

Crystal Structure of Sodium Pentafluorooxovanadate(V), $\text{Na}_2[\text{VF}_5\text{O}]$, and Potassium *catena*- μ -Fluoro-difluorodioxovanadate(V), $\text{K}_{2n}[(\text{VF}_3\text{O}_2)_n]$, Two Decomposition Products in the System $\text{V}_2\text{O}_5/(\text{MF},\text{HF})/\text{H}_2\text{O}_2/\text{H}_2\text{O}$

Rolf Stomberg

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

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The crystal structures of two fluorooxovanadates(V), $\text{Na}_2[\text{VF}_5\text{O}]$ (1) and $\text{K}_{2n}[(\text{VF}_3\text{O}_2)_n]$ (2), appearing in the system $\text{V}_2\text{O}_5/(\text{MF},\text{HF})/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ($\text{M} = \text{Na}, \text{K}$), have been determined and refined by the least-squares method from single-crystal X-ray diffractometer data collected at room temperature. $\text{Na}_2[\text{VF}_5\text{O}]$ crystallized in the cubic space group $Fm\bar{3}m$ (No. 225) with $a = 8.454(3)$ Å and $Z = 4$, and contained disordered vanadium atoms ($R_F = 0.052$ for 87 observed independent reflexions). $\text{K}_{2n}[(\text{VF}_3\text{O}_2)_n]$ crystallized in the orthorhombic space group $Pnma$ (No. 62) with $a = 7.383(1)$, $b = 5.646(1)$, $c = 11.426(2)$ Å and $Z = 4$ ($R_F = 0.023$ for 1269 observed independent reflexions). Vanadium was six-coordinated in the octahedral mode in both compounds. The light red crystals of $\text{K}_{2n}[(\text{VF}_3\text{O}_2)_n]$, containing infinite chains of octahedra, linked by *cis* bridging fluorine atoms, were structurally identical with the yellow ones of $\text{K}_2[\text{VF}_3\text{O}_2]$, whose structure has been previously determined. Bond distances in $\text{Na}_2[\text{VF}_5\text{O}]$: $\text{V}=\text{O}_{\text{apical}} 1.607(6)$, $\text{V}-\text{F}_{\text{equatorial}} 1.892(3)$ and $\text{V}-\text{F}_{\text{apical}} 2.140(6)$ Å. Bond distances in $\text{K}_{2n}[(\text{VF}_3\text{O}_2)_n]$: $\text{V}=\text{O} 1.641(1)$ and $\text{V}-\text{F} 1.872(1)$, $1.922(1)$ and $2.189(1)$ Å.

In transition metal catalyzed oxidation reactions in which oxygen or hydrogen peroxide are used as oxidizing agents, peroxometallates are often intermediates.¹⁻³ The knowledge of the formation and the structures of peroxometallates as well as their decomposition products greatly facilitates the interpretation of reaction paths.

Much interest has lately been focussed on peroxovanadates. Among the purely inorganic peroxovanadates, especially those formed in the system $\text{MVO}_3/(\text{MF},\text{HF})-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ ($\text{M} = \text{NH}_4, \text{K}$), have been studied recently. Schwendt *et al.*⁴⁻⁷ have performed extensive synthetic and analytical work on this system (a summary of fluoro-peroxovanadates formed in acidic medium is given in Table 1 in Ref. 4), and at this Depart-

ment, the crystal structures of a number of fluoro-peroxovanadates, such as $\text{K}_2[\text{VFO}(\text{O}_2)_2]$,⁸ as well as $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$,⁹ $(\text{NH}_4)_2[\text{VFO}(\text{O}_2)_2]$,¹⁰ and also $(\text{NH}_4)_3[\text{VF}_2\text{O}(\text{O}_2)_2]$ ¹¹ have been elucidated. The last one, synthesized for the first time by the present author,¹¹ is unique. It is the first example of a mononuclear seven-coordinated oxoperoxovanadate with only monodentate ligands, disregarding the peroxo group. The corresponding potassium analogue has not been observed hitherto. The possibility of hydrogen bonding in $(\text{NH}_4)_3[\text{VF}_2\text{O}(\text{O}_2)_2]$ is probably one of the reasons for its existence. A further dissimilarity between potassium and ammonium fluoro-oxoperoxovanadates is shown by $\text{K}_2[\text{VFO}(\text{O}_2)_2]$ and $(\text{NH}_4)_2[\text{VFO}(\text{O}_2)_2]$. Although they have similar

