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CHARACTERISATION AND THERMAL ANALYSIS OF VANADIUM(II) OXALATE

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Abstract

The synthesis, compositional formula and mode of thermal decomposition of a compound for which there existed only a single literature reference [1] have been investigated in this work.

The product of the aqueous phase reaction between vanadium(II) ions and oxalate ions at low *pH* has been identified: vanadium(II) oxalate dihydrate, $VC_2O_4{\cdot}2H_2O$, has been characterised by thermal methods of analysis supported by a range of complementary analytical techniques.

The findings of a previous author [1] have been confirmed and extended in this work. In addition, a synthetic procedure for the preparation of gram quantities of vanadium(II) oxalate dihydrate, $VC_2O_4{\cdot}2H_2O$, is reported here for the first time.

The oxalate compound prepared was found to be remarkably stable in relation to aerial oxidation, unlike other representative solid state compounds of the vanadium(II) oxidation state. Vanadium(II) oxalate dihydrate may, therefore, serve as an important intermediate in the future synthesis of other vanadium(II) compounds.

Keywords: vanadium(II) oxalate

Introduction

Dollimore, Griffiths and Nicholson have studied the thermal decomposition of some first-row (3d-) transition metal oxalates of general formula $MC_2O_4{\cdot}2H_2O$, for which M=Mn(II), Fe(II), Co(II) and Ni(II) [2]. Other first-row oxalates studied in this work were reported as chromium oxalate, $Cr_2(C_2O_4)_3{\cdot}6H_2O$; iron(III) oxalate, $Fe_2(C_2O_4)_3{\cdot}xH_2O$ and copper oxalate, $CuC_2O_4{\cdot}1/2H_2O$.

The focus of the present work was the synthesis and thermal characterisation of an additional member of the series which had not been included in the earlier study.

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Vanadium(II) oxalate has not been widely reported and no reference to it has been made in any known review of representative solid-state compounds of the vanadium(II) oxidation state.

An on-line computer search of Chemical Abstracts revealed only a single reference to vanadium(II) oxalate [1].

No other reference could be identified in the chemical literature, except that it is listed in Comprehensive Coordination Chemistry [3], where it is cited to the previously existing reference [1].

Experimental methods

(For full details see [4]).

Materials	Origin	Grade
Oxovanadium(IV) Sulphate, $VOSO_4 \cdot 5H_2O$	BDH	
Granulated zinc	BDH	Analar
Mercury(II) chloride	BDH	Analar
Vanadium(II) chloride, VCl_2	Fluka	Purum
Oxalic Acid	BDH	Analar
2,2-dimetoxypropane	Sigma	not stated
Nitrogen	BOC	Industrial
Nitrogen (white spot)	BOC	OFN

Techniques

Thermal analysis was carried out in a dynamic atmosphere of flowing air or nitrogen using the Stanton Redcroft STA 780 TG-DTA Simultaneous Thermal Analyser. Sample sizes were typically 10 mg and a heating rate of 3°C per minute was employed throughout.

Atomic Absorption Spectrometry was carried out using the PU9 100X Series Atomic Absorption Spectrometer. Infrared Absorption Spectra were run on KBr discs of the sample using the Philips PU 9706 Infrared Spectrophotometer. Magnetic susceptibility measurements were carried out using the Evans Magnetic Susceptibility Balance. X-Radiation Diffraction was carried out using the Philips PW 1729 X-ray generator in conjunction with the PW 1710 diffractometer control.

The total vanadium content of samples was determined using a standard procedure [5]. The oxalate content of samples was determined by a modified procedure involving complete removal of vanadium by refluxing in aqueous sodium carbonate solution and subsequent redox titration, following acidification of the filtrate.

Results

(For a full account of all experimental work performed see [4]).

Synthesis of vanadium(II) oxalate

Jones reduction of oxovanadium(IV) sulphate, $VOSO_4 \cdot 5H_2O$

Jones reduction resulted in samples of vanadium(II) oxalate which were highly contaminated with zinc (30%), as indicated by the atomic absorption spectrometry measurements.

Chemical and thermal analysis indicated that the zinc was present as zinc oxalate, comprising approximately 85% of the sample. Titrimetric analysis for total vanadium produced a value of 5% vanadium, equivalent to approximately 17% as vanadium(II) oxalate, dihydrate.

