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Reactivity of vanadium oxytrichloride with β-diketones and diesters as precursors for vanadium nitride and carbide

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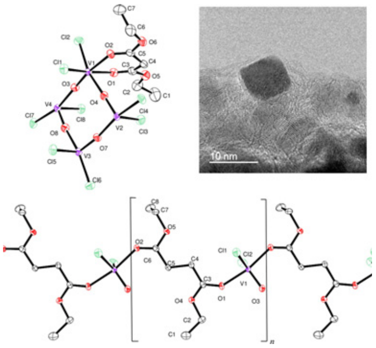
HIGHLIGHTS

- The synthesis of vanadium compounds Dichloro(oxo) (2,4-pentanedione) vanadium(V), Dichloro(oxo) (diethyl malonate) vanadium(IV) and Dichloro(oxo) (2,4-pentanedione) vanadium(V) are reported
- The compounds were evaluated as single source precursors for vanadium nitride and carbide.
- The synthesis of vanadium nitride or carbide could be effected by altering the gas under which these compounds were annealed at 1200 °C from nitrogen to argon.
- Dichloro(oxo) (diethyl malonate) vanadium(IV) produced phase pure vanadium nitride and carbide.

GRAPHICAL ABSTRACT



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ABSTRACT

Vanadium(V) oxytrichloride was reacted with 2,4-pentanedione, diethyl malonate, and diethyl succinate under inert conditions, forming compounds: dichloro(oxo)(2,4-pentanedione) vanadium(V) [**1**], dichloro(oxo)(diethyl malonate) vanadium(IV) [**2**] and dichloro(oxo)(diethyl succinate) vanadium(IV) [**3**]. Compounds **1**–**3** are coordinated to the vanadium centre through the two carbonyl oxygen atoms of the bidentate ligand. It was determined by X-ray crystallography that the structures of the resulting complexes were significantly different, resulting in a monomeric complex (**1**), a tetrameric ring (**2**) and a 1D coordination polymer (**3**). Following the synthesis and isolation of **1**–**3**, they were tested as precursors for vanadium nitride and vanadium carbide by annealing under nitrogen and argon respectively at 1200 °C for 24 h. The resulting materials were characterised by: XRD, EDS, XPS and TEM.

1. Introduction

Vanadium nitride (VN) and vanadium carbide (VC) are the subject of investigation for materials scientists due to their exceptional hardness, high melting points, high thermal conductivities and solid lubricating

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properties [1–3]. The Vickers hardness of VC has been measured at 2600–3200 kg mm^{-2} [4,5], considerably harder than tungsten carbide [6] and similar to titanium carbide (2400 kg mm^{-2} & 1 1900–3200 kg mm^{-2} respectively) [7] as well as a measured Young's modulus comparable with that of tungsten carbide [5,8,9]. VN exhibits similar properties, with a Vickers hardness of 1500 kg mm^{-2} and high melting point (2619 K) comparable to VC (3103 K) [1,10].

VN is widely used to harden steel, with a layer of VN created on the surface of the steel by annealing at high temperatures under a flow of nitrogen. This increases wear resistance for use in high performance steels [11,12]. VN is also a strong coupled superconductor, with nanocrystalline VN having potential use in supercapacitors [13].

VN is often synthesised by controlled direct nitridation using nitrogen or ammonia gas at varying temperatures. In this way, foams of VN were formed through the nitridation of vanadium oxides with ammonia gas with high control over foam morphology [14]. Other methods include microwave synthesis [15–17], hydrothermal synthesis [18] and high temperature plasma routes [19].

VN thin films have been synthesised from molecular precursors such as $NH(SiMe_3)_2$ [20], VCl_4 [21,22] and $V(NEt_2)_5$ with a carrier gas composed of 10% NH_3 in He using atmospheric pressure chemical vapour deposition (APCVD) [23]. VN has also been produced from a variety of molecular precursors including: the direct reaction of vanadium tetrachloride with sodium amide [24], vanadium-urea complexes [25,26], chloroimidovanadium compounds and metal oxide nanoparticles with cyanamide and urea [27].

VC has been shown to be a highly effective additive to tungsten carbide in improving the hardness and thermal conductivity of highly durable ceramic-metal "cermet" composites [28], and an ideal material for improving the wear resistance of tools [29-33]. Furthermore precipitation of vanadium carbide nanoparticles into ferrite-martensite dual phase steel has been shown to cause a consistent improvement to Vickers hardness over a range of synthesis conditions [27–29]. It has been reported that depositing a layer of vanadium carbide onto the surface of high carbon steel *via* a salt bath has been shown to improve its surface hardness by six times [34]. A similar report detailed VC coatings deposited onto a die steel substrate *via* high temperature reactive diffusion using a NH_4Cl/ferro-vanadium/naphthalene precursor, resulting in surface hardness improved approximately fivefold [35].

Numerous methods for the formation of vanadium carbide nanoparticles exist in the literature. A family of preparations using vanadium(V) oxide (V_2O_5) with various carbonaceous species and reducing gaseous environments at high temperatures are widely used [28,36,37]. Refluxing V_2O_5 powder in *n*-dodecane has been shown to yield VC nanoparticles after several days [38], as has decomposition of V_2O_5 with magnesium filings and acetone in an autoclave [28,39–41]. Nanostructured thin films of vanadium carbide have been deposited using the chemical vapour deposition of single source molecular precursors such as: vanadocene [42], vanadocene dichloride and dimethyl vanadocene [43] and cyclopentadienyl vanadium tetracarbonyl [44].

