SHORT PAPER

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Potassium bis(2-[α-hydroxyalkyl/aryl] benzimidazolato) dioxovanadates(V) through base assisted aerial oxidation of the corresponding oxovanadium(IV) complexes[†]

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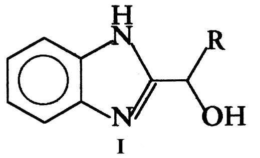
Bis(2-[α-hydroxyalkyl/aryl]benzimidazolato)dioxovanadates(V) dihydrates, as their potassium salts, were prepared by the reaction of [VO(acac)$_2$] with the respective benzimidazole followed by aerial oxidation in presence of KOH. An octahedral structure has been proposed for these complexes on the basis of IR, electronic and ^{1}H NMR spectral studies, and thermogravimetric analysis.

Keywords: bis(2-[-α-hydroxyalkyl/aryl]benzimidazolato) dioxovanadates(V) dihydrates

Perhaps interaction of vanadate ion with the coordinating ligands is the most suitable and general procedure to obtain complexes having a *cis*-[VO$_2$]$^+$ core.[1-4] However, this method is limited to ligands soluble in water or made soluble in water using suitable base such as KOH or NaOH.[5] Recently stabilisation of vanadium(V) complexes from the corresponding oxovanadium(IV) species via aerial oxidation has been achieved successfully.[5-7] However, such complexes are usually binuclear with the [(VO)$_2$μ-O]$^{4+}$ core. In the presence of a suitable base such association can be stopped and oxidised species can be isolated with the *cis*-[VO$_2$]$^+$ core.[5,8,9] Isolation of dioxovanadium (V) complexes using this process is, however, limited to only tridentate ligands.

In the present investigation, we have adopted the same procedure to isolate dioxovanadium(V) complexes of the biologically important mono basic bidentate ligands **I** (Scheme 1) and have observed that a base (*e.g.* KOH) not only accelerates the oxidation of oxovanadium(IV) complexes formed in solution, it also provides a suitable counter cation (K$^+$) to stabilise the oxidized species as the monomer K[VO$_2$L$_2$].2H$_2$O (LH= **I**).



I

R = H (Hhmbmz)
R = CH_3 (Hhebmz)
R = C_6H_5 (Hhbbmz)

Scheme 1

Results and discussion

Reaction of [VO(acac)$_2$] with ligand I (*c.f.* Scheme 1) in refluxing methanol followed by aerial oxidation in presence of KOH leads to the formation of dioxovanadium(V) complexes of general formula K[VO$_2$L$_2$].2H$_2$O (LH = **I**). KOH not only accelerates the oxidation of the oxovanadium (IV) species formed in solution, it also provides a suitable counter cation. The reaction can be represented by the simple eqns (1) and (2).

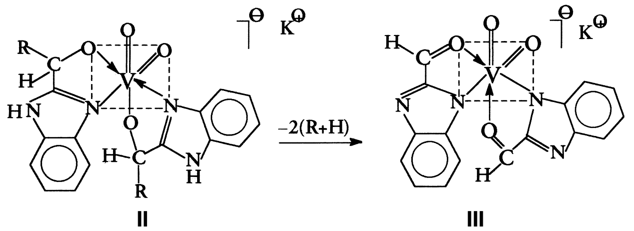
$$[V^{IV}O(acac)_2] + 2LH \xrightarrow{MeOH} [V^{IV}OL_2] + 2acacH \quad (1)$$

$$[V^{IV}OL_2] + KOH + O_2 \xrightarrow{MeOH} K[V^{V}O_2L_2].2H_2O \quad (2)$$

These complexes exhibit two absorption bands in the UV region with a slight shift in the band positions from that of the free ligands (276 and 283 nm). This is indicative of the coordination of ligands to the vanadium. Similarly, ^{1}H NMR spectra of these complexes exhibit signals due to aliphatic as well as aromatic protons at nearly the same position as that of respective free ligand.[10] The signal due to the –NH proton could not be observed between 0 and 15 ppm.

