

Crystal Structure and Spectroscopic Characterization of a Green V^{IV} Compound, Na₈(VO)₂(SO₄)₆

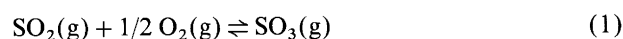
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A mixture of green crystals was precipitated at 467 °C from around 1.5 mL of a melt, consisting of Na₂S₂O₇ and V₂O₅ in the molar ratio Na/V=4. The melt was in contact with a 10% SO₂–90% N₂ mixed gas atmosphere. A minor amount of the product consisted of the green V^{III} compound NaV(SO₄)₂, previously investigated. The majority consisted of another kind of crystal, whose X-ray structure is reported here. The obtained formula was Na₈(VO)₂(SO₄)₆, crystallizing in the monoclinic space group *P*2₁/*c*, with *a*=8.6454(2), *b*=16.0027(4), *c*=15.5074(4) Å and β=90.017(1)° at 22 °C and *Z*=4. Surprisingly the crystals were not blue as would be expected from the +4 oxidation state of the vanadium. The structure consists of two kinds of octahedrally coordinated vanadium atoms, each closely bound to an O²⁻ (forming the vanadyl group VO²⁺) and five sulfato groups, the one trans to oxide at a longer distance. A complicated 3-dimensional network of V–O–SO₂–O–V bonding is described, in between which the Na⁺ ions are found. Infrared and Raman spectra of the compound were obtained and assigned to modes of the sulfato and vanadyl ions, but many fewer fundamentals were found than prescribed by the factor group analysis based on the unit cell.

In our continuing studies^{1,2} on the sulfuric acid catalyst model system M₂S₂O₇/V₂O₅–SO₂/O₂/SO₃/N₂ (M=K, Na and/or Cs) in the temperature range 400–600 °C, we have found that below about 420 °C, the catalytic activity for the reaction



decreases sharply, presumably due to precipitation of several kinds of vanadium(III), (IV) and mixed (IV)–(V)-compounds, among these KV(SO₄)₂,³ NaV(SO₄)₂,^{4,5} Na₃V(SO₄)₃,⁵ CsV(SO₄)₂,⁶ Na₂VO(SO₄)₂,⁷ K₄(VO)₃(SO₄)₅,⁸ β-VOSO₄,⁹ K₆(VO)₄(SO₄)₈¹⁰ and Cs₂(VO)₂(SO₄)₃,¹¹ which have been isolated from the model system. Several of these compounds have been recognized¹² as catalyst deactivation products by *in situ* ESR measurements on industrial catalysts. Here, by means of an X-ray investigation, we present the crystal structure of yet another deactivation product, the V^{IV} compound Na₈(VO)₂(SO₄)₆, formed in the Na₂S₂O₇/V₂O₅–SO₂/O₂/N₂ liquid–gas system at temperatures below ~470 °C. As far as we know there has been no previous report on the existence of such a sodium

compound or the formation of this compound in industrial catalysts or model melts.

Experimental

The experimental set-up (reactor flow cell in a furnace at ~500 °C and gas mixing unit) used for the preparation of the crystals has been described in detail in Refs. 1, 4 and 8. Na₂S₂O₇ was obtained by thermal decomposition of dry Na₂S₂O₈ (Fluka, pro analysi). V₂O₅ [Cerac, Pure (99.9%)] was used without further treatment. All handling of chemicals, including filling the reactor cell, was performed in a nitrogen atmosphere glovebox.

Synthesis of green crystalline Na₈(VO)₂(SO₄)₆. The cell, loaded with chemicals, was transferred from the glove box, mounted in the furnace, quickly connected to the gas supply and vent tubes, and heated.⁷ A mixture of green crystals slowly formed at 467 °C when a molten mixture (<1.5 mL) of Na₂S₂O₇ and V₂O₅ with mole ratio Na/V=4 was gently purged overnight with a 10% SO₂–90% N₂ gas mixture. The gas flow then was reversed, whereby the crystals were filtered on the porous disc. After cooling, the reactor cell was opened and gently flushed with water to dissolve residual Na₂S₂O₇, leaving

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the non-hygroscopic product. A minor amount of the product consisted of the green V^{III} compound NaV(SO₄)₂ which had been previously investigated.⁴ Surprisingly, most of the crystals, consisting mainly of a V^{IV} compound, were green. (V^{IV} compounds are usually blue.) The formula of the green compound was found to be Na₈(VO)₂(SO₄)₆ during the investigation presented here. A suitable single crystal was selected by use of a polarization microscope. In a similar way, a V^{IV} compound in the form of a blue needle-shaped Na₂VO(SO₄)₂ crystal has recently been isolated from a melt of molar ratio Na/V = 10 at 400 °C and the crystal structure reported.⁷

IR and Raman spectroscopy. The IR spectra were recorded on a Perkin–Elmer 1000 infrared Fourier transform spectrometer. The sample was ground in dry KBr and pressed into a transparent disk. Raman spectra were obtained with the 514.5 and 488.0 nm lines of a Spectra-Physics argon ion laser,⁵ directly on a sample of the green crystal mixture. We are not sure that all the crystals were of the Na₈(VO)₂(SO₄)₆ type, so the spectra should be taken as tentative. However, the spectral characteristics⁴ of the most likely contaminant, NaV(SO₄)₂, cannot be identified in the spectra.

