

Dinuclear metal complexes of Schiff base ligands as catalysts for oxidation and epoxidation reactions

P S ZACHARIAS*, B SRINIVAS and H ANEETHA

School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

Abstract. Dinuclear copper(II) complexes ($\text{Cu}_2\text{L}^n\text{Cl}_3$), nickel(II) complexes ($\text{Ni}_2\text{L}^n\text{Cl}_3$) and cobalt(II) complexes ($\text{Co}_2\text{L}_2^m\text{Cl}_2$) from Schiff base ligands are synthesised, characterised and used as catalysts for oxidation of 3,5-DTBC to 3,5-DTBQ. ($\text{Cu}_2\text{L}^n\text{Cl}_3$) are found to be more efficient than the other complexes. Dinuclear iron(III) complexes of composition ($\text{Fe}_2\text{L}_2^m\text{Cl}_2$) and ruthenium(III) complexes of composition $\text{Ru}_2\text{L}_2^m\text{Cl}_6(\text{PPh}_3)_2$ and $\text{Ru}_2\text{L}_2^m\text{Cl}_2(\text{PPh}_3)_2$ catalyse epoxidation of styrene and cyclohexene. Catalytic activities of ruthenium(III) complexes are much greater than those of analogous iron(III) complexes.

Keywords. Dinuclear complexes; oxidation, epoxidation, catalyst concentration.

1. Introduction

A number of magnetically interacting dinuclear copper(II) complexes are shown to be catalytically active in the oxidation of 3,5-di-*t*-butyl catechol (3,5-DTBC) in presence of oxygen (Oishio *et al* 1980; Casellato *et al* 1983; Srinivas *et al* 1991). While planar mononuclear copper(II) complexes have little or no catalytic activity, dinuclear planar complexes are catalytically efficient provided the internuclear distance falls in the range of 3.0 to 4.0 Å. In addition, many of the dinuclear copper(II) complexes undergo facile reduction to copper(I) in presence of two electron donors such as ascorbic acid (Oishio *et al* 1980). Compared to dinuclear copper(II) complexes, catalytic activity of analogous dinuclear nickel(II) and cobalt(II) complexes is investigated to a lesser extent.

In recent years transition metal complexes have become quite useful as catalysts for the epoxidation of olefins because of the flexibility in their synthesis and their ability for selective oxidation (Samsel *et al* 1985; Murch *et al* 1986; Jacob *et al* 1989; Jorgensen 1989; Rao *et al* 1994). In epoxidation reactions catalysed by iron(III) complexes using iodosyl benzene as oxygen source, formation of reactive oxo-iron intermediate was proposed (Jorgensen 1989). Catalytic efficiency decreases due to the formation of this species as epoxidation progresses. Formation of such species is facile in mononuclear complexes while it is more difficult in dinuclear complexes. Hence catalytic efficiency of dinuclear systems in epoxidation reactions is expected to be more than that of the mononuclear systems.

In comparison, several ruthenium(II), ruthenium(III) and dioxo ruthenium complexes have been used as catalysts for selective oxidation of primary alcohols to aldehydes and secondary alcohols to ketones (Sharpless *et al* 1976; El-Hendawy *et al* 1992, 1993; Aneetha and Zacharias 1995). Formation of ruthenium(IV) super oxo complexes or oxo ruthenium(V) complexes was suggested during the reaction of

*For correspondence

ruthenium(III) Schiff base complexes with O₂ or iodosyl benzene (Taqi Khan *et al* 1988, 1992). The ruthenium complexes are found to be better catalysts than dioxo ruthenium systems (Dengel *et al* 1990).

It is noteworthy that formation of oxo species decreases the catalytic efficiency of both iron(III) and ruthenium(III) complexes. Dinuclear complexes can minimise formation of such intermediate oxo species which in turn should increase the catalytic efficiency of these complexes. Results on the catalytic activity of some dinuclear copper(II), nickel(II) and cobalt(II) complexes of simple Schiff base ligand systems in oxidation reactions and that of dinuclear iron(III) and ruthenium(III) complexes in epoxidation reactions are discussed in the following sections.

