

**PS08.01.09 NEW ALKALI CHALCOGENOSTANNATES(IV) WITH ISOLATED ZINTL ANIONS:** Ferdinand Fabian & Kurt O. Klepp, Dept. of Inorg. Chemistry, Kepler University, Altenbergerstr. 69, A-4040 Linz, Austria

A number of new alkali chalcogenostannates were synthesized by high temperature methods and structurally characterized from CAD4-data obtained with MoK $\alpha$ -radiation. Their common structural feature is the formation of discrete anionic groups with Sn(IV) in tetrahedral chalcogen coordination. Apart from mononuclear species, binuclear, Sn<sub>2</sub>Se<sub>6</sub><sup>4-</sup>, and trinuclear, Sn<sub>3</sub>Se<sub>8</sub><sup>4-</sup>, anions are formed by condensation via common tetrahedral edges. Cs<sub>8</sub>Sn<sub>2</sub>Te<sub>9</sub> contains two different anionic species, SnTe<sub>4</sub><sup>4-</sup> and SnTe<sub>5</sub><sup>4-</sup>, in the latter an end on coordinated ditelluride group acts as a ligand on the central atom. A detailed discussion of the crystal structures is to be given on the meeting.

**Crystal Data:**

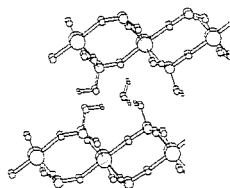
Formula	s.g.	a (Å)	b(Å)	c (Å)	$\beta$ (°)	Z
K <sub>4</sub> SnTe <sub>4</sub>	Pnma	15.874(6)	11.17(1)	8.623(6)		4
Rb <sub>4</sub> SnSe <sub>4</sub>	Pnma	15.06(1)	10.633(7)	8.663(5)		4
Rb <sub>4</sub> SnTe <sub>4</sub>	Pnma	15.957(2)	11.298(3)	9.059(2)		4
Cs <sub>4</sub> SnS <sub>4</sub>	P2 <sub>1</sub> /c	14.13(1)	7.263(3)	13.690(9)	116.20(4)	4
Cs <sub>4</sub> SnSe <sub>4</sub>	P2 <sub>1</sub> /c	14.74(2)	7.733(5)	14.15(2)	116.71(4)	4
Rb <sub>4</sub> SnS <sub>4</sub>	P $\bar{4}$ 3n	13.452(1)				8
Cs <sub>8</sub> Sn <sub>2</sub> Te <sub>9</sub>	Pmc2 <sub>1</sub>	12.248(3)	9.812(3)	14.636(3)		2
Rb <sub>4</sub> Sn <sub>2</sub> Se <sub>6</sub>	P $\bar{1}$	7.180(2)	8.223(29)	8.934(2)		1
		88.63(2)°	109.1(1)°	119.11(9)°		
Na <sub>4</sub> Sn <sub>2</sub> Se <sub>8</sub>	C2/c	26.73(1)	8.289(4)	7.440(4)	95.74(5)	4
K <sub>3</sub> NaSn <sub>3</sub> Se <sub>8</sub>	P4/nbm	8.1334(4)		13.701(2)		2
K <sub>3</sub> AgSn <sub>3</sub> Se <sub>8</sub>	P4/nbm	8.110(1)		13.440(4)		

This study was supported by the Austrian National Science Foundation under project nr. P09981

**PS08.01.10 DETERMINATION OF HYDROGEN-ATOMS ON LAMELLAR TITANIUM PHOSPHATES FROM NEUTRON POWDER DIFFRACTION DATA** S.García-Granda<sup>a</sup>, M.A.Salvadó<sup>a</sup>, P.Pertierra<sup>a</sup>, J.Rodríguez<sup>b</sup>, J.R.García<sup>b</sup> and M.T.Fernández-Díaz<sup>c</sup>. <sup>(a)</sup>Departamento de Química-Física y Analítica, <sup>(b)</sup>Area de Química Inorgánica Universidad de Oviedo (Spain), <sup>(c)</sup>Institut Laue-Langevin, Grenoble (France).

The layered phosphates of IV group elements have been widely investigated<sup>1</sup> for their interest in practical applications in many fields: ion exchange, intercalation, proton conduction, catalysis, etc. In order to understand the behaviour of these compounds the determination of hydrogen-atom positions became a fundamental issue. In spite of the large incoherent contribution, full information about the position of hydrogen atoms can be obtained using neutron powder diffraction, furthermore the presence of hydrogen bonds implies changes in the fine structure when hydrogen is substituted by deuterium.

