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A linear potassium metalated vanadium(IV) polymeric alkoxide: Structural and spectroscopic studies

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Abstract

We have been interested in the preparation of alkoxometallate "bricks" of the $M'\{M(OR)_n\}$ type, with M' = alkaline metal, M = vanadium(IV) and R = isopropyl or *tert*-butyl, to be employed as starting materials in salt-elimination reactions with other transition metal complexes. Here, we report the synthesis, spectroscopic characterisation and molecular structure of $[\{K_2(VO)_2(OPr^i)_6(Pr^iOH)_2\}_\infty]$ (**1**), prepared by a combination of Lewis acid–base and micro-hydrolysis reactions. The linear polymeric chain contains planar four-membered $\{(V{=}O)_2(\mu\text{-}OPr^i)_2\}$ rings with vanadyl groups in *anti-coplanar* configuration; the rings are connected by "bridging" $K(HOPr^i)^+$ units. Powder and solution EPR spectra suggest a spin triplet ground state, with a very weak ferromagnetic interaction between the vanadium(IV) centres at room temperature.

Keywords: Vanadium(IV); Potassium; Coordination polymer; Alkoxide; Mixed-metal

1. Introduction

Heterobimetallic alkoxides $(M'_xM''_y(OR)_z)$ are attractive as molecular precursors of mixed metal oxides because they can be prepared and isolated as pure, crystalline materials with defined M′:M″ proportions. These features, in particular the well-characterised metal stoichiometries, are useful in the preparation of specific oxides [1–4] by sol–gel, chemical vapour deposition (CVD) and physical vapour deposition (PVD) techniques [5–8]. The products obtained from these precursors are important candidates for high-technology applications, especially those dependent on oxide purity and highly homogeneous metal distribution in the solids.

In spite of the recent developments in heterometal alkoxide chemistry, mixed metal oxides containing vanadium ($KBaVO_4$, $KSrVO_4$, $Ba_2V_2O_7$, KVO_3, $FeVO_4$, $Ag_2V_4O_{11}$, $MgCu_2V_2O_8$, etc.) have been prepared almost exclusively from mixtures of homometal alkoxides, β-diketonates and/or carboxylates, frequently involving high-temperature and solid-state reactions [9–11]. A limiting factor in the development of new or improved V-containing heterometal oxides has been the lack of suitable *single-source precursors,* that is, reactive complexes with the different metal elements in the same molecular unit, and in defined stoichiometry. The preparation of these precursors requires suitable vanadium(IV) and vanadium(V) starting materials.

Several homometal (oxo)alkoxides of vanadium(V) synthesised from V_2O_5, NH_4VO_3, $VOCl_3$, or by ester exchange reactions have been reported [12]. On the other hand, oxovanadium(IV) alkoxides can be prepared from the same vanadium(V) starting materials, but only under specific reducing conditions. As an example, the reaction between $VOCl_3$ and sodium 1-methoxy-2-propanoxide yields a $V^{IV}{=}O$ derivative, while the attempt to apply the same procedure to ammonium metavanadate produces only a different oxovanadium(V) alkoxide [13].

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In the "non-oxo" form, that is, without the vanadyl group, vanadium(IV) alkoxide complexes are more elusive than V^V-containing alkoxides. Aiming at the synthesis of mixed-metal oxide precursors, we recently reported the preparation of the "non-oxo" vanadium(IV) alkoxide $[\{V(OPr^i)_3\}_2(\mu\text{-}OPr^i)_2]$ [14] and its reaction with $[\{FeI_2\}\text{-}(\mu\text{-}I)_2\{Fe(HOPr^i)_4\}]$ [15] to give the *single-source* $[FeI_2\text{-}(\mu\text{-}OPr^i)_2V(OPr^i)_2(HOPr^i)]$ [16].

We then became interested in developing a new, easier access to heterometal alkoxide assemblies containing both vanadium(IV) and a second transition metal through the preparation of $M'\{M(OR)_n\}$ species ($M' = K^+$ and R = *tert*-butyl or isopropyl), to be used as starting materials in salt-elimination reactions with transition metal halides. In order to do so, we decided to adapt, to vanadium, the classical method employed for titanium(IV) and zirconium(IV) alkoxides [17].

2. Experimental

2.1. General

All operations were carried out under an N_2 atmosphere with the use of standard Schlenk or glove-box techniques, unless otherwise stated. The solvents were dried by standard procedures [18] and distilled twice prior to use.