X-Ray single crystal investigation

The crystal symmetry and space group were determined from Weissenberg photographs. Crystal data and other experimental results are given in Table 1. Intensity data were collected at room temperature on a Siemens SMART diffractometer with graphite monochromated Mo K α radiation (0.710 73 Å). The unit-cell dimensions were determined by least-squares refinements based on the complete data set. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved and refined in the space group *P*2₁/*c*. The calculations were done using Sheldrick's programs,¹³ and included full-matrix least-squares *F*² refinements of positional and anisotropic thermal parameters. Anomalous dispersion corrections and atomic scattering factors given in Ref. 14 were used. Three of the 5494 reflections having very negative *F*² were omitted from the refinement. The crystal was twinned with coinciding (*h k l*) and (*h k -l*) reflections; the twin scale factor for the second component was 0.566(1). Atomic coordinates, equivalent isotropic thermal parameters, bond lengths and bond angles are listed in Tables 2 and 3. *R*- and *R*_w-values are given in Table 1. An approximate (isotropic) treatment of cell e.s.d. is used for estimating e.s.d. involving least-square planes. A list of observed and calculated structure factors as well as anisotropic thermal parameters (*U*_{*ij*}) is obtainable from the authors. Visualisations of the structure are shown in Figs. 1 and 2.

Description and discussion of the structure. The asymmetric unit contains eight sodium ions, two vanadium(IV)

Table 1. Crystal data for Na₈(VO)₂(SO₄)₆.

Formula	Na ₈ (VO) ₂ (SO ₄) ₆
<i>M</i> _w /g mol ⁻¹	894.16
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> /Å	8.6454(2)
<i>b</i> /Å	16.0027(4)
<i>c</i> /Å	15.5074(4)
β /°	90.017(1)
<i>V</i> /Å ³	2145.44
<i>D</i> _c /g cm ⁻³	2.768
<i>T</i> /K	293(2)
<i>Z</i> and <i>F</i> (000)	4 and 1752
μ (Mo K α)/cm	17.46
Extinction expression refined	$F_c^* = kF_c[1 + 0.001F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction parameter	0.0020(2)
Total no. of reflections	14753 (5494 independent)
	<i>R</i> _{int} = 0.063
Min, max in 2 θ /°	2.54, 59.33
Min, max in <i>h, k, l</i>	<i>h</i> : -9, 12; <i>k</i> : -22, 18; <i>l</i> : -20, 21
Reflections with <i>I</i> > 2 σ (<i>I</i>)	4450
No. of parameters	381
Crystal size/mm	0.15 × 0.08 × 0.03
Weight function	$w^{-1} = s^2(F_o^2) + (0.0071P)^2 + 7.3562P$, with $P = (F_o^2 + 2F_c^2)/3$
<i>R</i> ₁ = $\sum F_o - F_c / \sum F_o $	0.0732 for all reflections; 0.0479 for reflections with <i>F</i> _o > 2 σ (<i>F</i> _o)
$wR_2 = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.0954 for all reflections; 0.0810 for reflections with <i>F</i> _o > 2 σ (<i>F</i> _o)
Goodness of fit	1.189 for all reflections; 1.134 for reflections with <i>F</i> _o > 2 σ (<i>F</i> _o)
Residual charge density/e Å ⁻³	-0.78 < ρ < 0.86

oxide (vanadyl, VO²⁺) ions, and six sulfate ions. The bonding scheme connecting the atoms can be immediately derived from the content of Table 3 and Fig. 2. The coordination around the two vanadium atoms is very much the same: Each coordinative polyhedron is a distorted octahedron, with one short V=O bond (V1–O1 or V2–O7), with four longer equatorial V–O bonds (V1 to O2, O3, O4, O5, and V2 to O8, O9, O10, O11, respectively) and one very long V–O bond (V1–O6 and V2–O12), in a axial position trans to the vanadyl bond, as expected. The V=O bonds point approximately in the crystallographic *a*-direction, and the vanadyl oxygen atoms, O1 and O7, are not further coordinated. One of the equatorial V–O bonds incorporates a sulfato group that is not otherwise coordinated, V1–O4–S3 (with O17, O18 and O19 not further bound) and V2–O8–S5 (with O22, O23 and O24 not further bound). The three other equatorial and the trans V–O bonds involve sulfato groups which are further coordinated to other vanadium atoms: the four sulfato bridges branching off from each vanadium atom are of two kinds, one involving V1–O–S1–O–V2 or V1–O–S4–O–V2 and thus connecting V1 and V2 (hetero-bridging) and the other involving V1–O–S2–O–V1 or V2–O–S6–O–V2, thus connecting V1 with V1 or V2 with V2 (homo-bridging). The homo-bridging

Table 2. Fractional coordinates and equivalent isotropic thermal parameters for the atoms in $\text{Na}_8(\text{VO})_2(\text{SO}_4)_6$.^a

