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Crystal Structure and Vibrational Spectra of $Na_2VO(SO_4)_2$

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Blue crystals of the compound $Na_2VO(SO_4)_2$ suitable for X-ray structure determination have been obtained by dissolving V_2O_5 in molten $Na_2S_2O_7$ at a temperature of 400 °C and bubbling a 10% SO_2–90% N_2 gas mixture through the solution. In a few hours, blue needle-shaped crystals precipitated. The unique crystal structure belongs to the orthorhombic system in space group $P2_12_12_1$ (No. 19), with $a = 6.303$ (1) Å, $b = 6.803$ (1) Å, $c = 16.682$ (2) Å, and $Z = 4$. The structure consists of sodium ions and a three-dimensional network of vanadyl ions (VO^{2+}), interlinked by two kinds of bridging sulfate ions. Sulfate coordinates to the vanadium unidentately, forming a distorted VO_6 octahedron with one V–O bond length of 1.595 (2) Å, four in-plane bonds between 2.01 and 2.07 Å, and one bond opposite to the short one, with a length of 2.150 (2) Å. The O–V–O angles are distorted from 90° by less than 12°. The sulfate groups are slightly deformed and tilted, in such a way that the V–O–S bond angles are around 130 ± 3°. Short sodium–oxygen contacts (2.35–2.41 Å) are encountered. Sulfate groups 1 and 2, respectively, contain one (O(7)) and two (O(8) and O(9)) oxygen atoms, which are uniquely bound by short bonds to S(1) and S(2), respectively. Infrared and Raman spectra of the compound have been recorded and interpreted.

Introduction

This paper is one of a series[2-8] describing our efforts to explore the chemistry of the sulfuric acid catalyst. The liquid–gas system $M_2S_2O_7/V_2O_5–SO_2/O_2/SO_3/N_2$ (M = 80% K and 20% Na) is considered[9] to be a realistic model of the industrial catalyst, catalyzing the reaction

$$SO_2(g) + {}^1\!/_2O_2(g) \rightleftarrows SO_3(g) \qquad (1)$$

in the temperature range 400–600 °C. Below about 420 °C, the activity of the catalyst decreases sharply, and we have recently shown[8] that this deactivation for SO_2-rich gas compositions is caused by the precipitation of V(IV) and V(III) compounds.

Previously,[6,7] we have isolated the V(III) and V(IV) compounds $KV(SO_4)_2$ and $K_4(VO)_3(SO_4)_5$ from molten $KHSO_4/V_2O_5$ and $K_2S_2O_7/V_2O_5$ mixtures, respectively, in an SO_2-rich atmosphere. These K compounds have been recognized[8] as deactivation products in the above mentioned catalyst model system.

The present paper concerns compound formation in the $Na_2S_2O_7/V_2O_5–SO_2/O_2/N_2$ liquid–gas subsystem. It is shown that the V(IV) compound $Na_2VO(SO_4)_2$ is formed in sodium pyrosulfate below a temperature of ca. 470 °C, and its crystal structure and vibrational spectra are presented. The V(III) compound $NaV(SO_4)_2$ was also isolated. This compound will be characterized elsewhere.[10] The Na compounds were also recognized[8] as products of deactivation in the above mentioned catalyst model system. There seems to be no previous report on the formation of sodium compounds containing vanadium in the +IV or +III oxidation state from the working catalyst or from catalyst model melts. However, the existence of the compound $Na_2VO(SO_4)_2$ has been reported previously,[11] isolated from the $Na_2O/V_2O_4/SO_3$ system. The similar K compound $K_2VO(SO_4)_2$ has also been isolated from the analogous $K_2O/V_2O_4/SO_3$ system.[12]

Table I. Crystallographic Data for Sodium Vanadyl Sulfate

formula: $Na_2VO(SO_4)_2$	fw = 305.04
$a = 6.303$ (1) Å	space group: $P2_12_12_1$ (No. 19)
$b = 6.803$ (1) Å	$T = 300$ K
$c = 16.682$ (2) Å	λ(Mo Kα) = 0.71069 Å
$\alpha = \beta = \gamma = 90°$	$\mu = 20.46$ cm^{-1}
$V = 715.32$ Å^3	abs cor: none
$Z = 4$ formula units/cell	$R(F_o) = 0.0260$
$\rho_{exp} = 2.80$ g cm^{-3}	$R_w(F_o^2) = 0.0275$
$\rho_{calcd} = 2.83$ g cm^{-3}	

