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Reductive transformation of V(III) precursors into vanadium(II) oxide nanowires†

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Vanadium(III) oxide nanostructures are promising materials for supercapacitors and electrocatalysis because of their excellent electrochemical properties and high surface area. In this study, new homoleptic vanadium(III) complexes with bi-dentate O,N-chelating heteroarylalkenol ligands (DmoxCH=COCF₃, PyCH=COCF₃ and PyN=COCF₃) were synthesized and successfully transformed by reductive conversion into VO nanowires. The chemical identity of V(III) complexes and their redox behaviour were unambiguously established by single crystal X-ray diffraction studies, cyclic voltammetry, spectrometric studies and DFT calculations. Transformation into the metastable VO phase was verified by powder X-ray diffraction and thermo-gravimetry. Transmission electron microscopy and X-ray photoelectron spectroscopy data confirmed the morphology and chemical composition of VO nanostructures, respectively.

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Introduction

The long-standing interest in vanadium oxide chemistry has been due to its relevance to several industrial processes as well as its unique redox chemistry.¹ The redox activity and layered structures of crystalline vanadium oxides make these materials useful as intercalation cathodes for Li-ion batteries.^{2,3} Vanadium oxides have also been applied in catalytic and electrochemical fields due to their outstanding structural and valence flexibility.^{4,5} Currently, the search for different polymorphs of vanadium oxides that possess electrically induced valence switching properties is advancing rapidly due to their potential in heterogeneous catalysis and energy storage materials.^{6,7}

Several vanadium oxides show interesting properties in energy generation and conservation such as smart window for energy savings,^{8,9} cathode materials for Li-ion batteries¹⁰ and perovskite solar cells.¹¹ Vanadium monoxide (VO) represents a metastable phase in the V–O binary phase diagram that is interesting because of its unique redox chemistry and satisfactory electrical conductivity due to its partially filled conduction band.¹² Nevertheless, a reproducible synthesis of VO is challenging due to the coexistence of a large number of polymorphs of vanadium oxides¹³ (Fig. 1, ref. 14 and 15).



Fig. 1 Schematic vanadium–oxygen phase diagram based on the experimental data from Wriedt and the calculated data from Kang.^{14,15} The Magnélie phases V_nO_{2n-1} are highlighted in blue and the Wadsley phases V_nO_{5n-2} in green.

Nanostructured vanadium oxides have been obtained by sol-gel,¹⁶ pyrolysis,¹⁷ hydrothermal methods,¹⁸ chemical vapor deposition,¹⁹ electrospinning²⁰ and thermal reduction in the presence of a catalyst.²¹ However, reports on the controlled synthesis of vanadium(π) oxide nanomaterials especially from molecular precursors are still unexplored to a larger extent mainly due to the unavailability of suitable vanadium(π) oxide. Our research group has recently reported on the synthesis of volatile complexes from transition and main group metals using substituted heteroarylalkenol ligands, which offer a stabilizing effect by building six-membered metallacycles upon coordination to the central atom, which can also influence the physico-chemical

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properties by an additional positive inductive effect generated by different exchangeable heteroaryl moieties and a negative inductive effect of the CF_3 -groups (Scheme 1).^{22–24}

We therefore report here a reductive and quantitative transformation of vanadium(III) heteroarylalkenolate [V(DmoxCH=COCF₃)₃] (Scheme 3) into vanadium(II) oxide nanowires.

Results and discussion

Synthesis

The heteroarylalkenol ligands (1–3) used in this work were synthesized following the report by Kawase *et al.*²⁶ that was modified by Mathur *et al.*²⁷ *via* a reaction of a methylheteroaryl or aminoheteroaryl with trifluoroacetic anhydride (TFAA) and pyridine as a base as shown in (Scheme 2). The good electron donating and accepting properties of aryl-substituted alkenols make them bifunctional ligands providing both structural stability and electronic saturation around the metal centre that renders the resulting complex air-stable.

Via a salt metathesis reaction, three air-stable homoleptic vanadium(m) complexes were synthesized by reacting anhydrous VCl₃ with three equivalents of the respective deprotonated heteroarylalkenol ligands in tetrahydrofuran (THF) at room temperature (Scheme 3). The homoleptic vanadium(m) complexes (4–6) were isolated as orange powder and purified by sublimation under dynamic vacuum conditions (130 °C, 10^{-3} mbar) for further analysis. All the sample characterization studies were performed under ambient conditions including crystal mounting, which confirm that all the complexes are airstable.

