

**PS08.01.17 STRUCTURAL DIVERSITY IN THALLIUM CHEMISTRY.** Margaret James, Department of Chemistry, Mount Saint Vincent University, Halifax, Nova Scotia, Canada B3M 2J6; Anthony Linden, IOC - University of Zürich, CH-8057 Zürich, Switzerland; Bruce James, John Liesegang, Vilma Zuzich, Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

The structures of several chlorothallate (III) salts will be reported and analyzed. Of special interest is the variety of modes for obtaining high coordination at Tl. These modes include monomeric  $TlCl_5^{2-}$  species, a dimer and a variety of anionic chain forming species. The role of the cation and hydrogen bonding in the compound is investigated.

**PS08.01.18 TERNARY ALCALINE EARTH, LANTHANOID, AND ACTINOID TRANSITION METAL CARBIDES.** W. Jeitschko, Anorganisch-Chemisches Institut, Universität Münster, Wilhelm-Klemm-Str. 8, D-48149 Münster, Germany

Some 500 ternary carbides have been prepared during the past ten years. They crystallize with almost 50 different structure types. In many of these the carbon atoms are isolated from each other, even though the carbon content may be high, e.g. in  $Ho_2Cr_2C_3$ ,  $UW_4C_4$ , or  $U_5Re_3C_8$ . In others the carbon atoms form pairs as, for instance, in  $Gd_3Mn_2C_6$ ,  $La_{3.67}FeC_6$ ,  $GdRuC_2$ ,  $Sc_3RuC_4$ ,  $Er_8Rh_5C_{12}$ , and in the many carbides with  $CeNiC_2$ -,  $CeCoC_2$ -, and  $UCoC_2$ -type structures. In  $Dy_{10}Mn_{13}C_{18}$ ,  $La_{12}Re_3C_{15}$ ,  $Er_7Ru_2C_{11}$ ,  $Ca_4Ni_3C_5$ ,  $Yb_4Ni_2C_5$ ,  $Th_4Ni_3C_5$ , and  $U_2NiC_3$  carbon pairs are found together with isolated carbon atoms.  $Sc_3Re_2C_7$  contains  $C_3$  units derived from propadiene. The C-C bond lengths usually correspond to double bonds, however, the hydrolyses usually result in saturated and unsaturated hydrocarbons ranging from methane to the various isomers of hexane and hexene. The positions of the metal atoms in the carbides  $UCr_4C_4$ ,  $LaMn_{11}C_2$ ,  $Pr_2Mn_{17}C_3$ ,  $Tb_2Mn_{17}C_3$ ,  $Pr_2ReC_2$ , and  $La_5O_3C_4$  correspond to those of the binary structure types  $MoNi_4$ ,  $BaCd_{11}$ ,  $Th_2Zn_{17}$ ,  $Th_2Ni_{17}$ ,  $Co_2Si$ , and  $Mn_5Si_3$ . Most of these carbides are metallic conductors, others ( $LaRhC_2$ ,  $CeRhC_2$ ,  $Sc_3Re_2C_7$ , and  $ScCrC_2$ ) are semiconductors;  $Y_2FeC_4$  is superconducting below 3.6 K. The tetragonal structure of  $YCoC$  is most simple with no variable positional parameter. It contains a linear  $[-Y-C]_n^{-3n}$  polyanion. In the carbides  $Pr_2ReC_2$ ,  $Gd_{12}Ru_{7.5}C_{20}$ ,  $Th_2NiC_2$ , and  $Th_3Ni_5C_5$  the 18-electron rule seems to be obeyed for the transition metal atoms. The structures may be classified by the extension of the transition metal-carbon polyanions, which may be isolated from each other, or they form infinite chains, nets, and three dimensional networks.

**PS08.01.19 THE STRUCTURE AND CATION DISTRIBUTION IN SOLID SOLUTION  $(Al_{0.75}Cr_{0.25})(H_2O)_6(NO_3)_3 \cdot 3H_2O$ .** A.Kapor<sup>1</sup>, S.Rakic<sup>1</sup>, N.Furmanova<sup>2</sup>, Institute of Physics, Faculty of Sciences, University of Novi Sad, Yugoslavia<sup>1</sup>, Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia<sup>2</sup>

Starting from the isostructural compounds hexaquaaluminium (chromium)(III) nitrate trihydrate [1,2], a saturated aqueous solution was prepared with mass ratio of the components 75: 25. Highly higroscopic single crystals of the solid solution were obtained by the slow evaporation at room temperature and atmospheric pressure. Reflection intensities were collected on the automatic single crystal diffractometer using  $MoK\alpha$  radiation. Unit cell parameters:  $a = 13.882(9)\text{\AA}$ ,  $b = 9.612(4)\text{\AA}$ ,  $c = 10.918(5)\text{\AA}$ ,  $\beta = 95.43(4)^\circ$ ,  $V = 1450(6)\text{\AA}^3$ ,  $M_r = 381.39$ ,  $D_x = 1.746\text{Mg m}^{-3}$  and the space group  $P2_1/c$  indicate to isomorphism and probably isostructuralism with component compounds. The structure was refined starting from the coordinates of hexaquaaluminium(III) nitrate trihydrate using the program SHELXL 93 with the variable value of the occupation factor of Al and Cr atoms, beginning from 0.75 and 0.25 respectively (molar ratio was 0.762: 0.238). The final results ( $R1 = 0.038$ ,  $3245F_o > 4\sigma(F_o)$ ,  $np = 279$ ,  $wR2 = 0.117$ ,