2. Experimental

The ligands L¹ to L⁵ have been prepared by condensation of 2,6-diformyl-4-methyl phenol with appropriate aromatic monoamines (Gagne *et al* 1981; Srinivas and Zacharias 1991). The ligands L⁶ and L⁷ were prepared by reacting 3,3'-disubstituted-4,4'-diamino biphenyl and pyridine 2-aldehyde in 1:2 molar ratio (Rao *et al* 1994). The ligands L⁸ and L⁹ were prepared by the diazo coupling of biphenyl amines with alkyl hydroxylamine (Zacharias and Ramachandriah 1985). The ligand L¹⁰ was prepared by reacting substituted anilines with pyridine 2-aldehyde in absolute ethanol.

Copper(II), nickel(II) and cobalt(II) complexes of ligands L¹-L⁵ were prepared by reacting the ligands with appropriate metal salt and purifying the product. Iron(III) and ruthenium(III) complexes were obtained by reacting ligands in absolute alcohol with metal chlorides under dry nitrogen.

Catalytic activity of complexes in the oxidation of 3,5-DTBC to the corresponding quinone (3,5-DTBQ) was followed by spectroscopic methods. In a typical experiment, a methanolic solution of 3,5-DTBC (0.3 mmol dm⁻³) and copper(II) complex (0.003 mmol dm⁻³) in a 25 cm³ flask was kept under nitrogen. 3,5-DTBQ has a characteristic band at 400 nm which was taken as a measure of the oxidation. Epoxidations were carried out in a Schlenk tube under nitrogen. General procedure involved the following. To a solution of the catalyst (2.5 mM) in acetonitrile was added the alkene (cyclohexene; 1 cm³, 9.8 mM). Iodosyl benzene (0.5 mM) was added to this mixture over a period of 30 min and stirred for 3 hours. The product was distilled and analysed by gas chromatography.

The CHN analyses were carried out on a Perkin-Elmer 240C elemental analyser. IR spectra were recorded on a Perkin-Elmer 283 model in the range 400-200 cm⁻¹. Electronic spectra were recorded on Shimadzu UV 200 S double beam spectrophotometer. The room temperature magnetic susceptibility measurements were carried out on a Bruker BM-6 magnetic susceptibility set-up with a Sartorius digital balance. Catalysis experiments were carried out on a Shimadzu UV 200 S double beam spectrometer. Absorbance was measured at intervals of 10 minutes. The products of the epoxidation reaction were distilled off and analysed by GC using a carbowax 20 column at an injection temperature of 240°C.

3. Results and discussion

3.1. Copper(II), nickel(II) cobalt(II) complexes

Complexes of ligands L¹ to L⁵ were characterised by CHN analytical, IR and spectral

