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CATALYTIC OXIDATION OF TWO-ELECTRON DONORS BY DINUCLEAR COPPER(II), NICKEL(II) AND COBALT(II) COMPLEXES AND EPOXIDATION OF OLEFINS USING IRON(III) COMPLEXES

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Abstract—Dinuclear copper(II), nickel(II), cobalt(II) and iron(III) complexes derived from the Schiff base ligands obtained from the condensation of 3,3′-dimethyl-4,4′-diaminobiphenyl and pyridine-2-aldehyde and mononuclear iron(III) complexes of Schiff bases from substituted anilines and pyridine-2-aldehyde have been synthesised. Conductivity measurements on dilute solutions revealed that the dinuclear complexes are 1 : 4 electrolytes while the mononuclear complexes are 1 : 2 electrolytes. The geometry of the complexes is assigned based on spectral and magnetic susceptibility values. Catalytic activity of these complexes for the oxidation of two-electron donors such as 3,5-di-t-butylcatechol (3,5-DTBC) and ascorbic acid is examined. Dinuclear iron(III) complexes show greater activity than the mononuclear complexes for the epoxidation of olefins, namely cyclohexene and styrene using iodosyl benzene as oxygen source.

A number of dinuclear transition metal complexes where the metal ions are in close proximity have been synthesised and characterised because of their interesting spectral, magnetic, electron transfer, and catalytic properties which are markedly different from the analogous mononuclear complexes.[1–3] Out of the large number of bridged dinuclear systems, only a few biphenyl bridged systems are known.[4,5] One such system is obtained from bis[3,3′-dimethoxy-4,4′-bis(3-methyl-triazene-3-oxide)biphenyl] and the copper–copper distance in the dicopper complex is *ca* 12 Å. The geometry at the copper(II) centres is distorted square planar with D_{2d} point group.[6] The torsional angle between the two phenyl planes in each biphenyl bridge is *ca* 26° which results in an inclination of 70° between the coordination planes of the two copper centres.

It has been shown that magnetically interacting dinuclear complexes are catalytically active for the oxidation of two-electron donors such as 3,5-di-t-butylcatechol (3,5-DTBC) and ascorbic acid.[7–9] The proposed pathway for the electron transfer between ascorbic acid and dinuclear copper(II) complex involves a 'steric match' between the donor and the acceptor[7] which necessitates the metal–metal distance to be *ca* 3–4 Å. While planar mononuclear copper(II) complexes have little or no catalytic activity, dinuclear complexes are catalytically efficient. It becomes clear that dinuclear complexes of biphenyl bridged ligand systems will behave more like mononuclear complexes in catalysis experiments because of the large metal–metal distance. In addition, transition metal complexes

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have become important catalysts for the epoxidation of olefins because of the ability of metal complexes for selective oxidation, and the flexibility in the synthesis of complexes with specific structures.[10–16]

Therefore, it was of interest to investigate the catalytic activity, including the epoxidation of some new dinuclear copper(II), nickel(II), cobalt(II) and iron(III) complexes of biphenyl bridged ligand systems along with some mononuclear iron(III) complexes. This paper presents and discusses results on these dinuclear and mononuclear complexes of Schiff base ligands from 3,3′-dimethyl-4,4′-diaminobiphenyl and pyridine-2-aldehyde.

EXPERIMENTAL

Synthesis of ligand L^1

The ligand L^1 was obtained by reacting the diamine, 3,3′-dimethyl-4,4′-diamino biphenyl and pyridine-2-aldehyde in 1 : 2 molar ratio. In a typical procedure, 20 mM of the diamine was dissolved in absolute ethanol (50 cm^3) and 40 mM of pyridine-2-aldehyde was added in absolute alcohol (50 cm^3) and the mixture was refluxed for 3–4 h. The resulting yellow solid was filtered and washed with absolute alcohol. This ligand was used for the synthesis of the complexes without further purification.

