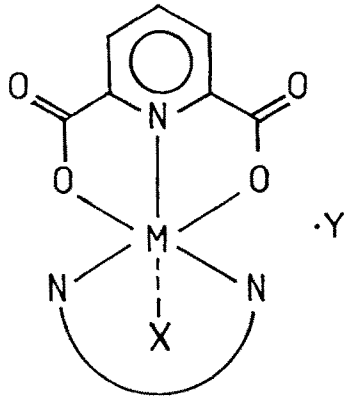
# CHAPTER 3
# Iron(III) and Chromium(III) mixed ligand complexes

It has been observed earlier that both polypyridyl and amino carboxylate complexes of Ru(III) and Fe(III) act as good catalysts for oxidation reactions. It has also been noted that the complexes with π-aromatic amines have a higher oxidation potential than those with saturated amines [1] The polypyridyl ligands impart stability to the ruthenium complexes and also increase the oxidation potential of Ru=O complex, thus weakening the Ru=O bond. The mixed ligand complexes Ruthenium(III)(DPA)(Diamine) were shown to have advantage of both the polypyridyl and carboxylate moieties [2]. $Ru^{V}$=O was generated with different oxidants, viz., PhIO and t-BuOOH The Ru(V)=O species was capable of epoxidizing olefins in an efficient manner It is expected that the corresponding Cr(III) and Fe(III) complexes should also be able to demonstrate such a catalytic behaviour. The five coordinate dpa-diamine ligand system appears to be appropriate for designing complexes to be used as catalysts. It gives complexes with octahedral geometry, in which one axial coordinating site is occupied by replaceable water molecule and is available for the reaction to occur

This chapter describes synthesis and characterization of mixed ligand complexes of Cr(III) and Fe(III) with dipicolinic acid and diamines - ethylenediamine (en), 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen) - and their evaluation as catalysts for the epoxidation of various olefins with iodosylbenzene as an oxidant

$$M^{III}X + dpa \longrightarrow M^{III}(dpa)X \xrightarrow{\overset{\frown}{NN}} M^{III}(dpa)(\overset{\frown}{NN})X$$




| Complex | M | $\overset{\frown}{N\ N}$ | X | Y |
|---|---|---|---|---|
| 1 | Cr | en | Cl | — |
| 2 | Cr | bpy | Cl | — |
| 3 | Cr | phen | Cl | — |
| 4 | Fe | en | $H_2O$ | Cl, $H_2O$ |
| 5 | Fe | bpy | $H_2O$ | Cl |
| 6 | Fe | phen | Cl | $H_2O$ |

## Experimental

### Materials and Methods

All the reagents were of AR grade and were used as received. The solvents were purified by standard literature methods [3]. Iodosylbenzene was prepared by a reported procedure [4]. Instruments used for the characterization of the complexes and GC used for monitoring the progress of the catalytic reactions were as described in chapter 2. An EG & G PAR model 273 Potentiostat/Galvanostat in conjunction with IBM PS/2 equipped with Model 270 Electrochemical Analysis System Software was used for electrochemical measurements. A three electrode system, consisting of Pt disk working, Pt wire counter and Ag wire reference were used. All potentials were converted to the SCE scale Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte and all measurements were carried out at room temperature The voltage scan rate was 0 1 V/s The working electrode surface was polished before recording each voltammogram Acetonitrile-water (1:1) was used as the medium for all the electrochemical measurements, unless otherwise mentioned.

### Synthesis of Complexes

*Cr(dpa)(en)Cl* (**1**). A solution of dipicolinic acid (1 mmol) in ethanol (50 ml) was added dropwise to a stirred solution of $CrCl_3.6H_2O$ (1 mmol) in ethanol (50 ml) and the mixture stirred further at room temperature for 1h To the resultant deep green solution was added dropwise, ethylenediamine (1 mmol) in ethanol (50 ml). The clear solution was stirred for 1h, stoppered, and left at room temperature for 3 days The precipitated purple solid was suction-filtered, washed thoroughly with ethanol and dried at 80 °C under vacuum for 4h. m p. 275°C (d); IR ($cm^{-1}$) 3200(b), 1660(s,b), 1300(s), 1165(m,sh), 1095(w,sh), 910(w), 780(w), 745(w)

*Cr(dpa)(bpy)Cl* (**2**). Preparation as for **1**. Colour, purple; m.p. >300 °C; IR ($cm^{-1}$): 1660(s), 1450(sh), 1330(s), 1160(s), 1085(s), 910(s), 770(w), 740(m), 670(w).