Structural characterization

The IR spectra (4000–400 cm⁻¹) of $[V(DmoxCH=COCF_3)_3]$ (4), $[V(PyCH=COCF_3)_3]$ (5) and $[V(PyN=COCF_3)_3]$ (6) showed the hydroxyl –OH mode in the ligands to be absent in the deprotonation of hydroxyl-oxygen. The absorption band due to the ν (C–O) mode observed at 1320 cm⁻¹ in an uncoordinated ligand shifted to a higher wave number (1354 cm⁻¹) in the complex due to the coordination to an electrophilic metal



 $X = CH_3, NH_2$





Scheme 3 Synthesis of homoleptic vanadium(III) heteroarylalkenolates.

centre. Also, the absorption band of the conjugated olefin ν (C=C) mode observed at 1566 cm⁻¹ in an uncoordinated ligand shifted to a higher wave number (1618 cm⁻¹) in the complex due to the formation of a metallacycle. In addition, the bands belonging to ν (V–N) and ν (V–O) could be assigned to 530 cm⁻¹ and 450 cm⁻¹, respectively, thereby suggesting the formation of a vanadium complex²⁸ (Fig. SI 1†).

X-ray crystallography

Single crystal X-ray diffraction analysis of complexes **4–6** showed the bonding arrangement of the ligands in a meridional fashion with an octahedral coordination geometry around vanadium centres (Fig. 2).

Compound 4 crystallized in the monoclinic space group $P2_1/c$ with four molecules per unit cell with a slightly distorted octahedral geometry around the vanadium centre originating from the geometric constraints of the DmoxCH=COCF₃ ligand. The main crystallographic data are given in Table S1.† The O6–V1–N3 angle is 88.56° while O2–V1–N1 and O4–V1–N2



Scheme 1 Structural and electronic modification of beta-heteroarylalkenols.²⁵



Fig. 2 Molecular structures of 4 (left), 5 (middle) and 6 (right). Thermal ellipsoids for V, O and N atoms are shown at the 50% probability level, and the H atoms have been omitted for the sake of clarity.

angles are 86.13° and 85.12°, respectively, showing deviation from the ideal octahedral geometry (90°). The oxygenvanadium bonds (1.954 Å (V1-O2) and 1.937 Å (V1-O4)) are in the range of typical vanadium-oxygen bond lengths found in octahedrally coordinated vanadium compounds (1.61 Å to 2.32 Å).²⁹ The vanadium-nitrogen bonds are in the typical range (2.01 Å to 2.18 Å) with the observed bond lengths being between 2.103 Å (V1-N3) and 2.128 Å (V1-N1). The bond lengths, bond angles and bite angles in 4 are similar to the values reported by Morosin, and Montgomery³⁰ for octahedral α - and β -tris(2,4-pentanedionato) vanadium(m). The two other complexes show a similar coordination arrangement in which compounds 5 and 6 crystallized in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The bond angle and distance in the two compounds are closely related with just minor differences. The crystallographic R-values of compound 6 are a bit high, due to the fast rotation of the CF₃-groups in the ligand backbone, which could not be reduced by low temperature measurement. For this reason, each fluorine atom was splitted at the C1 atom with an occupancy of 0.5. Elemental analysis confirms the formation and purity of the synthesized compounds. Small discrepancies for 5 (%N off) and 6 (H% off) could have been caused by the remaining solvent molecules.

Electron ionization mass spectra recorded with an ionization energy of 20 eV showed that compounds **4**, **5** and **6** fragmented into distinctive radical cations that proved the existence of the species in the gas phase since the calculated isotopic patterns of the signals were found to match with the measured ones. The EI-mass spectra of compound **4** demonstrated a considerable thermal stability with parent molecular ions $[V(C_8H_7O_2NF_3)_3]^{*+}$ $[m/z \ 669; \ 6\%]$ and $[V(C_8H_7O_2NF_3)_2O]^{*+}$ $[m/z \ 479; \ 100\%]$ as the base peak with the highest intensity. Other important fragment ions also observed in the complex are $[V(C_8H_7O_2NF_3)_2]^{*+}$ $[m/z \ 463; \ 5\%]$ and $[C_8H_7O_2NF_2]^{*+}$ $[m/z \ 189; \ 25\%]$ (Fig. SI 2†).