The commercial $KOBu^t$ (Aldrich) was used without purification. Anhydrous propan-2-ol (Aldrich) was distilled twice, from sodium and from calcium hydride. $[V(OBu^t)_4]$ was prepared according to the methods of Haaland and co-workers [19]. After solvent removal, the royal-blue liquid was distilled in 88% yield. Found for $[V(OBu^t)_4]$: C, 55.0; H, 10.5%. $C_{12}H_{36}O_4V$ requires: C, 56.0; H, 10.5%. IR, hexane solution (cm^{-1}): 1165 s, ν(C–O); 1032, ν(C–C); 941 and 789 s, carbon skeleton vibrations; 615, ν(V–O). EPR (hexane, 77 K): $A_\parallel = 135 \times 10^{-4}\ cm^{-1}$, $A_\perp = 31 \times 10^{-4}\ cm^{-1}$, $g_\parallel = 1.934$, $g_\perp = 1.980$. Electronic spectrum (hexane, 1×10^{-3} mol dm^{-3}, S_4 symmetry, nm): 848 ($^2B \rightarrow {}^2A$) and 729 ($^2B(E) \rightarrow {}^2B(T_2)$).

Microanalyses were carried out by Medac Laboratories Ltd., Egham, Surrey, UK. Vanadium analyses were performed by ICP–OES at the Institute of Chemistry, University of São Paulo – SP (IQ-USP), Brazil, using a Spectroflame Sequential equipment from Spectro Co., operating at 1.2 kW. The samples were dissolved in 3 mol dm^{-3} HCl before analysis.

IR data (Nujol mulls) were recorded on Bomem Hartmann & Braun equipment (MB series) in the 400–4000 cm^{-1} range. Samples were spread on KBr plates. EPR data (X-band, 9.5 GHz) were recorded on a Bruker ESP-300E instrument from solid samples or toluene/propan-2-ol solutions at room temperature and 77 K. EPR parameters were determined from spectrum simulation with Simphonia® (Bruker). UV–Vis spectra were recorded at room temperature from Nujol mulls in an HP 8452A spectrophotometer.

Magnetic susceptibility measurements by a modified Gouy method were carried out in the solid state at room temperature using a MKII magnetic susceptibility balance from Johnson-Matthey. Corrections for the diamagnetism of the ligands were applied (Pascal constants) [20,21].

2.2. Synthesis of $[\{K_2(VO)_2(OPr^i)_6(Pr^iOH)_2\}_\infty]$ (1)

A royal-blue solution of $[V(OBu^t)_4]$ (4.4 g; 9.3 mmol) in 30 cm^3 of toluene was added with stirring to a suspension of $KOBu^t$ (0.73 g; 4.6 mmol) in 20 cm^3 of toluene. The mixture was stirred at room temperature for 19 h. The resulting blue suspension was filtered to give a violet solid (0.15 g) containing no vanadium, which was discarded. The filtrate was evaporated under vacuum to 10 cm^3 and propan-2-ol (40 cm^3) was added. After 24 h at room temperature, light-green crystals of **1** were filtered off, washed with propan-2-ol and dried under vacuum. Yield: 1.45 g (45%). *Anal.* Calc. for $C_{24}H_{58}K_2O_{10}V_2$ (**1**): C, 41.9; H, 8.5. Found: C, 41.4; H, 8.6%.

2.3. Single-crystal X-ray diffraction analysis

Data were collected on a Nonius Kappa CCD area detector diffractometer at the Chemistry Department, University of Sussex, Brighton, UK. A highly moisture-sensitive light green crystal of **1** ($0.2 \times 0.2 \times 0.1\ mm^3$) was mounted on a glass fibre and cooled to 173(2) K. Cell dimensions were based on all 4985 observed reflections ($I > 2\sigma_I$). The structure was solved by direct methods using the program package WinGX [22] and refined by full-matrix least-squares on F^2 with SHELXL-97 [23]. Drawings were made with ORTEP-3 for Windows [24]. Absorption corrections were carried out with MULTISCAN. All non-hydrogen atoms were refined anisotropically.

3. Results and discussion

The 1:2 reaction of $KOBu^t$ and $[V(OBu^t)_4]$ in toluene was carried out using a synthetic route analogous to that employed for the preparation of "$K\{Ti_2(OPr^i)_9\}$" and $[K\{Zr_2(OPr^i)_9\}]$ [17,25,26]. The procedure gave a very air sensitive royal-blue solution and a violet solid; the latter did not contain vanadium. The addition of propan-2-ol to the mother liquor produced light-green crystals of **1** at room temperature. Product **1** is insoluble in toluene, propan-2-ol, hexane, dichloromethane, tetrahydrofuran and diethyl ether. This lack of solubility in common organic solvents is consistent with the behaviour of a number of polymeric $M(OR)_n^-$ anions [27]. Surprisingly, the crystals of **1** are highly soluble in a 2:1 toluene/propan-2-ol mixture; this behaviour is probably associated with structural changes (see below).

Analytical and spectroscopic data for **1** are consistent with the formulation $[\{K_2(VO)_2(OPr^i)_6(Pr^iOH)_2\}_\infty]$ determined by X-ray analysis. The crystalline, light green prod-