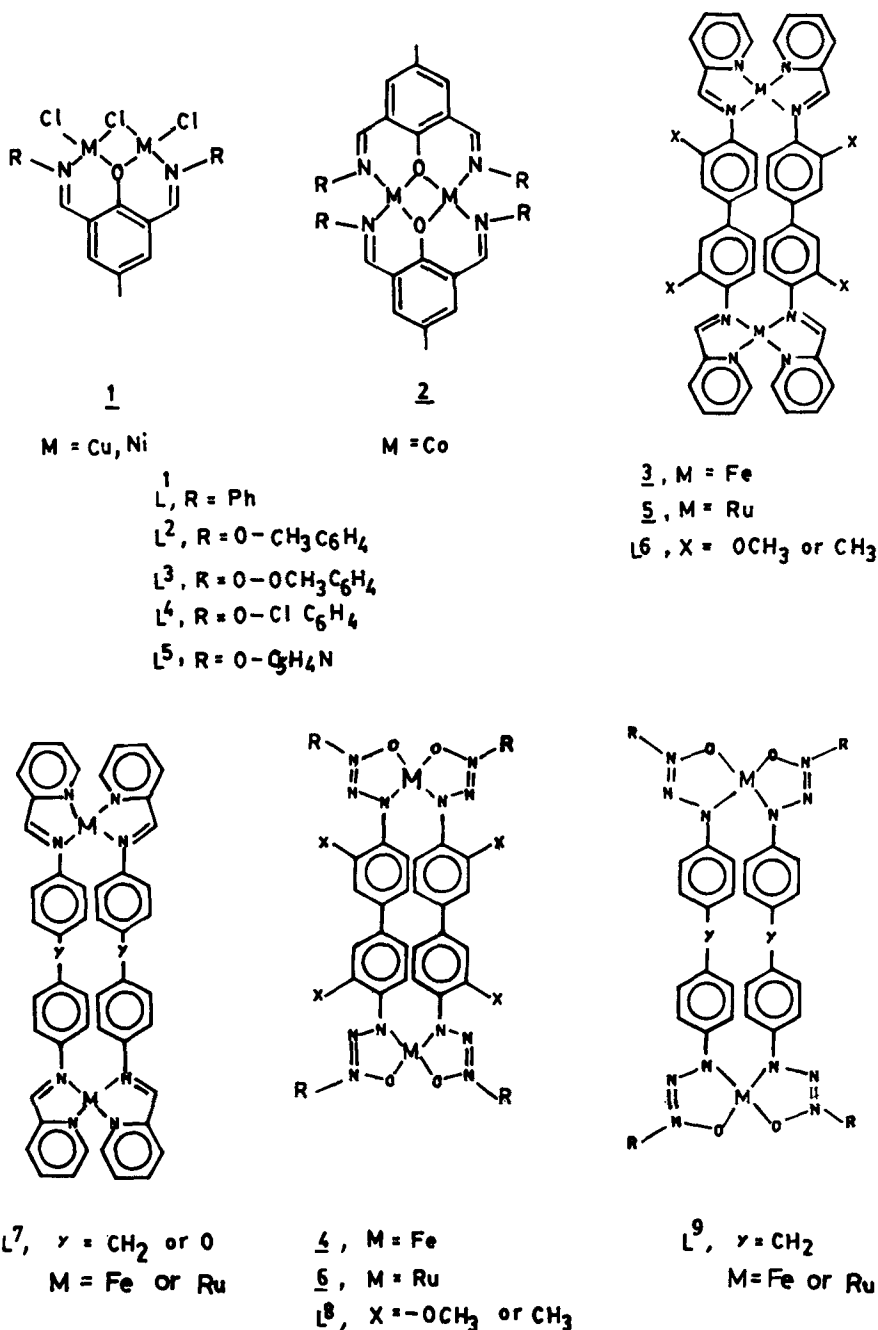


Figure 1. Proposed structures of various dinuclear complexes.

methods. The copper(II) and nickel(II) complexes of these ligands are shown to be dinuclear in nature with a chloro bridge (Srinivas *et al* 1991). The proposed structure of these complexes is shown in structure 1 of figure 1. For convenience they will be

Table 1. IR, electronic spectral and magnetic moment values of dinuclear copper(II), nickel(II) and cobalt(II) complexes.

Complex	IR bands(cm^{-1})			$\lambda(\epsilon)$ (nm)	μ_{eff} (BM)
	C=N	C-O	M-Cl-M		
$\text{Cu}_2\text{L}^1\text{Cl}_3$	1620	1340	320, 300	737(330)	1.30
$\text{Cu}_2\text{L}^2\text{Cl}_3$	1630	1360	320, 300	727(280)	0.83
$\text{Cu}_2\text{L}^3\text{Cl}_3$	1620	1350	325, 300	742(310)	0.93
$\text{Cu}_2\text{L}^4\text{Cl}_3$	1620	1330	330, 290	724(267)	0.95
$\text{Cu}_2\text{L}^5\text{Cl}_3$	1620	1325	320, 300	745(267)	1.0
$\text{Ni}_2\text{L}^1\text{Cl}_3$	1625	1340	325, 300	a	2.92
$\text{Ni}_2\text{L}^2\text{Cl}_3$	1630	1330	320, 295	a	2.82
$\text{Ni}_2\text{L}^3\text{Cl}_3$	1630	1360	300, 295	a	2.81
$\text{Ni}_2\text{L}^4\text{Cl}_3$	1620	1340	325, 300	a	2.64
$\text{Ni}_2\text{L}^5\text{Cl}_3$	1620	1335	325, 290	a	2.84
$\text{Co}_2\text{L}^1\text{Cl}_2$	1620	1350	—	a	4.54
$\text{Co}_2\text{L}^2\text{Cl}_2$	1630	1335	—	a	4.50
$\text{Co}_2\text{L}^3\text{Cl}_2$	1630	1335	—	a	4.80
$\text{Co}_2\text{L}^4\text{Cl}_2$	1625	1340	—	a	4.72
$\text{Co}_2\text{L}^5\text{Cl}_2$	1625	1350	—	a	4.67

^aNo band observed

abbreviated as $\text{M}_2\text{L}^n\text{Cl}_3$. The presence of the chloro bridge is evident from the observation of two IR peaks at 320 and 300 cm^{-1} characteristic of chloro-bridged dinuclear complexes (Estes *et al* 1978). Important IR frequencies are presented in table 1. Electronic spectra of $\text{Cu}_2\text{L}^n\text{Cl}_3$ complexes in dichloromethane exhibit a $d-d$ transition around 720 nm. The position of this band for various complexes is given in table 1. Dinuclear planar copper(II) complexes with chloro bridges are reported to have $d-d$ bands at around 725 nm (Dickson and Robson 1974). Electronic spectra of $\text{Ni}_2\text{L}^n\text{Cl}_3$ complexes show only a high intensity band at ~ 400 nm of ligand origin. Because of this intense absorption band no $d-d$ transition could be observed.

