

## 12-B heteropolyanions as ligands: Synthesis, spectral characterisation and solution studies of $[\text{Mn}^{\text{IV}}\text{ThMo}_{12}\text{O}_{42}]^{4-}$ , $[\text{Mn}^{\text{IV}}\text{UMo}_{12}\text{O}_{42}]^{4-}$ and $[\text{V}^{\text{IV}}\text{CeMo}_{12}\text{O}_{42}]^{4-}$

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**Abstract.** Interaction of 12-B heteropolyanions,  $[\text{XMo}_{12}\text{O}_{42}]^{8-}$ , where  $X = \text{Ce}$ , Th and U, with tetravalent transition metal ions  $\text{Mn}^{\text{IV}}$  and  $\text{V}^{\text{IV}}$  results in the formation of three well defined complexes, viz.,  $(\text{NH}_4)_4[\text{Mn}^{\text{IV}}\text{ThMo}_{12}\text{O}_{42}] \cdot 10\text{H}_2\text{O}$  (I),  $(\text{NH}_4)_4[\text{Mn}^{\text{IV}}\text{UMo}_{12}\text{O}_{42}] \cdot 8\text{H}_2\text{O}$  (II) and  $(\text{NH}_4)_4[\text{V}^{\text{IV}}\text{CeMo}_{12}\text{O}_{42}] \cdot 8\text{H}_2\text{O}$  (III), which are characterised by IR, Raman and EPR spectroscopies. Negative shift in the stretching frequency of Mo–O<sub>2</sub> bond in IR spectra and appearance of a strong band at  $818\text{ cm}^{-1}$  in Raman spectra support the formation of these complexes. EPR spectra of complexes (I) and (II) show a predominant signal at  $g = 4$  and a weak signal at  $g = 2$  (with hyperfine coupling from  $^{55}\text{Mn}$ ), characteristic of  $d^3$  system, ( $S = 3/2$  and  $I = 5/2$ ) with large zero field splitting, showing distortion from octahedral symmetry. EPR parameters of the vanadium complex (III) show the  $d$ -electron to be more localised on vanadium(IV) supporting the formulation of vanadium not to be a part of the “ $\text{Mo}_{12}$ ” unit. The oxidising property of complexes (I) and (II) is studied using glucose as the substrate.

**Keywords.** 12-B heteropolyanion; manganese; vanadium; synthesis; EPR.

### 1. Introduction

Synthesis of complexes with complete or lacunary heteropolyanions as ligands is a rapidly growing area in polyanion chemistry, since such chemistry is considered to be particularly pertinent to the mechanisms of catalysis on metal oxide surfaces and to the development of new catalysts<sup>1–6</sup>. Exploiting the topology and electron acceptor ability of heteropolyanions, multinuclear complexes have been prepared<sup>7</sup>. While complete heteropolyanions form complexes through the terminal oxygen atoms, the lacunary heteropolyanions form complexes by enclosing cations in the vacancies<sup>7</sup>. There have been several investigations of reactions of transition metal ions with lacunary heteropolyanions<sup>4,6,8,9</sup> which are known to act as multidentate ligands. Since 12-B heteropolyanions have high negative charge and suitable number of oxygen atoms, they form

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complexes with f- and d-block elements without the destruction of  $\text{MoO}_6$  octahedron<sup>10</sup>. However, relatively very few complexes are known where an intact heteropolyanion is found to act as the ligand. A few typical examples are, (i) complexes formed by paradecatungstate  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  with  $\text{Mn}^{\text{II}}$  and  $\text{Eu}^{\text{III}}$ , where paradecatungstate acts as monodentate ligand<sup>7</sup>, (ii) species like  $[\text{Co}(\text{H}_2\text{O})_4(\text{H}_2\text{W}_{12}\text{O}_{42})_n]^{6n-}$  where paradodecatungstate acts as a tetradentate ligand<sup>11</sup> through the terminal oxygen atoms and (iii) complexes like  $\text{CuH}_6\text{UMo}_{12}\text{O}_{42} \cdot 12\text{H}_2\text{O}$ <sup>12</sup> and  $[(\text{UMo}_{12}\text{O}_{42})\text{Th}(\text{OH}_2)_3]^{4n-}$ <sup>13</sup>, where the 12-B heteropolyanion  $[\text{UMo}_{12}\text{O}_{42}]^{8-}$  acts as a hexadentate ligand and the external metal atom thorium is attached to the opposite sides of the heteropolyanion *via* three terminal oxygen atoms of the three adjacent  $\text{MoO}_6$  octahedra.  $[\text{CeMo}_{12}\text{O}_{42}]^{8-}$  and  $[\text{ThMo}_{12}\text{O}_{42}]^{8-}$  anions are isostructural with  $[\text{UMo}_{12}\text{O}_{42}]^{8-}$  and it is also known that they form weak complexes in aqueous solution<sup>14</sup> with transition metal ions such as divalent Mn, Fe, Co, Cu and trivalent Y, Er and Yb. Hence it was thought to be worth exploring the potential of  $[\text{XMo}_{12}\text{O}_{42}]^{8-}$  [X = Ce, Th and U] as multidentate ligands.