*Cr(dpa)(phen)Cl* (**3**). Preparation as for **1**. Colour, purple; m.p. 280 °C(d); IR ($cm^{-1}$): 1670(s), 1435(sh), 1330(s), 1165(s), 1095(sh), 920(m), 850(sh), 750(w), 720(w), 670(sh)

*Fe(dpa)(en)($H_2O$)$_2$Cl* (**4**) Preparation as for **1** except that $FeCl_3$ (1 mmol) was taken in absolute ethanol The complex separates out immediately on adding diamine solution Colour, light yellow; m.p. 230 °C (d); IR ($cm^{-1}$) . 3500-3200(s,b), 2000(sh), 1650(s), 1580(sh), 1500(sh), 1420(s), 1315(s), 1170(sh), 1070(s), 900(s), 800(w), 765(sh), 735(sh), 670(sh)

*Fe(dpa)(bpy)($H_2O$)Cl* (**5**). Preparation as for **4**. Colour, yellow; m.p. 270 °C(d), IR ($cm^{-1}$)· 3400(s,b), 1595(s), 1570(s), 1470(s), 1440(s), 1245(m), 1170(m,sh), 1100(sh), 1020(sh), 760(m), 725(sh), 650(sh).

*Fe(dpa)(phen)($H_2O$)Cl* (**6**). Preparation as for **4**. Colour, Orange; m.p. 280 °C (d); IR ($cm^{-1}$): 3400(b,s), 1670(s), 1515(s), 1430(s), 1315(m), 1160(m,sh), 1070(sh), 905(m), 765(m), 670(sh).

**Procedure for oxidation studies**

All the oxidation reactions were carried out in a Schlenk tube under $N_2$ atmosphere. To a solution of catalyst (0 012 mmol) in $CH_3CN$-$H_2O$ mixture (3+1 ml) was added a solution of olefin (3.0 mmol) in $CH_3CN$ (3 ml) and the mixture deaerated by bubbling $N_2$ for 10 min PhIO (0 6 mmol) was added and the mixture stirred under $N_2$ at 25 °C for 6h. A suitable internal standard was added to the reaction mixture and the products analyzed by gas chromatography.

## Results and discussion

**Characterization**

All the complexes are amorphous in nature The complexes **1-6** gave satisfactory elemental analysis for C,H,N and metal corresponding to 1·1:1 stoichiometry of the metal : DPA : diamine in the complexes, and chloride as counterion (Table 1). All of them decompose at temperatures above 230 °C except **2** which does not melt upto 300°C. The conductance for complex **2** in $CH_3NO_2$-$CH_3OH$ solvent mixture (7·3) is 28 showing that it is a nonelectrolyte (Table 1). However, in $CH_3CN$-$H_2O$ (6:1) **2** shows 1:1 electrolytic behaviour. Conductance for **3** in $CH_3NO_2$-$CH_3OH$ (7:3) is 16 This shows that, in these complexes the chloride remains coordinated to metal in a weakly coordinating solvent but is replaced by $H_2O$ in an aqueous- organic solution. Elemental analyses of iron complexes **4-6** show presence of $H_2O$ molecules in the complexes in solid state which is confirmed by IR spectra. Moreover, conductance of **5** in acetone, a weakly coordinating solvent, is 87, corresponding to 1:1 electrolytic behaviour It can be said that in **5**, the sixth coordination site is occupied by $H_2O$

molecule and Cl resides outside the coordination sphere in solid state. However, **6** does not show 1·1 electrolytic behaviour in $CH_3NO_2$-$CH_3OH$ (Table 1). Complexes **1** and **4** do not dissolve in $CH_3NO_2$-$CH_3OH$ solvent