Atom	x/a	y/b	z/c	$U_{\text{eq}}/\text{\AA}^2$
V1	0.47314(11)	0.42560(6)	0.13920(6)	0.0106(2)
V2	0.97328(11)	0.42132(6)	0.36893(6)	0.0115(2)
S1	0.5732(2)	0.42470(9)	0.33878(9)	0.0129(3)
S2	0.4600(2)	0.38763(8)	-0.06143(9)	0.0117(3)
S3	0.4382(2)	0.22106(8)	0.13468(9)	0.0122(3)
S4	0.0624(2)	0.45290(8)	0.16026(9)	0.0117(3)
S5	0.9456(2)	0.22126(8)	0.34087(9)	0.0124(3)
S6	0.9083(2)	0.39854(8)	0.57436(9)	0.0117(3)
Na1	0.3072(3)	0.0477(2)	0.0104(2)	0.0229(6)
Na2	0.1471(3)	0.2794(2)	0.0304(2)	0.0253(6)
Na3	0.3227(3)	0.2824(2)	0.3113(2)	0.0216(6)
Na4	0.1648(3)	0.5700(2)	0.0093(2)	0.0316(7)
Na5	0.3170(3)	-0.2193(2)	0.0321(2)	0.0253(6)
Na6	0.1855(3)	-0.2169(2)	0.3195(2)	0.0211(6)
Na7	0.3522(3)	0.5873(2)	0.2549(2)	0.0205(5)
Na8	-0.2112(3)	0.5793(2)	0.2284(2)	0.0334(7)
O1	0.6490(5)	0.3970(3)	0.1300(3)	0.0183(9)
O2	0.4669(5)	0.4503(2)	0.2665(2)	0.0141(8)
O3	0.3991(5)	0.4325(2)	0.0163(3)	0.0151(9)
O4	0.3805(5)	0.3091(2)	0.1542(3)	0.0170(9)
O5	0.5329(5)	0.5505(2)	0.1338(2)	0.0152(8)
O6	0.2290(5)	0.4729(3)	0.1558(3)	0.0168(9)
O7	1.1431(5)	0.3934(3)	0.3954(3)	0.0240(10)
O8	0.9056(5)	0.3121(2)	0.3230(3)	0.0166(9)
O9	0.8624(5)	0.3981(3)	0.4798(3)	0.0178(9)
O10	1.0091(5)	0.4690(3)	0.2501(3)	0.0182(9)
O11	0.9578(5)	0.5425(2)	0.4143(2)	0.0151(8)
O12	0.7295(5)	0.4571(2)	0.3204(3)	0.0154(9)
O13	0.5708(6)	0.3340(3)	0.3436(3)	0.0323(12)
O14	0.5151(5)	0.4623(3)	0.4172(3)	0.0350(13)
O15	0.3511(6)	0.3228(3)	-0.0845(3)	0.0256(11)
O16	0.6146(5)	0.3571(3)	-0.0460(3)	0.0224(10)
O17	0.6003(5)	0.2246(3)	0.1112(3)	0.0209(10)
O18	0.3463(6)	0.1877(3)	0.0641(3)	0.0252(10)
O19	0.4173(6)	0.1728(3)	0.2140(3)	0.0230(10)
O20	0.0318(5)	0.3668(2)	0.1349(3)	0.0247(10)
O21	-0.0230(5)	0.5099(3)	0.1041(3)	0.0251(10)
O22	1.0988(5)	0.2063(3)	0.3081(3)	0.0256(11)
O23	0.8306(5)	0.1735(3)	0.2940(3)	0.0196(10)
O24	0.9374(5)	0.2073(3)	0.4343(3)	0.0219(10)
O25	0.9568(5)	0.3150(2)	0.5977(3)	0.0186(9)
O26	0.7761(5)	0.4300(3)	0.6200(3)	0.0213(10)

^aAll 42 atoms are on sites e of multiplicity 4 and with no site symmetry. E.s.d.s are given in parentheses. U_{eq} is defined as $1/3 \sum U_{ij} a_i^* a_j^* a_i a_j$ and values are given in \AA^2 . The anisotropic temperature parameters U_{ij} are given as supplementary material which can be obtained from the authors.

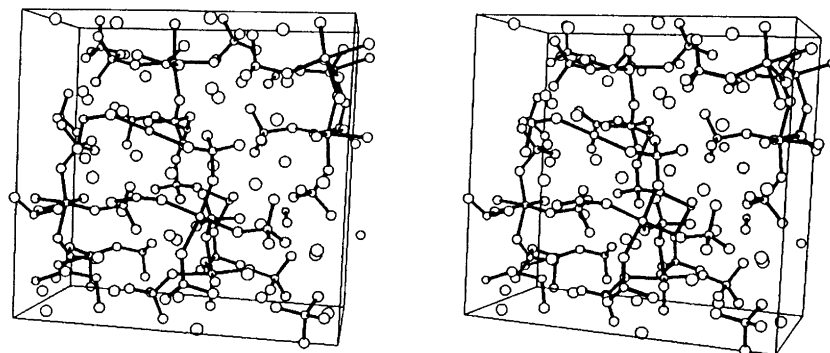


Fig. 1. Stereo plot of the unit cell of $\text{Na}_8(\text{VO})_2(\text{SO}_4)_6$, seen along the a -axis. Horizontal axis is b ; vertical axis is c .

Table 3. Bond distances and bond angles for VO₆ octahedra and SO₄ tetrahedra in Na₈(VO)₂(SO₄)₆.