Of the various complexes formed by the reaction of  $[\text{XMo}_{12}\text{O}_{42}]^{8-}$  with  $\text{Mn}^{\text{IV}}$  and  $\text{V}^{\text{IV}}$ , only three, viz.,  $[\text{Mn}^{\text{IV}}\text{ThMo}_{12}\text{O}_{42}]^{4-}$  (I),  $[\text{Mn}^{\text{IV}}\text{UMo}_{12}\text{O}_{42}]^{4-}$  (II) and  $[\text{V}^{\text{IV}}\text{CeMo}_{12}\text{O}_{42}]^{4-}$  (III) were found to be well defined. Here we report the synthesis and spectral characterisation of these three complexes (I), (II) and (III). Due to the significance of  $\text{Mn}^{\text{IV}}$  in a number of biologically important compounds<sup>15,16</sup>, we have also studied the oxidising property of  $\text{Mn}^{\text{IV}}$  complexes (I) and (II), by choosing glucose as the substrate.

## 2. Experimental

### 2.1 Materials

Uranyl acetate, ammonium molybdate, manganese sulphate, thorium nitrate and vanadyl sulphate used were of AR grade. Ammonium ceric sulphate and sodium peroxy disulphate were obtained from E-Merck and used without further purification. Doubly distilled water was used for kinetic measurements.

### 2.2 Preparation of the complexes

Complexes (I) and (II) were prepared by mixing a solution of thorium sulphate ( $0.2 \text{ mole dm}^{-3}$ ) or uranyl acetate ( $0.2 \text{ mol dm}^{-3}$ ) to a boiling aqueous solution of ammonium molybdate ( $0.25 \text{ mole dm}^{-3}$ ) with stirring. To the resulting solution, aqueous solution of manganese sulphate ( $0.2 \text{ mole dm}^{-3}$ ) containing oxidant, sodium peroxy disulphate ( $0.19 \text{ mole dm}^{-3}$ ) was added with continuous stirring. The solution was filtered, cooled and saturated with ammonium nitrate to salt out the complexes, which were further purified by recrystallisation from hot water.

(I) Found: Mn, 2.19; Th, 9.50; Mo, 48.01.  $(\text{NH}_4)_4 [\text{MnThMo}_{12}\text{O}_{42}] \cdot 10\text{H}_2\text{O}$  requires Mn, 2.27; Th, 9.60; Mo, 47.64%.

(II) Found: Mn, 2.26; U, 9.84; Mo, 47.56.  $(\text{NH}_4)_4 [\text{MnUMo}_{12}\text{O}_{42}] \cdot 8\text{H}_2\text{O}$  requires Mn, 2.27; U, 9.82; Mo, 47.52%.

Complex (III) was prepared by adapting a similar procedure used for the preparation of complexes (I) and (II). However, no oxidant was added and vanadyl sulphate was used in the place of manganese sulphate. Complex (III) was also recrystallised from hot water. Found: V, 2.30; Ce, 6.12; Mo, 50.20.  $(\text{NH}_4)_4 [\text{V}^{\text{IV}}\text{CeMo}_{12}\text{O}_{42}] \cdot 8\text{H}_2\text{O}$  requires V, 2.19; Ce, 6.07; Mo, 50.0%.

### 2.3 Analytical and physical methods

Molybdenum and uranium were estimated gravimetrically as oxinates. Thorium and cerium were estimated gravimetrically as  $\text{ThO}_2$  and  $\text{CeO}_2$ . Vanadium and manganese were estimated spectrophotometrically<sup>17</sup>. The amount of water content was found by heating the sample at 120°C, until constant weight was obtained. IR spectra were recorded on a Perkin Elmer 783 spectrometer as KBr disks. Raman spectra were recorded using DILOR 24 Raman spectrometer with spectra physics 164 Argon Laser (488 nm, 300 mw), by pressing the sample in a matrix. EPR spectra were recorded using Varian E112 spectrometer equipped with 100 KHz field modulation. DPPH was used as an internal field marker.