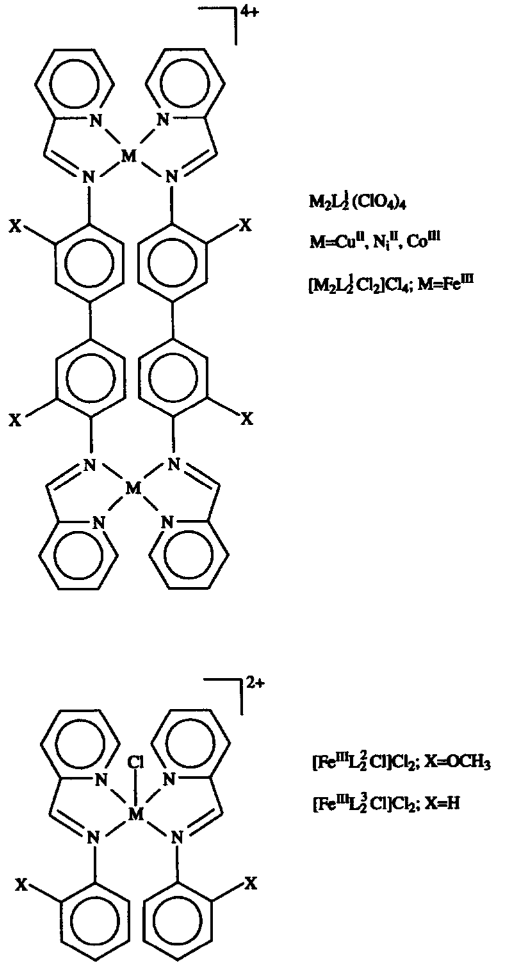

Fig. 1. Structures of dinuclear and mononuclear complexes.

Synthesis of complexes

To a suspension of the ligand L^1 (0.390 g, 1 mM) in absolute ethanol, $Cu(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1 mM) in absolute alcohol was added and the mixture was refluxed for 3 h. The resulting dark brown solid was filtered, washed with alcohol and dried *in vacuo* for 8 h.

Similar procedure was used for the analogous cobalt(II) and nickel(II) complexes by using their respective metal perchlorates. The iron(III) complexes were obtained by the same procedure but the experiments were conducted under dry nitrogen using anhydrous ferric chloride.

Mononuclear iron(III) *complexes*

To a solution of the substituted anilines (3 mM) and pyridine-2-aldehyde (3 mM) in absolute ethanol (50 cm^3), $FeCl_3$ (0.162 g, 1 mM) was added while refluxing. The reaction mixture was refluxed for 4 h. A black product was obtained upon keeping the reaction mixture overnight at room temperature.

Epoxidation of olefins

Epoxidations were carried out in a Schlenk tube under nitrogen. To a solution of the catalyst (iron(III) complex; 2.5 mM) in acetonitrile was added the alkene (cyclohexene; 1 cm^3, 9.8 mM). Iodosylbenzene (0.110 g; 0.5 mM) was added to this mixture over a period of 30 min. The mixture was stirred at ambient temperature for 3 h. The product was distilled off and analysed by GC using a carbowax 20 column (injection temperature 240°C).

Physical measurements

The carbon, hydrogen, and nitrogen analyses were carried out on a Perkin–Elmer 240C elemental analyser. IR spectra were recorded on a Perkin–Elmer IR-283 spectrophotometer in KBr pellets. Electronic absorption spectra were recorded on Schimadzu UV-200S double beam spectrophotometer. Magnetic susceptibility measurements were carried out by the Faraday method, at ambient temperature using a CAHN magnetic balance setup. Diamagnetic corrections were made using Pascal's constants.[17] Epoxides were estimated using a Shimadzu GS 14A Gas Chromatograph (GC column (3M), carbowax 20M, 15% on Chromosorb W, carrier gas nitrogen, detector FID, injection temperature 240°C). Conductivity experiments were done on CM-82T Elico conductivity meter at 25°C.

Catalysis experiments were monitored on a Perkin–Elmer UV–vis spectrophotometer with a Lambda-3B data station. Experiments were carried out using methanol as solvent. In a generalised procedure a MeOH solution of 3,5-DTBC (0.5 mM) and the copper(II) complex (0.005 mM) in a 50 cm^3 standard flask was kept under N_2. 3,5-DTBQ has a characteristic absorption at 400 nm which was taken as a measure of the quinone formation [ε (mol^{-1} dm^3 cm^{-1}) = 1900 in MeOH].[18] Absorbance was measured at 30 min intervals immediately after exposing the solution to air. A similar procedure was adopted for reactions with ascorbic acid, the *d–d* band being monitored.