The presence of two intense bands in the *ca* 900 cm^{-1} region due to the *cis*-VO$_2$ group in the IR spectra clearly indicates the oxidation of [VO]$^{2+}$ species to [VO$_2$]$^+$. Other spectral features due to the co-ordination of ligand to the vanadium are comparable to that reported for dioxomolybdenum(VI) and dioxotungsten(VI) complexes.[11] All the complexes show a broad feature in the 2600 – 2900 cm^{-1} region, due to the involvement of the NH proton in hydrogen bonding with lattice water. However, the intensity of the band decreases in the order **1**>**2**>**3**, indicating the presence of a similar order of hydrogen bonding in these complexes.

The TGA profile of one representative complex **3** is given in Fig. 1. All three complexes lose weight equivalent to two water molecules in the first step. The weakest hydrogen bonded complex **3** loses these water molecules at lower temperature while **1**, having highest hydrogen bonding, loses them at higher temperature. On further heating each coordinated ligand in **2** and **3** loses methyl or phenyl groups, respectively, in the second step of the thermogram. The loss of methyl or phenyl groups is followed by the abstraction of N-H hydrogen from the benzimidazole moiety as shown in Scheme 2



Scheme 2 (R = H, CH_3, C_6H_5)

This abstraction causes a series of electronic rearrangement to give **III**, and converting coordinated imino nitrogen and

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

anionic oxygen into amido and aldehydo groups, respectively. Due to the poor stability of **III**, further increment of temperature causes decomposition of the remaining part of the complex up to the formation of KVO_3 as the end product. The % weight loss of the residue obtained matches the theoretical value. In the complex **1**, ligand decomposition starts after the loss of water and continues until the formation of KVO_3 at ~620°C. It is very likely that **1** also undergoes a transformation like that shown in Scheme 2, but since $2H_2$ is lost it does not show up in the TGA traces. Structure **III**, is therefore, a common intermediate decomposition product of all three initial compounds. The transformation of intermediate products into KVO_3 in the same temperature range further suggests the common intermediate decomposition product, **III** for these complexes. However, isolation and characterisation of this species spectroscopically was not possible in any compound due to the poor stability of **III**.

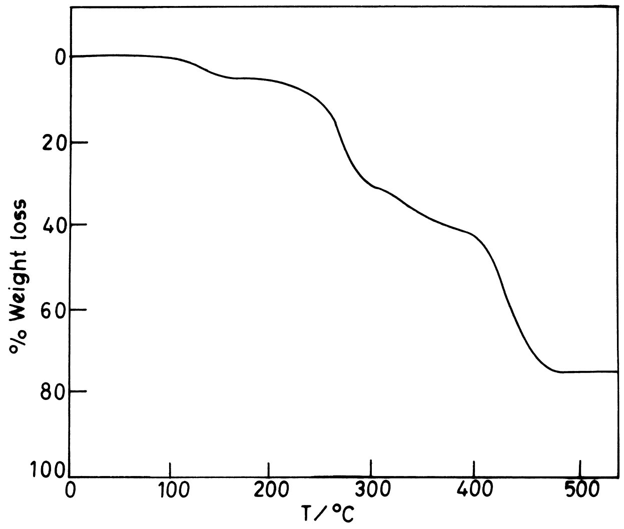

Fig. 1 TGA profile of complex **3**.

On the basis of the physico-chemical evidence presented above, an octahedral structure **II**, has been proposed for these complexes. The structure of a related *cis*-dioxovanadium(V) complex, $NH_4[VO_2(pic)_2]$ (pic = 2-picolinic acid), where the two oxo groups are *trans* to one N and one O donor atoms of the 2-picolinic acid, has been confirmed by a single-crystal X-ray study.[4]

Although the synthetic route reported herein for dioxovanadium (V) complexes has hitherto only been proven useful for some tridentate ligands, we have applied this process for monobasic bidentate ligands successfully. It is expected that aerial oxidation of oxovanadium(IV) complexes in presence of base to dioxovanadium(V) would be a suitable general synthetic route to isolate mononuclear dioxovanadium(V) complexes.

