Synthesis of hexa-aza macrocyclic ligand complexes of manganese(III), iron(III) and cobalt(III) and their evaluation as epoxidation catalysts

P B Samnani, V Manjula & P K Bhattacharya
Chemistry Department, Faculty of Science, M.S. University of Baroda, Vadodara 390002, India
Received 27 July 1996; revised 27 May 1997

Complexes of manganese(III), iron(III) and cobalt(III) with the macrocyclic ligands derived from 2,3-butanedione and an aliphatic amine, diethylenetriamine, have been synthesized and characterized. These have been evaluated as catalysts for epoxidation of olefins using iodosylbenzene as oxidant.

Several studies of oxygenation of hydrocarbons have been carried out using metal complexes as catalysts to understand the mechanism of cytochrome P-450 catalyzed biological oxygenation processes. Studies of synthetic models mimicking cyt P-450 fall into two broad categories, namely, those involving metal-porphyrins and those involving non-porphyrinic complexes. Non-porphyrinic complexes used are mainly of open ligands, though a macrocyclic ligand complex is a closer model to cyt P-450. Very few studies have been devoted to non-porphyrinic macrocyclic ligand complex models, except some recent reports of oxidation studies using iron(II), iron(III), ruthenium(II), ruthenium(III), cobalt(II) and nickel(II) cyclam and related complexes.

This note reports synthesis of a hexa-aza macrocyclic ligand by condensation of 2,3-butanedione with the aliphatic amine, diethylenetriamine, and preparation of complexes of manganese(III), iron(III) and cobalt(III) with the macrocyclic ligand. The complexes have been characterized and used as catalysts for epoxidation of olefins.

Experimental
2,3-Butanedione (Merck), diethylenetriamine, sodium tetraphenylborate, sodium perchlorate, tetrabutylammonium iodide and iodosylbenzene (Fluka) were used as received. All other reagents used were of AR grade and were used as received. Methanol for synthesis was super dried and stored over 4A molecular sieves.

Acetonitrile for catalysis was distilled from P2O5 and stored over 4A molecular sieves. Iodosylbenzene (PhIO) was obtained using the literature method. Tetrabutylammonium perchlorate (TBAP) for cyclic voltammetric studies was prepared from tetrabutylammonium iodide and sodium perchlorate, and was recrystallized thrice in ethanol-water solvent mixture.

Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. A Perkin Elmer Lambda 15 spectrophotometer was used for UV-vis measurements and IR studies were carried out on a Shimadzu 408 spectrophotometer. Room temperature magnetic measurements were carried out by Gouy method using Hg[Co(SCN)4] as standard. Gas chromatographic analyses were performed on a Shimadzu 7A instrument equipped with C-RIB chromatopac, using FID, carbowax 20M 15% on chromosorbe W column (3M) and N2 as the carrier gas. An EG & G PAR model 175 Programmer in conjunction with model 174 Polarographic Analyzer and model 303 system and RE 0089 XY Recorder was used for electrochemical measurements. A three electrode system, comprising platinum disc as working electrode, Pt wire as auxiliary electrode and Ag/AgNO3 as reference electrode was used. The solutions were 0.1 M in TBAP as the supporting electrolyte.

Synthesis of complexes
The general procedure followed for the synthesis of the complexes 1-3 is given below. Super dry method was used for all the syntheses.

To 50 ml methanol solution containing 1.22 x 10⁻³ M of amine was added dropwise. 50 ml methanol solution of 1.2 x 10⁻³ M 2,3-butanedione, with vigorous stirring. The solution was then refluxed for 30 mm whereupon it turned yellow. Refluxing was
Table I — Elemental analyses and magnetic moments for complexes 1-3

<table>
<thead>
<tr>
<th>Complex</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>(\mu_{\text{eff}}) (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>79.4 (80.1)</td>
<td>6.5</td>
<td>6.9</td>
<td>4.81</td>
</tr>
<tr>
<td>2</td>
<td>81.0 (80.1)</td>
<td>6.2</td>
<td>6.7</td>
<td>3.76</td>
</tr>
<tr>
<td>3</td>
<td>79.2 (79.9)</td>
<td>6.4</td>
<td>6.8</td>
<td>4.72</td>
</tr>
</tbody>
</table>

stopped and to the warm ligand solution, 20 ml methanol solution of metal salt \((1.2 \times 10^{-3} \text{ M})\) \((\text{MnCl}_2 \cdot 4\text{H}_2\text{O}, \text{FeCl}_3, \text{CoCl}_2 \cdot 4\text{H}_2\text{O})\) was added dropwise with stirring and then the reaction mixture was refluxed for 25 h. The resulting dark solution was cooled and \(3.7 \times 10^{-6} \text{ M}\) of \(\text{NaBPh}_4\) salt was added to it. The dark complex thus precipitated was suction filtered, washed with the minimum volume of cold, dry, methanol and vacuum dried at room temperature.

**Epoxidation studies**

All the oxidation reactions were carried out in a Schlenk tube under high purity nitrogen atmosphere and at room temperature. For a typical catalysis study, 0.01 mmol of catalyst dissolved in 3 ml acetonitrile was mixed with 2.5 mmol of olefin in 3 ml acetonitrile. Nitrogen was slowly bubbled through this mixture for 10 min, 0.5 mmol of \(\text{PbIO}\) was added and the mixture stirred under nitrogen atmosphere for 6 h. A known amount of suitable internal standard was added to this and the reaction mixture analyzed by GC for products.

