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The one dimensional chain structures of vanadyl glycolate and vanadyl acetate†

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The solvothermal reaction, at 200 °C, of vanadium pentoxide and lithium hydroxide in acetic acid or ethylene glycol leads to the formation of vanadyl acetate and vanadyl glycolate respectively. The structure of the acetate contains vanadium in octahedral coordination whereas the glycolate contains VO_5 square pyramids. The VO_6 octahedra in the acetate, $VO(CH_3COO)_2$, are joined through the vanadyl groups, giving a rather long V=O bond of 1.684(7) Å and a short *trans* V-O bond of 2.131(7) Å, and by bridging acetate groups. The vanadium atoms interact along the ⋯V=O⋯V=O⋯ chain giving one-dimensional antiferromagnetic behavior. In contrast in the glycolate, the apical V=O bond is shorter, 1.58(1) Å, and the square pyramids share edges in a two up–two down fashion to give chains of formula $VO(OCH_2CH_2O)$. Magnetic susceptibility of vanadyl glycolate is consistent with an isolated spin dimers model.

Introduction

Hydrothermal synthesis is proving to be a fruitful technique for producing new transition metal oxides.[1] This technique often yields metastable, open, or layered compounds. In the case of vanadium oxide, five new compounds have been formed simply by changing the pH of the reaction medium.[2] In that study the pH was buffered by the use of weak acetic acid in the presence of tetramethylammonium ions. In most cases the tetramethyl-ammonium ions are incorporated between vanadium oxide extended sheets giving the compositions $TMAV_3O_7$, $TMAV_4O_{10}$, $TMAV_8O_{20}$ and $TMA_{0.17}V_2O_5$ as the pH is reduced from 8 to 2.6, but in two cases $Li_xV_{2-\delta}O_{4-\delta}$ and Li_3VO_4 the TMA was excluded from the structure.[3] The coordination around the vanadium increases from 4 to 6 through this series of compounds, as the pH of the reaction medium is reduced. Little work has been performed in non-aqueous media, and in the present study acetic acid and ethylene glycol were used as the reaction medium and no organic cation such as TMA was present. Microwave heating of the reaction medium was also explored, as that appears to substantially reduce the reaction time as noted for titanium phosphates[4–6] and $TMAV_4O_{10}$.[6] In the course of this study we have synthesized two chain compounds containing vanadyl groups that are of potential interest as battery material precursors. The synthesis and characterization of $VO(OCH_2CH_2O)$ and $VO(CH_3COO)_2$ are described herein. The presence of water led to the formation of the known phases $V_3O_7·H_2O$ or the sol–gel form of $Li_xV_2O_5$.

Experimental

Synthesis

V_2O_5 and LiOH were purchased from Alfa, acetic acid from Fisher Scientific, and ethylene glycol from Aldrich; they were used without further purification. The vanadyl acetate was synthesized by solvothermal methods. In a typical preparation 0.224 g of a 1:1 molar ratio of V_2O_5 to LiOH was stirred for 24 hours in a flask containing 50 ml of glacial acetic acid. The resulting orange solution was poured into a 125 ml Teflon lined Parr reactor and heated in a conventional oven for 2 days at 200 °C. After cooling for 12 hours the tan crystals were filtered, washed with distilled water, and dried at 50 °C. The lithium hydroxide is not essential in the formation of $VO(CH_3COO)_2$ but its presence resulted in the formation of larger crystals. When water was added to the acetate reaction medium, the known compound $V_3O_7·H_2O$ was formed; this synthesis is, however, simpler than those previously described.[7,8] Micro-wave heating at 200 °C, in a CEM Model MDS 2100 oven, produced $VO(CH_3COO)_2$ in one hour but only in the presence of LiOH; the pressure of the vessels attained 80–120 psi. The microwave products were always contaminated with unreacted V_2O_5. Purple crystals of $VO(OCH_2CH_2O)$ were prepared by heating in a Parr reaction vessel V_2O_5 and LiOH in a 1:2 molar ratio dissolved in 50 ml of ethylene glycol for 2 days at 200 °C. In each case, the organic acted as the reducing agent; the organic oxidized products formed were not identified.

