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Mixed ligand complexes of chromium(III) and iron(III): synthesis and evaluation as catalysts for oxidation of olefins

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Abstract

The mixed ligand complexes $\text{Cr}^{\text{III}}(\text{dpa})(\text{L})\text{Cl}$ and $\text{Fe}^{\text{III}}(\text{dpa})(\text{L})(\text{H}_2\text{O})_n\text{Cl}$ (where dpa = dipicolinic acid, L = ethylenediamine, 2,2-bipyridine or 1,10-phenanthroline, $n = 1$ or 2) were synthesized and characterized by elemental analysis and spectral, magnetic, conductance and electrochemical studies. The complexes were evaluated for their activity as catalysts for the epoxidation of olefins. The chromium complexes catalyzed epoxidation of olefins, viz., norbornene, *cis*-cyclooctene, styrene and cyclohexene with iodobenzene, to give corresponding epoxides. Oxidation of cyclohexene gave allylic oxidation products besides the epoxide. The iron complexes were nearly inactive as epoxidation catalysts under these conditions. Spectrophotometric and electrochemical measurements were used to deduce the cause of low catalytic activity.

Keywords: Oxidation; Epoxidation; Catalyst; Chromium; Iron

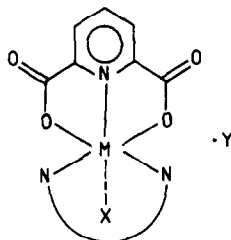
1. Introduction

There is currently much interest in the transition metal-catalyzed oxidation reactions as chemical models for the monooxygenase, cytochrome P-450 [1,2]. The work in this area is aimed at inventing new methods for catalytic oxidation of hydrocarbons in a selective manner under mild conditions [3]. During our work on the development of biomimetic epoxidation systems, we have evaluated several non-porphyrin transition metal complexes as catalysts [4–11].

It was observed that the mixed ligand complexes of ruthenium(III) with dipicolinic acid (dpa) and diamine ligands generate $\text{Ru}^{\text{V}}=\text{O}$ intermediate with a variety of oxidants, viz., PhIO, *t*-BuOOH and dioxygen [10]. The $\text{Ru}^{\text{V}}=\text{O}$ species was capable of epoxidizing olefins efficiently. 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 available for the reaction to occur. This paper reports synthesis and

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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.



Complex	M	N-N	X	Y
1	Cr	en	Cl	–
2	Cr	bpy	Cl	–
3	Cr	phen	Cl	–
4	Fe	en	H ₂ O	Cl, H ₂ O
5	Fe	bpy	H ₂ O	Cl
6	Fe	phen	Cl	H ₂ O

2. Experimental

2.1. Materials and methods

All the reagents were of AR grade and were used as received. The solvents were purified by standard procedures [12]. Iodosylbenzene was prepared by a published procedure [13]. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer. UV–Vis spectra were recorded on Shimadzu UV-160A and IR spectra on Shimadzu IR-408 spectrophotometers. Conductivity measurements were carried out on a Toshniwal conductivity bridge. Magnetic susceptibility measurements were performed at room temperature by the Guoy method using Hg[Co(CNS)₄] as calibrant. Gas chro-

matographic analyses were done on a Shimadzu GC-7A equipped with Shimadzu C-R4A Chromatopac, using FID, Carbowax 20 M, 15% on Chromosorb W column (3 M) and N₂ as carrier gas. An EG and G PAR model 273 potentiostat/galvanostat in conjunction with an 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 electrode, Pt wire counter electrode and Ag wire reference electrode 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 each voltammogram recording. Acetonitrile–water (1:1) was used as the medium for all the electrochemical measurements unless otherwise mentioned.

2.2. Synthesis of complexes

2.2.1. Cr(dpa)(en)Cl (1)

A solution of dipicolinic acid (1 mmol) in ethanol (50 ml) was added dropwise to a stirred solution of CrCl₃ · 6H₂O (1 mmol) in ethanol (50 ml) and the mixture stirred further at room temperature for 1 h. To the resultant deep green solution was added dropwise, ethylenediamine (1 mmol) in ethanol (50 ml). The clear solution was stirred for 1 h, 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 4 h. 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).

2.2.2. 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).

2.2.3. $Cr(dpa)(phen)Cl$ (**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).

2.2.4. $Fe(dpa)(en)(H_2O)_2Cl$ (**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).

2.2.5. $Fe(dpa)(bpy)(H_2O)Cl$ (**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).