**Results and discussion**

The high dilution method has been used in the synthesis of the macrocyclic ligands to avoid polymerization. The reaction leading to the formation of the cyclic ligand is shown below (Scheme 1).

Solubility of the complexes of the macrocyclic ligand is very high in methanol and a large counter ion, \(\text{BPh}_4^-\), is required to precipitate them. The isolated complexes can be assigned the following structure (I).

Table 1 shows elemental analyses for these complexes, which correspond to the expected formulae. IR spectra for all the complexes were broadly similar.

They showed absence of -\(\text{NH}_2\) and \(>\text{C}=\text{O}\) stretching vibrations in the region 3200 and 1700 cm\(^{-1}\) respectively, indicating formation of macrocycles. Strong bands in the region of 1645 - 1625 cm\(^{-1}\) confirm presence of imine linkages. Magnetic susceptibility values for the complexes correspond to their +3 oxidation state (Table 1).

All the complexes 1-3 act as catalysts for epoxidation of olefins (Table 2). Complexes 1-3 are expected to be distorted octahedral, with two-\(\text{NH}\) on axial sites, hence, as observed, the hexa-aza complexes are expected poor epoxidation catalysts due to nonavailability of vacant sites for reaction. The weak catalytic activity of the hexa-aza complexes may be because the two axial nitrogens are weakly bound to metal ion and can easily be displaced either by solvent or by the oxidant. Further, for complexes 1-3, change of metal ion does not affect the epoxidation yield for cis-cyclooctene (Table 2).
Table 2 — Complexes 1-3 as epoxidation catalysts

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Complex</th>
<th>Epoxide yield % (PhIO based)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norbornene</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>1</td>
<td>6(22b, 11c)</td>
</tr>
<tr>
<td>Styrene</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>cis-Cyclooctene</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>cis-Cyclooctene</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>cis-Cyclooctene</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

* Cat PhIO : Olefin mole ratio = 1:50:250, cat = 0.01 m mol

Complex 3 does not show any characteristic absorption in acetonitrile from 300 to 700 nm. Complexes 1 and 2 both show absorptions at 364 nm. Addition of PhIO to the solution of 1-3 does not generate any new absorption band and the original absorptions remain intact. Cyclic voltammetry of the complexes 1-3 in water-dioxane (1:1 v/v) does not show any clear discernible feature. Complexes 1-3 show no redox peak in the 1st cathodic cycle from 0.00 V to -1.00 V. In the anodic cycle from -1.00 to +1.00 V, a diffused redox peak is seen at +0.62 V, for which the corresponding reduction wave is not observed. Complexes 1-3 show similar behaviour in DMF solvent. In the first sweep from 0.00 to -1.00 V, no cathodic peak is seen, and on sweeping from -1.00 to +0.70 V, a clear anodic peak at +0.56 V is observed, for which, the corresponding reduction peak at +0.50 V is not well resolved. This redox couple shifts with scan rate. Addition of PhIO does not bring any change in the voltammograms. Since for the complexes 1 and 2, the redox couple, in both presence and absence of PhIO, is seen at the same potential, a probable assignment could be ligand-based oxidation rather than metal centered oxidation. These observations suggest that in the complexes, change in the oxidation states is not facile, and this is reflected in the poor catalytic activity of the complexes. UV-vis measurements and CV studies show that reaction of the complexes with PhIO does not generate the high-valent metal-oxo species, required to explain the oxygen rebound mechanism followed by the cyt P-450 mimics (Scheme 2).

\[
\text{LM}^{+11} + \text{PhIO} \rightarrow \text{LM}^{\text{V}=\text{O}} + \text{PhI}
\]

\[
\text{LM}^{\text{V}=\text{O}} + \text{C} = \text{C} \rightarrow \text{LM}^{+11} + \text{O}
\]

These complexes gave limited epoxidation yields probably by the Lewis-acid catalysis, as suggested by Valentine, which does not require formation of the high-valent metal-oxo species (Scheme 3).

**Scheme 3**

The above mechanism is supported by the observation that similar cyclooctene oxide yields are obtained by using the three complexes containing different metal ions as catalysts. Tentatively, the difference in the catalytic activity and pathway of the open chain Schiff base complexes studied earlier (oxygen rebound mechanism) and the macrocyclic Schiff base ligand complexes studied in the present investigation (Lewis acid mechanism) can be attributed to the constraint imposed by the hexadentate macrocyclic ligand.

**Acknowledgement**

The authors are thankful to the Head, Chemistry Department, M S University, Vadodara, for providing laboratory facilities. Their thanks are also due to the Director, Research Centre, Indian Petrochemicals Corporation Limited (IPCL), Vadodara, for permission to use the GC and to Dr S Satish and Dr P.A. Ganeshpure, Research Centre, IPCL, Vadodara, for useful discussions. VM and PBS also acknowledge their thanks to CSIR, New Delhi, India, for financial assistance.
References