$S = 0.947$ ,  $\Delta/\sigma = 0.002$ ,  $\Delta\rho_{\max} = 0.33\text{ e/\AA}^3$ ) confirm the isostructurality. The distribution of the cations  $Al^{+3}$  and  $Cr^{+3}$  in the special position (0,0,0, 1/2,0,1/2) shows from the final values of occupation factors  $K_1(Al) = 0.381(18)$ ,  $K_1(Cr) = 0.115(9)$ , ( $K_2(Al) = 0.222(19)$ ,  $K_2(Cr) = 0.256(10)$ ) that the total relative abundance of Al cations with respect to Cr cations is 0.603(18): 0.371(10). Preferential occupation of the position 2 by Cr ions indicates that at the room temperature the structure is below the point of statistical ordering.

[1] D.Lazar, B.Ribar, B.Prelesnik: Redetermination of the structure of Hexaquaaluminium(III)nitrate trihydrate, Acta Cryst.C47,2282,(1991)

[2] D.Lazar, B.Ribar, V.Divjakovic, Cs.Mezzaros: Structure of Hexaquaachromium(III) nitrate trihydrate, Acta Cryst.C47,1060,(1991).

**PS08.01.20 SUB- AND SUPERSTRUCTURE OF  $AgPbBr_3$ .** H.-L. Keller, H.Ullmann, Chemistry Department/Inorganic Chemistry, University of Dortmund, Germany

Substructure and superstructure of  $AgPbBr_3$  are discussed.

The compound  $AgPbBr_3$  exists beside the compounds  $AgPb_2Br_5$  and  $AgPb_3Br_7$  in the system  $AgBr-PbBr_3$  [1].

$AgPbBr_3$  melts congruently at 282°C. The crystal structure was determined from a single crystal with X-ray methods.  $AgPbBr_3$  crystallizes in the orthorhombic spacegroup type  $Cmcm$  (No. 63) with four formula units per unit-cell. Silver is surrounded by a slightly distorted octahedron of bromine. These octahedra are interconnected by two trans-edges and two trans-corners. For that reason  $AgBr_{6/2}$ -layers are formed parallel to the [010]-plane. The octahedra within the layers are arranged in a way that lead is coordinated trigonal-prismatic by bromine and two side-planes of the prisms are capped by additional bromines. This coordination around lead corresponds to the coordination in the  $PbCl_2$ -structuretype.

The structure refinement for both the lead as well as the silver positions shows unsatisfying large thermal displacement parameters. X-ray film measurements of longer annealed crystals lead to a number of additional weak reflections. Indexing of X-ray powder diffractions shows a new metric in the same crystalsystem as before, but with the short axis three times enlarged. The superstructure was refined with data received from powder diffraction using Rietveld-methods in the original spacegroup type  $Cmcm$  ( $a' = 3a$ ).

[1] Y. Otsubo, Y. Tanaka, M. Miyahara  
Nippon Kagaku Zasshi 92(8) (1971) 735

**PS08.01.21 NEW CHALCOGENOMETALLATES OF IVA AND VA METALS WITH LAYERED COMPLEX ANIONS.** Kurt O. Klepp, Doris Gurtner and Dietmar Sturmayer, Dept. of Inorg. Chemistry, Kepler University, Altenbergerstr. 69, A-4040 Linz, Austria.

An investigation of the sections  $Tl_{3-x}M_xTVX_4$  ( $M = Cu, Ag$ ;  $T = V, Nb, Ta$ ,  $X = S, Se$ ) led, among others [1], to the *pseudo* two-dimensional compounds  $Tl_2Cu_4T_2S_8$  and  $Tl_4Ag_2Ta_2S_8$ . In the former  $CuS_4$  and  $TS_4$  tetrahedra share edges to form corrugated layers which can be interpreted as fragments of the sulvanite type structure. Tetrahedral coordination of the transition metals is also found in  $Tl_4Ag_2Ta_2S_8$ . Almost planar layers, built up by double tetrahedra  $[S_2AgS_2TaS_2]$  sharing their free corners, run through the structure parallel to (101).

The complex anions in the isostructural series  $Tl_2Cu_2TIV_3X_8$  consist of corrugated layers which are built up by edge and corner sharing  $TIVX_6$  octahedra which run parallel to (201). Corrugation of these layers leads to the formation of distorted tetrahedral niches which are occupied by Cu. The  $Tl^{+}$ -ions between the layers are in a bicapped trigonal prismatic chalcogen coordination. Homologous layers are found in  $Rb_2Cu_2Hf_3Se_8$ , however here their stack-