2.2.6. $Fe(dpa)(phen)(H_2O)Cl$ (**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).

2.3. 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.

3. Results and discussion

All the complexes are amorphous. The complexes **1–6** gave satisfactory elemental analysis for C, H, N and metal (Table 1). All of them decompose at temperatures above 230°C except **2** which does not melt below 300°C. The conductance for complex **2** in CH_3NO_2 – CH_3OH solvent mixture (7:3) is $28\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ showing that it is a non-electrolyte (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 $16\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$. This shows that in these complexes the Cl 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 the presence of H_2O molecules in the complexes in the solid state which is confirmed by IR spectral data. Moreover, conductance of **5** in acetone, a weakly coordinating solvent, is $87\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$, corresponding to 1:1 electrolytic behaviour. It

Table 1
Elemental analyses, conductance and magnetic data for the complexes **1–6**

Complex	Analysis found (Calc.), %				Conductance ^a ($\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$)	μ_{eff} (uncorr.) BM
	M(Fe/Cr)	C	H	N		
1	16.3 (16.6)	34.4 (34.6)	3.6 (3.5)	13.5 (13.4)	–	2.80
2	12.5 (12.7)	49.7 (49.9)	2.9 (2.7)	10.0 (10.3)	28(90) ^b	2.85
3	12.1 (12.0)	52.4 (52.7)	2.8 (2.6)	9.6 (9.7)	16	2.90
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)	9.7 (9.8)	87 ^c	5.45
6	11.1 (11.4)	50.5 (50.2)	3.2 (2.9)	9.3 (9.2)	33	5.61

^a In CH_3NO_2 – CH_3OH (7:3).

^b In CH_3CN – H_2O (6:1).

^c In acetone.

can be said that in **5**, the sixth coordination site is occupied by a H₂O molecule and the Cl resides outside the coordination sphere in the solid state. However, **6** does not show 1:1 electrolytic behaviour in CH₃NO₂-CH₃OH (Table 1). Complexes **1** and **4** do not dissolve in CH₃NO₂-CH₃OH solvent.

Magnetic susceptibility values for chromium complexes **1–3** lie in the range of 2.8–2.9 BM corresponding to 3 unpaired electrons in the metal centre. This is consistent with the +3 oxidation state of the metal centre in the complexes. μ_{eff} values for iron complexes correspond to 5 unpaired electrons for the +3 oxidation state of iron. Characteristic IR bands due to $\nu_{\text{asymm}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ 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 that coordination of the carboxylic functions is 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 ν_{sym} and ν_{asymm} vibrations of -NH₂ in **1**. In complex **4**, the N-H bands merge with that due to H₂O and a single broad band is observed at 3500–3200 cm⁻¹.

The chromium complexes **1** and **2** show two redox couples in the potential range of 0.0 V to -0.9 V (Fig. 1). The first wave corresponding to the Cr³⁺/Cr²⁺ 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 Cr²⁺/Cr⁺ redox couple. Two redox couples in the same range are observed for the iron complexes **4–6** (Table 2). The first, corresponding to Fe³⁺/Fe²⁺ system, is quasi-reversible for **4** and **6** and is irreversible for **5**. The Fe²⁺/Fe⁺ redox couple is quasi-reversible for the complexes **4–6**.

The potentials for chromium are more negative than those for the iron complexes (Table 2). Further, for both metal systems, the redox potentials with bpy ligand appear at more positive

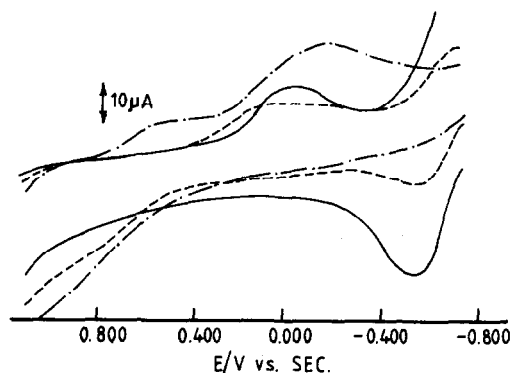


Fig. 1. Cyclic voltammograms of chromium complexes: — **1**; - - - **2**; - · - **2** after addition of PhIO. Conditions as in Table 2.

potentials than those for corresponding en analogues. This trend is expected to be due to the strong σ -donor tendency of the en moiety and the strong π -acceptor ability of bpy ligand.