The complete crystal structure including hydrogen-atom positions of  $\alpha$ -Ti(HPO<sub>4</sub>)<sub>2</sub>H<sub>2</sub>O ( $\alpha$ -TiP) and  $\alpha$ -Hf(HPO<sub>4</sub>)<sub>2</sub>H<sub>2</sub>O ( $\alpha$ -HfP) were determined by Rietveld refinement and Fourier synthesis, using constant-wavelength neutron diffraction data<sup>2</sup>. This work is one of few recent examples of determination of hydrogen atoms using neutron powder diffraction with an intense source. Orientation of water molecules in the cavities of  $\alpha$ -TiP is similar that previously found for  $\alpha$ -ZrP. For  $\alpha$ -HfP (see figure) although hydrogen bonding scheme is identical, orientation of water molecules in similar cavities was found to be different.



1. R.Llavona, J.R.García, M.Suárez and J. Rodríguez, *Thermochimica Acta* (1985) 86, 281.

2. M.A.Salvadó, P.Pertierra, S.García-Granda, J.R.García, J.Rodríguez and M.T.Fernández-Díaz, *Inorganic Chemistry* (Submitted).

**PS08.01.11 EVOLUTION OF DEFECT STRUCTURE OF GROSSLY NONSTOICHIOMETRIC Ca<sub>1-x</sub>R<sub>x</sub>F<sub>2+2x</sub> CRYSTALS (R<sup>3+</sup> = La, Nd, Dy, Ho, Yb).** Grigorieva N.B., Otroschenko L.P., Maximov B.A., Sobolev B.P., Simonov V.I. Inst. of Crystallography, Leninsky pr. 59, Moscow 117333, Russia

The structure of Ca<sub>0.65</sub>La<sub>0.35</sub>F<sub>2.35</sub> (I); Ca<sub>0.65</sub>Nd<sub>0.35</sub>F<sub>2.35</sub> (II); Ca<sub>0.8</sub>Dy<sub>0.2</sub>F<sub>2.2</sub> (III); Ca<sub>0.65</sub>Ho<sub>0.35</sub>F<sub>2.35</sub> (IV); Ca<sub>0.8</sub>Yb<sub>0.2</sub>F<sub>2.2</sub> (V) crystals was studied by X-ray diffraction technique. AgK $\alpha$  (II, III, IV) and MoK $\alpha$  (I, V) was used. The crystals have sp. gr. Fm $\bar{3}$ m with the parameters of cubic cells: a=5.6452(9); a=5.6095(3); a=5.5115(3); a=5.5292(3); a=5.4815(7) Å respectively. R-factor over F(hkl) averaging are 0.0246; 0.0169; 0.0172; 0.0186; 0.0157.

There are two types of anionic defects in this crystals: vacancies at basic position 8c and interstitial F-ions near the center of unit cell. The number of sites of different interstitial F-ions is reduced with the decrease in ionic radius of R<sup>3+</sup>.

In crystals (I) and (II) interstitial F-ions occupy position 32f. They statistically occupy two positions (32f and 48i) in (III) and (IV). In (V) interstitial F-ions occupy position 48i. In crystals (I, II, III, IV) part of F-ions relaxed from basic position 8c along axis 3.

**PS08.01.12 THE CORRECT STRUCTURE OF THE ACID RHODO COMPLEX - A CLASSICAL COORDINATION COMPOUND.** Pernille Harris, Henrik Birkedal, and Sine Larsen, Centre for Crystallographic Studies, Department of Chemistry, University of Copenhagen, Denmark

The acid rhodo chromium(III) compound has been known for more than a century. It is a dimeric complex with two Cr(NH<sub>3</sub>)<sub>5</sub><sup>3+</sup> moieties linked by a  $\mu$ -hydroxo group. The electronic and magnetic properties of crystalline [(NH<sub>3</sub>)<sub>5</sub>Cr-OH-Cr(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>5</sub>H<sub>2</sub>O have been extensively studied (H. Riesen and H.U. Gudel, *Inorg. Chem.* 25, (1986), 3566) but these results were obviously at variance with the published crystal structures, assigned to the tetragonal space groups P4<sub>2</sub>/mmm and P4<sub>2</sub>12. Making use of an extensive set of low temperature diffraction data we have acquired, what we believe is the correct structural description of this classical coordination compound. Our result is in accordance with the spectral and magnetic measurements. The structure has been solved in the orthorhombic space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with cell dimensions a= 16.157(5) Å, b= 16.164(5) Å and c= 14.766(3) Å. The crystals emulate tetragonal symmetry by having a reflection twin in the (110) plane. There are two crystallographically different dimers, i.e. four chromium sites, in the asymmetric unit. The four chromium sites are connected by pseudo-tetragonal symmetry, corresponding to a cell with c' = c/2. This means that reflections with l = 2n + 1 are systematically weak, a feature that gave rise to further complications in the structure determination. The Cr-O-Cr angle of the two dimers is 154.8(3)° and 152.8(4)°, respectively; this small difference is also apparent from ESR-measurements. The angle between the Cr-O-Cr planes of the two dimers is 90.2(1)° - in agreement with optical measurements. It has not been possible for us to locate hydrogen atoms. This is most probably due to the twinned nature of the data. The final model has an R-value of 0.059 for 6949 reflections having F<sub>0</sub> > 4  $\sigma$ (F<sub>0</sub>).