Characterization

Powders were X-rayed using a Scintag XDS 2000 automatic diffractometer (θ–θ geometry, flat plate sample, CuKα radia-tion). The data were collected from 10° to 90° 2θ at a scan rate of 0.02° 2θ per step and 30 seconds per point. Thermal gravimetric analysis was carried out on a Perkin-Elmer Model TGA 7 instrument in flowing oxygen at a heating rate of 5 °C per minute from 50–400 °C. IR spectra were obtained on a Bruker Equinox 55 spectrophotometer using KBr discs, and a Jeol XJA 8900A Electron Microprobe was used to obtain the SEM images. Magnetic susceptibility was measured using a Quantum Design SQUID magnetometer from room tempera-ture to 2 K in a 1000 Oe magnetic field. The EPR spectrum was obtained on a Bruker CW/EPR spectrometer; a 1 cm high portion of the sample was placed in a thin quartz tube and scanned over a field range of roughly 2000 Gauss at room temperature.

X-Ray crystallography

The X-ray powder diffraction showed a lattice spacing of 7.069 Å for the vanadyl acetate. The pattern was indexed with orthorhombic symmetry with possible space groups $Cmcm$, $C2cm$ and $Cmc2_1$. The crystal structure of vanadyl acetate was solved by direct methods in the non-centrosymmetric $Cmc2_1$ space group using 140 integrated intensities from pattern decomposition. The first two reflections, below 18° 2θ, were excluded from the final refinement due to high errors in intensity.

For the vanadyl glycolate the X-ray diffraction pattern showed a lattice spacing of 6.635 Å. The pattern was indexed in the monoclinic system with possible space groups $C2/c$ and Cc. The crystal structure of vanadyl glycolate was solved by direct methods in the centrosymmetric $C2/c$ space group using 261 integrated intensities from pattern decomposition.

All refinements were done using the CSD program.[9]

CCDC reference numbers 192052 and 192053. See http://www.rsc.org/suppdata/jm/b2/b208100h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Vanadyl acetate

The vanadyl acetate has a tan color and comprises long needles that radiate from a single nucleation site. The crystals have dimensions of around 2 μm × 1 μm × 100 μm. The ends of the crystals appear hexagonal. The X-ray diffraction pattern indicated essentially a single phase with a trace amount of V_2O_5. Thermal gravimetric analysis showed onset of decomposition around 200 °C with completion by 300 °C; analysis of the product after heating to 400 °C showed pure orange V_2O_5, indicating the absence of any lithium in the acetate. The observed weight loss of 50% compares well with the expected weight loss of 50.9%. X-Ray and TGA showed no difference between the products formed from lithium containing or lithium free reactants.

The FTIR of the vanadyl acetate supports the presence of the carboxylate ion (-CO_2^-) from the absence of the carbonyl stretch (around 1700 cm^{-1}), and the presence of two peaks at 1507 and 1405 cm^{-1} which represent the asymmetric and symmetric vibrations of the carboxylate group respectively.

The structure of the vanadyl acetate is comprised of VO_6 octahedra with a double bonded oxygen (V=O 1.684(7) Å) at one apex. This oxygen also bonds with the next vanadium (V⋯O 2.131(7) Å) forming an infinite one-dimensional chain ⋯V=O⋯V=O⋯. The double bond falls toward the upper length of normal V=O bonds, 1.55–1.75 Å, whereas the V⋯O bond is one of the shortest V⋯O *trans* bonds, which usually range from 2.1–2.6 Å (V_2O_5 itself has bonds of 1.58 and 2.79 Å respectively in the ⋯V=O⋯V= chain). The base of the octahedron consists of four oxygen atoms, from bridging acetate groups, with V–O distances 1.931(4) and 2.002(3) Å, fairly typical of V–O bond distances. As shown in Fig. 1, the alternating acetate bridges bend the octahedra chain making it wavelike (V=O⋯V angle is 131.2(3)°) but the octahedral geometry is not affected (O=V⋯O angle is 174.6(2)°). The symbolic formula of this chain of corner sharing octahedra would be "{O.}" according to ref. 10. This structure is similar to that predicted from magnetic studies.[11]