The UV-vis spectral data (200-900 nm) of $[V(DmoxCH=COCF_3)_3]$ (4) recorded in acetone showed two bands corresponding to d-d and charge-transfer transitions (Fig. SI 3[†]). In the visible region two moderately intense

absorption maxima were observed at 616 nm ($\varepsilon = 200 \text{ l mol}^{-1} \text{ cm}^{-1}$) and 756 nm ($\varepsilon = 183 \text{ l mol}^{-1} \text{ cm}^{-1}$) assignable to d–d transitions (${}^{3}\text{T}_{1g}(\text{F}) \rightarrow {}^{3}\text{T}_{1g}(\text{P})$ and ${}^{3}\text{T}_{1g}(\text{F}) \rightarrow {}^{3}\text{T}_{2g}$), respectively. The absorbance of the concentrated sample was too high to determine the absorption maxima of the intra-ligand charge transfer. However, upon dilution, a decrease in absorbance was observed with new absorption maxima at 327 nm ($\varepsilon = 10\ 000 \text{ l mol}^{-1} \text{ cm}^{-1}$) and 211 nm ($\varepsilon = 7400 \text{ l mol}^{-1} \text{ cm}^{-1}$) corresponding to intra-ligand n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ charge transfer transitions.³¹

Electrochemical investigations using cyclic voltammetry were carried out to determine the redox behaviours of the synthesized complexes. The cyclic voltammogram of compound 4 with a scan rate of 100 mV s⁻¹ in 0.1 M solution of *n*-Bu₄NPF₆ (electrolyte) in absolute THF showed a well-defined redox process at -1.77 V corresponding to the formation of the V(III)/V(II) couple (Fig. 3). The one-electron electrochemically reversible process observed at -1.77 V was unaffected upon varying the scan rates, however, further reduction to V(1) at -2.40 V was found to be irreversible. The CV also showed a quasi-reversible oxidation, presumably the oxidation of V(III) to V(IV). Since quasi-reversibility suggests that the electron transfer process was slow relative to the voltage scan rate (voltammogram depends strongly on the kinetic parameter). Therefore, the electrochemical study of the oxidized species was kinetically analysed by measuring them at three different feed rates. With rapid measurement (500 mV s^{-1}), the waveform showed a higher reversibility than at normal settings (100 mV s^{-1}). In a very slow feed rate (20 mV s^{-1}), the reversibility was lost, possibly because the voltage scan rate was not enough to initiate the electron transfer process. In situ UV/vis spectro-electrochemistry measurement of the complex in comparison with the free ligand was also performed for better understanding of the electronic transition in the reduced compound as shown in Fig. 3(c & d). A broad d-d transition with an absorption maximum at 557 nm of the diluted solution appears after the metal centred reduction, which correlates to the reversible formation of V(II) species in the CV. The intraligand charge transfer absorption at 303 nm increased during



Fig. 3 (a) Cyclic voltammogramms of 4 at 298 K, 100 mV s⁻¹ scan rate. (b) Kinetic measurement of 4 oxidized at three different feed rates. (c) UV/ vis-spectroelectrochemistry of 4. (d) UV/vis-spectroelectrochemistry of DmoxCH=COCF₃ (1).

the reduction of the complex as well in the free ligand, which indicates dissociation of a free ligand after reduction.

Theoretical (DFT) investigation

For further interpretation and better understanding of the electrochemical measurements, we carried out a DFT-based geometry optimization of complex 4 that elaborated the localization of the molecular orbitals (HOMO and LUMO states). The calculations showed that both the HOMO and LUMO are mostly centred on the vanadium atom with an additional small density on the ligands (Fig. 4). Since applied redox-chemistry obviously occurs in these orbitals, the oxidation and



Fig. 4 HOMO and LUMO molecular orbitals of the [V $(DmoxCH=COCF_3)_3$] complex.

at least the first reversible reduction found in the cyclic voltammetry is probably vanadium centred. This implies that the reversible reduction observed from V(m)/V(n) at -1.77 V takes place on the vanadium centre as evident from the DFT calculation. The well-defined reversible redox process at -1.77 V corresponding to the formation of the V(m)/V(n) couple suggests the potential catalytic application of the complex especially in oxygen reduction reactions according to the report of Zagal *et al.* that the potential of the M(m)/M(n) redox couple is an important parameter in determining the electrocatalytic activity toward the ORR in metallophthalocyanine catalysts.³²

Thermal studies

Thermogravimetric analysis (TGA) of complexes 4–6 revealed the trend in the stability and volatility of the complexes as shown in Fig. 5. Thermal decomposition of $[V(PyCH=COCF_3)_3]$ (6) starts around 200 °C. After that, the precursor undergoes a gradual decomposition from 200 °C up to 370 °C, to leave approximately 13% of the initial mass which corresponded to crystalline V₂O₃ (12%) as the end product. Based on the TGA results it is reasonable to conclude that during the single large decomposition step the organic residue of the single-source precursor is removed leaving behind vanadium(m) oxide.