Experimental Section

The equipment used has earlier been described in detail.[7,8] It included a mixing unit for SO_2, O_2, SO_3, and N_2 gases to obtain any desired $SO_2/O_2/SO_3/N_2$ ratio for the gas led to the reactor cell. This was placed in a tiltable double-quartz-walled transparent tube furnace, in which the temperature of the melt could be regulated to ±0.5 °C within the range of 20–500 °C to simulate the conditions of a working catalyst. The reactor cell, made of borosilicate glass, contained a porous sintered-glass filter disk as support for the melt. The gas was introduced below the disk and bubbled through the melt. This cell construction enabled us to separate precipitates on the filter disk and isolate the melt filtrate in the bottom ampule for separate analysis.

Materials. The $Na_2S_2O_7$ used was synthesized by thermal decomposition of $Na_2S_2O_8$ (Fluka, pro analysi) and stored in sealed ampules until used. The nonhygroscopic V_2O_5 (Cerac, Pure (99.9%)) was used without further purification. All handling of chemicals including the filling of the reactor cell was performed in a glovebox with a nitrogen atmosphere that was continuously dried to around 5 ppm of H_2O by means of circulation through a column with molecular sieves. Commercial gases in steel bottles were used: SO_2 (>99.9%), O_2 (99.8% O_2 + 0.2% N_2 and Ar), and N_2 (<40 ppm of $O_2 + H_2O$).

Synthesis of Crystalline $Na_2VO(SO_4)_2$. In the glovebox, $Na_2S_2O_7$ and V_2O_5 were added to the reactor cell at mole ratios Na/V = 3, 4, 4.7, and 10. Usually the volume of the components did not exceed 1.5 mL (when fused) to avoid excessive foaming, which might stop the gas flow by solidification of the melt in the cold part of the tube leading out of the reactor. The closed cell was transferred to the reactor furnace and quickly connected to the gas supply and vent tubes. During heating of the mixture in the temperature range 400–470 °C, the $SO_2/O_2/N_2$ or SO_2/N_2 gas mixture of the desired composition was gently bubbled through the melt, at a total flow in the range 10–40 mL/min. Inde-

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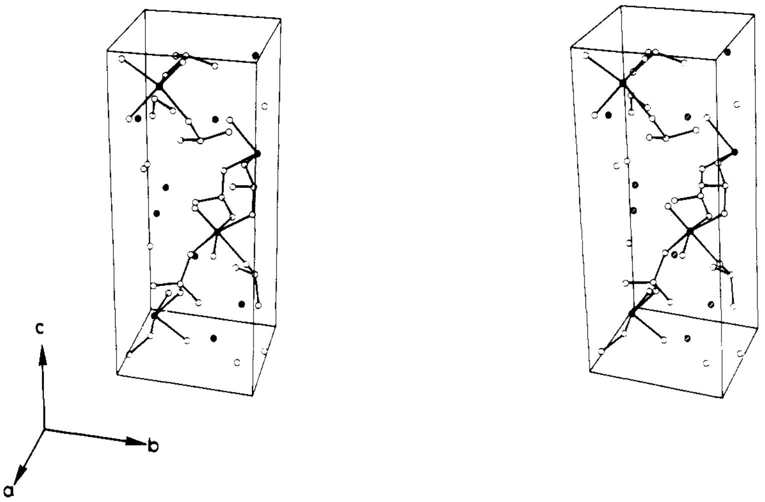

Figure 1. Stereo plot of the unit cell of $Na_2VO(SO_4)_2$, seen along the *a* axis.

Table II. Coordinates of the Atoms in the $Na_2VO(SO_4)_2$ Structure in Space Group $P2_12_12_1$[a,b]

atom	*x*/*a*	*y*/*b*	*z*/*c*
Na(1)	0.6756 (4)	0.1511 (3)	0.5906 (1)
Na(2)	−0.6288 (2)	0.1057 (2)	0.2388 (1)
V	0.5326 (8)	0.1497 (7)	0.9107 (3)
S(1)	0.0345 (1)	0.0859 (1)	0.9321 (1)
S(2)	0.8573 (1)	0.1030 (1)	0.2497 (1)
O(1)	0.2181 (3)	0.2014 (4)	0.9047 (2)
O(2)	0.5227 (4)	0.4033 (3)	0.9790 (1)
O(3)	0.5169 (4)	0.3591 (3)	0.8144 (1)
O(4)	0.8482 (3)	0.1880 (3)	0.8966 (1)
O(5)	0.5125 (4)	−0.0523 (3)	0.8225 (1)
O(6)	0.5371 (5)	−0.0083 (4)	0.9813 (1)
O(7)	0.0483 (4)	−0.1164 (4)	0.9074 (2)
O(8)	0.2735 (4)	−0.2281 (4)	0.2328 (2)
O(9)	−0.2740 (4)	−0.0631 (4)	0.2245 (1)

[a] The temperature factor parameters can be obtained from the authors upon request. [b] All atoms are at general positions.

