

## Template synthesis, characterization and catalytic behaviour of oxovanadium(IV) macrocyclic complexes

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The oxovanadium(IV)-directed condensation of 2,4-pentane dione with diamines [ethylenediamine(a), 1,2-diaminopropane(b), 1,3-diaminopropane(c) and *o*-phenylenediamine(d)] in ethanol produces macrocyclic complexes of the type  $[\text{VO}(\text{L})(\text{SO}_4)]_3 \cdot 3\text{H}_2\text{O}$  [**1a-1d**] in high yields. The complexes have been characterized by elemental analyses, conductance measurements, IR, electronic and ESR spectra. They act as active catalysts at room temperature for olefin epoxidation in the presence of *t*-butylhydroperoxide (TBHP). Norbornene gives exo epoxide. Competitive epoxidation of cycloolefins follows the order: norbornene > cyclohexene. The anionic surfactants (SLS) promote epoxide formation when catalysts **1a** and **1c** are used.

The past few years have witnessed an increasing interest in the synthesis of macrocyclic products using metal ion template procedure<sup>1-4</sup>. The chemistry of vanadium(IV) complexes is largely dominated by that of oxovanadium(IV) ion because of its unusually high stability. There are some reports on the synthesis of oxovanadium(IV) complexes with macrocyclic ligands<sup>5-7</sup>. However, there is distinct sparsity in the catalytic activity of such complexes<sup>8</sup>. In the present investigation, we report a new route for the synthesis of oxovanadium(IV) macrocyclic complexes, their characterization and catalytic behaviour.

### Experimental

The elemental analysis was performed using a CARLO ERBA 110 elemental analyser. Sulphate was estimated gravimetrically as BaSO<sub>4</sub>. The conductance data were recorded in DMF (10<sup>-3</sup> M) using a digital conductivity meter DCM 900. The IR spectra in KBr were recorded on a Perkin Elmer 883 IR spectrophotometer. The electronic spectra in methanol were recorded on a Shimadzu UV 160A spectrophotometer. X-band ESR spectra were recorded on a Varian E-112 spectrometer at 77K (liquid nitrogen). Diphenylpicryl hydrazyl (DPPH) (*g*=2.0037) was used as

an external standard. Analytical gas chromatography was done on a Nucon Amil 5700 series gas chromatograph fitted with Shimadzu. CR 3A data processor.

Vanadyl sulphate, 2,4-pentanedione, *o*-phenylenediamine, 1,3-diaminopropane, 1,2-diaminopropane and ethylenediamine were obtained from Aldrich and Merck. Cyclohexene and norbornene (Aldrich) were purified before use<sup>9</sup>. Sodium lauryl sulphate (SLS), cetyl trimethylammonium bromide (CTABr) and triton-X-100 used were of high purity.

### Synthesis of complexes $[\text{VO}(\text{L})(\text{SO}_4)]_3 \cdot 3\text{H}_2\text{O}$ [**1a-1d**]

To a boiling solution of vanadyl sulphate (0.43 g, 2 mmol) and 2,4-pentanedione (0.45 g, 4 mmol) in ethanol (20 mL), an ethanolic solution of diamine (4 mmol) [ethylenediamine (a), 1,2-diaminopropane(b), 1,3-diaminopropane(c), and *o*-phenylenediamine(d)] was added slowly with constant stirring and refluxed for 3 h when a light green compound separated out. The product was filtered, washed with ethanol and dried in air, yield 78%.

### Epoxidation of cyclohexene

Cyclohexene (5 mmol), *t*-butyl hydroperoxide (0.9 mmol) and catalyst (5 mg) were added in acetonitrile (10 ml). The contents were stirred for 1 h under nitrogen at room temperature. Dodecane (0.1 ml) was used as internal standard. The products were analysed by gas chromatographic technique.

The effect of various additives viz. sodium lauryl sulphate, cetyltrimethylammonium bromide and triton-X-100 was studied by adding 0.1 g or 100 ml of the additives to the reaction mixture.

The competitive oxidation of cyclohexene and norbornene was studied by taking cyclohexene (5 mmol) and norbornene (5 mmol) together in a flask, and to them were added catalysts (5 mg), TBHP (0.9 mmol), dodecane (0.1 ml) in acetonitrile (10 ml).

