Studies of Ammonium Dioxovanadium(V) Bisoxalate Dihydrate

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Complexes of vanadium containing VO_2^+ are rare. Ammonium dioxovanadium(V) bis(oxalate) tetrahydrate was prepared by Rosenheim[1] by treating an ammonium oxalate solution with vanadium pentoxide; his compound was said to be remarkably stable. Although this oxalato complex has been known since 1893, its physico-chemical properties, except the conductivity of its aqueous solution,[2] have not been investigated. During the course of our investigations of oxovanadium(IV) complexes, it was thought desirable to study some properties of the ammonium dioxovanadium(V) bis(oxalate) complex and to assign it a structure.

Experimental

Materials Employed.—The oxalic acid dihydrate, ammonium oxalate monohydrate and ammonium meta-vanadate were of reagent grade. Vanadium pentoxide was prepared by heating ammonium meta-vanadate (A. R.) at 450°C for about 2 hr.

Preparation.—When a solution of ammonium oxalate is boiled with vanadium pentoxide,[1] ammonium dioxovanadium(V) bis(oxalate) is not easily obtained. Hence, an easy method was developed to prepare the complex from ammonium meta-vanadate on the basis of the following possible reaction:

$$NH_4VO_3 + H_2C_2O_4 + (NH_4)_2C_2O_4 \rightarrow (NH_4)_3[VO_2(C_2O_4)_2] + H_2O$$

When calculated amounts of oxalic acid and ammonium oxalate were added to an aqueous solution of the metavanadate so that the molar ratio of $NH_4VO_3 : H_2C_2O_4 : (NH_4)_2C_2O_4$ was 1 : 1 : 1, a quick reaction occurred, giving a deep yellow solution. An excess of oxalic acid has to be avoided to prevent the reduction of pentavalent vanadium. A drop or two of dilute hydrogen peroxide was added to prevent any reduction of vanadium(V). The solution was warmed on a water bath to decompose the hydrogen peroxide and filtered through a sintered glass funnel. The filtrate was concentrated by passing a current of dry air at room temperature; when yellow crystals were obtained in about two days. The crystals were separated from the mother liquor and recrystallized from water. The crystals were then air-dried and analysed.[3]

Vanadium was estimated by igniting a known amount of the complex (about 200 mg.) to vanadium pentoxide, the oxalate by oxidation with potassium permanganate and ammonia by its liberation with aqueous alkali. The water was determined by the weight loss of the complex over anhydrous phosphorus pentoxide in a vacuum The V_2O_5, $C_2O_4^{2-}$, NH_4^+ and H_2O found were 26.1, 50.0, 15.1 and 10.2% respectively, while the corresponding calculated values for $(NH_4)_3[VO_2 \cdot (C_2O_4)_2] \cdot 2H_2O$ are 26.07, 50.42, 15.51 and 10.32% respectively. Thus, the complex obtained is a dihydrate and not the tetrahydrate.[1]

The complex is highly soluble in water, but insoluble in most of the organic solvents. When the complex was kept over fused calcium chloride, it lost both the molecules of water, giving a pale yellow powder. The complex is highly susceptible to reduction by oxalic acid and acid vapours. Ion-migration experiments in an aqueous solution indicated that vanadium was present wholly in the anion. The molecular weight determination in aqueous solutions by Beckmann's cryoscopic method showed that the complex dissociated into four ions.

Apparatus.—*Magnetic Susceptibility*.—The magnetic susceptibilities of the powdered samples were determined by the Gouy method[4] at room temperature, using $Hg[Co(NCS)_4]$ as the calibrant.

Thermal Studies.—The thermal behaviour of the complex was studied by both the differential thermal (DTA) and thermogravimetric (TGA) analyses. The DTA studies were carried out by a standard manual apparatus[5] using chromel-alumel thermocouples. The powdered samples (200 mg.) were pyrolysed at a heating rate of 8±1°C per minute in atmospheric air. The TGA studies were carried out with a quartz spring balance using 150~160 mg. of the substance, the rate of heating being maintained at 3°C per minute.

Absorption Spectral Studies.—The electronic spectrum of an aqueous solution of the complex was studied with a Hilger-Uvispek spectrophotometer, model H 700, using a pair of 1 cm. matched quartz cells. The infrared spectrum of the complex in Nujol mull was taken with a double-beam Perkin-Elmer Infracord spectrophotometer, model 137, employing sodium chloride optics.

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Results and Discussion

The magnetic susceptibility measurements indicated the compound to be diamagnetic, showing the pentavalent oxidation state of vanadium. The diamagnetic susceptibility found was $\chi = -0.51 \times 10^{-6}$ c. g. s. units.