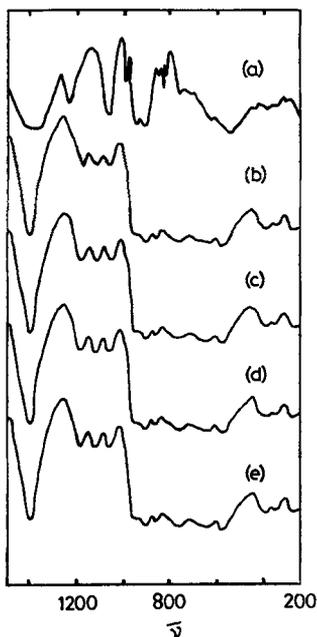
### 2.4 Kinetic measurements

The kinetic measurements were carried out under pseudo-first-order conditions,  $[\text{oxidant}] < [\text{D-glucose}]$  in aqueous medium by using Hitachi model 200–20 UV-Vis spectrophotometer equipped with a thermostatically controlled cell compartment. The disappearance of UV maximum at 340 nm was followed for the heteropolyanion based complexes. To determine the stoichiometry of the reaction, several reaction mixtures with  $[\text{oxidant}] > [\text{reductant}]$ , at fixed sulphuric acid concentration, were prepared. After the completion of the reaction, the unreacted manganese which exists in the form of  $\text{Mn}^{\text{III}}$  in acid solution was estimated spectrophotometrically. In all cases the stoichiometry was found to be 2:1 [oxidant:reductant]. The organic product, arabinose was identified by thin layer chromatography, using 1-butanol-acetic acid-water as the solvent. The other product formic acid, was identified by treating the product with  $\text{Zn}/\text{HCl}$  followed by the addition of chromotropic acid<sup>18</sup>. The resulting product of oxidant, was confirmed by EPR spectroscopy to be  $\text{Mn}^{\text{II}}$ . pH measurements were made using Systronics 273 pH meter.

## 3. Results and discussion

### 3.1 Infrared spectra

IR spectra of the ligand (12-B heteropolyanion) and the complexes (I), (II) and (III) are given in (figure 1) along with the complex  $(\text{NH}_4)_4 [\text{ThUMo}_{12}\text{O}_{42}] \cdot 3\text{H}_2\text{O}$  (IV), the structure of which has been well established<sup>13</sup>. The band frequencies and tentative assignments are given in table 1. IR spectroscopy is evolving as a promising technique to study the fine changes in the structure of heteropolyanions<sup>14</sup>. Typically the heteroatom of a 12-B heteropolyanion is present at the centre of a regular icosahedron and it is surrounded by six pairs of  $\text{MoO}_6$  octahedra. Each of the six pairs is face shared. As a result of the face sharing, each pair becomes an  $\text{Mo}_2\text{O}_9$  unit<sup>19</sup>. Each metal atom in the  $\text{Mo}_2\text{O}_9$  unit has two mutually *cis* unshared oxygen atoms<sup>20</sup>. The  $\text{Mo}_2\text{O}_9$  unit has three different types of molybdenum-oxygen stretching frequencies. They are, molybdenum-terminal oxygen ( $\text{Mo}-\text{O}_t$ ) and molybdenum-intra and inter bridging oxygen atoms ( $\text{Mo}-\text{O}_b$ -intra and  $\text{Mo}-\text{O}_b$ -inter). During the complex formation, the molybdenum-intra bridging oxygen is disturbed, whereas molybdenum-inter bridging oxygen is not disturbed<sup>13</sup>. In the free ligands  $[\text{XMo}_{12}\text{O}_{42}]^{8-}$  these bands occur at the following frequencies.  $\text{Mo}-\text{O}_t$ : 1240 and 1070  $\text{cm}^{-1}$ ;  $\text{Mo}-\text{O}_b$ -intra: 990  $\text{cm}^{-1}$ ;  $\text{Mo}-\text{O}_b$ -inter: 950 and 930  $\text{cm}^{-1}$ . In the case of *cis*  $\text{MoO}_2$  group there are two types of terminal oxygen bonds, hence it exhibits two bands in the IR spectra<sup>21</sup>. The bands at 1240 and



**Figure 1.** IR spectra of (a)  $[\text{CeMo}_{12}\text{O}_{42}]^{8-}$ , (b)  $[\text{MnThMo}_{12}\text{O}_{42}]^{4-}$ , (c)  $[\text{MnUMo}_{12}\text{O}_{42}]^{4-}$ , (d)  $[\text{VCeMo}_{12}\text{O}_{42}]^{4-}$  and (e)  $[\text{ThUMo}_{12}\text{O}_{42}]^{4-}$  as KBr disks.