formulae, they are not isostructural. They crystallize in different space groups and vanadium has different coordination geometry, being six-coordinated in $K_2[VFO(O_2)_2]$ and seven-coordinated in $(NH_4)_2[VFO(O_2)_2]$.^{8,10} Vanadium differs from its heavier congener. In the system $Nb_2O_5/(MF, HF)/H_2O_2/H_2O$, the pentafluoromonoperoxoniobate(V), $[NbF_5(O_2)]^{2-}$, dominates, as is evident from the synthetic and structural work performed by the author,¹²⁻¹⁶ while the corresponding peroxovanadate seems not to exist. In fact, only recently, a fluoromonoperoxovanadate, $(NH_4)[VF_4O(O_2)]$, was recognized in the system $NH_4VO_3/NH_4F/HF/H_2O_2/H_2O$.¹⁷

The thermal decomposition of fluoroperoxovanadates has been studied by Schwendt and Joniaková,^{6,18} and by Jere *et al.*¹⁹ During the decomposition of a fluoroperoxovanadate, oxygen is lost and coordination saturation is achieved by chain formation, exemplified by $K_2[VF_3O_2]$,²⁰ or by reactions with molecules in the surrounding medium exemplified by $K_3[VO(O_2)_2(CO_3)]$, the structure of which has recently been solved.²¹

The isothermal decomposition of substances formed in the system $V_2O_5/(MF, HF)/H_2O_2/H_2O$, while in contact with the mother liquor, leads to products other than those obtained during the

decomposition in the solid state. The possibility of obtaining substances with a lesser amount of peroxide is obvious. In the present study, the products ultimately formed in the system $V_2O_5/(MF, HF)/H_2O_2/H_2O$ ($M = Na, K$), with initial compositions leading to $M_3[HV_2F_4O_2(O_2)_3] \cdot 2H_2O$, have been characterized and their structures determined. The sodium compound appeared as orange, octahedral crystals while the potassium compound crystallized as light red prisms.

Experimental

Preparation. (1.) 0.36 g V_2O_5 (2 mmol) was dissolved in 1.6 ml 30% H_2O_2 and 10 ml H_2O , and 0.50 g NaF (12 mmol) and 6 ml 1 M HF were added. The resulting solution was left to evaporate at 5 °C. After about a week, orange crystals of the sodium compound were formed.

(2.) 0.23 g V_2O_5 (1.3 mmol) was dissolved in 6 ml 30% H_2O_2 and 10 ml H_2O , and 0.48 g KF (9 mmol) and 5 ml 1 M HF were added. The resulting solution was evaporated isothermally at 5 °C. Initially $K_3[HV_2F_4O_2(O_2)_3] \cdot 2H_2O$ was formed as bundles of rod-shaped crystals followed by the

Table 1. Crystal data and conditions for data collection

	$Na_2[VF_5O]$	$K_{2n}[(VF_3O_2)_n]$
F.W.	207.91	218.13 · n
Crystal system	Cubic	Orthorhombic
Space group	<i>Fm3m</i>	<i>Pnma</i>
a (Å)	8.454(3)	7.383(1)
b (Å)		5.646(1)
c (Å)		11.426(2)
V (Å ³)	604.1(4)	476.3(1)
Z	4	4
D _x (g cm ⁻³)	2.286	3.042
μ(MoKα) (mm ⁻¹)	1.91	3.88
Crystal size (mm)	0.14 × 0.18 × 0.18	0.21 × 0.21 × 0.26
<i>Data collection</i>		
Collection method	ω-2θ	ω-2θ
Scan speed (° min ⁻¹)	1.5-19.5	2.6-19.5
2θ range (°)	3.5-80	3.5-80
Number of independent reflexions collected	128	1762
Number of observed independent reflexions (<i>I</i> > 3 σ(<i>I</i>))	87	1269
<i>R</i> _F (= Σ <i>F</i> _o - <i>F</i> _c /Σ <i>F</i> _o)	0.052	0.023
Diff. Four. max. (e Å ⁻³)	0.62	0.42

Table 2. Atomic fractional coordinates and equivalent isotropic thermal parameters, B_{eq} , for Na₂[VF₅O]; space

$$\text{group } Fm\bar{3}m; B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_j \mathbf{a}_i \cdot \mathbf{a}_j$$

Atom	Site	Occupancy	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
V	24e	$\frac{1}{6}$	0.0315(6)	0	0	1.96(8)
Na1	4b	1	$\frac{1}{2}$	0	0	1.98(2)
Na2	8c	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2.80(4)
F,O	24e	1	0.2216(3)	0	0	2.65(4)

appearance of K₂[VFO(O₂)₂] and ultimately bright red prismatic crystals of the potassium compound.