Table III. Bond Lengths (Å) and Angles (deg) in $Na_2VO(SO_4)_2$

V–O(6)	1.595 (2)	O(6)–V–O(1)	99.88 (13)
V–O(1)	2.016 (2)	O(6)–V–O(2)	98.99 (10)
V–O(5)	2.017 (2)	O(6)–V–O(4)	98.96 (12)
V–O(4)	2.020 (2)	O(6)–V–O(5)	94.60 (11)
V–O(2)	2.068 (2)	O(6)–V–O(3)	178.17 (28)
V–O(3)	2.150 (2)	O(3)–V–O(1)	78.59 (9)
		O(3)–V–O(2)	81.81 (9)
		O(3)–V–O(4)	82.68 (9)
		O(3)–V–O(5)	84.45 (9)
		O(1)–V–O(2)	81.50 (10)
		O(1)–V–O(5)	91.18 (10)
		O(2)–V–O(4)	89.24 (10)
		O(4)–V–O(5)	93.70 (10)
		O(2)–V–O(5)	165.47 (11)
		O(1)–V–O(4)	160.09 (10)
		V–O(1)–S(1)	131.68 (16)
		V–O(2)–S(1)	126.10 (13)
		V–O(3)–S(2)	133.00 (15)
		V–O(4)–S(1)	132.12 (14)
		V–O(5)–S(2)	135.25 (15)
S(1)–O(1)	1.471 (2)	O(1)–S(1)–O(2)	108.82 (14)
S(1)–O(2)	1.488 (2)	O(1)–S(1)–O(7)	111.99 (16)
S(1)–O(4)	1.488 (2)	O(1)–S(1)–O(4)	104.34 (14)
S(1)–O(7)	1.439 (3)	O(2)–S(1)–O(7)	109.64 (14)
		O(2)–S(1)–O(4)	109.56 (13)
		O(7)–S(1)–O(4)	112.33 (14)
S(2)–O(3)	1.491 (2)	O(9)–S(2)–O(5)	111.29 (13)
S(2)–O(5)	1.506 (2)	O(9)–S(2)–O(3)	108.03 (13)
S(2)–O(8)	1.444 (2)	O(9)–S(2)–O(8)	110.48 (15)
S(2)–O(9)	1.462 (3)	O(5)–S(2)–O(3)	104.51 (12)
		O(5)–S(2)–O(8)	109.32 (14)
		O(3)–S(2)–O(8)	113.10 (14)
Na(1)–O(2)	2.398 (3)	O(9)–Na(1)–O(7)	87.90 (11)
Na(1)–O(9)	2.394 (3)	O(2)–Na(1)–O(9)	114.25 (11)
Na(1)–O(7)	2.352 (3)	O(2)–Na(1)–O(7)	149.92 (12)
Na(2)–O(8)	2.355 (2)	O(3)–Na(2)–O(9)	76.45 (9)
Na(2)–O(3)	2.414 (3)	O(3)–Na(2)–O(8)	80.70 (9)
Na(2)–O(9)	2.414 (3)	O(8)–Na(2)–O(9)	147.59 (11)

pendent of whether the gas consisted[8] of a 10% SO_2, 11% O_2, and 79% N_2 or a 10% SO_2 and 90% N_2 gas mixture, green and blue precipitates were observed after equilibration at any temperature in the range 400–470 °C over night. Large crops of crystals were obtained especially at low temperatures. After filtration and cooling, the reactor cell was opened and flushed gently with water overnight to dissolve the residual crystallized $Na_2S_2O_7$ solvent on the disk. In this way, slightly soluble bright blue crystals and sometimes[8] also green crystals remained.