$1070\text{ cm}^{-1}$  observed for the ligand may be assigned to two  $\text{Mo}-\text{O}_t$  terminal bonds of the *cis*  $\text{MoO}_2$  groups present in the  $\text{Mo}_2\text{O}_9$  unit. The band at  $990\text{ cm}^{-1}$  corresponds to  $\text{Mo}-\text{O}_b$ -intra. There are two types of  $\text{Mo}-\text{O}_b$ -inter bonds and hence the doublet appearing at  $950$  and  $930\text{ cm}^{-1}$  for ligand may be assigned to  $\text{Mo}-\text{O}_b$ -inter bonds. Spectra of the complexes (I–IV) show considerable changes in the region  $1300$ – $1000\text{ cm}^{-1}$ . To understand these changes a brief discussion of the structure of complex (IV) follows<sup>13</sup>. Thorium atom in complex (IV) bridges the two  $[\text{UMo}_{12}\text{O}_{42}]^{8-}$  anions, which act as hexadentate ligand and form the complex through their terminal oxygen atoms. The complex (IV) has four different types of molybdenum–oxygen bond lengths, *viz.*, molybdenum-terminal oxygen, bonded only to one molybdenum; molybdenum-oxygen shared with thorium; and molybdenum-bridging oxygen (intra and inter) respectively<sup>13</sup>. Hence in the IR spectra, four different types of molybdenum-oxygen stretching frequencies are expected. These frequencies are observed in the complexes (I–IV) (table 1). However, some of these frequencies are shifted from those of the ligand. These shifts may be accounted as follows.

When the ligand heteropolyanion, forms the complex through the terminal oxygen atom (one of the oxygen atoms present in the *cis*  $\text{MoO}_2$  groups), bond order of  $\text{Mo}-\text{O}_t$  gets decreased and hence  $\text{Mo}-\text{O}_t$  frequency suffers downward shift from  $1240$  to  $1190\text{ cm}^{-1}$ . However, the stretching frequency of its counterpart *i.e.*, the other  $\text{Mo}-\text{O}_t$  bond moves from  $1070$  to  $1100\text{ cm}^{-1}$ . This may be due to the distortion occurring in the  $\text{MoO}_6$  octahedron such that the Mo shifts towards the other terminal oxygen. Similarly, it is of interest to analyse the consequence of the complex formation on the co-ordination of the molybdenum-bridging oxygen stretching frequencies. As a result

Table 1. IR Spectral data<sup>§</sup> for complexes (I), (II), (III) and (IV)\*\*

Ligand	I	II	III	IV	Band assignment
$[\text{XM}_{0.12}\text{O}_{42}]^{8-}$	$[\text{MnThM}_{0.12}\text{O}_{42}]^{4-}$	$[\text{MnUM}_{0.12}\text{O}_{42}]^{4-}$	$[\text{VCeM}_{0.12}\text{O}_{42}]^{4-}$	$[\text{ThUM}_{0.12}\text{O}_{42}]^{4-}$	
X = Ce*					
1240	1190	1190	1190	1190	Mo-O <sub>i1</sub>
1070	1100	1100	1100	1100	Mo-O <sub>i2</sub>
990	1050	1050	1050	1050	Mo-O <sub>b</sub> , intra
950	950	950	950	950	Mo-O <sub>b</sub> , inter
930	930	930	930	930	Mo-O <sub>b</sub> , inter
—	800	800	800	800	M-O-Mo
					M = V <sup>IV</sup> and Mn <sup>IV</sup>

<sup>§</sup>KBr disk, cm<sup>-1</sup>

\* Isostructural with  $[\text{ThM}_{0.12}\text{O}_{42}]^{8-}$  and  $[\text{UM}_{0.12}\text{O}_{42}]^{8-}$

\*\* Ammonium is the counter cation for all the complexes (I-IV)

of the terminal oxygen co-ordination, the molybdenum-intra bridging oxygen bond length decreases<sup>14</sup>. This in turn will lead to increase in the stretching frequency of molybdenum-intra bridging oxygen. Hence the Mo–O<sub>b</sub>-intra frequency shows positive shift from 990 to 1050 cm<sup>-1</sup>. The M–O<sub>b</sub>-inter is not affected by complex formation and no remarkable changes in the stretching frequency of molybdenum-inter bridging oxygen bonds are expected as seen in table 1. All the complexes (I–IV) exhibit a strong and broad band at 800 cm<sup>-1</sup> which is not seen in the ligand. This may be assigned to the Mn<sup>IV</sup> or V<sup>IV</sup>–O bond formed due to the complex formation.

### 3.2 Raman spectra

Raman spectra of the complexes (I–IV) along with the ligand are shown in figure 2. The spectral data and band frequencies are given in table 2. The 12-B heteropolyanions exhibit bands at 963 and 926 cm<sup>-1</sup> corresponding to molybdenum-intra bridging oxygen stretching frequencies. The other bands at 716 and 670 cm<sup>-1</sup> may be assigned