The Thermal Behaviour of the Complex.—The differential thermogram of the complex is given in Fig 1. The small endothermic peak at 75°C is due to the loss of absorbed moisture. The medium endothermic peak at 125°C in the range from 85 to 145°C is due to the complete loss of two water molecules. The big endothermic peak at 225°C in the 170~270°C range was identified by heating the complex at 200°C for about 15 min. and by then analysing[3] the solid product, which corresponded to ammonium di-oxovanadium-(IV) trisoxalate, $(NH_4)_2[(VO)_2(C_2O_4)_3]$. (Analysis found in %: V_2O_5, 41.3 and $C_2O_4^{2-}$, 61.4, while the calculated % were V_2O_5, 41.94 and $C_2O_4^{2-}$, 60.83). The reaction taking place at 200°C can be represented as follows:

$$2(NH_4)_3[VO_2(C_2O_4)_2] \rightarrow (NH_4)_2[(VO)_2(C_2O_4)_3] + 2CO_2 + 4NH_3 + 2H_2O \quad (1)$$

The complex formed at 200°C is bluish-grey in colour and is paramagnetic, indicating the quadrivalency of vanadium. The complex is soluble in water, giving a bluish-green solution. Recently, it has been shown that europic(III) oxalate gives rise to europous(II) oxalate during the thermal decomposition of the former.[6] A number of other metal oxalato complexes, for example, those of nickel,[7] ferric[8] and plutonium[9], are also known to behave in a similar fashion.

The exothermic peak at 300°C is due to the decomposition of the dioxovanadium(IV) oxalato complex formed, giving rise to vanadium dioxide. This peak is followed by a big exothermic peak, with a maximum at 350°C. This peak was identified as due to the oxidation of vanadium dioxide to vanadium pentoxide.

The percentage-weight-loss vs. temperature curve is given in Fig. 2. The break in the curve corresponding to 170°C shows the completion of the loss of two water molecules from the complex, giving rise to the anhydrous oxalato complex. The anhydrous complex is found to be stable below 200°C. The formation of the intermediate compound $(NH_4)_2 \cdot [(VO)_2(C_2O_4)_3]$ starts from 200°C and is complete near 260°C (loss: 38%). The intermediate compound then starts decomposing, yielding vanadium(IV) oxide. The oxidation of vanadium(IV) oxide to vandium(V) oxide is not clearly shown by the TGA curve, probably because of the small gain in weight and the small contraction of the quartz spring with the increase in temperature.[10]

The Electronic Spectrum of the Complex.—In the ultraviolet region, there is a band below 220 mμ ($\log \varepsilon > 4.5$) and a shoulder at 265 mμ ($\log \varepsilon = 3.9$). These strong absorption

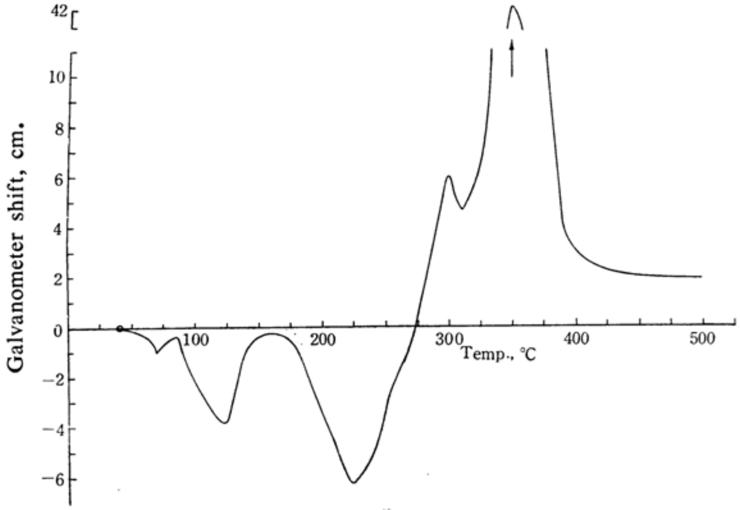

Fig. 1. DTA curve of $(NH_4)_3[VO_2(C_2O_4)_2] \cdot 2H_2O$.

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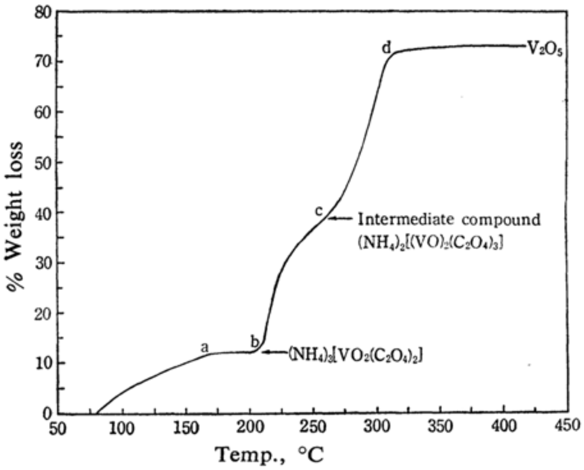

Fig. 2. TGA curve of $(NH_4)_3[VO_2(C_2O_4)_2]\cdot 2H_2O$.