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. Complex **3** was only partially soluble in the CH₃CN:H₂O (6:1) solvent mixture used for the oxidation reaction. This may be the reason for the lower yield of epoxide using complex **3** as a catalyst. Oxidation of *cis*-cyclooctene, norbornene and styrene exclusively gave corresponding epoxides, whereas,

Table 2
Electrode potentials for various complex systems vs. SCE^a

Complex ^b	E_{pc} (V)	E_{pa} (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 CH₃CN:H₂O = 10 + 10 ml. TBAP 0.1 M.

^b 0.07 mmol.

Table 3
Oxidation of olefins catalyzed by complexes 1–3^a

Olefin	Catalyst	Epoxide yield ^b (%)
<i>cis</i> -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 CH₃CN+H₂O (6+1 ml); time, 6 h.

^b Based on the oxidant taken.

^c Only partially soluble.

^d Cyclohex-2-en-1-ol.

^e Cyclohex-2-en-1-one.

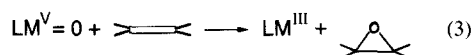
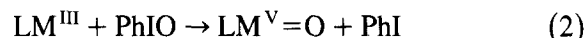
cyclohexene gave substantial amounts of allylic oxidation products in addition to cyclohexene oxide. The turnover numbers in the range of 2–5 indicate that the reaction is catalytic.

The iron complexes 4–6 show poor activity as catalysts 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 CH₃CN. A brown solid precipitated out within a few minutes which was filtered, washed with diethyl ether and dried at room temperature under vacuum. The 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 Fe–O–Fe group [14]. Room temperature magnetic susceptibility measurements correspond to value of 4.82 BM per metal centre for this complex. This confirms presence of Fe⁴⁺ oxidation state in the complex. Further support for this comes from cyclic voltammetric studies of 7 in acetonitrile (Fig. 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 (Fig. 2). The

peak at 0.383 V was assigned to Fe⁴⁺/Fe³⁺ reduction. Addition of PhIO to the CH₃CN solution of 5 also gives a cathodic peak at 0.375 V (Fig. 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.



In case of the chromium complexes 1 and 2, reaction with PhIO causes slow disappearance of the peaks corresponding to Cr³⁺/Cr²⁺ and Cr²⁺/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 (Fig. 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 Cr³⁺ 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.



Kochi et al. [15] 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]⁺.

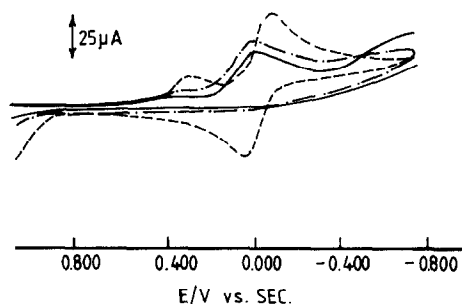


Fig. 2. Cyclic voltammograms of iron complexes in acetonitrile: — 7; --- 5; - · - 5 after addition of PhIO. Conditions as in Table 2.

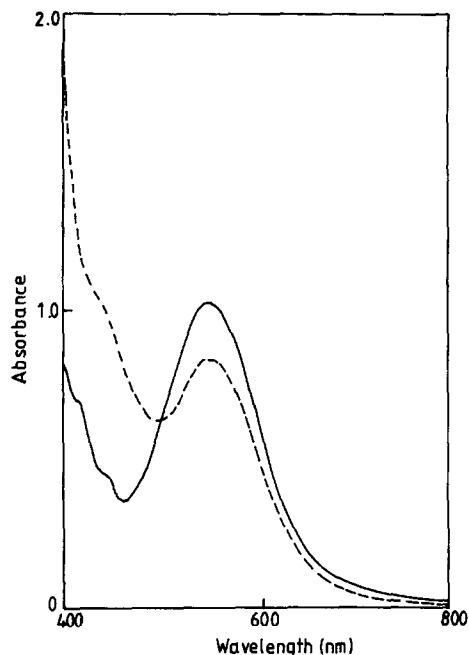


Fig. 3. UV-Vis spectrum of chromium complex in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (1:1): — **2**, 0.5×10^{-3} M; --- **2** after addition of PhIO, 0.5×10^{-3} M.

The complex **2** shows a d-d transition band in the 540 nm region (Fig. 3). Reaction of PhIO changes the purple colour of the complex solution to wine red. However, the d-d band due to $\text{Cr}^{\text{V}}=\text{O}$ is not seen due to d-d band of the original complex (Fig. 3). The d^5 iron(III) com-

plexes being both, spin and orbital forbidden, do not show any clear features in their UV-Vis spectra.

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