The structures of the strontium and lead vanadyl vanadates $M_2VO(VO_4)_2$[12,13] are constructed in a similar way to vanadyl acetate (Fig. 2a). The VO_6 octahedra share corners to form a one-dimensional chain surrounded with tetrahedral VO_4 groups. However, there are two such groups: the bidentate VO_4 tetrahedron plays the same bridging role as acetate in the title compound, but the second VO_4 group shares only one corner with the octahedral chain. Thus the symbolic formula
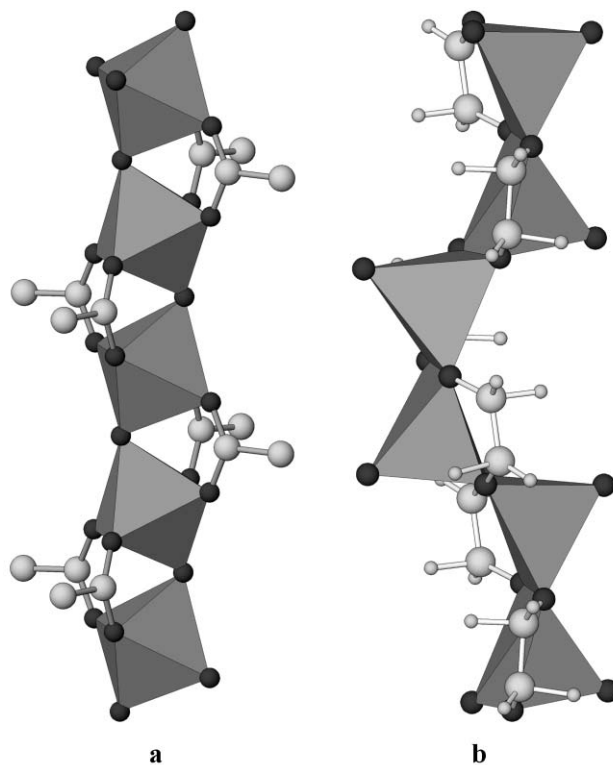

Fig. 1 (a) The 1-dimensional chain of the VO_6 octahedra in the $VO(CH_3COO)_2$ structure and (b) the 1-dimensional chain of the VO_5 square pyramids in the $VO(OCH_2CH_2O)$ structure.
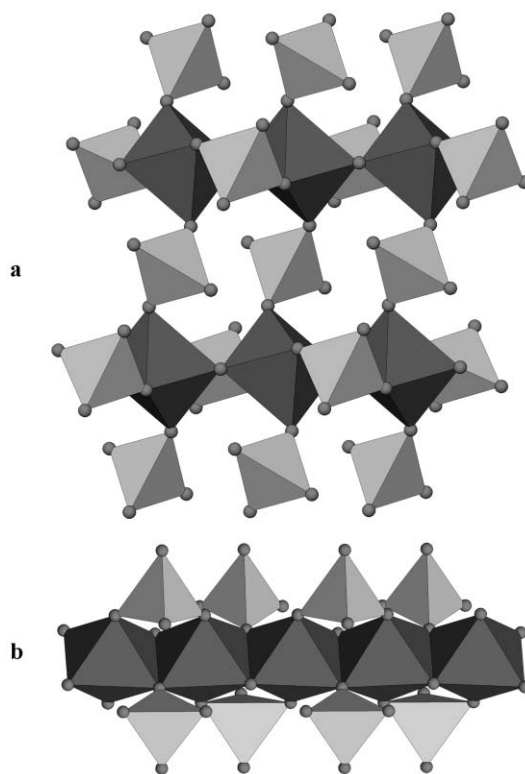

Fig. 2 The chains of (a) corner and (b) edge sharing VO_6 octahedra with adjuncted monodentate and bridged VO_4 tetrahedra in structures $Sr_2V_3O_9$ and $Ba_2V_3O_9$.

of the V_3O_9 chain is "{T:{O.}.T}" which reflects the chain of corner sharing octahedra (O) surrounded by tetrahedra (T) sharing two and one corners respectively. The $Ba_2V_3O_9$ structure[14,15] shown in Fig. 2b also contains a one-dimensional chain. However its chain, despite having the same composition
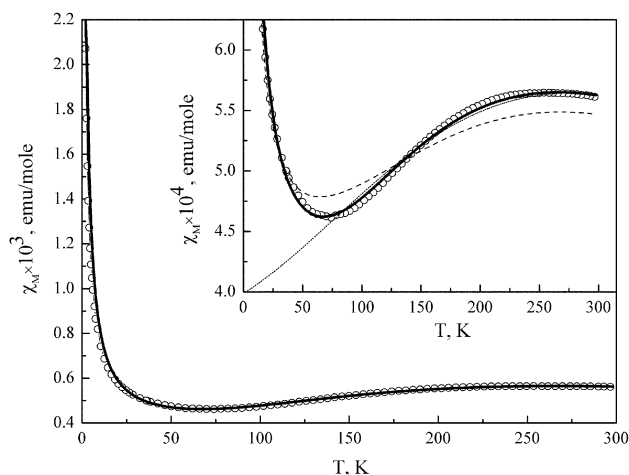
Fig. 3 Temperature dependence of magnetic susceptibility of vanadyl acetate, inset magnifies the high-temperature region. Dotted line: fit over the high-temperature region to the 1D Heisenberg chain model ($|J/k|$ = 215 K, g = 2), dashed line: fit over the whole investigated temperature range to the sum of 1D Heisenberg infinite chains and the paramagnetic Curie susceptibilities, solid line: fit to the sum of the paramagnetic susceptibility and the susceptibility of Heisenberg infinite and short chains.

as the Sr and Pb compounds, consists of octahedra sharing edges but not corners. The symbol of this chain is "T:{o}.T".