### Result and discussion

The template condensation of 2,4-pentanedione and various diamines in the presence of vanadyl sulphate in ethanol yields a greenish compound of composition  $[\text{VO}(\text{L})(\text{SO}_4)]_3 \cdot 3\text{H}_2\text{O}$  [**1a-1d**]. The ele-

Table 1 — Characterization data of the complex

| Complex  | Found (Calcd), % |                |                  |                  | $\Lambda_M$<br>( $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ) |
|--|------------------|----------------|------------------|------------------|--|
|  | C                | H              | N                | SO <sub>4</sub>  |  |
| [VOL <sub>a</sub> (SO <sub>4</sub> )] <sub>3</sub> H <sub>2</sub> O<br>( <b>1a</b> ) | 33.01<br>(32.95) | 6.10<br>(5.95) | 12.59<br>(12.81) | 22.21<br>(21.96) | 33   |
| [VOL <sub>b</sub> (SO <sub>4</sub> )] <sub>3</sub> H <sub>2</sub> O<br>( <b>1b</b> ) | 34.36<br>(34.51) | 6.30<br>(6.41) | 12.41<br>(12.38) | 21.39<br>(21.24) | 27   |
| [VOL <sub>c</sub> (SO <sub>4</sub> )] <sub>3</sub> H <sub>2</sub> O<br>( <b>1c</b> ) | 34.68<br>(34.51) | 6.53<br>(6.41) | 12.58<br>(12.38) | 21.49<br>(21.24) | 31   |
| [VOL <sub>d</sub> (SO <sub>4</sub> )] <sub>3</sub> H <sub>2</sub> O<br>( <b>1d</b> ) | 39.19<br>(39.58) | 5.39<br>(5.36) | 11.63<br>(11.54) | 20.01<br>(19.79) | 36   |

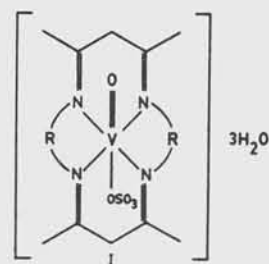
mental analyses values were found to be in close agreement with the calculated values for the molecular formulae assigned to these complexes (Table 1). The molar conductance values show that these complexes behave as non-electrolytes. The IR spectra of **1** shows one band in the region 960-975  $\text{cm}^{-1}$  indicative for a  $[\text{V}=\text{O}]^{2+}$  stretch. The absorption bands in the region 1580-1610  $\text{cm}^{-1}$  is assigned to the stretching vibration of unsaturated  $\nu\text{C}=\text{N}$ . No absorption band associated with  $-\text{NH}$  stretch at 3260  $\text{cm}^{-1}$  is observed. All the complexes show a broad band  $\sim 3400 \text{cm}^{-1}$  due to water molecules. Sulphate is coordinated to vanadium as evident from the splitting of  $\nu_3(\text{SO}_4)$  and  $\nu_4(\text{SO}_4)$  into two components (1120, 1040  $\text{cm}^{-1}$  and 635, 615  $\text{cm}^{-1}$  respectively); these are indicative of  $C_{3v}$  symmetry of monodentate sulphate<sup>10</sup>.

The electronic spectra of complexes exhibited two absorption bands in the region 500-550 and 800-830 nm in addition to charge transfer bands. For vanadyl(IV) complexes, it is generally observed that the unpaired electron is in a  $d_{xy}$  orbital and transitions occur to  $[d_{xz}, d_{yz}]$  ( $\nu_1$ ),  $d_{x^2-y^2}$  ( $\nu_2$ ) and  $d_{z^2}$  ( $\nu_3$ ) orbitals with increasing energies<sup>11</sup>. Usually, the band energy of  $\nu_3$  lies in the charge transfer region. The ESR spectrum of polycrystalline VO(IV) complexes is anisotropic with  $g$  values of  $g_{\parallel} = 2.157$ ,  $g_{\perp} = 1.985$ ,  $g_{av} = 2.042$ ,  $A_{\parallel} = 162 \times 10^{-4} \text{cm}^{-1}$  for **1b** and  $g_{\parallel} = 2.172$ ,  $g_{\perp} = 1.986$ ,  $g_{av} = 2.048$ ,  $A_{\parallel} = 160 \times 10^{-4} \text{cm}^{-1}$  for **1d** at 77K respectively, which are in good agreement with the reported values<sup>7,12</sup>. The trend  $g_{\perp} > g_{av} > g_{\parallel}$  in the complex indicates that the unpaired electron is present in  $d_{xy}$  orbital<sup>13</sup>. This observation supports the assignment made on the basis of electronic spectra. The  $\alpha^2$  values [0.6379 (**1b**) and 0.6468 (**1d**)] suggested that the complex is covalent in nature<sup>14</sup>. Thus an-