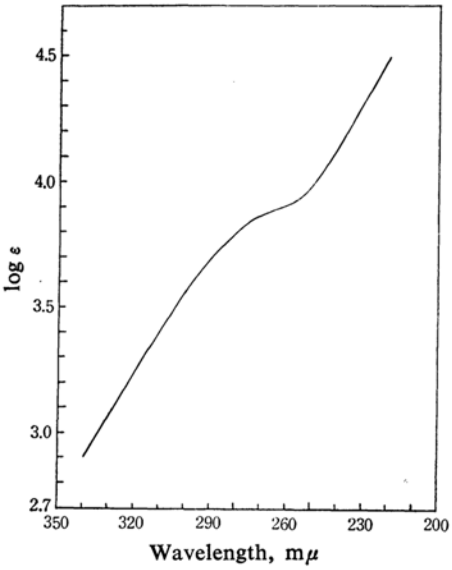

Fig. 3. Electronic absorption spectrum of $(NH_4)_3[VO_2(C_2O_4)_2]\cdot 2H_2O$ in water. Concn., 1×10^{-4} M.

TABLE I. THE ASSIGNMENT OF THE OBSERVED FREQUENCIES* IN cm^{-1} OF THE INFRARED SPECTRUM OF $(NH_4)_3[VO_2(C_2O_4)_2]\cdot 2H_2O$

Frequency	Assignment
3550 s	$\nu_a(H_2O)$
3080 vs	$\nu(NH)$
1720 s	$\nu_a(C{=}O)\ (\nu_7)$
1669 s	$\nu_a(C{=}O)\ (\nu_1)$
1629 s	$\delta(H_2O)$ and $\delta(NH_4)$ (asy)
1381 vs	$\nu_s(C\text{-}O)+\nu(C\text{-}C)\ (\nu_2)$ [overlapped by Nujol band]
1270 s	$\nu_s(C\text{-}O)+\delta(O\text{-}C{=}O)\ (\nu_8)$
924 s	$\nu_a(O\text{-}V\text{-}O)$
876 s	$\nu_s(C\text{-}O)+\delta(O\text{-}C{=}O)\ (\nu_3)$
866 s	$\nu_s(O\text{-}V\text{-}O)$
800 m	$\delta(O\text{-}C{=}O)+\nu(M\text{-}O)\ (\nu_9)$

* s = strong, vs = very strong, m = medium ν = stretching, ν_s = symmetrical stretching, ν_a = antisymmetric stretching, and δ = in-plane deformation vibrations

bands can be assigned to the charge transfer arising from the promotion of an electron from the π-orbital of oxygen to the vacant 3d orbitals of the vanadium of the $VO_2{}^+$ group. In the oxovanadium complex containing the VO^{2+} ion, there is a band below 220 mμ (log ε = 4.0) and a shoulder at 245 mμ (log ε = 3.2); these are assigned as electron-transfer bands arising from the promotion of an electron from the oxygen π-orbital to the 3d levels of the vanadium of the VO^{2+} ion.[11] In the present complex containing the $VO_2{}^+$ ion, the absorption bands have shifted to higher wavelengths with an increase in the intensity. This effect may be due to the presence of another oxygen atom, with a certain amount of π-bonding to vanadium, along the V–O axis and a higher valence state of vanadium in the $VO_2{}^+$ ion.

The ultraviolet absorption spectra of a large number of oxalato complexes resemble those of dimethyl oxalate and molecular oxalic acid, with a low intensity band in the 250∼270 mμ[12] region. This carboxylate band in the present compound has obviously merged with the intense electron-transfer band occurring in the ultraviolet region. No absorption peak was observed in the visible region, but the ultraviolet absorption band extends up to nearly 400 mμ. The light yellow colour of the compound, therefore, appears to be due to the charge transfer.