Material synthesis

The synthesis of vanadium(n) oxide nanowires was performed *via* the solvothermal process using [V(DmoxCH=COCF₃)₃] (4) as the precursor in toluene under high pressure and tempera-



Fig. 5 (a) TG profiles of 4, 5 and 6. (b) XRD pattern of 6 residues after TG.

ture that facilitates the interaction of precursors during the synthesis with the help of oleylamine as the surfactant and reducing agent to influence the morphology of the formed oxide materials.

Powder X-ray diffractogram revealed the formation of a welldefined crystalline phase. The diffraction peaks exhibited peak patterns corresponding to crystalline vanadium(n) oxide (VO) with diffraction peaks assignable to VO (JCPDS 77-2173). The broad shoulder at lower 2θ values indicates the presence of a poorly crystalline phase which could be carbon impurity from oleylamine. The reduction from vanadium(III) to (II) observed in the synthesized material is probably induced by the surfactant oleylamine, which has been reported to be suitable as a solvent, a surfactant and a reducing agent.³³

The morphological properties, size and crystallographic growth directions of the synthesized VO nanostructures were investigated using transmission electron microscopy (TEM). The TEM micrograph of vanadium(II) oxide as shown in Fig. 6b

200 nm



Fig. 6 (a) XRD pattern of VO nanowires at 500 °C. (b) TEM image of VO nanowires.



Fig. 7 (a) Typical survey quantitative XPS analysis spectra of VO nanowires (b) High-resolution quantitative XPS analysis spectra of VO.

revealed non-uniform nanowires with clearly distinguishable size and morphology with diameters of 30–50 nm. The particlelike impurity observed in the TEM image could be the presence of the poorly crystalline phase carbon impurity left over from the surfactant as indicated in the XRD.

XPS analysis performed on vanadium(II) oxide nanowires (Fig. 7) showed the presence of multiple oxidation states (V(0),V(II), V(IV) and V(V)). The peaks observed at 514.3 eV and 521.65 eV are assignable to the V $2p_{3/2}$ and V $2p_{1/2}$ of V(II), respectively. The broad peaks observed at 516.0 eV and 523.5 eV are indexed to the V $2p_{3/2}$ and V $2p_{1/2}$ of V(IV) and another pair of peaks located at 517.9 eV (V 2p_{3/2}) and 524.4 eV $(V 2p_{1/2})$ are attributed to V(v). This variety of vanadium oxide species is mainly due to sample storage under ambient conditions and with the surface oxidation of the sample. The observation of peaks corresponding to the vanadium metal (512.4 eV and 519.55 eV) indicates a disproportionation during the solution reaction. Next to the O 1s peaks for lattice oxide (530.1 eV) and hydroxide (531.4 eV), another peak was observed which is shifted to a lower binding energy at 527.09 eV. The presence of adsorbed oxygen on the surface of VO nanowires could be from the reductive degradation of V₂O₅ under X-ray exposure to V(IV) species.³⁴

Conclusion

New air-stable vanadium(Π) heteroarylalkenolate complexes reported in this work are promising precursors to selectively obtain a sub-valent oxide (VO) by an *in situ* solution reduction process. The stabilization of V(Π) oxide in solution indicates the influence of crystal chemistry in producing an anisotropic structure, however the exposure of VO nanowires in air oxidizes their surface to create multiple oxidation states that could facilitate surface-related chemical processes such as oxygen reduction reactions.

Experimental section

General procedures

All syntheses were performed under an inert nitrogen atmosphere using a modified Stock glass vacuum line. The solvents used were dried and distilled over sodium benzophenone and stored over molecular sieves. All chemicals used were of analytical grade and used without further purification. Potassium *tert*-butoxide (K^tOBu) was obtained from Fisher Scientific and purified by sublimation under reduced pressure. Vanadium(III) chloride (VCl₃) was obtained from Acros Organics (97% purity) and activated in dried THF by stirring for two days at room temperature. Mass spectra were recorded on a Finnigan MAT 95 (EI, 20 eV) in *m*/*z* (intensity in %). UV/ vis absorption spectra were recorded with a Varian Cary50 Scan spectrophotometer. Microanalysis for C, H, and N was carried out using a Hekatech CHNS EuroEA 3000 analyzer with helium as the carrier gas, TG/DTA measurements were