X-Ray methods. Rotation and Weissenberg photographs were taken of (1) (CuK radiation) and powder photographs of (2) (Guinier-Hägg camera, CuK α radiation, Pb(NO₃)₂ as internal standard at 21 °C).

Intensity data were recorded at room temperature with a Syntex P2₁ automatic four-circle single crystal X-ray diffractometer (graphite-monochromated MoK α radiation) for both compounds. Crystal data and conditions for the data collection are given in Table 1. Integrated intensity values were obtained by the Lehmann-Larsen profile analysis method.²² Periodical measurement of two test reflexions for (1) and three for (2) showed no loss in intensity during the collection of the data. The intensities were corrected for Lorentz, polarization and absorption effects but not for extinction. The unit cell dimensions of (1) were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions and of (2) from a least-squares fit of 46 indexed lines in the powder photograph.

Structure determination

(1.) The structure was solved by Patterson and electron density calculations. Initially, the four vanadium atoms in the unit cell were considered to occupy site 4a of space group $Fm\bar{3}m$ and the sodium ions, Na1 and Na2, the four- and eight-fold sites 4b and 8c, respectively. Both vanadium and Na2 showed high B values, 4.0 and 5.6 Å², respectively. In the electron density map, Na2 appeared with a peak height of only half the magnitude of that observed for Na1. The abnormally high B value of vanadium was taken to be due to

disorder while the observation made for Na2 indicated half occupancy of site 8c. A model with vanadium occupying site 24e ($x, 0, 0$ with occupancy = $\frac{1}{6}$) and Na2 8c (occupancy = $\frac{1}{2}$) was tried. Refinement led to a vanadium position 0.27 Å from the origin. Starting from a position either closer to or more remote from the origin gave the same result. Full matrix least-squares refinement of positional and anisotropic thermal parameters led to a final R value of 0.052 ($R = \sum |F_o| - |F_c| / \sum |F_o|$). Other possible space groups were tried, but no further improvement was achieved. The weighting scheme $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$ with $a = 10$, $c = 0.01$ and $d = 0.001$ was used.²³ Since the fluorine and oxygen atoms could not be distinguished, the weighted mean of the scattering factors for these atoms, $\frac{5}{6}f_F + \frac{1}{6}f_O$, was used.

(2.) The cell dimensions of (2) were the same as those of K₂[VF₃O₂] within 3 σ , strongly indicating identity despite the difference in colour. The observed structure factors differed, however, in some cases considerably (by more than 30% in a few cases). This indicated slight differences, e.g., the presence of small amounts of peroxide in (2) (the crystals of (2) consumed slight amounts of permanganate), replacing fluorine or oxygen atoms without noticeable change in the cell dimensions. This type of replaceability has been observed for other peroxometallates.²⁴⁻²⁷ As a starting point, the parameters obtained for K₂[VF₃O₂] were used.²⁰ It soon became evident that the structure of (2) could be refined without the introduction of further atoms (the z coordinate of vanadium is, however, erroneous in Table 2 in Ref. 20; it should be 0.06940). The observed difference in colour between crystals of (2) and K₂[VF₃O₂] was attributed to inclusion of hydrogen peroxide. This may also have influenced the mosaic structure, thus explaining the large differ-

Table 3. Atomic fractional coordinates and equivalent isotropic thermal parameters, B_{eq} , for $K_{2n}[(VF_3O_2)_n]$; space group $Pnma$. $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_i \mathbf{a}_i \cdot \mathbf{a}_j$