Distances/Å		Angles/°		Nonbonded/Å	
V1-O1	1.594(4)	O1-V1-O3	103.5(2)	Na1-O14	2.312(5)
V1-O3	2.013(4)	O1-V1-O2	99.8(2)	Na1-O14	2.342(5)
V1-O2	2.014(4)	O3-V1-O2	155.3(2)	Na1-O18	2.414(5)
V1-O4	2.042(4)	O1-V1-O4	97.0(2)	Na1-O7	2.466(5)
V1-O5	2.067(4)	O3-V1-O4	91.9(2)	Na1-O11	2.574(5)
V1-O6	2.257(4)	O2-V1-O4	93.3(2)	Na1-O9	2.812(5)
		O1-V1-O5	92.0(2)	Na1-O26	2.856(5)
		O3-V1-O5	89.3(2)	Na1-O12	3.015(5)
		O2-V1-O5	81.7(2)		
		O4-V1-O5	170.3(2)		
		O1-V1-O6	176.7(2)		
		O3-V1-O6	78.0(2)		
		O2-V1-O6	78.3(2)		
		O4-V1-O6	85.8(2)		
		O5-V1-O6	85.1(2)		
V2-O7	1.588(5)	O7-V2-O8	96.7(2)	Na2-O18	2.322(5)
V2-O8	1.976(4)	O7-V2-O9	99.7(2)	Na2-O24	2.357(5)
V2-O9	2.004(4)	O8-V2-O9	90.2(2)	Na2-O20	2.361(5)
V2-O10	2.019(4)	O7-V2-O10	101.5(2)	Na2-O25	2.466(5)
V2-O11	2.067(4)	O8-V2-O10	92.9(2)	Na2-O15	2.602(5)
V2-O12	2.310(4)	O9-V2-O10	158.0(2)	Na2-O4	2.825(5)
		O7-V2-O11	103.7(2)		
		O8-V2-O11	159.0(2)		
		O9-V2-O11	81.4(2)		
		O10-V2-O11	88.1(2)		
		O7-V2-O12	175.6(2)		
		O8-V2-O12	80.3(2)		
		O9-V2-O12	83.6(2)		
		O10-V2-O12	75.5(2)		
		O11-V2-O12	79.6(2)		
S1-O14	1.448(4)	O14-S1-O13	111.5(3)	Na3-O22	2.288(5)
S1-O13	1.453(4)	O14-S1-O12	109.5(3)	Na3-O15	2.347(5)
S1-O12	1.475(4)	O13-S1-O12	112.0(3)	Na3-O13	2.352(5)
S1-O2	1.506(4)	O14-S1-O2	107.5(3)	Na3-O19	2.455(5)
		O13-S1-O2	107.5(3)	Na3-O4	2.525(5)
		O12-S1-O2	108.6(2)	Na3-O7	2.695(5)
S2-O16	1.444(4)	O16-S2-O15	113.7(3)	Na4-O16	2.307(5)
S2-O15	1.445(4)	O16-S2-O5	108.1(3)	Na4-O21	2.392(5)
S2-O5	1.498(4)	O15-S2-O5	108.4(3)	Na4-O21	2.496(5)
S2-O3	1.499(4)	O16-S2-O3	110.8(3)	Na4-O24	2.524(5)
		O15-S2-O3	108.3(2)	Na4-O1	2.746(5)
		O5-S2-O3	107.5(2)	Na4-O6	2.807(5)
				Na4-O20	2.985(6)
				Na4-O3	2.992(5)
S3-O17	1.449(4)	O17-S3-O18	110.7(3)	Na5-O16	2.292(5)
S3-O18	1.453(5)	O17-S3-O19	110.6(3)	Na5-O13	2.321(5)
S3-O19	1.463(4)	O18-S3-O19	111.8(3)	Na5-O17	2.336(5)
S3-O4	1.525(4)	O17-S3-O4	109.3(2)	Na5-O9	2.443(5)
		O18-S3-O4	108.0(2)	Na5-O24	2.547(5)
		O19-S3-O4	106.3(2)	Na5-O8	3.002(5)
S4-O20	1.457(4)	O20-S4-O21	109.8(3)	Na6-O17	2.336(5)
S4-O21	1.461(4)	O20-S4-O6	111.7(3)	Na6-O25	2.372(5)
S4-O6	1.477(4)	O21-S4-O6	109.2(3)	Na6-O8	2.391(5)
S4-O10	1.490(4)	O20-S4-O10	111.1(3)	Na6-O20	2.414(5)
		O21-S4-O10	107.0(3)	Na6-O1	2.446(5)
		O6-S4-O10	107.9(3)	Na6-O23	2.489(5)
S5-O22	1.439(5)	O22-S5-O23	111.5(3)	Na7-O23	2.231(5)
S5-O23	1.449(4)	O22-S5-O24	111.6(3)	Na7-O26	2.253(5)
S5-O24	1.468(4)	O23-S5-O24	112.4(3)	Na7-O2	2.413(4)
S5-O8	1.519(4)	O22-S5-O8	107.7(3)	Na7-O19	2.465(5)
		O23-S5-O8	104.9(2)	Na7-O5	2.512(4)
		O24-S5-O8	108.4(2)	Na7-O6	2.616(5)

Table 3. (Continued.)

Distances/Å		Angles/°		Nonbonded/Å	
S6–O26	1.435(4)	O26–S6–O25	115.5(3)	Na8–O22	2.322(5)
S6–O25	1.447(4)	O26–S6–O11	109.6(2)	Na8–O12	2.474(5)
S6–O11	1.504(4)	O25–S6–O11	109.1(3)	Na8–O19	2.493(5)
S6–O9	1.519(4)	O26–S6–O9	105.6(3)	Na8–O10	2.619(5)
		O25–S6–O9	108.2(2)	Na8–O5	2.693(5)
		O11–S6–O9	108.5(2)	Na8–O21	2.756(6)
				Na8–O15	2.982(6)

Table 4. Selected bond distances in vanadyl VO_6 octahedra and coordinated SO_4 tetrahedra.

