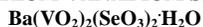


### HYDROTHERMAL SYNTHESIS AND SINGLE-CRYSTAL STRUCTURE OF BARIUM VANADIUM SELENITE HYDRATE



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Brown needle-like crystals of the compound  $\text{Ba}(\text{VOSeOH})$ , prepared by hydrothermal synthesis at  $180^\circ$  for five days, were characterized by single crystal X-ray diffraction. The structure is monoclinic  $P2c$  with  $a = 10.803(2)$ ,  $b = 5.1126(8)$ ,  $c = 17.905(3)$  Å  $\beta = 92.048(2)^\circ$   $V = 988.2(5)$  Å<sup>3</sup>  $Z = 4$ ,  $\rho = 3.865$  gcm<sup>-3</sup>  $M = 575.14$ ,  $R = 0.038$ ,  $R = 0.0389$  for 3681 observed, independent reflections with  $I > 2\sigma(I)$ , measured at 150 K. The structure contains a complex three-dimensional network of VO VO SeO and BaO polyhedra, linked into chains along [101], with coordinated water molecules in the spaces between chains. The chains contain pairs of  $\text{V}^+$  octahedra sharing an edge ( $\text{V}^0$  dimers), and pairs of  $\text{V}^{5+}$  square pyramids also sharing an edge (V dimers), with the dimers connected to each other by barium-centered, mono-capped square antiprisms and SeO trigonal pyramids. The chains are linked to each other via -V-O-Se-, -V-O-Ba- and -Ba-O-Se- bonds with Se coordinated to oxygen at distances of 1.669(4) to 1.748(4) Å which is typical for Se(IV) with a lone pair of electrons occupying the fourth coordination position in the pseudotetrahedral SeO-group. The structural features and interchain arrangement of the title compound are similar to the related, interlayer compounds VOSeOH (1) and Ba(VOSeOHSeO) (2) described previously.

#### References

1. G. Huan, J.W. Johnson, A.J. Jacobson and D.P. Goshorn, Chem. Mater. 3, 539-41 (1991).
2. W.T.A. Harrison, J.T. Vaughey, A.J. Jacobson, D.P. Goshorn and J.W. Johnson, J. Solid State Chemistry, 116, 77-86 (1995).

**Keywords:** BARIUM-VANADIUM, SELENITE, CRYSTAL STRUCTURE

### SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NITROGEN CONTAINING HIGH ENERGY DENSITY MATERIALS

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Polynitrogen compounds are of great interest as High Energy Density Materials (HEDM). Single crystal X-ray crystallography plays a crucial role in the characterization of these materials and their precursors. In this paper, we report the crystal structures of the novel  $\text{N}_5^+$  cation in  $\text{N}_5^+ \text{Sb}_2\text{F}_{11}^-$ , which is the first stable polynitrogen species to be discovered in a century since the discovery of the azide ion. The other HEDM materials synthesized and characterized are  $\text{N}_2\text{F}^+ \text{M}_x\text{F}_{2x+1}^-$  ( $M = \text{As}$  or  $\text{Sb}$ ),  $\text{NOF}_2^+ \text{AsF}_6^-$ ,  $\text{NF}_4^+ \text{Sb}_2\text{F}_{11}^-$ ,  $\text{NH}_3\text{F}^+ \text{SO}_3\text{CF}_3^-$ ,  $\text{M}(\text{N}_3)_3$  ( $M = \text{As}$  or  $\text{Sb}$ ) and  $\text{SbCl}_x (\text{N}_3)_{6-x}$  ( $x = 2$  or  $4$ ). In the case of oxofluorides, oxygen fluorine disorder is frequently encountered and a new method for obtaining valuable structural information from disordered structures is briefly discussed for the  $\text{NOF}_2^+$  cation. The techniques employed for handling these energetic materials for X-ray diffraction studies will also be described.

**Keywords:** HEDM, POLYINITROGEN, AZIDES

### SYNTHETIC LAYER COMPOUNDS OF Se(IV) AND Te(IV) OXOHALOGENIDES

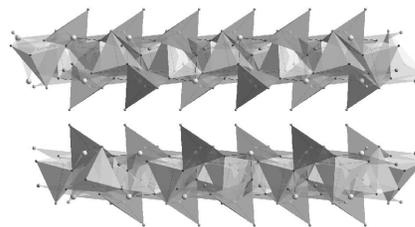
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The combination of elements with stereochemically active lone pairs and halogen atoms has proven to be very efficient as structural scissors. An example of a structure type drawing the full capacity of this characteristic is the family of layer compounds with the general formula  $\text{ZnMLO}_3\text{X}_2$ . Two oxygen and two halogen atoms adopt a distorted tetrahedral coordination around Zn. M is a transition metal e.g. Zn or Cu with a distorted octahedral or square pyramidal coordination of four oxygen atoms in the basal plane and apical halogen atom(s). L is a lone pair element; Se(IV) or Te(IV); coordinating three oxygens in a pyramidal geometry and with the lone pair directed out of the layer. X is one of the halogenides Cl and Br; terminating further bonding. These three building units constitute the infinite layers which are held together through dispersion interactions between the halogen atoms directed out of the layers and possibly also interactions involving the active Se/Te lone pairs. Only one structure of a compound belonging to this family has till now been published;  $\text{Zn}_2\text{SeO}_3\text{Cl}_2$  [1] a mineral from the fumaroles at the famous Tolbachik volcano in Kamchatka; Russia. A projection of the structure of  $\text{CuZnTeO}_3\text{Cl}_2$  down [100] is given below.

[1] T.F. Semenova; I.V. Rozhdestvenskaya; S.K. Filatov & L.P. Vergasova: Crystal structure and physical properties of sophiite;  $\text{Zn}_2 (\text{SeO}_3)\text{Cl}_2$ ; a new mineral;

Mineralogical Magazine; 56 (1992) 241-245.



**Keywords:** INORGANIC COMPOUNDS LAYER STRUCTURE MAIN GROUP ELEMENTS

### CRYSTALLOGRAPHY OF ENOLATE FORMATION AND REACTIONS

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New structural results derived from X-ray diffraction analysis concerning a variety of synthetically important carbanions will be discussed. Generally, the targets of our structural work are either enolate anions, amide bases used to generate enolates or some alkyl lithium reagents that are widely utilized in a variety of synthetic applications. Recently we have characterized some chiral amide/alkyl lithium reagents. The structures of these reagents will be presented and their ability to induce stereoselectivity in organic reactions will be discussed.

**Keywords:** ORGANOLITHIUM, ENOLATE, NMR