Magnetic susceptibility values for chromium complexes **1-3** lie in the range of 2.8 - 2.9 B M., corresponding to 3 unpaired electrons in the metal centre This is consistent with the +3 oxidation state of metal centre in the complexes. $\mu_{eff}$ values for iron complexes correspond to 5 unpaired electrons as expected for +3 oxidation state of iron. Characteristic IR bands due to $\nu_{COO}$ vibrations in free dpa appear at 1700 and 1300 $cm^{-1}$, respectively In the chromium complexes the bands are shifted to 1600-1670 $cm^{-1}$ and 1330 cm-1 respectively, indicating coordination of the carboxylic functions to the metal centre. In iron complexes, the corresponding bands appear at 1595-1670 $cm^{-1}$ and 1420-1440 $cm^{-1}$. A broad band at 3200 $cm^{-1}$ is observed due to merging of $\nu_{sym}$ and $\nu_{asymm}$ vibrations of $-NH_2$ in **1**. In the complex **4**, the $\nu_{N-H}$ bands merge with that due to $H_2O$ and a single broad band is observed at 3500-3200 $cm^{-1}$.

**Electrochemistry**

The chromium complexes **1** and **2** show two redox couples in the potential range of 0.0 V to -0.9 V (Figure 1). The first wave corresponding to the $Cr^{+3}/Cr^{+2}$ redox system is irreversible in the case of **1** and **2**. The second redox wave in the more negative potential range is quasi-reversible for both the complexes This is attributed to the $Cr^{+2}/Cr^{+}$ redox couple. Two redox couples in the same range are observed for the iron complexes **4-6** (Table 2). The first, corresponding to $Fe^{+3}/Fe^{+2}$ system, is quasi-reversible for **4** and **6** and is irreversible for **5** The $Fe^{+2}/Fe^{+}$ redox couple is quasi-reversible for the complexes **4-6**.

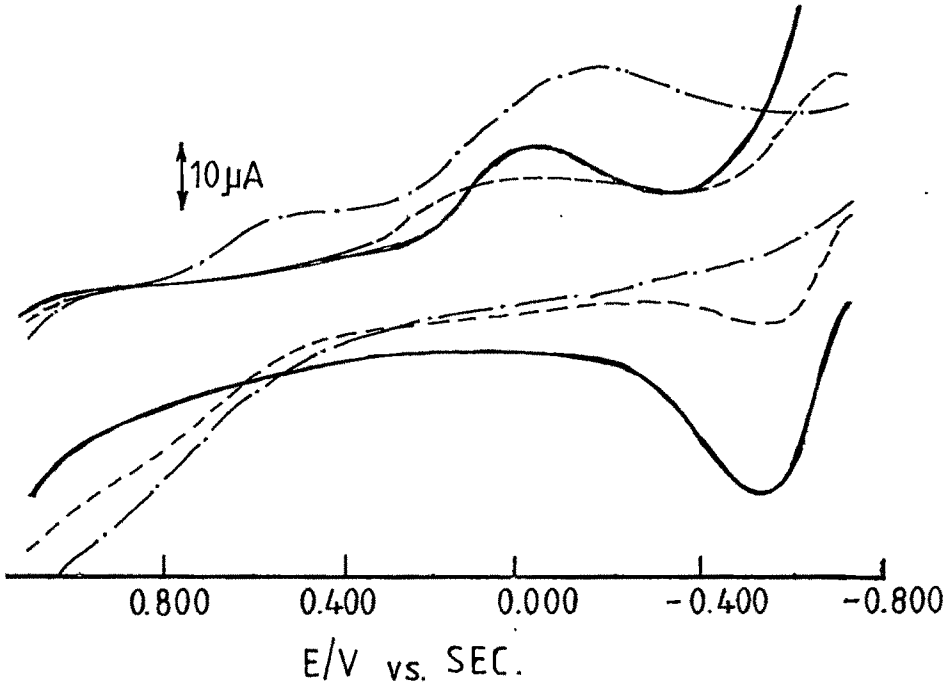



**Figure 1** Cyclic voltammetry of chromium complexes :——**1**; ----------**2**; ----------**2** after addition of PhIO. Conditions as in Table 2.

A comparison of potentials for chromium and iron complexes (Table 2) shows that the values for the former are more negative as compared to those for the latter. Further, for both metal systems, the redox potentials with bpy ligand appear at more positive potentials compared to those for corresponding en analogues. This trend is expected to be due to the strong σ-donor tendency of en moiety and strong π-acceptor ability of bpy ligand.