Indirect synthesis via vanadium(II) sulphate $VSO_4 \cdot 7H_2O$

The proposed reaction for the indirect synthesis was:

$$VCl_2\,(s) + H_2SO_4(aq) \rightarrow VSO_4(aq) + 2HCl(aq)$$

$$\downarrow\ (COOH)_2 \cdot 2H_2O$$

$$V(C_2O_4) \cdot 2H_2O + H_2SO_4(aq) + 2HCl(aq)$$

No precipitation of vanadium(II) oxalate occurred due to the *pH* of the solution being too low. However, increasing the *pH* led to the formation of a green solution indicative of oxidation of V(II) to V(III), and no precipitation occurred.

Direct synthesis via vanadium(II) chloride

Preparation of vanadium(II) oxalate by direct synthesis from vanadium(II) chloride produced reasonable yields (30–36%) of a very dark black/purple finely divided crystalline solid. The method of preparation was easily reproducible.

Drying conditions

A number of different methods were used to dry the samples, including refluxing with a nonaqueous solvent and drying at elevated temperatures, at atmospheric and reduced pressure, for varying periods of time (see Discussion).

Characterisation of vanadium(II) oxalate

Thermal analysis

Simultaneous TG/DTA curves of the product were run between ambient temperature and 725°C in air (Fig. 1) and nitrogen (Fig. 2).

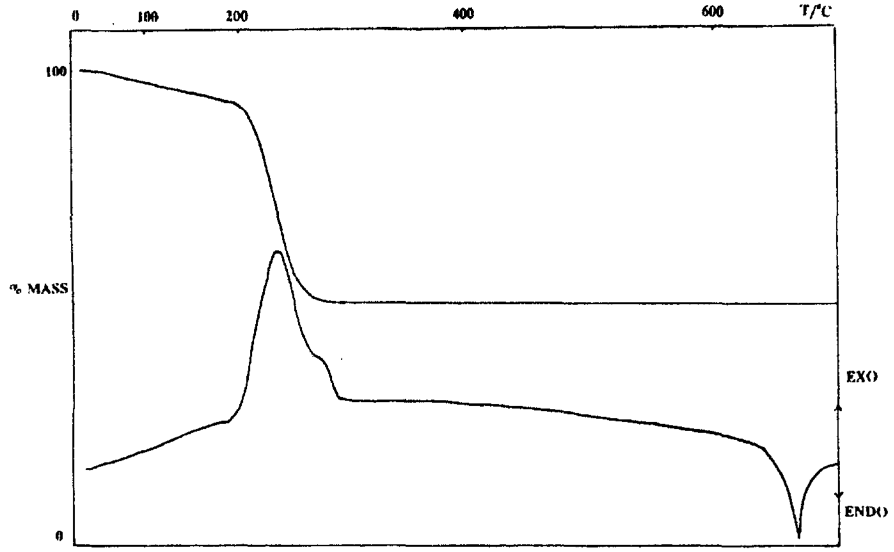

Fig. 1 TG/DTA of vanadium(II) oxalate (air)

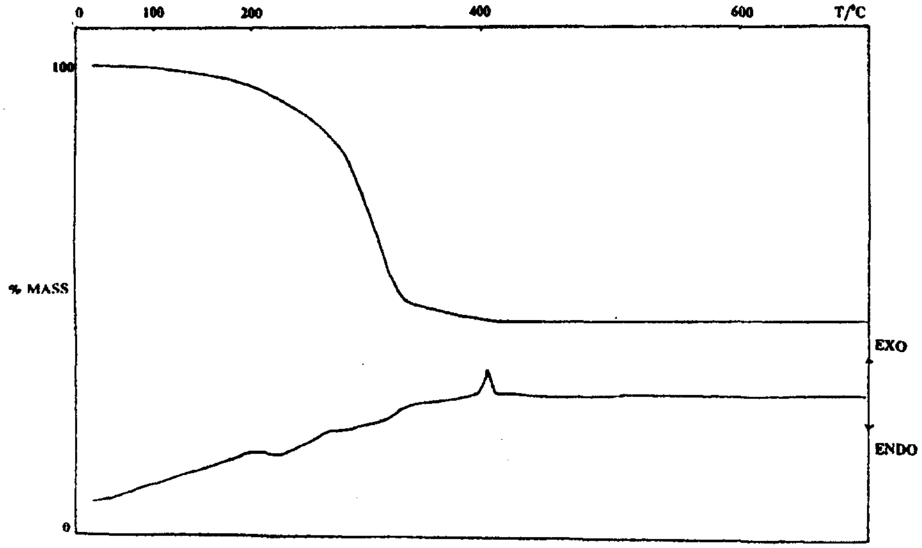

Fig. 2 TG/DTA of vanadium(I) oxalate (nitrogen)

Complementary analytical data

Infrared absorption spectroscopy

The infrared absorption spectrum of the sample shows the presence of the following functional groups:

OH, C=O, and C–O (Fig. 3).