The infrared band assignments of the complex are given in Table I. The presence of a strong band around 3550 cm^{-1} indicates crystal lattice water. The strong band at 3080 cm^{-1} is due to the NH stretching of NH_4 groups.[13] The band at 1629 cm^{-1} may be due to the bending of water. The bands arising due to the oxalate group are assigned after Fujita, Martell and Nakamoto.[14] The spectrum shows a very strong absorption at 1720 cm^{-1}, indicating a highly covalent character of the bonds between the metal and the oxalate group.[15]

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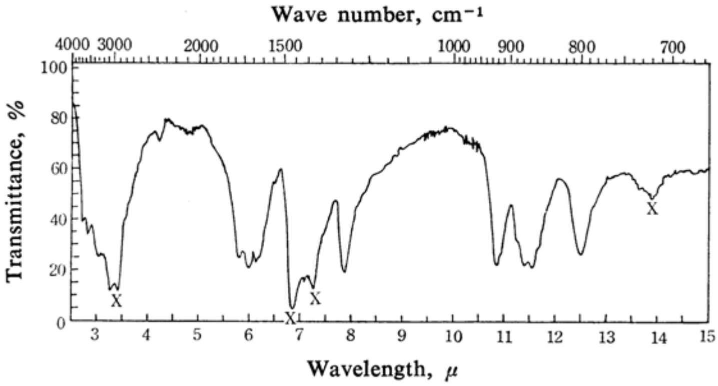


Fig. 4. Infrared spectrum of $(NH_4)_3[VO_2(C_2O_4)_2]\cdot 2H_2O$.

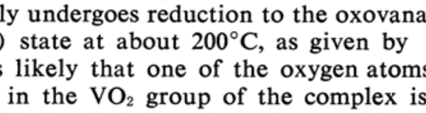
The infrared spectrum of the complex is given in Fig. 4

The band at 924 cm^{-1} is assigned to O–V–O asymmetrical stretching frequency, although it is predominantly a V–O mutiple-bond stretching frequency. Selbin et al.[16] assigned the strong band around 980 cm^{-1} to the V–O stretching in the oxovanadium compounds. It is interesting to note that the V–O stretching in the present complex occurs at a frequency much lower than that of the V–O stretching in hydrated oxovanadium(IV) oxalates (985 cm^{-1}) and in ammonium oxovanadium(IV) bisoxalates (978 cm^{-1}).[16] The lowering of the V–O frequency in the present case is due to the oxygen atom in the sixth position (of an octahedral structure) along the V–O axis, which is vacant in the above oxalates.[16] Such a position of oxygen will have the effect of slightly weakening the V–O bond, with also some reduction in its π-bond character. Nakamoto et al.[17] reported the lowering of the V–O stretching from 995 to 964 cm^{-1} in the solid complexes the addition of one pyridine molecule to oxovanadium(IV) bisacetylacetonate, $VO(acac)_2$.

Another band at 866 cm^{-1}, occurring as a doublet, may be due to the symmetrical stretching of O–V–O. The appearance of this second band may be due to the absence of the centre of symmetry of the O–V–O linear group, as has been suggested in the literature.[18,19]

The Structure of the Complex

Since the two water molecules in the complex are easily lost and since the infrared spectrum does not give any evidence of their being coordinated to the metal atom, they are considered to be lattice-held. Further, the infrared spectrum shows that the oxalate groups are covalently bonded. Hence, a six-coordinated octahedral structure with d^2sp^3 bonding can be assigned to the complex anion (I):



(I)

As there are no d electrons in vanadium(V), no distortion from the linear arrangement of the oxygen atom is expected in the VO_2^+ group of the complex.[18,19] Since the complex easily undergoes reduction to the oxovanadium(IV) state at about 200°C, as given by Eq. 1, it is likely that one of the oxygen atoms (say, O_1) in the VO_2 group of the complex is more weakly bonded than the other. This is supported by the similar instances of V_2O_5[20](V), $KVO_3\cdot H_2O$[21](V) and VO_2[22](IV), in which it has been found by X-ray diffraction studies that one of the V–O bonds is much shorter than the rest. A sulphate oxygen along the V–O axis, completing the octahedral structure in $VOSO_4\cdot 5H_2O$,[23] is held at a much longer distance than the four water molecules in the tetragonal plane, and the V–O bond of VO^{2+} complexes is much shorter than the other bonds.[23,24] This characteristic feature of the oxovanadium compounds can be attributed to the strong V–O bond with a predominantly high π character. The appearance of the two

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vibrational stretching frequencies of the O–V–O may thus be due to the differently bonded oxygen atoms.

Summary

A simple method for the preparation of the yellow diamagnetic complex, $(NH_4)_3[VO_2\cdot(C_2O_4)_2]\cdot 2H_2O$, is described. Around 200°C, the complex suffers decomposition, giving a bluish-grey paramagnetic compound $(NH_4)_2\cdot[(VO)_2(C_2O_4)_3]$. The infrared spectrum of the yellow complex shows a covalent bonding between vanadium and the oxalate groups. The absorption in the ultraviolet region is due to the electron transfer within the VO_2 group. An octahedral structure, with the two linearly-arranged oxide oxygens at unequal lengths from vanadium(V), is suggested for the complex anion.

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