Atom	Site	x	y	z	$B_{eq}/\text{\AA}^2$
V	4c	0.19960(4)	$\frac{1}{4}$	0.06930(2)	1.035(5)
K1	4c	0.19110(6)	$\frac{1}{4}$	0.40699(4)	1.694(7)
K2	4c	0.47788(6)	$\frac{1}{4}$	0.71734(4)	1.527(7)
O1	8d	0.3223(1)	0.0229(2)	0.1111(1)	1.71(2)
F1	4a	0	0	0	1.67(2)
F2	4c	0.0363(2)	$\frac{1}{4}$	0.1946(1)	1.790(2)
F3	4c	0.2731(2)	$\frac{1}{4}$	0.9079(1)	1.52(2)

ence between observed structure factors among the strong reflections (see above). According to Ryan *et al.*²⁰, large extinction effects were noticed and corrected for; this was not necessary for (2). Full matrix least-squares refinement of positional and anisotropic thermal parameters reduced the R value to 0.023. The parameters used in the above-mentioned weighting scheme were $a = 30$, $c = 0.015$ and $d = 0.0002$.

Absorption correction was applied for both (1) and (2,) using an empirical method for correcting diffractometer data for absorption effects due to Walker and Stuart.²⁸ The atomic scattering factors for K, Na, v, F and O were taken from Ref. 29. Calculations were carried out on an IBM 3033 computer, using the crystallographic programmes described in Refs. 30 and 31. Lists of structure factors and anisotropic thermal parameters for (1) and (2) as well as a table of observed, indexed lines in the powder photograph of (2) are available from the author on request.

Results and discussion

Atomic positional parameters and equivalent isotropic thermal parameters, B_{eq} , are given in Table 2 for (1) and in Table 3 for (2,) bond distances and angles in Table 4 for (1) and in Table 5 for (2.) Fig. 1 shows a stereoscopic view of the unit cell content in (1).

The crystals of $Na_2[VF_5O]$ ((1)) consist of sodium ions and isolated, close packed, octahedral pentafluorooxovanadate(V) ions, while those of $K_{2n}[(VF_3O_2)_n]$ ((2)) are composed of potassium ions and *catena*- μ -fluoro-difluorodioxovanadate(V) ions, forming zigzag chains of distorted VF_4O_2 octahedra (see Fig. 2 in Ref. 20). Despite

differences in colour between crystals of (2) and those described by Ryan *et al.*, probably due to the presence of peroxide in (2,) this investigation has shown that the structures are identical within the limits of experimental error and an elaborate description of the structure is given in Ref. 20.

The anions in $Na_2[VF_5O]$ seem to be disorderedly orientated. Although the corners of the regular octahedral anion are orientated along the coordinate axes, the oxygen atom is randomly

Table 4. Interatomic distances (\AA) and bond angles ($^\circ$) in $Na_2[VF_5O]$

V—O'	1.607(6)	O—V—F	98.1(2)
V—F ^a	1.892(3)	F—V—F	88.9(1)
V—F ^b	2.140(6)	F—V—F	81.9(2)
Na1...F,O'	2.353(3)	Symmetry codes:	
Na2...F,O	2.998(1)	i	(x00)
F,O...F,O	2.650(4)	ii	(0x0)
		iii	(x00)

Table 5. Interatomic distances (\AA) and angles ($^\circ$) within the coordination sphere of vanadium in the $[(VF_3O_2)_n]^{2m-}$ anion

V—F1	2.189(1)	O—V—O'	102.76(8)
V—F2	1.872(1)	O—V—F1	88.46(4)
V—F3	1.922(1)	O—V—F1'	168.77(4)
V—O	1.641(1)	O—V—F2	97.62(5)
F1...F1'	2.823(1)	O—V—F3	97.11(5)
F1...F2	2.648(1)	F1—V—F1'	80.31(1)
F1...F3	2.676(1)	F1—V—F2	80.98(3)
F1...O	2.700(1)	F1—V—F3	80.96(3)
F2...O	2.648(2)	F2—V—F3	156.30(6)
F3...O	2.677(2)	V—F1—V'	180
O...O	2.564(2)		