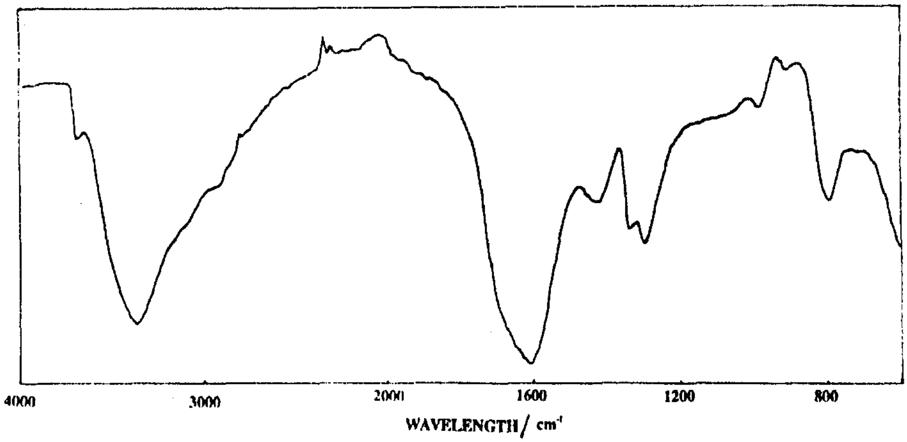

Fig. 3 Infrared absorption spectrum of vanadium(II) oxalate

X-radiation diffraction

X-radiation powder diffraction data were recorded for the sample using unfiltered CuK$_\alpha$ radiation, for which a mean value ($\alpha 1/\alpha 2$) of wavelength, λ, was taken as 1.5418×10^{-10} m (Table 1).

Magnetic susceptibility

Magnetic susceptibility measurements on the sample show it to be paramagnetic. However, the experimental value of 3.36 BM was significantly lower than the 'spin only' value for three unpaired electrons (3.87 BM).

Table 1 Recorded XRD of $VC_2O_4{\cdot}2H_2O$

2θ	10^{10}d.m	Counts	2θ	10^{10}d.m	Counts
18.566	4.7792	1385	37.694	2.3865	118
22.843	3.8931	402	39.971	2.2556	155
24.380	3.6509	107	42.785	2.1135	158
29.636	3.0144	383	46.688	1.9455	131
32.335	2.7686	88	48.045	1.8937	184
33.058	2.7097	85	50.375	1.8115	118
34.376	2.6088	304	57.306	1.6077	75
36.259	2.4775	70	88.262	1.1072	19

Chemical analysis

Qualitative analysis involving manganate(VII) oxidation of the sample in acidic aqueous solution indicated the presence of the oxalate ion. Reduction of the oxidized solution, firstly with sulphur dioxide and subsequently with zinc, revealed the presence of vanadium through the characteristic colours of its various oxidation states.

Quantitative analysis indicated that the total vanadium content of the sample and the oxalate content were reasonably consistent with the compositional formula $VC_2O_4{\cdot}2H_2O$, although the total vanadium content was a little lower than the theoretical requirement (Table 2).

Table 2 Compositional analysis of $VC_2O_4{\cdot}2H_2O$

% w/w vanadium		% w/w oxalate	
experimental	theoretical	experimental	theoretical
28.0	29.11	49.9	50.30

Discussion

It was clear from the results obtained in this work that Jones reduction was unsuitable as a means of synthesizing vanadium(II) oxalate due to gross contamination of the product by zinc ions from the column. It was also evident that indirect synthesis from vanadium(II) sulphate, $VS_2O_4{\cdot}7H_2O$, led to problems with regard to the *pH* dependent oxidation of V(II) to V(III). It would seem that at very low *pH*, no precipitate formed, presumably because the oxalic acid could not deprotonate, thereby preventing the oxalate ion from acting as an anionic ligand. However, at higher *pH*, oxidation of V(II) occurred to produce a green solution containing the octahedral tris-oxalato anionic complex, $[V(C_2O_4)_3]^{3-}$.

In the direct synthesis of vanadium(II) oxalate from solid vanadium(II) chloride and aqueous oxalic acid, it would seem that the slow rate of dissolution of solid vanadium(II) chloride, VCl_2, mediated the reaction by preventing rapid formation of the $[V(H_2O)_6]^{2+}$ ion and subsequent oxidation to $[V(H_2O)_6]^{3+}$ in aqueous solution, prior to reaction with the oxalic acid. The *pH* of the aqueous oxalic acid medium allowed formation of the precipitate which was then stable in respect of oxidation.

