Hall, London), 1971, 159.
- Russo U, Calogero S, Burriesci N & Petrera M, *J inorg nucl Chem*, **41** (1979) 25.
- Spj Kerman J J, Hall L H & Lambert J L, *J Am chem Soc*, **90** (1968) 2039.
- Nicholson R S, *Analyt Chem*, **37** (1965) 1351.
- Brown E R & Large R F, *Physical methods of chemistry*, part II A, edited by A Weissberger & B W Rossiter (Wiley-Interscience, New York), 1971, 423.
- Nicholson R S & Shain I, *Analyt Chem*, **36** (1964) 706.
- Golding R M, Lehtonen K & Ralph B J, *J inorg nucl Chem*, **36** (1974) 2047.
- Goel R G, Henry P M & Polyzou P C, *Inorg Chem*, **18** (1979) 2148.
- Ferraudi G, *Inorg Chem*, **19** (1980) 438.