We present a range of new molecular species derived from diester (2,4-pentanedione, diethyl malonate, and diethyl succinate) addition to $VOCl_3$ as single source precursors for vanadium nitride and carbide formation. The single source precursors presented herein are ideal for small scale laboratory preparations and applications of VN and VC, such as the synthesis of thin films, nanoparticles and nanofibres [45]. The chemistries and structures of the aforementioned molecular species were evaluated using X-ray crystallography (full structure determination and associated analysis), elemental analysis, ^1H and $^{13}C\{^1H\}$ nuclear magnetic resonance (NMR) spectroscopy. Each of the precursors was converted to vanadium nitride and vanadium carbide *via* heating in furnace under an inert atmosphere at 1200 °C, similar temperatures to those used in the formation of austenitic steel [46,47]. The conversion to the carbide or nitride was dependent on the carrier gas used, with nitrogen giving the nitride and argon the carbide. This demonstrates the versatility of the single-source precursors presented herein over multi-source methods, as by changing something as simple as the carrier gas, a completely different material is formed. It is also noteworthy that the vast majority of recent literature on the synthesis of both vanadium carbide and nitride focuses on the use of dual source precursors and complex formation *in situ* in the reaction vessel [48–53]. Reported scale-up and industrial scale processes use dual source routes, with vanadium pentoxide and carbon under different gaseous conditions for both vanadium carbide and nitride [54,55]. The use of single source precursors represents a significant step forward in precursor design for vanadium nitride and carbide, and offers potential advantages over dual source precursors for industrial scale-up as the amount of feedstocks would multiply, thus increasing costs. This route would also offer a more convenient synthetic method for lab-scale synthesis of both vanadium carbides and nitrides. The conversion to vanadium carbide and nitride was examined by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM).

2. Experimental

All starting materials were purchased from Sigma Aldrich and used without further purification. The solvents were dried over activated alumina by the Grubbs method using anhydrous engineering equipment, such that the water concentration was 5–10 ppm [56]. All products were synthesised under an atmosphere of nitrogen obtained from BOC in anhydrous solvents using standard Schlenk techniques. ^1H and $^{13}C\{^1H\}$ NMR spectroscopy was carried out on a Bruker A-600 MHz spectrometer, operating at 295 K and 600.13 MHz (^1H). Signals are reported relative to $SiMe_4$ ($\delta = 0.00$ ppm) and the following abbreviations are used s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), b (broad). Deuterated $CDCl_3$ was obtained from GOSS Scientific and was degassed and dried over 3 Å molecular sieves.

2.1. Synthesis of dichloro(oxo)(2,4-pentanedione) vanadium(V) [**1**]

2,4-Pentanedione (acacH) (0.5 cm^3, 4.87 mmol) was added dropwise to $VOCl_3$ (2 cm^3, 21.1 mmol) in 30 cm^3 of *n*-hexane and stirred under nitrogen for 2 h. A dark precipitate formed immediately, giving a solution that appeared black. The precipitate was filtered and washed with *n*-hexane and dried *in vacuo*. This afforded the dark red complex **1** (1.1 g, 75%). Crystals suitable for single crystal X-ray diffraction were grown by layering a saturated solution of **1** in dichloromethane with hexane. Large green crystals formed over the course of 2 days. ^1H NMR ($CDCl_3$): δ 2.39 (s, 6H, CH_3), 6.13 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.4 (CH_3), 105 (CH), 193 (C=O). Elemental analysis calculated for $VO_3Cl_2C_5H_7$: C, 25.34; H, 2.98. Found: C, 25.80; H, 3.02.

2.2. Synthesis of dichloro(oxo)(diethyl malonate) vanadium(IV) [**2**]

Diethyl malonate (0.5 cm^3, 3.3 mmol) was added dropwise to $VOCl_3$ (2 cm^3, 21.1 mmol) in 50 cm^3 of hexane and stirred under nitrogen for 2 h. An excess of $VOCl_3$ was used to ensure completion as unreacted $VOCl_3$ is facile to remove from the reaction. A very dark precipitate was formed in a dark red solution. The precipitate was filtered and washed 3 times with 20 cm^3 hexane and dried *in vacuo* to afford **2** in good yield (0.9 g, 78%). Some of the product was re-dissolved in 5 cm^3 dichloromethane and layered with 15 cm^3 hexane. Small crystals formed over approximately one week. ^1H NMR ($CDCl_3$): δ 1.34 (t, 6H, $-CH_3$, $J = 7.25$ Hz, 3.35 (s, 2H, $-CH_2$)), 4.18 (q, 4H, $-CH_2$, $J = 7.25$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.2 (CH_3), 55.9 (CH_2), 63.6 (CH_2CH_3), 163 (C=O). Elemental analysis calculated for $C_7H_{12}O_5Cl_2V$: C, 28.21; H, 4.06. Found: C, 26.38; H, 3.78.