The optimization of drying conditions proved critical in the synthesis of vanadium(II) oxalate. After each drying procedure the sample was analyzed by thermogravimetry (TG) and differential thermal analysis (DTA) in order to calculate the mass loss and to examine the shape of the DTA curve. The existence of unbound water in the sample could be detected by the occurrence of a higher percentage mass loss than the theoretical requirement for the dihydrate composition, $VC_2O_4{\cdot}2H_2O$. In addition the existence of a shallow endotherm upon

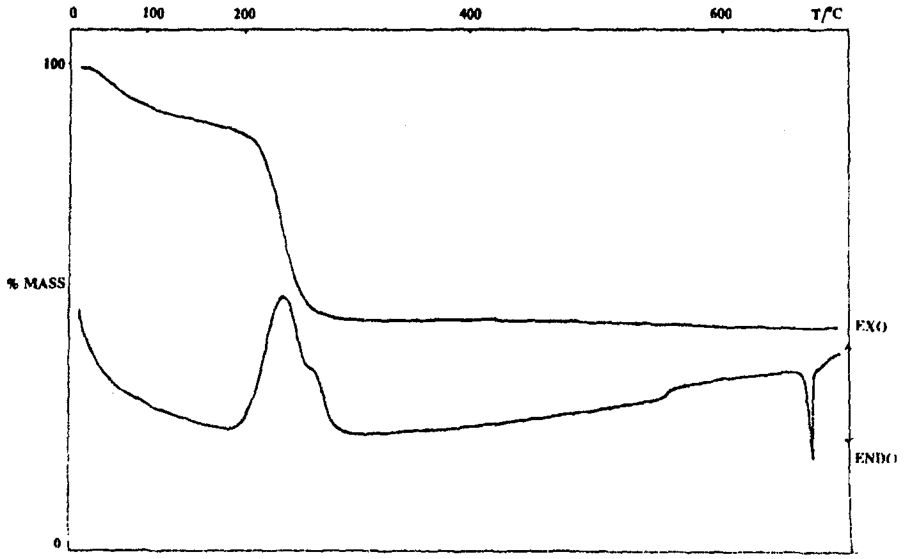

Fig. 4 TG/DTA of vanadium(II) oxalate containing unbound water

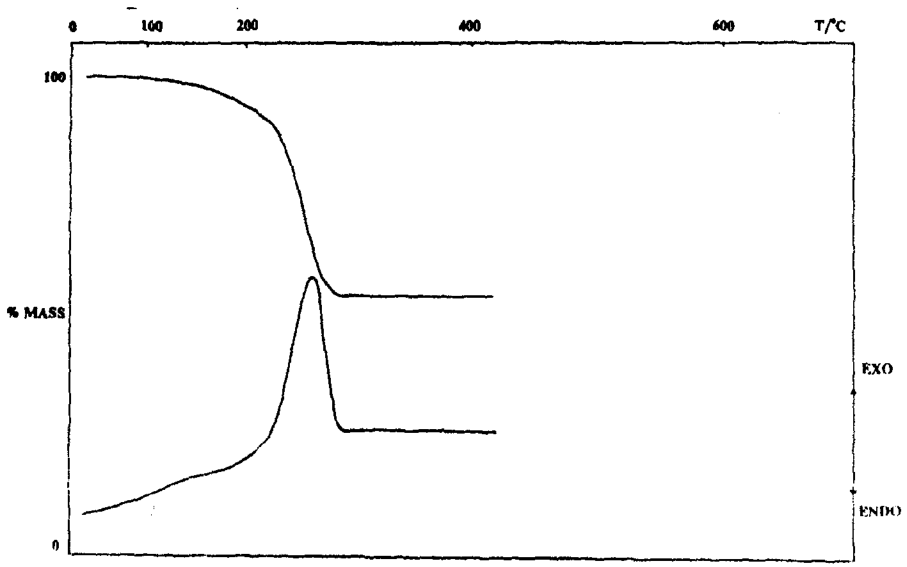

Fig. 5 TG/DTA of vanadium(II) oxalate (overdried)

which the exotherm due to oxalate decomposition (in air) was superimposed was indicative of the presence of unbound water in the sample (Fig. 4). Overdrying of the sample was indicated by the occurrence of a lower than expected mass loss (TG) and the disappearance of the shoulder in the DTA (Fig. 5).

It was found that if the product was dried at 110°C under a vacuum of 30"Hg then partial decomposition of the sample occurred but if the drying process was confined to ambient temperature without the application of diminished pressure, then unbound water remained in the sample. The use of a nonaqueous solvent such as 2,2-dimethoxypropane if often recommended for the removal of unbound water but in the present case refluxing the sample in this solvent for a period of one hour resulted in a sample in which the unbound water had been retained. A sample with minimal unbound water and in which no decomposition was apparent was obtained by leaving the sample for several days in a fairly high vacuum (30"Hg) at a temperature of 60°C. Complete characterisation was then carried out on samples dried under this optimised regime.