RESULTS AND DISCUSSION

All of the complexes were characterised by C, H and N analytical data and other spectral methods. IR spectra of the complexes showed bands at 1620 cm^{-1} corresponding to the coordinated azomethine C═N stretching and at 1330 cm^{-1} corresponding to the coordinated C═N stretching of the pyridyl ring. All the perchlorate complexes gave two bands at 1100 cm^{-1} and 625 cm^{-1} characteristic of ionic perchlorates. The analytical data are presented in Table 1. Conductivity values for the dinuclear complexes in DMF are in the range of 280–300 ohm^{-1} cm^2 mol^{-1} indicating they are 1 : 4 electrolytes. For the mononuclear iron(III) complexes the values are in the range 145–160 ohm^{-1} cm^2 mol^{-1}. The conductivity values along with some important IR frequencies are presented in Table 2. The diamine complexes are dinuclear since the analogous dicopper(II) complexes obtained from triazene-1-oxide ligands are structurally confirmed to be dinuclear.[6] This has further been supported by the high solubility of these complexes in organic solvents.

Magnetic and spectral data

Magnetic moment values per metal ion at room temperature are close to the corresponding mononuclear complexes implying the absence of measurable antiferromagnetic interaction between the two metal ions in the complexes. These values are presented in Table 2. The μ_{eff} value of copper(II) complex is 2.02 BM. The monomeric complexes of the present pyridine-2-aldimines are essentially planar.[19] Some complexes of pyrrole-2-aldimine are also shown to be planar with bands at 530 nm and 409 nm. But the geometry is sensitive to the nature of R group on the azomethine nitrogen. For example, for copper(II) complexes it was observed that when R is changed from *n*-propyl to t-butyl, absorption band shows a red shift of *ca* 3000 cm^{-1}, due to distortion towards tetrahedral geometry. For pseudotetrahedral pyrrole-2-aldimine complexes the band is observed at 645 nm.[20] For the present copper(II) complex, the band is at 740 nm with an additional band at 370 nm. Since the R group is replaced by bulkier biphenyl moiety tetrahedral distortion is expected to be more and hence a larger red shift is expected in the band position for the present complex. This is indeed observed. For analogous biphenyl bridged dinuclear complexes with distorted planar geometry the electronic absorption band is at 900 nm.[4]

The dinuclear nickel(II) complex has a μ_{eff} value of 2.94 BM and is comparable to the value of monomeric pseudotetrahedral complexes of pyrrole-2-aldimine and salicylaldimine complexes.[20] Planar

Table 1. Analytical data for the dinuclear copper(II), nickel(II), cobalt(II), iron(III) and mononuclear iron(III) complexes

	C, H and N analytical data Found (Calc)		
Complex	C	H	N
$[Cu_2L^1_2](ClO_4)_4$	47.3 (47.8)	3.6 (3.4)	8.7 (8.6)
$[Ni_2L^1_2](ClO_4)_4$	48.5 (48.2)	3.9 (3.4)	8.8 (8.6)
$[Co_2L^1_2](ClO_4)_4$	49.0 (48.6)	3.2 (3.4)	8.1 (8.6)
$[Fe_2{}^{III}L^1_2Cl_2]Cl_4$	56.3 (56.5)	5.4 (4.0)	9.3 (10.1)
$[Fe^{III}L^2_2Cl]Cl_2$	52.6 (52.9)	3.8 (4.1)	9.3 (9.5)
$[Fe^{III}L^3_2Cl]Cl_2$	53.4 (54.4)	4.0 (3.8)	10.0 (10.6)

Table 2. Spectral, magnetic and conductivity data on dinuclear copper(II), nickel(II), cobalt(II), iron(III) and mononuclear iron(III) complexes

Complex	Electronic spectral data λ/nm (ε/mol^{-1} dm^3 cm^{-1})	Characteristic IR bands (cm^{-1})	Magnetic moment μ_B (BM)	Conductivity data[a]
$[Cu_2L^1_2](ClO_4)_4$	740 (sh), 370	1610, 1340 1100, 625	2.02	284
$[Ni_2L^1_2](ClO_4)_4$	580 (2700), 530 (sh) 350	1620, 1320 1120, 625	2.94	292
$[Co_2L^1_2](ClO_4)_4$	670 (313), 606 (285) 597 (287), 350	1640, 1310 1100, 625	4.07	275
$[Fe_2{}^{III}L^1_2Cl_2]Cl_4$	1000 (sh), 500 (sh) 360	1640, 1320	5.84	298
$[Fe^{III}L^2_2Cl]Cl_2$	560 (sh), 340	1620, 1310	5.87	149
$[Fe^{III}L^3_2Cl]Cl_2$	590 (716)	1640, 1320	5.99	162

[a] Measured in 10^{-3} M DMF solutions, units: ohm^{-1} cm^2 mol^{-1}.

nickel(II) complexes are diamagnetic. Nickel in tetrahedral geometry shows bands at 910 nm and another with splitting in the region 830–550 nm. For the present nickel(II) complex, a band at 580 nm was observed besides a shoulder at 1000 nm to confirm pseudotetrahedral geometry.