recorded on a TGA/DSC 1 STAR system by Mettler with a gas controller GC 100. Samples were put in an aluminium cartridge (HEKAtech GmbH, 5 × 12 mm) and sealed, measurements were performed under a 25 ml N2 flow. Data collection for X-ray structure elucidation was performed on a STOE IPDS II diffractometer using monochromated Mo Ka radiation (0.71071 Å). Powder X-ray diffraction patterns were recorded using X-ray diffraction (XRD), operating in a Bragg-Brentano mode (XRD Stoe Stadi MP vertical diffractometer with Mo Ka; source). XPS analysis was performed with an ESCA M-Probe system from Surface Science Instruments. The samples were irradiated with Al K α rays (λ = 8.33 Å). Survey scans were recorded with a detector pass energy of 158.9 eV and highresolution spectra were recorded with a pass energy of 22.9 eV. All spectra were referenced to adventitious carbon (284.8 eV). The component for metallic vanadium was fitted using LA (1.2,5,8) line shape, all other components were fitted using GL (30) line shape with CasaXPS software from Casa Software Ltd. TEM measurement was performed using a TEM LEO912 omega from Zeiss company operated at 120 kV high tension. The programs used in this work are STOE's XAREA³⁵ and the WINGX suite of programs,³⁶ including SIR-92,³⁷ SHELX and SHELXTL³⁸ and PLATON³⁹ for structure solution and refinement. H atoms were calculated geometrically, and a riding model was applied during the refinement process.

[V(DmoxCH=COCF₃)₃] **(4).** 4 was prepared in a 250 mL flask containing 60 mL of toluene by addition of 5.30 g (25.5 mmol) of DmoxCH=COCF₃ (1) potassium *tert*-butoxide (K^tOBu, 2.85 g, 25.5 mmol) and stirred for 2 h. The potassium salt thus obtained was added *in situ* to 1.32 g (8.5 mmol) of tetrahydro-furan activated vanadium(m) chloride [VCl₃(THF)₃]. Orange-brown colouration was observed, and the reaction mixture was stirred for 2 h at ambient temperature. The solvent was removed under vacuum and the resulting orange-brown solid was sublimed at 130 °C (10⁻³ mbar) to obtain 4.30 g (6.4 mmol) orange powder with 76% yield. Orange crystals were obtained in a mixture of *n*-heptane and THF solution at −18 °C. Molar mass: (669 g mol⁻¹), elemental analysis showed C 42.82%, N 5.94%, H 3.06%, calculated: C 43.06%, N 6.28%, H 3.16%.

[V(PyCH=COCF₃)₃] (5). The synthetic procedure was similar to that described for compound 4 above, with three equivalents of deprotonated PyCH=COCF₃ (2) (3.53 g, 18.7 mmol) to obtain 81% yield (3.10 g, 5.0 mmol) of an orange solid. Orange-like crystals were obtained in *n*-heptane and THF at −18 °C. Molar mass: (615 g mol⁻¹), elemental analysis showed: C 46.83%, N 5.66%, H 2.47%, calculated: C 46.85%, N 6.83%, H 2.46%.

[V(PyN=COCF₃)₃] (6). The synthetic procedure was similar to that described for 4 & 5 above, with three equivalents of deprotonated PyN=COCF₃ (3) (2.50 g, 13.1 mmol) to obtain 79% yield (2.14 g, 3,5 mmol) of a brownish-orange solid. Orange-like crystals were obtained in *n*-heptane and THF solution at −18 °C. Molar mass: (618 g mol⁻¹), elemental analysis showed: C 40.46%, N 13.18%, H 2.02%, calculated: C 40.40%, N 13.46%, H 2.91%.

Synthesis of vanadium(II) oxide nanowires

A solvothermal synthesis of vanadium monoxide nanowires from a single precursor [V(DmoxCH=COCF₃)₃] was carried out. Typically, 0.015 mol (5 mL) of oleylamine (OM) was added to 30 mL of toluene solution containing 1.06 g [V(DmoxCH=COCF₃)₃] complex under stirring. The reaction solution was transferred to a 60 mL Teflon-tube positioned in a stainless-steel autoclave and heated at 250 °C for 10 h. The reaction system was cooled to room temperature and the vanadium(II) oxide product was centrifuged (11 000 rpm) and washed several times with ethanol and dried in a desiccator. The dried vanadium monoxide nanowires were then calcined at 500 °C under an argon atmosphere for 2 hours.

Computational details

Ground state electronic structure calculations have been done with a resolution of identity Coulomb approximation^{40,41} using the TURBOMOLE⁴² program package and the TMoleX 4.1^{43} user interface. For all atoms, the double- ξ -valence def-SV (P)⁴⁴ and the triple- ξ -valence def2-TZVP⁴⁵ basis sets were used with Becke's gradient-corrected exchange-energy functional BP86⁴⁶ The molecules were preoptimized at the def-SV(P) level and then optimized at the def2-TZVP-level.

Conflicts of interest

The authors declare there is no conflicts of interest.

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