Room temperature magnetic moment values of $\text{Cu}_2\text{L}^n\text{Cl}_3$ complexes are in the range 0.8–1.2 BM and are presented in table 1. The low μ_{eff} values indicate antiferromagnetic type interaction resulting from super-exchange mechanism. Room temperature magnetic moment values per nickel centre in $\text{Ni}_2\text{L}^n\text{Cl}_3$ complexes are in the range 2.7–2.9 BM and are tabulated in table 1. These values are commensurate with a nonplanar geometry, possibly pseudo tetrahedral.

The cobalt(II) complexes of the ligands L^1 – L^5 are of 1:1 stoichiometry and based on analytical and spectral data dinuclear structure 2 shown in figure 1 is proposed. For convenience they will be abbreviated as $\text{Co}_2\text{L}_2^n\text{Cl}_2$. It may be noticed that this structure is different from that of $\text{Cu}_2\text{L}^n\text{Cl}_3$ or $\text{Ni}_2\text{L}^n\text{Cl}_3$ complexes. The important IR frequencies are listed in table 1. The room temperature μ_{eff} values are in the range of 4.5–4.9 BM per cobalt centre expected for pseudo tetrahedral geometry. These values do not indicate any significant magnetic interaction in these cobalt complexes.

3.2 Oxidation reactions

Catalytic activity of $\text{Cu}_2\text{L}^n\text{Cl}_3$ complexes for the oxidation of 3,5-DTBC to 3,5-DTBQ has been examined. The activity for a methanolic solution of 1:100 complex to DTBC ratio was evaluated from the absorbance of the 400 nm band characteristic of 3,5-DTBQ. The conversion of 3,5-DTBC to 3,5-DTBQ was complete in about 90 min in presence of various dinuclear complexes. Time-dependent growth of 3,5-DTBQ in presence of $\text{Cu}_2\text{L}^1\text{Cl}_3$ is shown in figure 2. Catalytic efficiency of various complexes follow the order $\text{Cu}_2\text{L}^4\text{Cl}_3 > \text{Cu}_2\text{L}^2\text{Cl}_3 > \text{Cu}_2\text{L}^3\text{Cl}_3 > \text{Cu}_2\text{L}^5\text{Cl}_3 > \text{Cu}_2\text{L}^1\text{Cl}_3$. To a general approximation, greater catalytic efficiency is observed for dinuclear complexes with lower magnetic moment, that is systems with large magnetic exchange interaction. Similar trends have been observed in several dinuclear systems (Casellato *et al* 1983).

The $\text{Ni}_2\text{L}^n\text{Cl}_3$ and $\text{CoL}_2^n\text{Cl}_2$ complexes were also examined for their catalytic activity in the conversion of 3,5-DTBC. In the case of these complexes conversion is completed over a period of 6–7 hours for 1:100 catalyst to substrate systems. Catalytic activities of selected $\text{Ni}_2\text{L}^n\text{Cl}_3$ and $\text{Co}_2\text{L}_2^n\text{Cl}_2$ complexes are compared in figure 3. Catalytic activity of these systems is significant since there are only few dinuclear nickel