The dinuclear cobalt(II) complex has a μ_{eff} value of 4.07 BM. Although μ_{eff} values of high spin octahedral and high spin tetrahedral complexes overlap considerably, tetrahedral complexes have generally low μ_{eff} values, often in the range 4.2–4.5 BM, while octahedral complexes have a value around 4.8 BM. The μ_{eff} value of the present complex is close to that of tetrahedral geometry. Pseudotetrahedral cobalt(II) complex has a visible band whose components lie in the range 470–625 nm. The other transitions are generally in the far IR region.[20,21] The present cobalt(II) complex gives a complex envelope consisting of three bands at 670, 606 and 597 nm in agreement with pseudotetrahedral geometry.

The dinuclear iron(III) complex has a μ_{eff} value of 5.84 BM. This shows that the complex is high spin with ground-state configuration of $S = 5/2$. This ground-state configuration is possible for both five and six coordinate geometry. Iron(III) complexes of square pyramidal geometries are reported to have μ_{eff} values of *ca* 5.8 BM.[22] Some dinuclear iron(III) complexes of biphenyl bridged ligand systems are shown to be five coordinate[5] with a μ_{eff} value of *ca* 5.83 BM. Five coordinate square pyramidal type geometry is proposed for the iron centre with one chloride ion each occupying the fifth position. The electronic spectra of this shows shoulders at 1000 nm and 500 nm. For five coordinate iron(III) systems two reasonably intense *d–d* transitions are expected[23] at *ca* 500 and 400 nm. For six coordinate iron(III) complexes all *d–d* transitions are forbidden and hence generally absorption bands are not observed.

The monomeric $[Fe^{III}L^2_2Cl]Cl_2$ and $[Fe^{III}L^3_2Cl]Cl_2$ complexes have μ_{eff} values of 5.87 and 5.99 BM, respectively. These complexes also have electronic spectra similar to the dinuclear systems. Therefore, a five coordinate geometry is proposed for these complexes.

Catalytic activity of the copper(II), *nickel*(II) *and cobalt*(II) *complexes*

All the complexes were examined for catalytic activity in the oxidation of 3,5-DTBC by O_2 to the quinone DTBQ, formation of which is monitored by measurement of 400 nm ($\varepsilon = 1900$ mol^{-1} dm^3 cm^{-1}) absorption band characteristic of 3,5-DTBQ. Though the complete mechanism of the catalytic process is not yet established, the catalytic activity of the dinuclear complexes is suggested to involve a weak 1:1 adduct between the complex and the substrate which requires the metal–metal distance to be *ca* 3 Å. This adduct reacts with dioxygen to form the starting dicopper(II) complex and the oxidised substrate. Antiferromagnetically coupled systems are catalytically more active in the DTBC to DTBQ oxidation. Figure 2 gives a comparison of activity of the copper(II), nickel(II) and cobalt(II) dinuclear complexes. Cobalt(II) complex shows marginal activity even after 24 h. In the case of the copper(II) complex *ca* 60% conversion is observed in 24 h while only 25% DTBQ is formed for the same period in the case of nickel(II) complex.

Since the intermetallic distance in these dinuclear

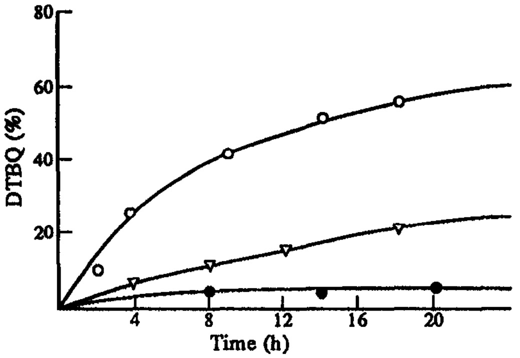

Fig. 2. Time dependent formation of 3,5-DTBQ in the presence of dinuclear copper(II) (○), nickel(II) (▽) and cobalt(II) (●) complexes.

complexes is 12 Å, any adduct formation with DTBC is not possible. Also there is no evidence for antiferromagnetic type interaction in these complexes. Therefore, in the catalysis experiments the metal centre is expected to behave as an independent unit, that is to say as mononuclear systems. Copper(II) complexes can be active because of pseudotetrahedral distortion. The order of catalytic efficiency for the dinuclear complexes is $Cu^{II} > Ni^{II} > Co^{II}$.