Similar blue and green compounds were also obtained by cooling to 325 °C $NaHSO_4/V_2O_5$ molten mixtures with the mole ratio Na/V = 16 equilibrated in Pyrex ampules sealed under a SO_2 pressure of 0.95 atm at room temperature. The green compound was the vanadium(III) compound $NaV(SO_4)_2$, which will be described elsewhere.[10]

The needle-shaped blue crystals were examined in a polarization microscope, and proper samples were selected for further investigations. The crystal used for the X-ray investigation was obtained from the $V_2O_5/Na_2S_2O_7$ system with the mole ratio Na/V = 10 and treated with a 10% SO_2 and 90% N_2 gas mixture at 400 °C overnight.

Infrared Spectra. The IR spectra were recorded on a Perkin-Elmer 577 spectrometer in the double-beam mode with a KBr disk as the reference.

Raman spectra were excited with the 514.5- or 488.0-nm line of a 4-W Spectra Physics argon ion laser. The scattered light was collected at an angle of 90° (vertical scattering plane) and analyzed with a Spex 1403 0.85-m double monochromator equipped with a −20 °C cooled RCA photomultiplier and EG&G/ORTEC photon counting and chopper lock-in amplifier electronics.

X-ray Single-Crystal Investigations. The crystal symmetry was determined from Weissenberg photographs. Crystal data and other experimental details of the structure solution method are given in Table I. Intensity data were collected at 300 K on an Enraf-Nonius CAD-4F diffractometer. The cell dimensions were determined by least-squares refinement based on the setting of 25 high-order reflections. Because of irregular shape of crystals and low absorption coefficients, no correction for absorption was attempted. Reflections with $I < 2\sigma(I)$ were omitted from the refinement. The weight function gave a uniform distribution of $w|\Delta F|^2$. The results from the fitting calculations, i.e. atomic coordinates, bond lengths, and bond angles, are listed in Tables II and III. Observed and calculated structure factors and atomic thermal parameters are included as supplementary material.

Results and Discussion

Description of the Structure. Figure 1 shows a stereo pair of the structure. The asymmetric unit contains one independent vanadyl, VO^{2+}, complex ion, two sulfate ions, and the corresponding two sodium ions. The sulfate coordination around vanadium forms a complicated three-dimensional network. The vanadium sits near the center of an octahedron consisting of the vanadyl oxygen and five oxygens from five different sulfate groups, which themselves are further coordinated to other vanadium atoms.

In Figure 2, a projection of the distorted $V–O_6$ octahedron is shown. The vanadyl O(6) is at a short distance (1.595 Å), the

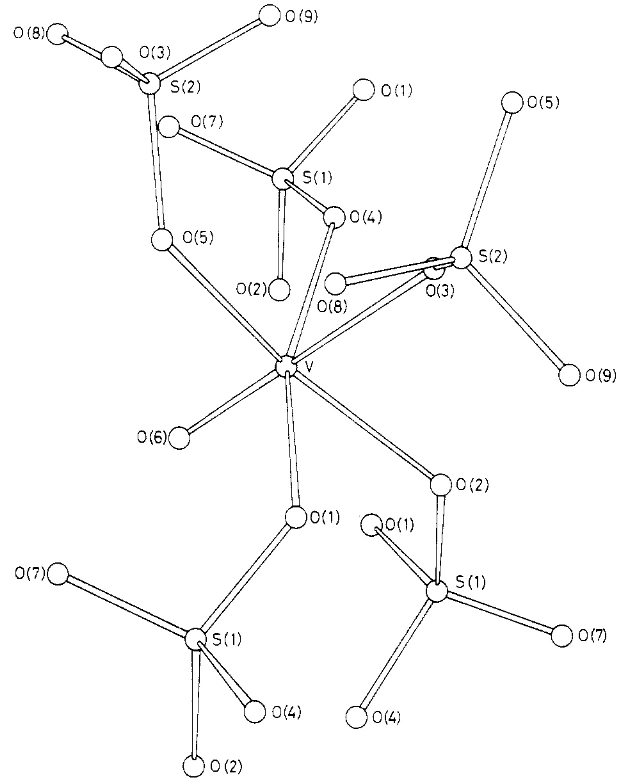

Figure 2. Labeling of atoms and thermal vibration ellipsoids for the distorted V–O_6 octahedron and for the two sulfate ions. Distances and angles are given in Table III.

other axial oxygen opposite to it, i.e. O(3), is at a long distance (2.150 Å), and the other four equatorial oxygens are at intermediate distances (2.02–2.07 Å). Two kinds of nearly 90° O–V–O angles are found (Table III), those involving the vanadyl O(6) and the four equatorial oxygens being around 95–100°, whereas those involving the other axial oxygen, O(3), and the four equatorial oxygens are consequently below 85°. The O(6)–V–O(3) angle involving the axial oxygens is 178°, indicating a small deviation from a collinear arrangement. The angles involved in the equatorial plane formed by oxygens 1, 2, 4, and 5 deviate somewhat (less than 9°) from 90°.