Position	Kind	Length	$\text{Na}_8(\text{VO})_2(\text{SO}_4)_6$ (this work)		$\text{Na}_2\text{VO}(\text{SO}_4)_2$ (Ref. 7)	$\text{K}_4(\text{VO})_3(\text{SO}_4)_5$ (Ref. 8)
			V1	V2		
		V–O bond/Å	1.588(5)	1.594(4)	1.595(2)	1.580(2) 1.584(2) 1.588(2)
Equatorially coordinated sulfate	Bridging	V–O bond/Å	2.013(4) 2.014(4) 2.067(4)	2.004(4) 2.019(4) 2.067(4)	2.016(2) 2.017(2) 2.020(2) 2.068(2)	12 bonds ^a within the range 2.023–2.058
		O–S bond/Å	1.498(4) 1.499(4) 1.506(4)	1.490(4) 1.504(4) 1.519(4)	1.471(2) 1.488(2) 1.488(2) 1.506(2)	12 bonds ^a within the range 1.482–1.497
		Unidentate	V–O bond/Å O–S bond/Å	2.042(4) 1.525(4)	1.976(4) 1.519(4)	— 1.546(2) ^b 1.548(2) ^b
Axial trans-coordinated sulfate	Bridging	V–O bond/Å	2.257(4)	2.310(4)	2.150(2)	2.230(2) 2.224(2) 2.216(1)
		O–S bond/Å	1.475(4)	1.477(4)	1.491(2)	1.476(2) 1.472(2) 1.459(2)
Na–O six shortest contacts/Å			Range 2.231–3.002		Range 2.352–2.414	—

^aSulfate with three or four oxygens coordinated to vanadium. ^bUnidentately bound sulfates in $\text{K}_7\text{M}(\text{SO}_4)_7$, $\text{M}=\text{Nb}^{\text{V}}$ and Ta^{V} , respectively.²²

takes place via equatorial V–O bonds (V1–O3–S2–O5–V1 and V1–O5–S2–O3–V1 or V2–O9–S6–O11–V2 and V2–O11–S6–O9–V2, respectively), approximately in the *bc*-plane. The hetero-bridging takes place via one equatorial V–O bond and one axial trans V–O bond: V1–O2–S1–O12–V2 and V2–O10–S4–O6–V1, respectively, and *vice versa*. Seen from the sulfato point of view, in other words, the hetero-bridging S1 sulfate has O12 bound to V2 in trans coordination, and O2 is coordinated equatorially to V1, whereas O13 and O14 are bound non-bridging; the homo-bridging S2 has O3 and O5 bridging to V1 atoms in equatorial coordination and O15, O16 non-bridging; the unidentate S3 is bound in equatorial coordination to V1 via O4 and with O17, O18 and O19 non-bridging; the hetero-bridging S4 has O6 bound to V1 in trans coordination, O10 is

coordinated equatorially to V2 and O20, O21 are bound non-bridging; the unidentate S5 is bound in equatorial coordination to V2 via O8 and with O22, O23 and O24 non-bridging; the homo-bridging S6 has O9 and O11 bridging to V2 atoms in equatorial coordination and with O25, O26 non-bridging.

In this way, a three-dimensional interlocked network of linked VO_6 octahedra and SO_4 tetrahedra is formed accommodating the required sodium ions. The bond distances (~ 2.0 and 1.47 Å) and angles (ideal values 90 and 109.47°) of the VO_6 octahedra and SO_4 tetrahedra take values which are typical for these well known species,^{15,16} as may be seen for example from Table 4, based on data from Refs. 7 and 8. It appears that the axial trans V–O bond lengths found are somewhat longer than seen previously.

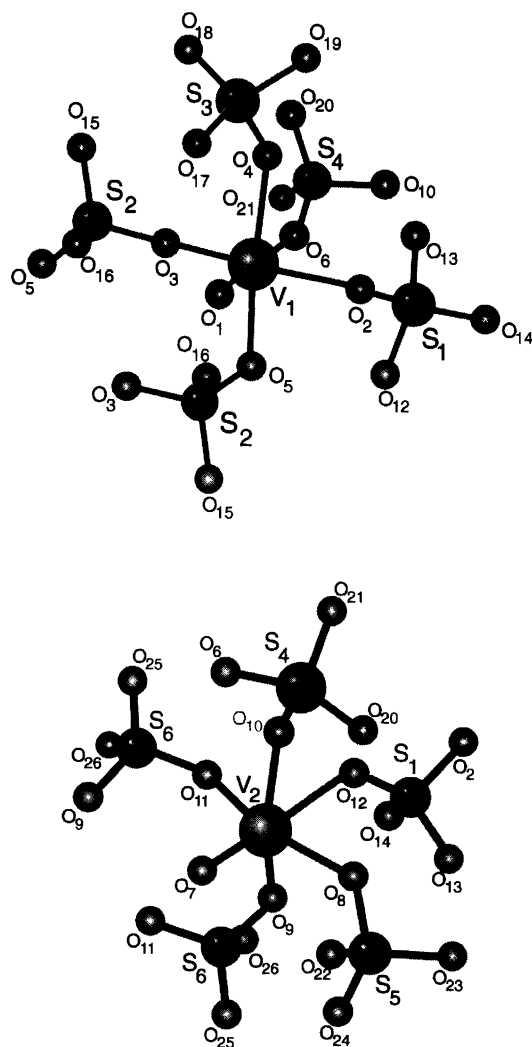


Fig. 2. Details of the coordination polyhedra of vanadium atoms V1 and V2.