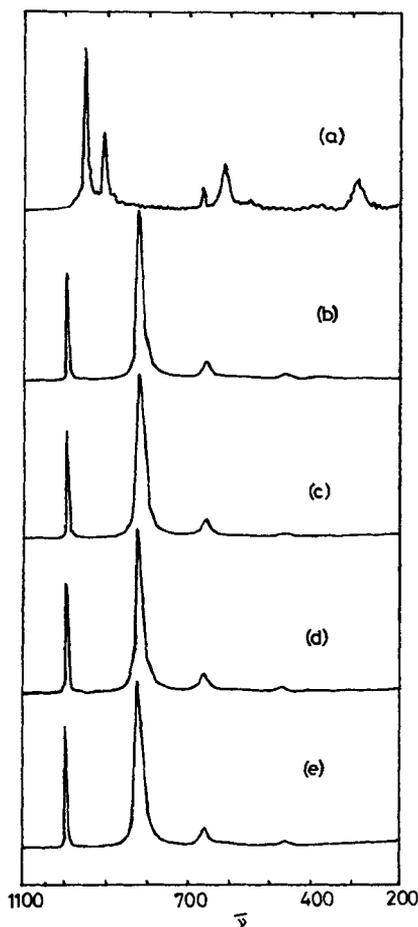


Figure 2. Raman spectra of (a) [CeMo<sub>12</sub>O<sub>42</sub>]<sup>8-</sup>, (b) [MnThMo<sub>12</sub>O<sub>42</sub>]<sup>4-</sup>, (c) [MnUMo<sub>12</sub>O<sub>42</sub>]<sup>4-</sup>, (d) [VCeMo<sub>12</sub>O<sub>42</sub>]<sup>4-</sup> and (e) [ThUMo<sub>12</sub>O<sub>42</sub>]<sup>4-</sup>

Table 2. Raman spectral data<sup>§</sup> for complexes (I), (II), (III) and (IV)\*\*

Ligand	I	II	III	IV	Band assignment
$[\text{XM}_{0_{12}}\text{O}_{42}]^{8-}$ X = Ce*	$[\text{MnThMo}_{12}\text{O}_{42}]^{4-}$	$[\text{MnUMo}_{12}\text{O}_{42}]^{4-}$	$[\text{VCeMo}_{12}\text{O}_{42}]^{4-}$	$[\text{ThUMo}_{12}\text{O}_{42}]^{4-}$	
963	992	992	991	992	Mo-O <sub>6</sub> intra
926	818	818	819	819	M-O-Mo M = V <sup>IV</sup> and Mn <sup>IV</sup>
716	662	663	659	662	X-O X = Ce, Th and U

<sup>§</sup>Solid sample, cm<sup>-1</sup>

\* Isostructural with  $[\text{ThMo}_{12}\text{O}_{42}]^{8-}$  and  $[\text{UMo}_{12}\text{O}_{42}]^{8-}$

\*\* Ammonium is the counter cation for all the complexes (I-IV)

to the stretching frequency of X–O ( $X = \text{Ce}, \text{U}$  and  $\text{Th}$ ) bond. The molybdenum-terminal oxygen stretching frequency is not seen in the spectra, because the molybdenum-terminal oxygen stretching is not a pure vibration, it has some deformation character; hence, it may not be seen in the Raman spectra<sup>22</sup>. While the ligand forms complexes through the terminal oxygen atoms with the tetravalent metal ions, the bond length of molybdenum-intra bridging oxygen is disturbed. The molybdenum-intra bridging oxygen stretchings at  $963 \text{ cm}^{-1}$  and  $926 \text{ cm}^{-1}$  for the ligand, undergo positive shift to  $992 \text{ cm}^{-1}$  for the complexes (I), (II) and (IV) and to  $991 \text{ cm}^{-1}$  for the complex (III). This is due to the shortening of molybdenum-intra bridging oxygen bond length, as discussed earlier. A sharp and strong band is found at  $818 \text{ cm}^{-1}$  for the complexes (I–III) and  $819 \text{ cm}^{-1}$  for the complex (IV), which may be due to the formation of a new bond [M–O–Mo bond where  $M = \text{V}^{\text{IV}}$  and  $\text{Mn}^{\text{IV}}$ ], indicating the formation of the complex between the ligand and the tetravalent transition metal ions. This band is not seen for the ligand. The same trend is revealed by the complex (IV) whose structure is well established. The X–O stretching (where  $X = \text{Ce}, \text{Th}$  and  $\text{U}$ ) appears at  $662 \text{ cm}^{-1}$  for the complexes (I) and (IV) and  $663$  and  $659 \text{ cm}^{-1}$  for the complexes (I) and (III) respectively.