The values for interatomic angles and distances are typical of what is found for other vanadyl compounds.[13] The structure can be described as a distorted VO_6 octahedron in which the vanadium atom is located slightly (around 0.3 Å) above the plane defined by the four equatorial oxygen ligands.

The V–O–S bonds deviate significantly from being collinear, forming angles around 130 ± 3° (Figure 2 and Table III). One sulfate group, S(1), has one oxygen (O(7)) that is not coordinated to V, while the other sulfate group, S(2), has two noncoordinated oxygens (O(8) and O(9)). The other oxygens for both kinds of sulfate are shared with vanadium in the formation of V–O–S coordination bridges. The lengths of the bonds between sulfur and the noncoordinated oxygens are relatively shorter (1.44–1.46 Å) than the sulfur–oxygen bonds (1.47–1.51 Å) found in the coordination bridges. Around the sulfur atoms, nearly tetrahedral angles are found, deformed in such a way that the O–S–O angles involving oxygen atoms bridging to vanadium on the whole are smaller (around 104.34–109.64°) than the ideal angle of 109.47°; see Figure 2 and Table III. This is probably due to repulsion from the short-bonded oxygens. The O–S–O angles not involving oxygen atoms bridging to vanadium are in the range 108.03–113.10° and generally enlarged to values above 109.47°. The S–O distances (Table III) depend on the angles in such a way that the larger the average of the three possible O–S–O angles involving a particular bond, the smaller is the S–O distance. This is shown in Figure 3, in which an approximately linear relationship

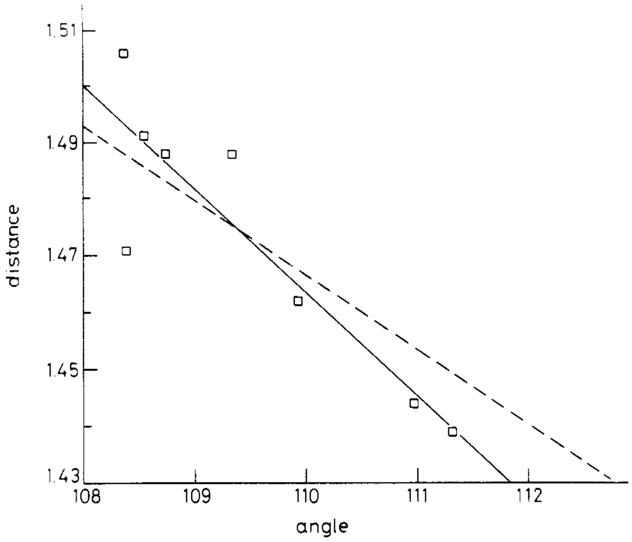

Figure 3. Plot of the S–O distances for a particular bond versus the average of the three angles involving this bond and the other three S–O bonds of the sulfate tetrahedra. The dashed line is taken from ref 7.

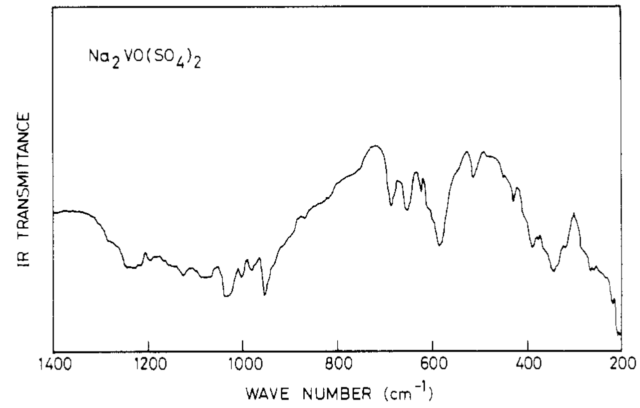

Figure 4. Infrared spectrum of $Na_2VO(SO_4)_2$ powder in a pressed KBr disk at room temperature. Resolution = ca. 5 cm^{-1}.