Sulfate group geometry. A relationship between the length of any particular bond between sulfur and oxygen (coordinated as well as non-coordinated) and the average O–S–O angle involving that particular S–O bond has been put forward previously.^{4,5,8,10,17} Around the sulfur atoms, nearly tetrahedral angles have been found; however, they are deformed in such a way that O–S–O angles involving an oxygen atom bridging to vanadium are smaller than the ideal tetrahedral angle of 109.47°. This is believed to be due to repulsion from the short-bonded oxygens. The O–S–O angles not involving oxygen atoms bridging to vanadium increased to values above 109.47°. The S–O distances have been found to 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. A plot of the relation is shown in Fig. 3, including results from Refs. 3–10 and 17. An approximately linear relationship is found, and the new points found here fit very well with the previous results (errors in average angles in [10] have been corrected). The relation in Fig. 3 indicates a general relation between bond distances and hybridization of the central atom in tetrahedral groups, as pointed out also for the case of the $[\text{AlBr}_4]^-$.^{18,19}

Vibrational spectra

Spectral expectations. The $\text{V}=\text{O}^{2+}$ ion only has one vibrational degree of freedom, and the mode is to be found near 1000 cm^{-1} .^{15,20} The internal vibrations of a regular SO_4^{2-} ion of T_d point group symmetry span the representation

$$\Gamma_{\text{vib}} = A_1(\nu_1) + E(\nu_2) + 2F_2(\nu_3 + \nu_4)$$

of which all symmetry species are Raman-permitted and F_2 is IR-permitted. The modes labelled ν_1 and ν_3 are bond stretchings, and ν_2 and ν_4 are mostly angle bendings in the SO_4^{2-} tetrahedron, in the usual approximation of

Table 5. Correlation diagram for the 24 SO_4^{2-} internal vibrations^a

24 isolated ions of T_d point group symmetry	24 ions on sites of no symmetry	24 ions in a crystal of C_{2h} factor group symmetry
24 A_1 [ν_1 (str)] [Raman activity: $x^2 + y^2 + z^2$]	216 A	54 A_g [$6\nu_1$ (str) + $12\nu_2$ (bend) + $18\nu_3$ (str) + $18\nu_4$ (bend)] [Raman activity: x^2, y^2, z^2, xy]
24 E [ν_2 (bend)] [Raman activity: $(2z^2 - x^2 - y^2, x^2 - z^2)$]		54 B_g [$6\nu_1$ (str) + $12\nu_2$ (bend) + $18\nu_3$ (str) + $18\nu_4$ (bend)] [Raman activity: xz, yz]
48 F_2 [ν_3 (str) + ν_4 (bend)] [Raman activity: (xz, yz, xy)] [Infrared activity: x, y, z]		54 A_u [$6\nu_1$ (str) + $12\nu_2$ (bend) + $18\nu_3$ (str) + $18\nu_4$ (bend)] [Infrared activity: z]
		54 B_u [$6\nu_1$ (str) + $12\nu_2$ (bend) + $18\nu_3$ (str) + $18\nu_4$ (bend)] [Infrared activity: x, y]

^aCode: ν_1 (str), ν_2 (bend), ν_3 (str), and ν_4 (bend) are the A_1 , E and $2F_2$ stretching and bending mode components of the SO_4^{2-} group under T_d symmetry.