### 3.3 EPR spectra

X-band EPR spectra of powder samples of complexes (I) and (II) are given in the figure 3. The EPR parameters derived from the spectra are given in table 3. Spectra of both the complexes are similar to each other and show a predominant signal at  $g \approx 4$  and a comparatively weak signal at  $g = 2$ . These EPR spectra directly support the formulation of manganese in these complexes to be  $\text{Mn}^{\text{IV}}$  ( $d^3$ -system with  $S = 3/2$  and  $I = 5/2$ ). The nature and complexity of the powder EPR spectrum of  $d^3$ -system depends

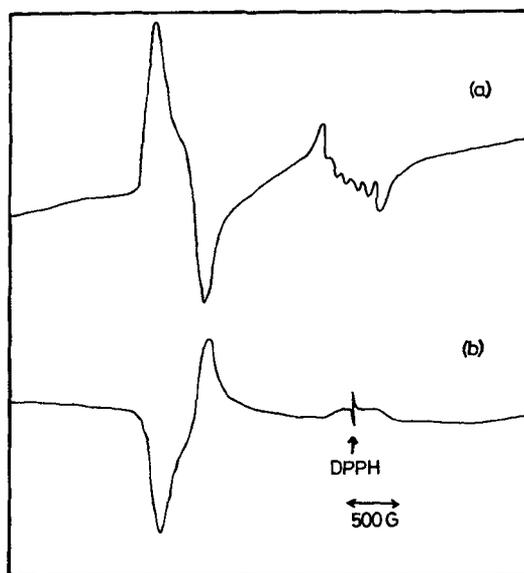


Figure 3. X-band polycrystalline EPR spectra of (a)  $[\text{Mn}^{\text{IV}}\text{ThMo}_{12}\text{O}_{42}]^{4-}$  and (b)  $[\text{Mn}^{\text{IV}}\text{UMo}_{12}\text{O}_{42}]^{4-}$  at 300 K.

**Table 3.** EPR parameters for (I), (II) and other Mn<sup>IV</sup> complexes

Complexes	$g_1$	$g_2$	$A_{Mn} \times 10^4 \text{ cm}^{-1}$
[MnThMo <sub>12</sub> O <sub>42</sub> ] <sup>4-</sup>	3.65	2.01	76.1
[MnUMo <sub>12</sub> O <sub>42</sub> ] <sup>4-</sup>	3.86	2.01	78.4
Mn(dtc) <sub>3</sub> <sup>*</sup>	4	2	84.7
Mn(saladph) <sup>**</sup>	5.2	2.07	79.4

\*16

\*\*33

upon the magnitude of the zero field splitting parameter <sup>23</sup>. The powder spectrum becomes complex when  $D$  is comparable to the microwave quantum (at X-band,  $h\nu = 0.30 \text{ cm}^{-1}$ ). However, simplification occurs under limiting conditions, where  $2D \gg h\nu$  or  $2D \ll h\nu$ . If  $2D \ll h\nu$ , then the spectrum shows predominant signal at  $g = 2$  and a weak signal at  $g = 4$ . On the contrary, if  $2D \gg h\nu$ , the  $g = 4$  peak is strong and  $g = 2$  peak becomes weak. Spectra given in (figure 3) correspond to the situation of  $2D \gg h\nu$ . The  $D$  value can be approximately obtained by assuming axial symmetry, using the equation <sup>24</sup>

$$D^2 \approx 3/8 [g_{\perp} (g_{\perp} \beta H)^2] / (2g_{\perp} - g_1).$$

Using the  $g_1$  values given in (table 3),  $|D|$  has been calculated to be  $0.71 \text{ cm}^{-1}$  for complex (I) and  $0.61 \text{ cm}^{-1}$  for complex (II). Since the  $D$  value is large ( $|D| > h\nu$  ( $0.31 \text{ cm}^{-1}$ )), transitions between upper and lower Kramers doublets are not accessible in the X-band region. Similar behaviour is observed for manganese(IV) catechol and manganese(IV) sorbitol complexes <sup>25</sup>. The higher values of  $D$  for complexes (I) and (II) are indicative of distortion from octahedral symmetry. Similar EPR spectra have also been reported for manganese(IV) porphyrin complex <sup>24</sup>. The asymmetric appearance of low-field signal and the crossing point of the signal being at  $g < 4$ , indicate noticeable rhombic distortion <sup>26</sup>. The EPR spectra of the complex (I) show hyperfine splitting in the region  $g = 2$ . The signal shows six lines with splitting constant  $A_{Mn} = 76.1 \times 10^{-4} \text{ cm}^{-1}$ . For complex (II),  $A_{Mn} = 78.4 \times 10^{-4} \text{ cm}^{-1}$ , but the hyperfine splitting is not well resolved.