(linear regression) is found similar to what was observed for the five different sulfate ions in the $K_4(VO)_3(SO_4)_5$ structure[7] (shown as the dashed line): There is no significant difference in slope between the two lines. This indicates similar hybridizations of the sulfur atoms of the sulfate groups, at least in these cases. The bond lengths and bond angles of the sulfate tetrahedra (Table III) are generally close to the usual values of 1.474 Å[14] and 109.47° for the sulfate group. Short sodium–oxygen contacts (2.35–2.41 Å) occur, as can be seen in Table III.

Comparison of $Na_2VO(SO_4)_2$ to Other Structures. Only a few sulfates of vanadium(IV) are known, and the only single-crystal structure determinations of which we are aware concern α-$VOSO_4$,[15,16] β-$VOSO_4$,[17] $VOSO_4{\cdot}3H_2O$,[18] $VOSO_4{\cdot}5H_2O$,[19] and $K_4(VO)_3(SO_4)_5$[7] (ref 7 gives further details). The short V═O bond of the vanadyl entity in the $VOSO_4$ compounds is in the range 1.56–1.63 Å, and the equatorial V—O bond lengths are in the range 1.99–2.08 Å, while the long axial V—O bond opposite the short vanadyl bond is in the range 2.22–2.47 Å. The angles between the short V—O bond and the equatorial V—O bonds are in the range 94–103°. For the three slightly different VO_6 octahedra of the $K_4(VO)_3(SO_4)_5$ structure[7] these four values were

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Table IV. Infrared and Raman Bands[a–c] (cm^{-1}) of $Na_2VO(SO_4)_2$[d] and $K_2VO(SO_4)_2$[e] and Their Assignments

	Raman (polycrystalline, needle crystals; λ = 488.0 nm)	IR		
		$Na_2VO(SO_4)_2$ (in KBr)	$Na_2VO(SO_4)_2$[d]	$K_2VO(SO_4)_2$[e]
$\nu_3(SO_4^{2-})$		1250	1253	
	1245 m	1245	1243	
		1225	1236	
		1215	1225	1220
	1127 m	1125	1137	1155
$\nu_1(SO_4^{2-})$	1085 m	1090	1095	
	1047 w	1035	1040	1045
	1022 s			
	1013 m	1003	1010	1005
	993 m	980	990	980
	972 s			
$\nu(V{=}O)$	964 vs	955	957	
	688 w	688	696	685
		655	662	665
$\nu_4(SO_4^{2-})$	636 w	625	634	645
		610	619	620
	603 m		610	600
		585	590	
		512		
$\nu_2(SO_4^{2-})$	536 w	450	440	475
	484 w	428		415
	390 w	390		
		375		
	322 w	320		
	287 m	285		
ν(lattice)	273 m	265		
	256 s	256		
ν(V—O str)	236 w	240		
	175 m			
	139 w			
	121 w			
	80 w			
	59 m			

[a] Powder samples at room temperature. [b] Intensity codes: w = weak; m = medium; s = strong; v = very. Raman intensities dependent on crystallite orientation. [c] Polystyrene sheet or argon laser plasma lines were used for frequency calibration (±2 cm^{-1}). [d] Reference 11; liquid paraffin mull. [e] Reference 12; liquid paraffin mull.

in the ranges 1.58–1.59 Å, 2.02–2.06 Å, 2.22–2.23 Å, and 95–101°, respectively, which compares well to the $VOSO_4$ structures. For the present compound, $Na_2VO(SO_4)_2$, the values are 1.60 Å, 2.02–2.07 Å, 2.15 Å, and 95–100°, respectively, in good accordance with the other compounds. However, the length of the V–O bond opposite the short V–O bond is only 2.15 Å in $Na_2VO(SO_4)_2$, which is shorter than in any of the other similar compounds mentioned above. Thus, the first coordination spheres seem to be arranged in similar ways in all compounds containing vanadyl and sulfate groups.

Infrared and Raman Spectra. IR spectra (Figure 4) of the blue $Na_2VO(SO_4)_2$ at room temperature were obtained on finely ground powders in pressed KBr disks. Raman spectra were obtained at room temperature on stationary polycrystalline samples by using either the 488.0-nm (Figure 5) or the 515.4-nm laser line. Raman spectra excited with the 514.5-nm line exhibited similar features, as shown in Figure 5.