**Catalytic activity**

The results of the oxidation of olefins with iodosylbenzene in the presence of the chromium complexes **1-3** as epoxidation catalysts are shown in Table 3. A control experiment using *cis*-cyclooctene under identical experimental conditions, but excluding metal complex, did not give any epoxide. The complex **3** was only partially soluble in $CH_3CN$:$H_2O$ (6:1) solvent mixture used for the oxidation reaction. This may be the reason for the relatively lower yield of epoxide using the complex **3** as a catalyst. Oxidation of *cis*-cyclooctene, norbornene and styrene gave corresponding epoxides exclusively, whereas, cyclohexene gave substantial amounts of allylic oxidation products besides cyclohexene-oxide The turnover numbers in the range of 2-5 indicate that the reaction is catalytic

The iron complexes **4-6** were found to possess poor activity as catalyst for epoxidation of the above olefins (yield of epoxides <1%). This can be attributed to the facile oxidation of the complexes with iodosylbenzene to give μ-oxo complexes $Fe^{IV}$-O-$Fe^{IV}$ or complex degradation In order to confirm this, an independent experiment was done where slightly more than 0 5 equivalent of PhIO was added to a solution of the complex **5** in $CH_3CN$. A brown solid precipitated out within a few minutes. This was filtered, washed with diethyl

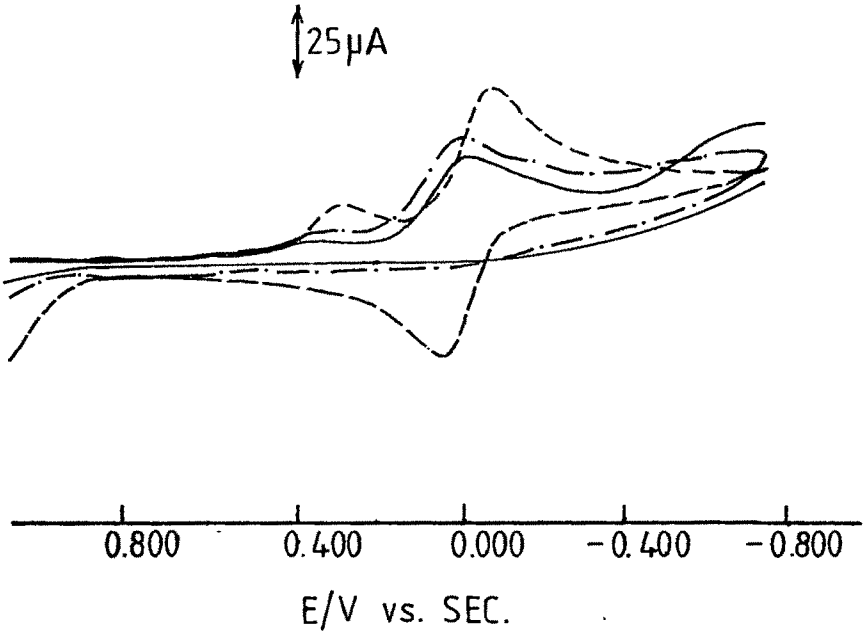



**Figure 2** Cyclic voltammogram of iron complexes in acetonitrile : —— 7; ----------5; ·-·-·-·- 5 after addition of PhIO. Conditions as in Table 2.

ether and dried at room temperature under vacuum. IR spectrum of this complex (7) was very similar to that of the complex **5** except that there is an additional strong band at 850 $cm^{-1}$. This band was assigned to stretching vibration of Fe-O-Fe group [5] Room temperature magnetic susceptibility measurements correspond to value of 4.82 BM per metal centre for this complex. This confirms presence of $Fe^{+4}$ oxidation state in the complex. Further support for this comes from cyclic voltammetric studies of 7 in acetonitrile (Figure 2). It shows two irreversible cathodic peaks at 0.383 V and 0.011 V and is different from the voltammogram of the complex **5** (Figure 2). The peak at 0.383 V was assigned to $Fe^{+4}/Fe^{+3}$ reduction. Addition of PhIO to the $CH_3CN$ solution of **5** also gives a cathodic peak at 0.375 V (Figure 2), similar to that in complex 7. These experiments confirm formation of μ-oxo species in the reaction of iron complexes with PhIO, leading to termination of the catalytic reaction (Eq. 1) and account for their inability to act as epoxidation catalysts.