Reaction with ascorbic acid

Since the copper complex was a better catalyst in the conversion of DTBC, its reaction with ascorbic acid was examined under nitrogen.

The reduction process was monitored by measuring the changes in absorbance of the *d–d* bands of the complexes. Figure 3 shows the spectral change due to the addition of ascorbic acid. The *d–d* band at 740 nm disappears on addition of ascorbic acid under nitrogen, reappearing when the solution is exposed to air. It has been shown[7] that only copper(II) complexes with distorted tetrahedral structure are reduced to copper(I) by ascorbic acid or 3,5-DTBC. Planar copper(II) complexes are not reduced by these two-electron donors. Reduction of copper(II) complexes by ascorbic acid is therefore indirect evidence for the distorted tetrahedral structure of the complexes. This has been inferred from spectral data (*vide supra*).

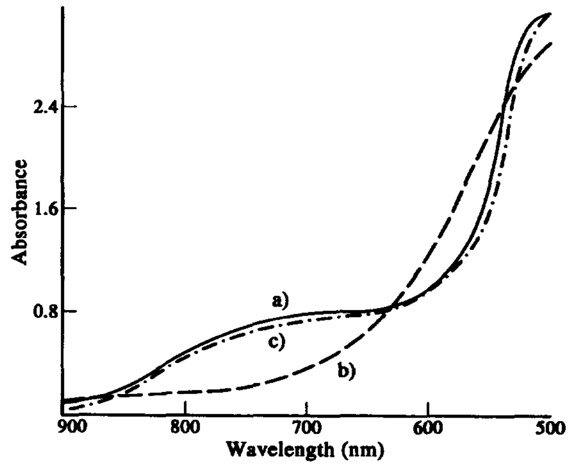

Fig. 3. Absorption spectra of dicopper(II) complexes in the presence of ascorbic acid: (a) complex alone (——); (b) complex + ascorbic acid under nitrogen (— — —); (c) solution (b) under air (— · — · —).

Epoxidation reactions

In epoxidation reactions catalysed by iron(III) complexes using iodosylbenzene as oxygen source, reactive oxo-iron is formed as an intermediate.[12,16] Catalytic efficiency decreases due to the possible formation of Fe^{IV}—O—Fe^{IV} species as epoxidation progresses. Formation of such species is facile in mononuclear complexes while it is more difficult in dinuclear complexes. Hence, the catalytic efficiency of dinuclear systems in epoxidation reactions will be more than those of the mononuclear systems. To generalise this, two mononuclear iron(III) complexes and a corresponding dinuclear iron(III) complex have been used for epoxidation of styrene and cyclohexene.

All three iron(III) complexes have been studied for their activity using both the substrates and the results are presented in Table 3. In comparison to the mononuclear complexes, the dinuclear complex is shown to be a more effective catalyst for the formation of epoxide. The yields are improved by *ca* 40% when the reactions are carried out for 24 h in comparison to the products obtained for reactions that are carried out for 3 h. No further conversions occur after 24 h. The epoxidation reaction occurs *via* an oxo-iron species as suggested in the case of iron porphyrin and some iron Schiff base systems.[12,16] The formation of Fe^{IV}—O—Fe^{IV} species is suggested to be the reason for the termination of catalytic activity. The possibility of formation of this species is less in the case of dinuclear complexes and hence they are more effective catalysts compared to the mononuclear complexes.

Conclusions

The catalytic efficiency of the dinuclear complexes are in the order $Cu^{II} > Ni^{II} > Co^{II}$ for the oxidation of two electron donors such as 3,5-DTBC and ascorbic acid. The dinuclear iron(III) complex is a better catalyst for epoxidation of styrene and

Table 3. Oxidation of olefins with iodosylbenzene in the presence of various iron(III) complexes at room temperature

Complex	Substrate	Time (h)	Yield of epoxide[a] (%)
$[Fe_2^{III}L_2^1Cl_2]Cl_4$	Styrene	3	133.47
	Cyclohexene	3	128.65
$[Fe^{III}L_2^2Cl]Cl_2$	Styrene	3	58.49
	Cyclohexene	3	56.28
$[Fe^{III}L_2^3Cl]Cl_2$	Styrene	3	57.92
	Cyclohexene	3	54.73

[a] Yields based on the catalyst concentration measured at 25°C.

cyclohexene than the corresponding mononuclear iron(III) complexes.

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