As can be seen from Figures 4 and 5, the IR and Raman spectra contain many bands and most of them are common to both kinds of spectra. The bands observed are listed and tentative assignments given in Table IV.

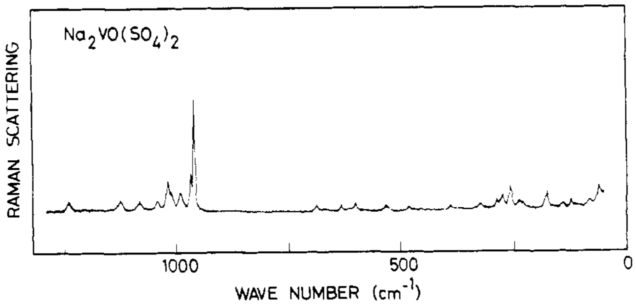

Figure 5. Raman spectrum of $Na_2VO(SO_4)_2$ powder at room temperature. λ_0 = 448.0 nm, power = 110 mW, and resolution = ca. 2 cm^{-1}.

The free-group vibrations of the $V{=}O^{2+}$ and SO_4^{2-} groups usually give stretching bands near 975 cm^{-1} for $\nu(V{=}O)$,[20] near 1000 cm^{-1} for $\nu_1(SO_4^{2-})$, and near 1100 cm^{-1} for $\nu_3(SO_4^{2-})$ and bending bands near 450 cm^{-1} ($\nu_2(SO_4^{2-})$) and 600 cm^{-1} ($\nu_4(SO_4^{2-})$).[21] Of these, $\nu_1(SO_4^{2-})$ and $\nu_2(SO_4^{2-})$ are not IR-permitted. However, in an ionic crystal lattice, the interaction between the ions can reduce the symmetry of the groups and can e.g. lift the degeneracies of the sulfate group vibrations. This may lead to a splitting of the ν_2, ν_3, and ν_4 bands of the SO_4^{2-} group into several components,[21] and it can cause ν_1 to gain in intensity in the IR spectrum. The presence in the IR and Raman spectra of $Na_2VO(SO_4)_2$ of a number of bands in the regions of 1000–1300, of 600–700, and near 500 cm^{-1} points to a lowering of the T_d symmetry of the free SO_4^{2-} group in the $Na_2VO(SO_4)_2$ crystal. This is in good accordance with the bond lengths and interionic distances found in the crystal. Furthermore, the presence of four asymmetric units in the unit cell also points to a complicated pattern of the vibrational spectra. The frequencies of the V═O bond vibrations are probably found in the region 950–1000 cm^{-1}, i.e. in the lower end of the frequency range for the SO_4^{2-} vibrations. The absence of the characteristic bands[3]

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of the $S_2O_7^{2-}$ ion constituting the solvent melt should be noted.

The IR spectrum of the compound $Na_2VO(SO_4)_2$, isolated previously,[11] shows a close analogy to the spectrum given here (Figure 4). This is also obvious from the frequencies listed in Table IV, which support the impression that we are dealing with the same compound. Apart from this, only a few sulfato compounds of V(IV) have been examined by IR spectroscopy, and so far, no Raman spectra have been published except[7] for that of the compound $K_4(VO)_3(SO_4)_5$. For α- and β-$VOSO_4$ the IR spectra show[12,15,22,23] that the ν(V═O) bands are found in the region 940–990 cm^{-1} while $\nu_1(SO_4^{2-})$ and split $\nu_3(SO_4^{2-})$ bands are present in the region 1000–1200 cm^{-1}. Several bands of the bending modes, $\nu_2(SO_4^{2-})$ and $\nu_4(SO_4^{2-})$, respectively, are found in the regions of ca. 400–500 and ca. 600–700 cm^{-1}. An identical compound, which probably can be represented by the formula $K_2(VO)_2(SO_4)_3$, seems to have been obtained in three different investigations according to the stoichiometry and the IR spectra of the compounds.[12,23,24] In these investigations ν(V═O) bands are found around 985 cm^{-1}, while the ν_1 and ν_3 stretching modes of the SO_4^{2-} groups are found in the region 1000–1270 cm^{-1} and the ν_2 and ν_4 bending modes in the regions ca. 400–460 and 600–660 cm^{-1}, respectively. The complicated IR and Raman spectra[7] of the compound $K_4(VO)_3(SO_4)_5$ show that the stretching modes ν(V═O), $\nu_1(SO_4^{2-})$, and $\nu_3(SO_4^{2-})$ most probably are found in the region 970–1270 cm^{-1} and the bending modes $\nu_4(SO_4^{2-})$ and $\nu_2(SO_4^{2-})$ at 600–700 and 440–520 cm^{-1}, respectively. For $K_2VO(SO_4)_2$, the potassium analogue of the sodium compound studied here, the IR spectrum shows[12] rather similar features, as can be seen in Table IV. The ν(V═O) bands seem to be found at lower frequencies in $Na_2VO(SO_4)_2$ than in $K_2VO(SO_4)_2$. The same is found by comparison to $K_4(VO)_3(SO_4)_5$.[7] This seems reasonable since the V═O bond length is longer in $Na_2VO(SO_4)_2$ than in $K_4(VO)_3(SO_4)_5$. This weakening of the V═O bond in $Na_2VO(SO_4)_2$ might be due to a stronger donation of electrons to the metal d orbitals by the sulfate ligand opposite the V═O bond. This is reflected by the unusual short opposite V—O bond length of 2.15 Å in $Na_2VO(SO_4)_2$ compared to 2.22–2.23 Å found in $K_4(VO)_3(SO_4)_5$. A general common feature for all V(IV) oxo–sulfato compounds discussed here seems to be—judged from the vibrational spectra—the presence of bi- or tridentate chelate or bridging sulfate ligands coordinated to a V═O^{2+} entity. The X-ray structure examinations made so far confirm this.