$$LM^{V}=O \quad + \quad LM^{III} \text{---> } LM^{IV}\text{-O-}M^{IV}L \qquad (1)$$

In case of the chromium complexes **1** and **2** reaction with PhIO causes slow disappearance of the peaks corresponding to $Cr^{+3}/Cr^{+2}$ and $Cr^{+2}/Cr^{+}$ redox couples. In complex **2**, a new couple appears with cathodic peak at 0.500 V and an anodic peak at 0.853 V (Figure 1) This can be attributed to high-valent $Cr^{V}=O$ complex. Thus it is seen from cyclic voltammetric studies that the $Cr^{V}=O$ species (Eq 2) is generated by the reaction of $Cr^{+3}$ with PhIO. The lower catalytic activity of the chromium complexes is probably due to the poor oxygen transfer ability of the $Cr^{V}=O$ complex.

$$LCr^{III} \quad + \quad PhIO \text{ -------> } LCr^{V}=O \quad + \quad PhI \qquad (2)$$

$LCr^{III}$ + PhIO -------> $LCr^{V}=O$ + PhI (2)

$LCr^{V}=O$ + === --------> $LCr^{III}$ +  (3)

Kochi et al.[6] have assigned a partially resolved band in the region 550 nm to $Cr^{V}=O$ in the Uv-vis spectrum of $[(salen)Cr^{V}=O]^{+}$ The complex **2** shows a d-d transition band in the 540 nm region (Figure 3) Reaction of PhIO changes the purple colour of the complex solution to wine red. However, the d-d band due to $Cr^{V}=O$ is not seen due to overlap with the d-d band of the original complex (Figure 3). The $d^5$ iron(III) complexes, in which electronic transitions are both, orbital and spin forbidden, do not show any clear features in their UV-vis spectra.