Figure 1 shows the recorded thermal decomposition curves (DTA/TG) for vanadium(II) oxalate in air. Thermogravimetry revealed an overall mass loss of approximately 49% which was consistent with the formation of V_2O_5 and this was confirmed by the DTA melting endotherm at 690°C which is characteristic of vanadium pentoxide [6].

$$VC_2O_4{\cdot}2H_2O \xrightarrow[\text{air}]{120\text{–}260^{\circ}C} 1/2V_2O_5 + CO + CO_2 + 2H_2O \qquad \%\ \text{mass loss} = 48.03$$

Decomposition of oxalate to give an equimolar ratio of carbon monoxide and carbon dioxide is an established principle and the DTA exotherm in Fig. 1 was attributed to the oxidation of carbon monoxide. The absence of a corresponding exotherm in the DTA curve for decomposition in nitrogen (Fig. 2) provived support for this view.

The overall mass loss for decomposition in nitrogen (approximately 53%) obtained from the TG curve was significantly greater than that for decomposition in air, as expected (Fig. 2). The composition of the thermally stable oxide phase was not identified unambiguously and the recorded mass loss was not consistent with the formation of vanadium(II) oxide, VO. However the possible formation of vanadium pentoxide could be excluded on the basis of the recorded mass loss data and the absence of the characteristic melting endotherm in the recorded DTA curve.

The recorded infrared spectrum of the sample (Fig.3) was consistent with the structure of other first-row (3d-) transition metal oxalates previously studied [2]. The absence of a strong sharp absorption band at around 1000 cm^{-1} excluded the possible presence of the vanadyl ion, $(V{=}O)^{2+}$, as expected.

No entry for $VC_2O_4{\cdot}2H_2O$ appears in the Joint Committee on Powder Diffraction Standards (JCPDS) index and the diffraction data were reported here, presumably for the first time. In the absence of reference data an attempt was made to index the recorded experimental data.

Of the sixteen diffraction lines observed, an integral relationship between the calculated $\sin^2\theta$ values appeared in only eight cases (with a common factor

Table 3 Derived XRD data for $VC_2O_4{\cdot}2H_2O$

q	10^{10} *d*/m	$100I/I_o$	$\sin^2\theta$ obs	q	10^{10} *d*/m	$100I/I_o$	$\sin^2\theta$ obs
q_1	4.7792	100	0.0260	q_9	2.3865	9	0.1044
q_2	3.8931	29	0.0392	q_{10}	2.2556	11	0.1168
q_3	3.6509	8	0.0446	q_{11}	2.1135	11	0.1331
q_4	3.0144	28	0.0654	q_{12}	1.9455	9	0.1570
q_5	2.7686	6	0.0775	q_{13}	1.8937	13	0.1657
q_6	2.7097	6	0.0809	q_{14}	1.8115	9	0.1811
q_7	2.6088	22	0.0873	q_{15}	1.6077	5	0.2299
q_8	2.4775	5	0.0968	q_{16}	1.1072	1	0.4848

of 0.013, values underlined) and half of the data could not be indexed on the basis of high order symmetry. Unless the sample was highly contaminated, the crystal system, almost certainly, was not isometric (cubic). It was of interest to note that most of the other lines were of low relative intensity ($100I/I_o$), and inspection of these lines suggested that, of the likely impurities, the possibility of contamination of the sample by oxalic acid, vanadium(II) chloride, VCl_2, vanadium(II) oxide, VO, and vanadium(III) chloride, VCl_3, could be excluded by reference to their respective JCPDS index data [7]. The monoclinic form of vanadium(III) oxide, V_2O_3, was excluded as a possible impurity, on the same basis [8]. However, inspection of the reference data for the hexagonal form of vanadium(III) oxide revealed a significant coincidence between the values of three of the major diffraction lines reported for this particular phase [8] and three of the minor lines (q_3, q_6 and q_8) in the corresponding diffraction data of the sample (Table 3). It was conceivable, therefore, that the sample was slightly contaminated with low levels of the hexagonal modification of vanadium(III) oxide, although this was by no means certain on the basis of the diffraction data alone. Moreover, the oxalate content of the sample was close to the theoretical value (Table 2) and, since oxalic acid had been excluded as a possible impurity on the basis of the XRD data, it was felt that any contamination by V_2O_3 was minimal (<1%).

* * *

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