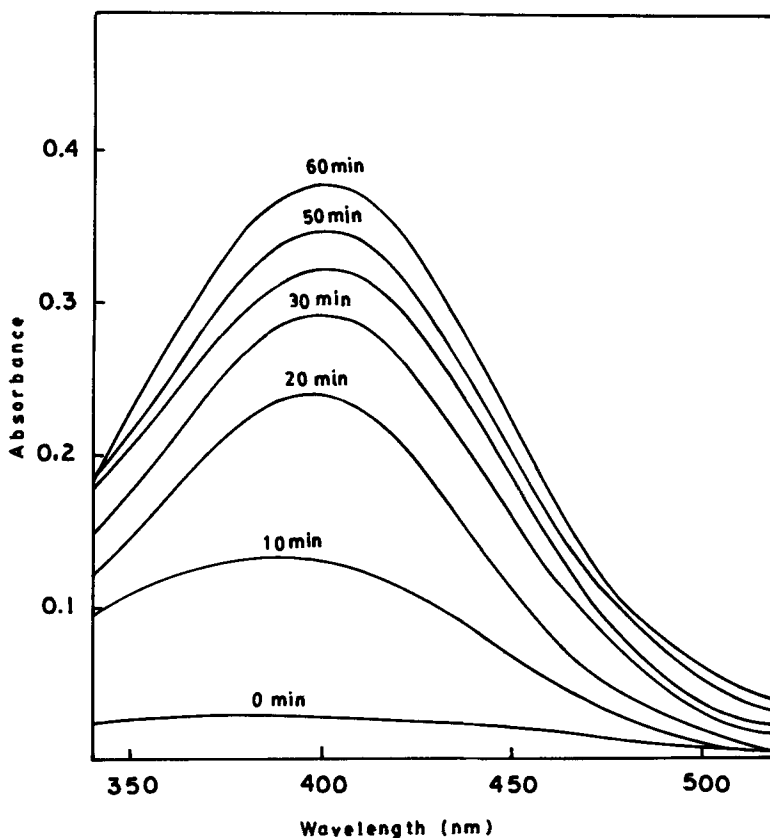


Figure 2. Time-dependent formation of 3,5-DTBQ in the presence of the dinuclear copper(II) complex, ($\text{Cu}_2\text{L}^1\text{Cl}_3$).

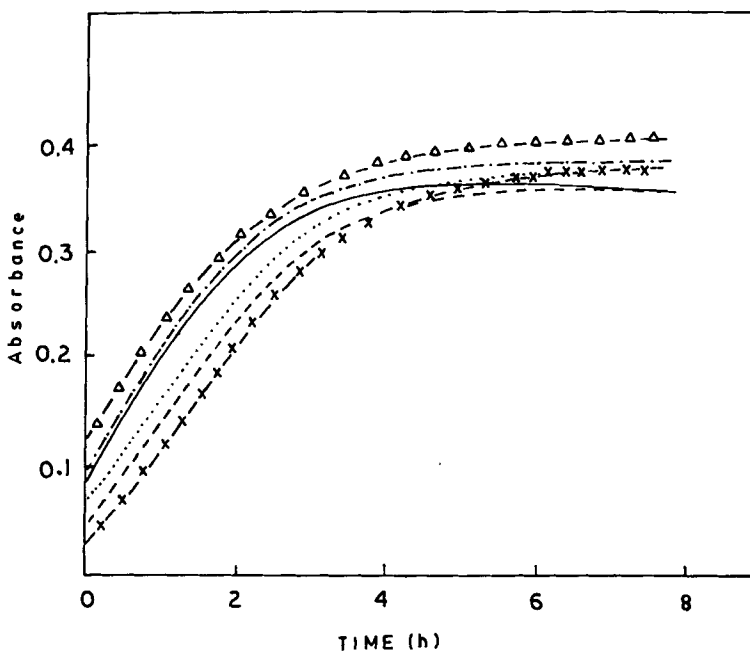


Figure 3. Time-dependent formation of 3,5-DTBC in the presence of dinuclear nickel(II) and cobalt(II) complexes. $\text{Ni}_2\text{L}^1\text{Cl}_3$ (—), $\text{Ni}_2\text{L}^2\text{Cl}_3$ (---), $\text{Ni}_2\text{L}^3\text{Cl}_3$ (.....), $\text{Co}_2\text{L}_2^1\text{Cl}_2$ (—x—), $\text{Co}_2\text{L}_2^2\text{Cl}_2$ (.....), and $\text{Co}_2\text{L}_2^3\text{Cl}_2$ (—Δ—).

Table 2. IR, electronic spectral and magnetic moments of dinuclear iron(III) and ruthenium(III) complexes.