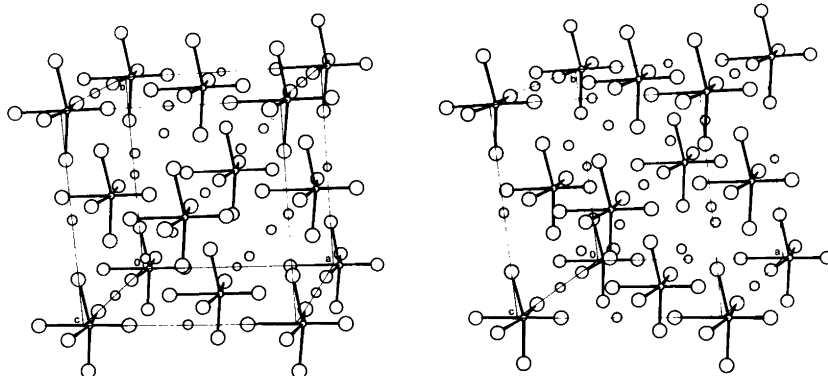


Fig. 1. Stereoscopic view of the unit cell of $\text{Na}_2[\text{VF}_5\text{O}]$. The site 8c is only half occupied. Since vanadium is disordered, only one of the six possible vanadium positions is shown.

distributed over the corners, i.e., the anion may have one or the other of six equally probable orientations. Due to the similar sizes of the oxygen and fluorine atoms, random orientation is far from uncommon among fluorooxometallates.

The present investigation has shown that the ultimate products formed during the isothermal evaporation of the solvent in the system $\text{V}_2\text{O}_5/(\text{MF}, \text{HF})/\text{H}_2\text{O}/\text{H}_2\text{O}$ depend on the cation, despite similar initial molar concentrations. Moreover, $\text{K}_3[\text{HV}_2\text{F}_4\text{O}_2(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ and, especially, $\text{K}_2[\text{VFO}(\text{O}_2)_2]$ in the potassium system, are easily formed,^{4,8} while the corresponding sodium compounds do not seem to be established.

In both (1) and (2) the *trans* effect is obvious, i.e., the V–F bond *trans* to a V=O bond is significantly longer, being 2.140(6) Å in $[\text{VF}_5\text{O}]^{2-}$ and 2.189(1) Å in $[(\text{VF}_3\text{O}_2)_n]^{2n-}$, than the other V–F bonds. The ultimate extreme due to the *trans* effect would be the total loss of a ligand *trans* to V=O. This was observed in $\text{K}_2[\text{VFO}(\text{O}_2)_2]$.⁸ The other V–F bond distances, 1.892(3) Å in $[\text{VF}_5\text{O}]^{2-}$ and 1.872(1) and 1.922(1) Å in $[(\text{VF}_3\text{O}_2)_n]^{2n-}$, have normal single bond values.

Despite similar stoichiometry, $\text{Na}_2[\text{VF}_5\text{O}]$ is not isomorphous with $\text{Na}_2[\text{NbF}_5\text{O}]$.³² The anions, being disorderedly orientated in both compounds, but in different ways, are, however, similar. They both have octahedral geometry, slightly distorted in $[\text{NbF}_5\text{O}]^{2-}$, and the metal atoms are displaced from their respective equatorial planes towards the double bonded oxygen atom, by 0.27 Å in the $\text{Na}_2[\text{VF}_5\text{O}]$ and 0.23 Å in $\text{Na}_2[\text{NbF}_5\text{O}]$.

Monomeric fluorooxovanadate(V) anions like $[\text{VF}_5\text{O}]^{2-}$ are uncommon, most being polynuclear as in the chain structures of $[(\text{VF}_3\text{O}_2)_n]^{2n-}$, $[(\text{VF}_2\text{O})_n]^{n-}$,^{33,34} and $[(\text{VF}_2\text{O}_2)_n]^{n-}$.³⁵ Vanadium(IV) shows, however, some examples of monomeric fluorooxovanadate ions like $[(\text{VF}_4\text{O})_n]^{n-}$,^{36–38} and $[\text{VF}_5\text{O}]^{3-}$.³⁹ In $\text{K}_2\text{Na}[\text{VF}_5\text{O}]$, the anions are disorderedly orientated, too, and an average V–(F,O) bond distance of 1.875 Å was observed.³⁹ In view of the results obtained in the present investigation, it seems possible to distinguish the V=O and V–F bond lengths also in the last named compound.