Experimental

V_2O_5 (Loba Chemie, India), lactic acid, mandelic acid, (E. Merck, India) and glycolic acid (Lancaster) were used as supplied. *o*-Phenylenediamine (E. Merck) was recrystallized from ethanol while acetylacetone (E. Merck) was distilled before use. 2-(α-hydroxymethyl)benzimidazole, 2-(α-hydroxyethyl)benzimidazole and 2-(α-hydroxybenzyl)benzimidazole were prepared by the literature method.[12] $[VO(acac)_2]$ was prepared by the method of Rowe and Jones.[13]

The micro analytical section of the National Chemical Laboratory, Pune, performed elemental analyses of the complexes. A simple manually-operated thermo-balance constructed in our laboratory was used to carry out thermogravimetric analyses. IR spectra were recorded as KBr pellet on a Perkin-Elmer model 1600 FT-IR spectrometer while electronic spectra were taken in DMF on a UV-1601 PC UV/vis spetrophotometer. ^1H NMR spectra were recorded in $(CD_3)_2SO$ using a Bruker DRX-300 FT-NMR spectrometer with TMS as internal standard.

Synthesis: $K[VO_2(hmbmz)_2]$. $2H_2O$ **1**. A methanolic solution of $[VO(acac)_2]$ (0.265 g, 1 mmol) was added to a well-stirred hot solution of Hhmbmz (0.296 g, 2 mmol) in MeOH (20 ml). The resulting reaction mixture was heated at reflux for 8 h and cooled to ambient temperature. KOH (0.056 g, 1 mmol) dissolved in 2 ml of MeOH was added to it and the flask was kept open for aerial oxidation at room temperature whereupon a cream coloured compound deposited on the wall of the flask. This was filtered, washed with MeOH and dried *in vacuo* (yield 60 %) (Found: C, 42.4; H, 4.0; N, 12.5%. $C_{16}H_{18}KN_4O_6V$ requires C, 42.5; H, 4.0; N, 12.4 %); ν_{max}/cm^{-1} 1622 (C=N), 1595 (C=C), 952 (V=O sym), 918 (V=O asym); λ_{max}/nm 272, 278; δ_H $[(CD_3)_2SO]$ 5.48 (2H, s, alkyl), 7.73 – 7.36(4H, m, aryl).

A similar procedure as mentioned for **1** was adopted for the synthesis of $K[VO_2(hebmz)_2].2H_2O$, **2** and $K[VO_2(hbbmz)_2].2H_2O$, **3** using ligand Hhebmz or Hhbbmz, respectively.

$K[VO_2(hebmz)_2].2H_2O$ **2**: Yield 55% (Found: C, 45.2; H, 4.4; N, 11.6%. $C_{18}H_{22}KN_4O_6V$ requires C, 45.0; H, 4.6; N, 11.7%); ν_{max}/cm^{-1}1622 (C=N), 1595 (C=C), 954 (V=O sym), 917 (V=O asym); λ_{max}/nm 272, 279; δ_H $[(CD_3)_2SO]$ 1.75 (3H, d, methyl), 5.44(1H, q, alkyl), 7.36 - 7.80(4H, m, aryl).

$K[VO_2(hbbmz)_2].2H_2O$ **3**: Yield 58% (Found: C, 55.5; H, 4.3; N, 9.1%. $C_{28}H_{26}KN_4O_6V$ requires C, 55.6; H, 4.3; N, 9.3%); ν_{max}/cm^{-1}1624 (C=N), 1598 (C=C), 945 (V=O sym), 924 (V=O asym); λ_{max}/nm 273, 280; δ_H $[(CD_3)_2SO]$ 6.39(1H, s, alkyl), 7.24 – 7.74(9H, m, aryl).

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10 δ_H $[(CD_3)_2SO]$ of Hhmbmz: 5.72 (2H, s, alkyl), 7.08 – 7.65(4H, m, aryl); Hhebmz: 1.75(3H, s, methyl), 5.53(1H, q, alkyl), 7.24 – 7.76(4H, m, aryl); Hhbbmz: 6.0 (1H, s, akyl), 7.06 – 7.60(9H, m, aryl).
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