Complex	IR bands (cm^{-1})	λ (nm)	μ_{eff} (BM)
$[\text{Fe}_2\text{L}_2^6\text{Cl}_2]\text{Cl}_4$	1640 1320	500(sh)	5.84
$[\text{Fe}_2\text{L}_2^7\text{Cl}_2]\text{Cl}_4$	1600 1250	570	5.88
$\text{Fe}_2\text{L}_2^8\text{Cl}_2$	1615 1260	570	5.62
$\text{Fe}_2\text{L}_2^9\text{Cl}_2$	1615 1270	520	5.72
$[\text{Ru}_2\text{L}_2^6(\text{PPh}_3)_2]\text{Cl}_6$	1620 1265	560	1.89
$[\text{Ru}_2\text{L}_2^7(\text{PPh}_3)_2]\text{Cl}_6$	1625 1265	520	1.86
$[\text{Ru}_2\text{L}_2^8(\text{PPh}_3)_2]\text{Cl}_2$	1590 1260	760	1.83
$[\text{Ru}_2\text{L}_2^9(\text{PPh}_3)_2]\text{Cl}_2$	1600 1275	780	1.89

and cobalt systems with reported catalytic activity for the oxidation of 3,5-DTBC. It is to be noted that Cu_2LCl_3 complexes are catalytically more efficient than the nickel and cobalt complexes with copper complexes showing strong magnetic interaction compared to nickel and cobalt complexes.

3.3 Iron(III) and ruthenium(III) complexes

Iron(III) complexes of ligands L^6 to L^9 were characterised by CHN analytical, IR and spectral methods. Analytical data agree with the dinuclear structures, which are as

shown in **3** and **4** of figure 1. Iron(III) complexes of ligands L^6 and L^7 are represented as $Fe_2L_2^6Cl_6$ and those of ligands L^8 and L^9 are represented as $Fe_2L_2^8Cl_2$. Important IR bands of these complexes are compiled in table 2. Room temperature magnetic moment values per iron atom are in the range of 5.6–5.8 BM. These values are close to the value of high spin mononuclear complexes ($S=5/2$) implying the absence of measurable antiferromagnetic interactions. Dinuclear iron(III) complexes of biphenyl bridged ligand system are shown to be five coordinate with μ_{eff} values of 5.8 BM (Mary Elizabeth and Zacharias 1985; Rao *et al* 1994). Based on experimental data and by comparison to analogous dinuclear systems five-coordinate square pyramidal type geometry is proposed for the complexes. One chloride ion occupies the fifth coordination position of each iron centre. Electronic spectra of $Fe_2L_2^8Cl_6$ complexes show a shoulder band at ~ 580 nm and $Fe_2L_2^9Cl_2$ complexes have a band at ~ 530 nm. For five coordinate iron(III) systems two $d-d$ transitions are expected at 500 nm and 400 nm while for six coordinate iron(III) complexes all $d-d$ transitions are forbidden.

Ruthenium(III) complexes of ligands L^6 to L^9 were synthesised from $RuCl_3(PPh_3)_2$ and were characterised by CHN analytical and spectral data. Generalised structure is shown in **5** and **6** of figure 1. Complexes of L^6 and L^7 are represented as $Ru_2L_2^6Cl_6(PPh_3)_2$ and those of L^8 and L^9 are represented as $Ru_2L_2^8Cl_2(PPh_3)_2$. The IR spectra of these complexes have several prominent bands which are listed in table 2. Presence of a PPh_3 unit has been confirmed by ^{31}P nmr spectra. Electronic spectra of $Ru_2L_2^6Cl_6(PPh_3)_2$ complexes have a broad band at ~ 500 nm and $Ru_2L_2^8Cl_2(PPh_3)_2$ complexes have a band at ~ 700 nm in dichloromethane. These high intensity bands are assigned to ligand to metal charge transfer (Mukherjee and Chakravorty 1983). The magnetic moment values of these complexes at room temperature are close to a spin only value corresponding to one unpaired electron suggesting low spin d^5 configuration. These values are tabulated in table 2.

3.4 Epoxidation reactions

Catalytic activity of $Fe_2L_2^8Cl_2$ complexes for epoxidation was investigated using cyclohexene and styrene as substrates and iodosyl benzene as oxidant. Catalytic activity calculated based on catalyst concentration is ~ 250 . For analogous mononuclear iron(III) complex of L^{10} this value is ~ 50 . These values are presented in table 3.

Table 3. Catalytic activity based on catalyst concentration for the oxidation of olefins with iodosyl benzene in presence of dinuclear iron(III) and ruthenium(III) complexes.