Table 2 — Epoxidation of cyclohexene with dry TBHP\* using oxovanadium(IV) complexes at room temperature for 1 h

| Catalyst   | Epoxide (mmol) | Cyclohexenol (mmol) | Cyclohexenone (mmol) |
|--|----------------|---------------------|----------------------|
| [VOL <sub>a</sub> (SO <sub>4</sub> )] <sub>3</sub> H <sub>2</sub> O<br>( <b>1a</b> ) | Traces         | 0.29                | 0.45                 |
| [VOL <sub>b</sub> (SO <sub>4</sub> )] <sub>3</sub> H <sub>2</sub> O<br>( <b>1b</b> ) | 0.94           | 0.47                | 1.24                 |
| [VOL <sub>c</sub> (SO <sub>4</sub> )] <sub>3</sub> H <sub>2</sub> O<br>( <b>1c</b> ) | Traces         | 0.02                | 0.05                 |
| [VOL <sub>d</sub> (SO <sub>4</sub> )] <sub>3</sub> H <sub>2</sub> O<br>( <b>1d</b> ) | 1.93           | 0.23                | 0.18                 |

\*0.9 mmol of oxidant



R = C<sub>2</sub>H<sub>4</sub>, 1,2-C<sub>3</sub>H<sub>7</sub>, 1,3-C<sub>3</sub>H<sub>7</sub> & C<sub>6</sub>H<sub>4</sub>

alytical and spectral evidences support a distorted octahedral structure I of the complex.

#### Catalytic activity

This is the first report of room temperature epoxidation of olefins using oxovanadium catalysts. The epoxidation of cyclohexene produced cyclohexene epoxide, cyclohexenone and cyclohexenol as the products (Table 2). Formation of the latter two products suggests that allylic oxidation is also taking place. The complex **1b** pro-

duced highest yield of products followed by **1d**, **1a** and **1c**. The formation of allylic oxidation products suggests that oxygen atom insertion in C=C and C-H bond is a competitive process resulting in the simultaneous formation of both epoxide and carbonyl compounds<sup>15-17</sup>. It also suggests that homolytic cleavage of hydroperoxide is taking place.

The addition of cationic surfactant (CTABr) decreases the yield of epoxide with **1b** (0.01 mmol) and **1d** (0.78 mmol) and completely inhibited the epoxide with **1c** and **1a** as catalyst. It suggests the involvement of some electron deficient centre during epoxidation. This fact is further supported by the addition of anionic surfactant (SLS) to the reaction mixture which increases the yield of products substantially with complex **1b** (1.97 mmol), **1d** (1.48 mmol), **1c** (0.20 mmol) and **1a** (0.35 mmol). The addition of non-ionic surfactant triton-X-100 did not affect the yield of products significantly.

The competitive epoxidation of cycloolefins showed that norbornene reacts faster than cyclohexene. This shows that coordination of olefin to metal centre is not the rate determining step<sup>18,19</sup>. Bond angle strain and torsional strain play an important role in determining the relative reactivity of cycloolefins<sup>20</sup>. The epoxidation of norbornene gave only one type of epoxide. This shows that the two C-O bond formations are quite fast giving no place to C-C bond rotation<sup>21</sup>. The yield of norbornene epoxide was quite high with complex **1b** (0.52 mmol) followed by **1d** (0.19 mmol), **1c** (0.12 mmol) and **1a** (0.11 mmol).



The addition of anionic, cationic and non-ionic surfactants gave yields 0.57, 0.06 and 0.53 mmol respectively. A decrease in yield on cationic surfactant addition shows that a positively charged intermediate is being destabilised. This behaviour is similar to that observed with cyclohexene. The above observations suggests a similar mechanism as reported earlier<sup>19,22</sup>.

Formation of very good yield of products under very simple reaction conditions suggests that these

complexes can function as catalysts in ambient condition of various substrates giving a very high catalyst turnover number at room temperature.

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