Polycrystalline EPR spectrum recorded at 300 K for complex (III), given in (figure 4) corresponds to axially symmetric vanadium(IV) complex. EPR parameters for the complex (III), collected in (table 4), correspond to typical oxygen co-ordination around vanadium. Using the EPR parameters of the complex (III),  $\alpha^2$ , fractional contributions of  $d_{xy}$  orbital and  $k$ , isotropic Fermi contact term were calculated using the equations <sup>27</sup>

$$A_{\parallel} = P [-4/7\alpha^2 - k + g_{\parallel} - 2.0023 + 3/7(g_{\perp} - 2.0023)]$$

$$A_{\perp} = P [2/7\alpha^2 - k + 11/14(g_{\perp} - 2.0023)]$$

A value of  $0.0128 \text{ cm}^{-1}$ , for  $P$  was used in this calculation <sup>27</sup>. The  $\alpha^2$  and  $k$  values calculated for vanado tungstates or vanado molybdates where vanadium replaces the tungsten or molybdenum, are generally found to be lower than that of an oxovanadium complex <sup>27,28</sup>, and this reduction is attributed to the delocalisation of the unpaired electron over the entire polyanion unit. However, in the present case the calculated value of  $\alpha^2(0.967)$  and  $k(0.768)$  for complex (III), indicate a lesser degree of electron delocalisation. This observation supports the formulation that vanadium is not a part of the "Mo<sub>12</sub>" unit.

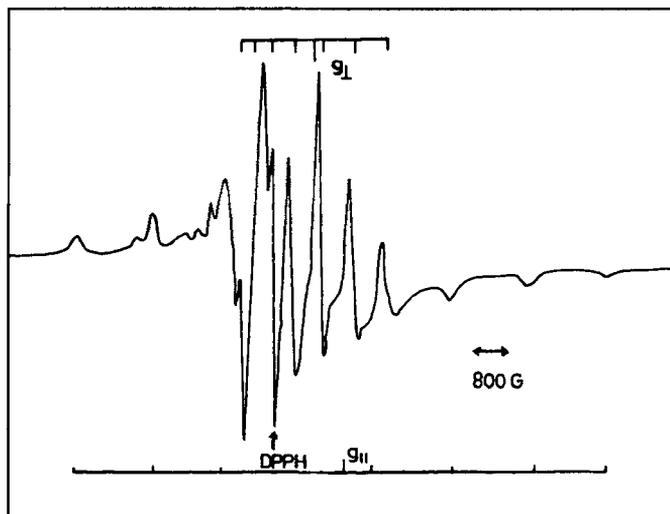


Figure 4. X-band polycrystalline EPR spectrum of  $[\text{V}^{\text{IV}}\text{CeMo}_{12}\text{O}_{42}]^{4-}$  at 300 K.

Table 4. EPR parameters for complex (III) and other  $\text{V}^{\text{IV}}$  complexes

Complexes	$g_{\parallel}$	$g_{\perp}$	$A_V \times 10^4 \text{ cm}^{-1}$		$\alpha^2$	k
			$A_{\parallel}$	$A_{\perp}$		
$[\text{V}^{\text{IV}}\text{CeMo}_{12}\text{O}_{42}]^{8-}$	1.908	1.978	155.6	54.4	0.967	0.768
$\text{V}^{\text{IV}}$ in $\alpha\text{-TeO}_2^*$	1.901	1.982	160.13	53.03	1.086	0.739
$[\text{VO}(\text{mquin})_2]^{**}$	1.949	1.983	157.3	55.5	0.984	0.724
$^a[\text{PVMo}_{11}\text{O}_{40}]^{5-}$	1.939	1.974	151.2	53.4	0.895	0.687
$^a[\text{PVW}_{11}\text{O}_{40}]^{5-}$	1.915	1.970	167.2	59.7	0.810	0.632

\*<sup>34</sup>

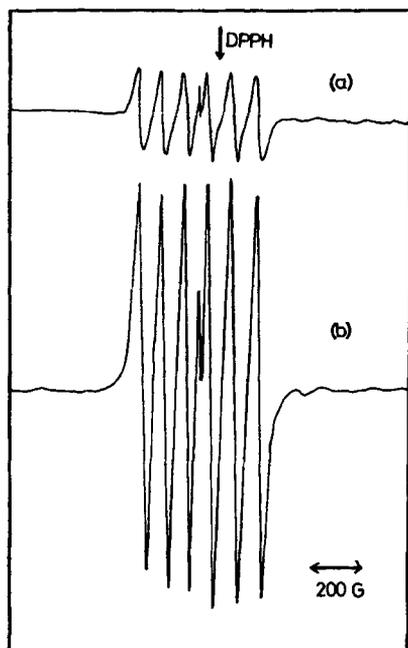
\*\*<sup>35</sup>

<sup>a</sup><sub>28</sub>

### 3.4 Solution studies

In recent years, studies on electron transfer reactions of heteropolyanions have attracted increased attention particularly with heteropolyanion having higher valent transition metal as a heteroatom<sup>29</sup>. Since  $\text{Mn}^{\text{IV}}$  is an unusual oxidation state for manganese in co-ordination chemistry; it plays a vital role in photosystem II to produce molecular oxygen, and acts as a catalyst in the reduction of hydrogen peroxide to water by pseudocatalase, isolated from *lactobacillus plantarum*<sup>16</sup>. Due to its interesting role in biological systems, oxidising property of  $\text{Mn}^{\text{IV}}$  in the complexes (I) and (II) merits attention. Selecting D-glucose, due to its importance in mammalian food supply and metabolism<sup>30</sup>, as the reductant, we have studied the rate of oxidation of D-glucose by complexes (I) and (II).