There is also a known vanadyl formate $K_4[VO(HCO_2)_4]$,[16] whose one-dimensional chain contains formic ions as bridges between VO_6 octahedra. There is no direct interaction between the octahedra, and the V^{4+} ions behave as isolated species according to magnetic studies.[16]

Magnetic susceptibility data for the vanadyl acetate are shown in Fig. 3; it is independent of field and whether the sample was cooled with the field on or off. A broad maximum observed at T = 275 K is typical for the susceptibility of antiferromagnetic linear chains, while a low-temperature increase of the susceptibility reflects the presence of paramagnetic impurities and/or short chains. After correction of the data for the temperature-independent susceptibility $\chi_0 = 6 \times 10^{-5}$ emu mol^{-1},[11,17] the temperature and the magnitude of the maximum were compared to the tabulated values for various one-dimensional (1D) models.[18] The data were found to be consistent with that for an S = 1/2 1D Heisenberg linear chain: from the relation $kT(\chi_{max})/|J| \approx 1.282$, the exchange constant $|J|/k$ is about 215 K, while the other relation $\chi_{max}|J|/Ng^2\mu_B^2 \approx 0.07346$ gives a g-factor $g \approx 2$ in agreement with the EPR value of 1.966, assuming the number of magnetic ions N = 6.02×10^{23} per mole. However an attempt to fit the whole curve to the sum of the paramagnetic Curie and the Heisenberg chain contributions[19] produced a poor fit (dashed line in Fig. 3). This led us to a more sophisticated model, which also accounts for the short chains. Reasonable agreement between the experimental data and the model was achieved by addition of the smallest linear clusters: dimers and triplets.[20] During the fit procedure, χ_0, g, $|J|/k$ were fixed at the values estimated above, and only the percentage of V^{4+} ions contributing as single paramagnetic impurities, doubles and triplets were varied. The best fit (solid curve in Fig. 3) was obtained with 90% of V^{4+} atoms in infinite Heisenberg chains, 6% in doublets and the remaining 4% distributed among singlets and triplets.

The results of the previous magnetic studies[11,17] of vanadyl acetate and our data are consistent in the temperature of the susceptibility maximum, but not in the shape of the curve: at high temperature, the data of Casey et al.[11] fit the 1D Izing model, while the data of Kalinnikov et al[17] fit the Heisenberg one. In the latter paper, the low-temperature increase of susceptibility is qualitatively explained by the presence of the

short chains in agreement with our model. The temperature dependences of the magnetic susceptibility of $Sr_2V_3O_9$ and $Pb_2V_3O_9$ show maxima at 45 K and 25 K,[13] respectively, which means that the exchange interaction in these compounds is much weaker than in vanadyl acetate. Surprisingly, the magnetic behavior of these nearly isostructural compounds is different: $Sr_2V_3O_9$ behaves like a uniform Heisenberg chain, while $Pb_2V_3O_9$ shows an alternating Heisenberg chain behavior. It may be concluded that the magnetic properties of such chains are very sensitive to the structure.

Vanadyl glycolate

The vanadyl glycolate has a purple color that darkens after prolonged exposure to air. SEM images show fiber-like strands, which correspond to growth along the long axis of the chains. Thermal gravimetric analysis of the vanadyl glycolate, $VO(OCH_2CH_2O)$, showed a 33.4 wt.% loss by 190 °C consistent with the 34.7% expected for loss of the organic and formation of the observed black VO_2; further heating to 400 °C resulted in the formation of orange V_2O_5 (overall weight loss was experimental 27.3%, calculated 28.4%). This orange color indicates the absence of any lithium in the glycolate.

The vanadyl glycolate structure is also composed of one-dimensional chains. The chain contains edge sharing VO_5 square pyramids, whose oxygens come from a vanadyl group (V=O), a chelating (-OCH_2CH_2O-) ligand and one end of two other (-OCH_2CH_2O-) ligands, as shown in Fig. 1. The vanadyl bond is at the apex of the square pyramid. The double bonded oxygen is terminal in this structure and therefore the V=O distance of 1.58(1) Å is noticeably shorter than in the acetate compound. The square pyramids are joined by "edge sharing" with two apices pointing "up" and two pointing "down", thus the chain formula can be given as {uudd}.[10] In a uu pair the vanadyl groups are tilted from each other by 43°. In contrast, the tilt between antiparallel vanadyl groups in a ud pair of square pyramids is only 9°. This type of tilting is also found in such layered vanadates as $tmaV_4O_{10}$,[21] CaV_4O_9[22] and $ppdV_4O_9$[23] where uu and ud pairs of square pyramids are also present.