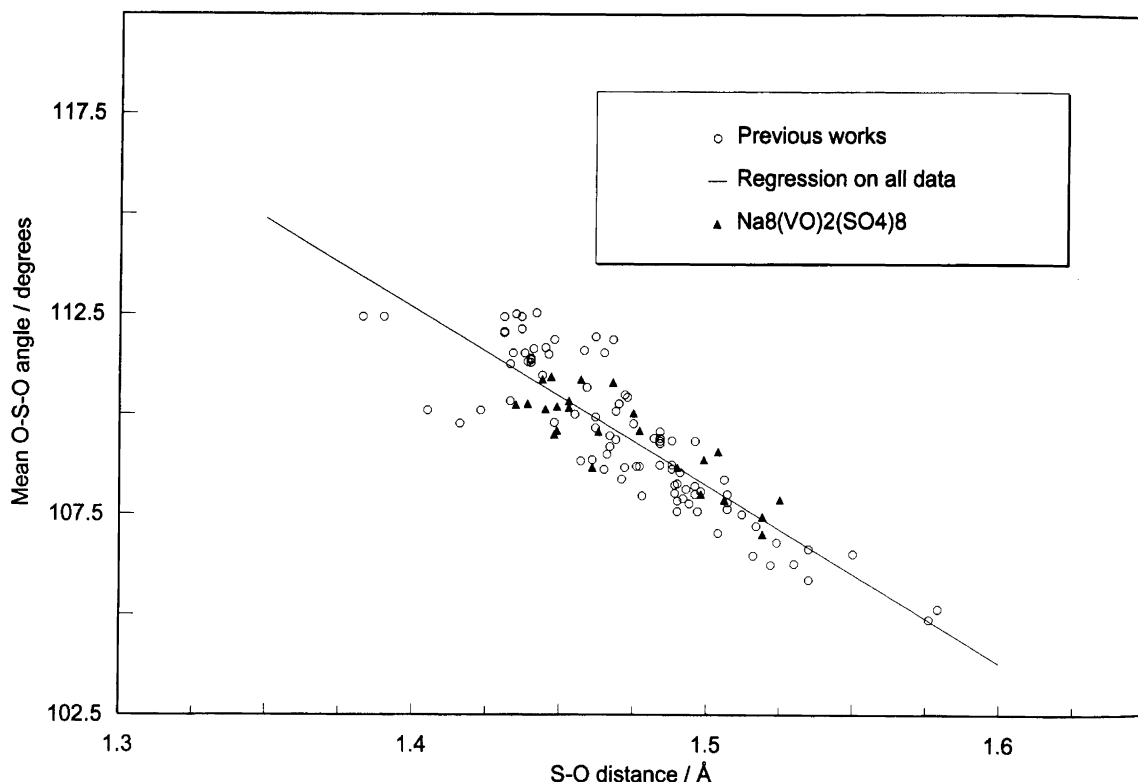


Fig. 3. Plot of S–O distances for a particular bond versus the average of the three angles involving that bond and the other S–O bonds of the sulfate tetrahedron (24 solid triangles). Also shown are points (open circles) from $\text{KV}(\text{SO}_4)_2$,³ $\text{NaV}(\text{SO}_4)_2$,⁴ $\text{Na}_3\text{V}(\text{SO}_4)_3$,⁵ $\text{CsV}(\text{SO}_4)_2$,⁶ $\text{Na}_2\text{VO}(\text{SO}_4)_2$,⁷ $\text{K}_4(\text{VO})_3(\text{SO}_4)_5$,⁸ $\beta\text{-VOSO}_4$,⁹ $\text{K}_6(\text{VO})_4(\text{SO}_4)_8$,¹⁰ and $\text{Cs}_4(\text{VO})_2(\mu\text{-O})(\text{SO}_4)_4$.¹⁷ The regression line $y=ax+b$ where y =mean O–S–O angle/ $^\circ$, x =S–O distance/ \AA , $a=-44.497$ and $b=174.97$ included all points. The r^2 correlation coefficient was 0.759 and the standard error on the estimated value of y was 0.85.

weak couplings. The wavenumbers of the fundamental transitions are well known:²⁰ $\nu_1(A_1) \approx 983 \text{ cm}^{-1}$, $\nu_2(E) \approx 450 \text{ cm}^{-1}$, $\nu_3(F_2) \approx 1105 \text{ cm}^{-1}$ and $\nu_4(F_2) \approx 611 \text{ cm}^{-1}$, according to Raman spectra of aqueous sulfate solutions.

The $8\text{V}=\text{O}^{2+}$ ions in the primitive unit cell of $\text{Na}_8(\text{VO})_2(\text{SO}_4)_6$ perform vibrations which will be distributed on the symmetry species of the cell. Under C_{2h}

factor group symmetry they span the representation

$$\Gamma_{\text{vib}}(\text{V}=\text{O}^{2+}) = 2A_g + 2B_g + 2A_u + 2B_u$$

of which the gerade species are Raman-permitted and the ungerade ones are IR-permitted. Since the VO^{2+} ions sit on sites with no symmetry, the normal modes will be evenly distributed all over the symmetry species.

Table 6. Factor group analysis^a for the $\text{Na}_8(\text{VO})_2(\text{SO}_4)_6$ salt crystallizing in space group C_{2h}^5 ($P2_1/c$, No. 14, $Z=4$).

C_{2h} symmetry	T_A	T	Optical active normal modes				Activity in
			$R(\text{SO}_4^{2-})$	$R(\text{VO}^{2+})$	$N_i(\text{SO}_4^{2-})$	$N(\text{VO}^{2+})$	
A_g	—	48	18	4	54	2	Raman: x^2, y^2, z^2, xy
B_g	—	48	18	4	54	2	Raman: xz, yz
A_u	1	47	18	4	54	2	Infrared: z
B_u	2	46	18	4	54	2	Infrared: x, y
Total	3	189	72	16	216	8	Totally: 504 degrees of freedom

^aThe primitive unit cell contains four formula units of 42 atoms each, i.e. a total of 168 atoms. The T and R classification is based on the same cell considered as containing the following 64 ions: 32 Na^+ ions, 8 VO^{2+} ions and 24 SO_4^{2-} ions, all on Wyckoff site e with no site symmetry. T_A =optically inactive acoustic modes, T =optic branch translatory modes of the 64 ions, ($T+T_A=3$ times 64), $R(\text{SO}_4^{2-})$ and $R(\text{VO}^{2+})$ =rotatory modes of the 24 SO_4^{2-} and 8 VO^{2+} ions, respectively, and $N_i(\text{SO}_4^{2-})$ and $N_i(\text{VO}^{2+})$ =internal vibrational modes of the 24 SO_4^{2-} ions and the 8 VO^{2+} ions, respectively.