All the reactions were found to follow first order kinetics as judged by the linearity of plots of  $\log(\text{absorbance})$  versus time. The dependence of rate on substrate concentration was studied for the  $\text{Mn}^{\text{IV}}$  complexes at  $35^\circ\text{C}$  with  $[\text{oxidant}] = 4.86 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.3 \text{ mol dm}^{-3}$  and  $[\text{substrate}]$  ranging from  $4.86 \times 10^{-3} \text{ mol dm}^{-3}$  to



**Figure 5.** X-band EPR solution spectra of the product  $\text{Mn}^{\text{II}}$ , as function of time (a) after 5 min (b) after 10 min.

$8.39 \times 10^{-3} \text{ mol dm}^{-3}$ . The order in substrate was found to be non-integral for the complexes. The dependence of rate on oxidant concentration was also studied at  $35^\circ\text{C}$  with  $[\text{D-glucose}] = 4.86 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.3 \text{ mol dm}^{-3}$  and the range of oxidant concentration varying from  $4.86 \times 10^{-4}$  to  $8 \times 10^{-4} \text{ mol dm}^{-3}$ . The rate constants show an initial increase followed by a decrease as the concentration of the oxidant is increased. This may be due to the formation of a complex between the substrate and the polyanion (PA) containing the trivalent manganese  $[\text{PA-Mn}^{\text{III}}]$ , resulting in the decreased total concentration of the complex or the reactive species. Similar behaviour has been observed in the oxidation of maleic acid by manganese(III) acetate<sup>31</sup>, phenacyl bromides by manganese(III) sulphate<sup>32</sup>. The possible reactive species in sulphuric acid are  $\text{Mn}(\text{OH})_2^+$ ,  $\text{Mn}(\text{HSO}_4)_2^+$ ,  $\text{Mn}(\text{SO}_4)^+$ ,  $\text{Mn}(\text{SO}_4)_2^-$  and  $\text{Mn}(\text{OH})_3(\text{HSO}_4)_3^-$  and their presence depends on experimental conditions. But in the present case, since  $\text{Mn}^{\text{III}}$  ion is encircled by other  $\text{MoO}_6$  moieties, the formation of the above mentioned reactive species may not be possible. The formation of  $\text{PA-Mn}^{\text{III}}$  substrate complex may be the reason for the decrease in the rate as the concentrations of the oxidant are increased. The reaction was found to go through free radical intermediate as confirmed by the polymerisation of acrylonitrile in the system. Acid dependence studies were carried out for manganese(IV) containing complexes with  $[\text{D-glucose}] = 4.86 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{oxidant}] = 4.86 \times 10^{-4} \text{ mol dm}^{-3}$  and  $[\text{H}^+] = 0.3$  to  $1.5 \text{ mol dm}^{-3}$  at  $35^\circ\text{C}$ . The rate increases as the concentration of acid increases. This may be due to the formation of a stable  $\text{PA-Mn}^{\text{III}}$  species in acidic medium. A similar trend has been observed in the oxidation of phenacyl bromides by manganese(III) sulphate<sup>32</sup>.

The reaction between manganese(IV) complexes and D-glucose was also monitored using the EPR technique, by following the formation of one of the products  $Mn^{II}$ . The reactants were mixed under experimental conditions and the EPR spectra were recorded. Typical spectra showing the formation of  $Mn(II)$  are given in figure 5.

Activation parameters were also evaluated for the reaction. The value of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the complexes (I) and (II) at  $30^\circ C$  are  $78.7 \text{ kJ mol}^{-1}$  and  $45.4 \text{ kJ mol}^{-1}$  respectively. Increase of temperature accelerates the rate of the reaction indicating the formation of a stable activated complex in the transition state. The negative value of  $\Delta S^\ddagger$  indicates the orderliness of the reaction and the formation of a more rigid activated complex. The high value of  $\Delta H^\ddagger$  indicates difficulty in the formation of the activated complex.

#### 4. Conclusion

Using 12-B heteropolyanions  $[XMo_{12}O_{42}]^{8-}$ , where  $X = Ce, Th$  and  $U$  as ligands three complexes, viz.,  $(NH_4)_4[Mn^{IV}ThMo_{12}O_{42}] \cdot 10H_2O$  (I),  $(NH_4)_4[Mn^{IV}UMo_{12}O_{42}] \cdot 8H_2O$  (II) and  $(NH_4)_4[V^{IV}CeMo_{12}O_{42}] \cdot 8H_2O$  (III) were prepared. These complexes have been characterised by IR, Raman and EPR spectral studies.

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