Conclusion

The compound $Na_2VO(SO_4)_2$ has been isolated from the liquid–gas system $V_2O_5/K_2S_2O_7$–$SO_2/O_2/N_2$ and its molecular structure determined. The deactivation of sulfuric acid catalysts at lower temperatures has been attributed[25] to the precipitation of V(IV) compounds. Indeed, our recent work[8] has shown that when V(III) and V(IV) compounds of the alkali metals Na, K, and Cs are formed in the $M_2S_2O_7/V_2O_5$–$SO_2/O_2/N_2$ liquid–gas system (M = Na, K, Cs), a similar dramatic decrease in the catalytic activity of the system is observed. Thus, the precipitation of the V(IV) compound $Na_2VO(SO_4)_2$ may contribute to the observed deactivation at low temperatures of the commercial catalyst containing sodium as a copromotor to potassium.

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Supplementary Material Available: Tables A and C, giving temperature factor parameters and all crystallographic data (2 pages); Table B, listing observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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$RbV_3P_4O_{17+x}$ ($x = 0.14$): A Novel Mixed-Valence Vanadium Pyrophosphate

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A novel mixed-valence vanadium pyrophosphate, $RbV_3P_4O_{17+x}$ ($x = 0.14$), was discovered, and its structure was determined from single-crystal X-ray diffraction data. This nonstoichiometric phase crystallizes in the tetragonal space group $P4_2/mnm$ with $a = 13.651$ (2) Å, $c = 7.289$ (2) Å, $V = 1358.3$ (4) Å^3, $Z = 4$, $R = 0.0366$, and $R_w = 0.0360$ for 835 unique reflections with $I > 2.5\sigma(I)$. The structure may be regarded as built from ReO_3-type infinite chains along the c axis (in which each VO_6 octahedron shares two opposite vertices) and finite chains parallel to the ⟨110⟩ directions, which are linked by P_2O_7 groups to form a three-dimensional structure. Each finite chain consists of four VO_6 subunits. The oxygen atom shared between the central and side octahedra in the four-membered chain is about two-thirds occupied. Variable-temperature powder magnetic susceptibility data suggest the presence of two V^{4+} and one V^{5+} per formula unit and support the formula determined from single-crystal X-ray diffraction data.

Introduction

The vanadium phosphorus oxide system has shown a rich structural chemistry owing to the accessibility of more than one oxidation state and the ability of vanadium polyhedra and phosphate tetrahedra to form a variety of frameworks. As a part of the search for novel mixed frameworks built up from corner-sharing octahedra and tetrahedra, we recently began an investigation of the vanadium phosphate system containing vanadium in oxidation states less than +5. By adding alkali-metal cations to this system, a variety of structural types with cage, tunnel, or layer structures have been generated. In the system M–V(IV)–P–O, $LiVOPO_4$,[1] $M_2VOP_2O_7$ (M = K, Rb, Cs),[2,3] and $M_2V_3P_4O_{17}$ (M = Cs, Rb, K)[4-6] are known to exist. The phos-

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