The four oxygens making up the polyhedron's base are almost planar, but not the glycol molecule. Its torsion angle O–C–C–O is 24°, which is far from the ideal 60°. The same angle in the $LiOCH_2CH_2OH$[24] compound is 54°, which is much closer to the ideal value. The FTIR pattern supports the presence of the CH_2O group and of V=O and V–O bonds at 1500, 1000 and 570 cm^{-1} respectively.

The magnetic susceptibility of the vanadyl glycolate is presented in Fig. 4; it indicates Curie–Weiss behavior up to T = 75 K followed by an increase of susceptibility above this temperature. From the fit of the low-temperature part of the curve to the Curie–Weiss law (straight line in inset (a) of Fig. 4) the concentration of S = 1/2 paramagnetic impurity is about 5%. Magnetic susceptibility after subtraction of the temperature-independent contribution $\chi_0 = 10^{-5}$ emu mol^{-1} and the Curie–Weiss contributions is shown in inset (b) of Fig. 4. Zero susceptibility at low temperature and the increase observed above 100 K are indicative of spin-gap behavior with a large energy gap. The curve fits the susceptibility of isolated dimers[18] $\chi_d = Ng^2\mu_B^2/[kT(3 + \exp(-2J/kT))]$ with the number of V^{4+} ions in dimers equal to 95% of their total amount, g-factor g = 2, which is in agreement with the EPR value g = 1.97, and exchange constant $J/k = -(460 \pm 1)$ K. This dimer behaviour of the vanadyl glycolate follows from its structure (Fig. 1b): exchange interaction between V^{4+} ions in two upward (or two downward) pyramids provided by direct exchange is much stronger than that between ions on the opposite sides of basal plane. Similar magnetic behaviour is typical of vanadium compounds built up of zigzag chains of VO_5 square pyramids connected in the same (two upward–two downward) manner.[25]
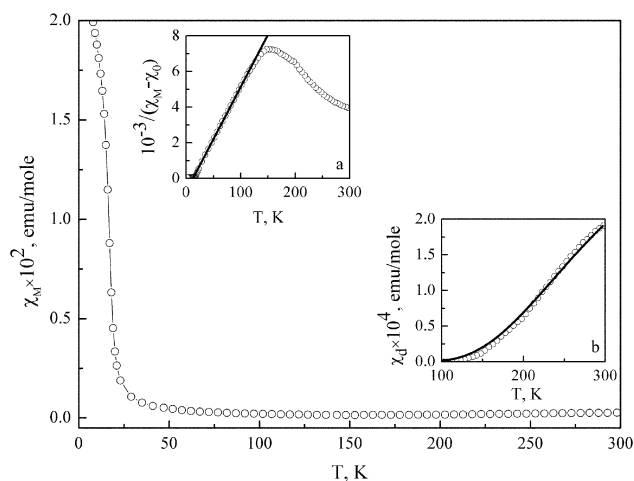
Fig. 4 Temperature dependence of magnetic susceptibility of vanadyl glycolate. Inset (a) shows reciprocal magnetic susceptibility corrected for the temperature independent contribution ($\chi_0 \approx 10^{-5}$ emu mol^{-1}) and its fit to the Curie–Weiss law. Inset (b) shows magnetic susceptibility after subtraction of the χ_0 and the Curie–Weiss contributions, solid line is the best fit to the susceptibility of isolated dimers.

Conclusions

In conclusion a vanadyl acetate and a vanadyl glycolate have been synthesized and their structures determined. Both compounds were produced by both traditional and microwave solvothermal reactions of vanadium pentoxide and lithium hydroxide in anhydrous acetic acid or ethylene glycol. For the acetate, the 1D antiferromagnetic behavior suggests strong interactions between the vanadium ions, $|J/k| = 215$ K, which is in agreement with the one-dimensional system of V=O···V bonds along the chain. In contrast to the acetate, the glycolate contains edge sharing VO_5 square pyramids. Pairs of upward and downward pyramids provide magnetic dimerisation of the chain with very strong intradimer exchange $|J/k| = 460$ K.

Acknowledgements

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