Complex	Yield of epoxide (%)	
	Cyclohexene	Styrene
$Fe_2L_2^8Cl_2$	170	245
$Fe_2L_2^9Cl_2$	140	245
$[Ru_2L_2^6(PPh_3)_2]Cl_6$	180	310
$[Ru_2L_2^7(PPh_3)_2]Cl_6$	140	280
$[Ru_2L_2^8(PPh_3)_2]Cl_2$	110	475
$[Ru_2L_2^9(PPh_3)_2]Cl_2$	100	460

From these data it is clear that the present dinuclear complexes are several magnitudes more efficient than the mononuclear complexes. The increase in the catalytic efficiency of the dinuclear complexes is partly explained on the basis of reduced possibility of formation of the oxo species of the type $\text{Fe}^{\text{IV}}\text{-O-Fe}^{\text{IV}}$ (Jacob *et al* 1989).

Ruthenium(III) complexes in general are catalytically more active than the iron(III) complexes. Catalytic activity of ruthenium(III) complexes based on catalyst concentration is ~ 400 for styrene and ~ 200 for cyclohexene. These values are presented in table 3. These values are much more than those observed for the corresponding iron(III) complexes. It is known that ruthenium forms less stable superoxo complexes (Taqi Khan *et al* 1988, 1992). Formation of less stable intermediate oxo species may be responsible for the higher catalytic activity of ruthenium(III) complexes in epoxidation reactions.

Acknowledgement

Financial assistance from the Council of Scientific and Industrial Research, and Department of Science & Technology, New Delhi (to BS, HA) is gratefully acknowledged.

References

- Aneetha H and Zacharias P S 1995 *Polyhedron* (submitted)
- Casellato U, Tamburini S, Vigato P A, Destefani A, Vidali M and Fenton D E 1983 *Inorg. Chim. Acta* **69** 45
- Dengel A C, El-Hendawy A M, Griffith W P, Mahoney E O and William D J 1990a *J. Chem. Soc., Dalton Trans.* 737
- Dengel A C, El-Hendawy A M, Griffith W P and Jolliffe J 1990b *Polyhedron* **9** 1751
- Dickson I E and Robson R, 1974 *Inorg. Chem.* **13** 1301
- El-Hendawy A M, Al Kubaisi A H, El-Kourashy A and Shanab M M 1993 *Polyhedron* **12** 2343
- El-Hendawy A M, El-Kourashy A and Shanab M M 1992. *Polyhedron* **11** 523
- Estes W E, Wasson J R, Hall J W and Hatfield W E 1978 *Inorg. Chem.* **17** 3659
- Gagne R R, Spiro C L, Smith T J, Hamann C A, Thies W R and Shiemke A K 1981 *J. Am. Chem. Soc.* **103** 4073
- Jacob M, Bhattacharya P K, Ganeshpure P A, Satish S and Sivaram S 1989 *Bull. Chem. Soc. Jpn.* **62** 1325
- Jorgensen K A 1989 *Chem. Rev.* **89** 431
- Mary Elizabeth J and Zacharias P S 1985 *Indian J. Chem.* **24A** 936
- Mukherjee R and Chakravorty A 1983 *J. Chem. Soc., Dalton Trans.* 955
- Murch B P, Bradley F C and Que L Jr 1986 *J. Am. Chem. Soc.* **108** 5027
- Oishio N, Nishida Y, Ida K and Kida S 1980 *Bull. Chem. Soc. Jpn.* **53** 2847
- Rao C R K, Aneetha H, Srinivas B, Zacharias P S and Ramachandraiah A 1994 *Polyhedron* **13** 2659
- Samsel E G, Srinivasan K and Kochi J K 1985 *J. Am. Chem. Soc.* **107** 7606
- Sharpless K B, Akashi K and Oshima K 1976 *Tetrahedron Lett.* **17** 2503
- Srinivas B, Arulsamy N and Zacharias P S 1991 *Polyhedron* **10** 731
- Srinivas B and Zacharias P S 1991 *Transition Met. Chem.* **16** 521
- Taqi Khan M M, Sreelatha C, Mirza S A, Ramachandraiah G and Abidi S H 1988 *Inorg. Chim. Acta* **154** 103
- Taqi Khan M M, Mirza S A, Shaikh Z A, Sreelatha C, Paul P, Shukla R, Srinivas D, Rao A, Abidi S H, Bhatt S D and Ramachandraiah G 1992 *Polyhedron* **11** 1821
- Zacharias P S and Ramachandraiah A 1985 *Polyhedron* **4** 1013