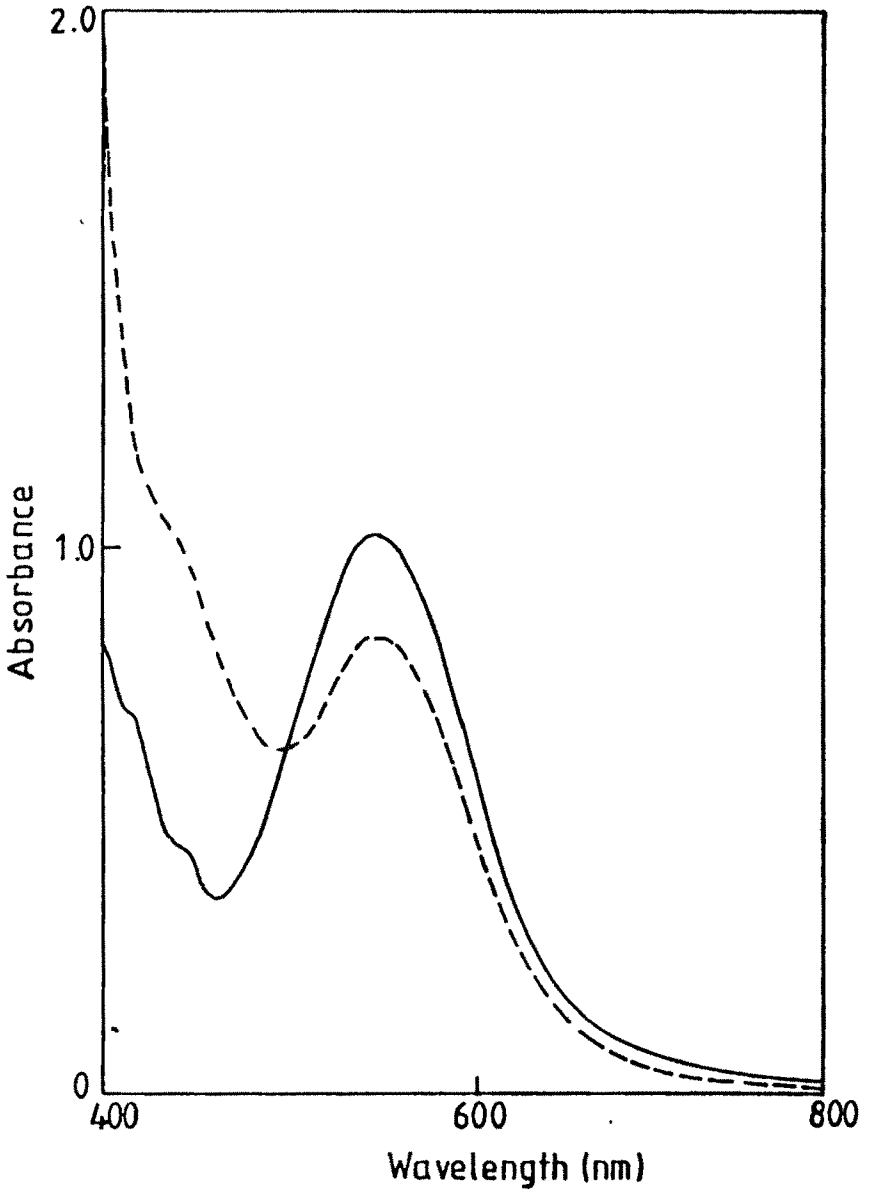



**Figure 3** Uv-vis spectrum of chromium complex in $CH_3CN$-$H_2O$ (1:1) · ——— **2,** 0.5 x $10^{-3}$M; ----------**2** after addition of PhIO, 0.5 x $10^{-3}$M.

## References


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**Table 1** Elemental analyses, conductance and magnetic data for the complexes **1-6**[a]

| Complex | Analysis found (Calc ) % | | | | Conductanc | $\mu_{eff}$ (uncorr.) |
|---|---|---|---|---|---|---|
| | M(Fe/Cr) | C | H | N | $Ohm^{-1}cm^2$ $mol^{-1}$ | B.M. |
| **1** | 16.3(16.6) | 34.4(34.6) | 3.6(3.5) | 13.5(13.4) | - | 2.8 |
| **2** | 12 5(12.7) | 49.7(49.9) | 2.9(2.7) | 10 1(10.3) | 28(90)b | 2.85 |
| **3** | 12.1(12.0) | 52.4(52.7) | 2 8(2.6) | 09.6(09.7) | 16 | 2.9 |
| **4** | 16.0(15.8) | 30 4(30.7) | 4.5(4 3) | 12 2(11.9) | - | - |
| **5** | 13.1(12.9) | 47.5(47.4) | 3.2(3.0) | 09.7(09.8) | 87c | 5 45 |
| **6** | 11.1(11.4) | 50.5(50.2) | 3.2(2 9) | 09.3(09 2) | 33 | 5.61 |

a In $CH_3NO_2$-$CH_3OH$ (7.3), b In $CH_3CN$-$H_2O$ (6.1), c in acetone

**Table 2** Electrode potentials for various complex systems vs SCE[a]

| Complex[b] | Epc (V) | Epa (V) |
|---|---|---|
| **1** | -0.020 | --- |
| | -0.713 | -0 527 |
| **2** | -0 007 | --- |
| | -0.673 | -0.499 |
| **4** | 0.007 | 0.087 |
| | -0 740 | -0 500 |
| **5** | 0.122 | --- |
| | -0 477 | -0 288 |
| **6** | 0.007 | 0.100 |
| | -0.473 | -0.347 |

a $CH_3CN:H_2O$ = 10+10 ml. TBAP 0.1 M.
b 0.07 mmole.

**Table 3** Oxidation of olefins catalyzed by complexes **1-3**[a]

| Olefin | Catalyst | Epoxide Yield[b](%) |
|---|---|---|
| cis-cyclooctene | **1** | 8 |
| | **2** | 8 |
| | **3**[c] | 3 |
| norbornene | **1** | 3 |
| | **2** | 3 |
| styrene | **1** | 5 |
| | **2** | 9 |
| cyclohexene | **1** | 5(7[d], 28[e]) |
| | **2** | 3(3[d], 6[e]) |

a Catalyst PhIO:Olefin mole ratio 1·50·250, catalyst 0.012 mmol, solvent $CH_3CN+H_2O$ = 6+1 ml, time 6h.
b based on the oxidant taken.
c only partially soluble.
d cyclohex-2-en-1-ol
e cyclohex-2-en-1-one.