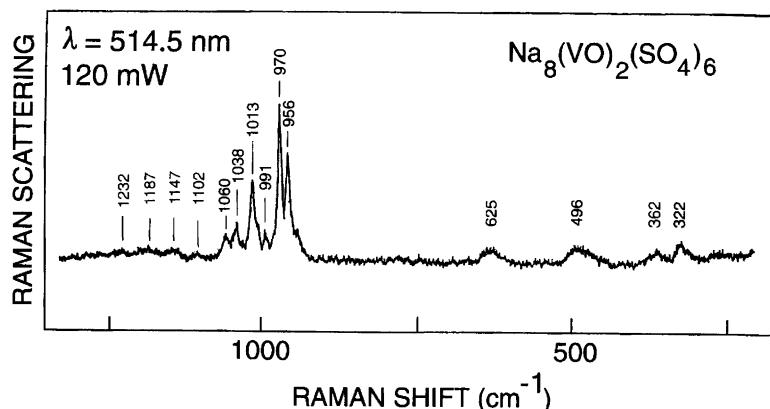


Fig. 4. Raman spectrum of a mixture of crystals of $\text{Na}_8(\text{VO})_2(\text{SO}_4)_6$. A contamination with other compounds, such as e.g. $\text{NaV}(\text{SO}_4)_2$, is possible but not likely.

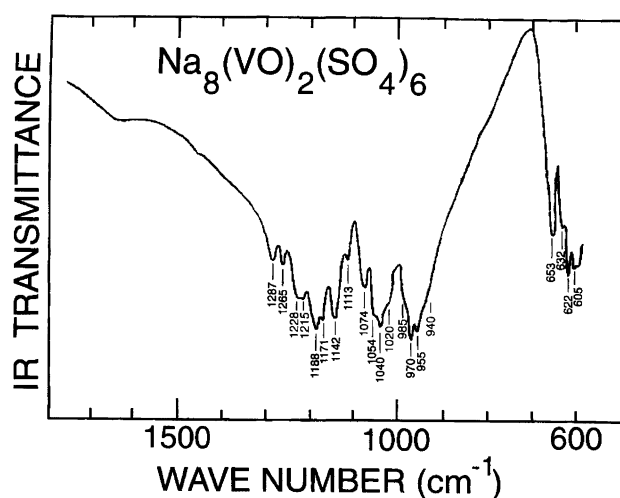


Fig. 5. Infrared spectrum of $\text{Na}_8(\text{VO})_2(\text{SO}_4)_6$ powder in a KBr disk at room temperature. A contamination with, e.g., $\text{NaV}(\text{SO}_4)_2$ is possible but not likely.

In a similar way the 24 SO_4^{2-} ions in the primitive unit cell each contribute nine internal degrees of vibrational freedom (inherent in the T_d sulfate modes ν_1 – ν_4), which again are distributed on the symmetry species of the cell, spanning the internal vibrations under the representation

$$\Gamma_{\text{vib}}(\text{SO}_4^{2-}) = 54 A_g + 54 B_g + 54 A_u + 54 B_u$$

distributed evenly over the symmetry types of the C_{2h}^5 factor group. Some of these modes are stretchings and some are mixtures of stretchings and bendings. The $\text{V}=\text{O}^{2+}$ modes occurring in the sulfate stretching range probably also couple to ν_1 and ν_3 sulfate modes. The correlation of the sulfate modes from the cubic T_d symmetry (free ion) to those of the ions in the bound state in the crystal is given in Table 5.

With the crystal structure known we can work out the complete selection rules based on the factor group analysis²¹ in the usual wavevector $k \cong 0$ approximation (Table 6). In total, for the crystal 252 Raman fundamentals ($126 A_g + 126 B_g$) and 249 IR fundamentals

Table 7. Infrared and Raman bands (in cm^{-1}) and assignments for $\text{Na}_8(\text{VO})_2(\text{SO}_4)_6$.^a

IR powder in KBr disc	Raman powder of quite big crystals ($\lambda = 514.5$ and 488 nm)	Tentative assignments
1287 m		} $\nu_3(\text{str}, \text{SO}_4^{2-})$
1265 w		
1228 m	1232 vw	
1215 m		
1188 s	1183 vw	
1171 w		
1142 m	1147 vw	
1113 w	1102 vw	
1074 m		
1040 m	1060 w	
	1038 m	
	1013 s	} $\nu(\text{V}=\text{O}^{2+})$
	991 w	
970 s	970 s	
955 w	956 s	} $\nu_4(\text{bend}, \text{SO}_4^{2-})$
940 vw		
653 s		
625 m	622 w, br	
605 w		} $\nu_2(\text{bend}, \text{SO}_4^{2-})$
	496 w, br	
	362 w	
	322 w	} $\nu(\text{str}, \text{V-O-S})$

^aIntensity codes: w = weak; m = medium; s = strong; v = very; br = broad. Calibration: laser plasma lines (Raman) and polystyrene sheet (IR).

($125 A_u + 124 B_u$) should be spectroscopically observable by use of suitably polarized light.

Interpretation of observed spectra. The observed Raman and IR spectra are depicted in Figs. 4 and 5, and the band positions and assignments are specified in Table 7. As can be seen, many bands are found in the spectra but much fewer than predicted. We observe roughly eight bands in the Raman spectrum and 12–16 bands in the

IR spectrum which can be tentatively interpreted as S–O stretchings.⁸ The characteristic vanadyl stretching commonly found at $\sim 975 \text{ cm}^{-1}$ should be noted.¹⁵ Unambiguous assignment of the bands are difficult because the requisite number is not observed. Extensive degeneracy of most of the normal modes must prevail.

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