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References

- Sheldon, R. A. and Koshi, J. K. In: *Metal-catalyzed oxidation of organic compounds*. Academic Press, New York 1981, p. 48.
- Lyons, J. E. In: Ugo, R. ed., *Aspects of homogeneous catalysis*. Reidel, D., Dordrecht 1977, p. 1.
- Patai, S. *The Chemistry of peroxides*. Wiley, New York 1983.
- Schwendt, P., Joniaková, D. and Ezr, V. *Chem. Zvesti* 39 (1985) 353.
- Schwendt, P. and Joniaková, D. *Polyhedron* 3 (1984) 287.
- Schwendt, P. and Joniaková, D. *Thermochim. Acta* 68 (1983) 297.
- Joniaková, D. and Schwendt, P. *Acta Fac. Rerum Natur. Univ. Comenianae (Chimia)* 32 (1984) 93.

8. Stomberg, R. *Acta Chem. Scand.* A38 (1984) 223.
9. Stomberg, R. and Olson, S. *Acta Chem. Scand.* A38 (1984) 821.
10. Stomberg, R. and Olson, S. *Acta Chem. Scand.* A38 (1984) 801.
11. Stomberg, R. *Acta Chem. Scand.* A38 (1984) 541.
12. Stomberg, R. *Acta Chem. Scand.* A34 (1980) 193.
13. Stomberg, R. *Acta Chem. Scand.* A35 (1981) 389.
14. Stomberg, R. *Acta Chem. Scand.* A35 (1981) 489.
15. Stomberg, R. *Acta Chem. Scand.* A36 (1982) 101.
16. Stomberg, R. *Acta Chem. Scand.* A37 (1983) 523.
17. Schwendt, P. and Joniaková, D. *Proc. Conf. Coord., 10th*, Bratislava (1985) 347.
18. Schwendt, P. and Joniaková, D. *Proc. Conf. Coord., 8th*, (1980) 369.
19. Jere, G. V., Gupta, M. K., Surendra, L. and Kausshik, S. M. *Thermochim. Acta* 58 (1982) 67.
20. Ryan, R. R., Mastin, S. H. and Reifeld, M. J. *Acta Crystallogr.* B27 (1971) 1270.
21. Stomberg, R. *Acta Chem. Scand.* A39 (1985) 725.
22. Lehmann, M. S. and Larsen, F. K. *Acta Crystallogr.* A30 (1974) 580.
23. Cruickshank, D. W. J. *Crystallographic Computing*, Munksgaard, Copenhagen 1970, p. 195.
24. Larking, I. and Stomberg, R. *Acta Chem. Scand.* 26 (1972) 3708.
25. Persdotter, I., Trysberg, L. and Stomberg, R. *Acta Chem. Scand.*, *In press*.
26. Persdotter, I., Trysberg, L. and Stomberg, R. *Acta Chem. Scand.*, *In press*.
27. Stomberg, R. *Acta Chem. Scand.*, *In press*.
28. Walker, N. and Stuart, D. *Acta Crystallogr.* A39 (1983) 158.
29. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV, p. 72.
30. Lindgren, O. *An integrated set of crystallographic programs*. In: *On the oxygen coordination of cerium in some sulfates and chromates*. Dissertation, Chalmers University of Technology and University of Göteborg, Göteborg 1977.
31. Andersen, L. *An integrated set of crystallographic programs*. In: *Structure determination of some symmetrical oxoanions of sulfur (IV), selenium (IV) and tellurium (IV) and implementation of a general set of programs for crystallographic computing*. Dissertation, Chalmers University of Technology and University of Göteborg, Göteborg 1985.
32. Stomberg, R. *Acta Chem. Scand.* A38 (1984) 603.
33. Bushnell, G. W. and Moss, K. C. *Can. J. Chem.* 50 (1972) 3700.
34. Rieskamp, H. and Mattes, R. *Z. Anorg. Chem.* 401 (1973) 158.
35. Mattes, R. and Rieskamp, H. *Z. Anorg. Allg. Chem.* 399 (1973) 205.
36. Rieskamp, H. and Mattes, R. *Z. Naturforsch.* 31b (1976) 541.
37. Mattes, R. and Foerster, H. *J. Solid State Chem.* 45 (1982) 154.
38. Schabert, M. Pausewang, G. and Massa, W. *Z. Anorg. Allg. Chem.* 506 (1983) 169.
39. Pausewang, G. and Rüdorff, W. *Z. Anorg. Chem.* 364 (1969) 69.

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