PS08.01.17 STRUCTURAL DIVERSITY IN THALLIUM CHEMISTRY. Margaret James, Department of Chemistry, Mount Saint Vincent University, Halifax, Nova Scotia, Canada B3M 2B6; Anthony Linden, IOC-University of Zürich, CH-8093 Zürich, Switzerland; Bruce James, John Liesegang, Vilma Zwickl, Department of Chemistry, La Trobe University, Bendora, Victoria 3083, Australia.

The structures of several clorothallate (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 TICI₂⁻ 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, Universitat Muenster, Wilhelm-Kleemann-Str. 8, D-48149 Muenster, Germany.

Some 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 Ho₂Cr₂C₃, U₂C₄ or U₃ReC₃. In others the carbon atoms form layers as, for instance, in Gd₃MnC₆, La₃FeC₄, Ce₃FeC₄, Ce₃CoC₄, Gd₃RuC₂, Gd₃RhC₂, Lu₃FeC₄, Tb₃FeC₄, Tb₃CoC₄, and Gd₃NiC₂. In the many carbides with Ce₃NiC₄, Ce₃CoC₄, and UC₃GeC₄ type structures, the space group contains C₃ as a three dimensional network.

Starting from the isostructural compounds hexaquaaluminium (chromium)(III) nitrate trihydrate [1], 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 slow evaporation at room temperature and atmospheric pressure. Reflection intensities were collected on the automatic single crystal diffractometer using MoKα radiation. Unit cell parameters: a = 13.882(9) Å, b = 9.612(4) Å, c = 10.918(5) Å, β = 95.43(4)°, V = 1450(6) Å³, M = 381.39, D = 1.746 g·cm⁻³ and the space group P2₁/c indicate to isomorphism and probably isostructuralism with component carbides. The structure was refined starting from the coordinates of hexaquaaluminium (chromium)(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 > 4σ(F o), np= 279; wR2=0.117, w= 0.947, Δ(σ)= 0.002, Δ(σ)max= 0.33 e·Å⁻³) confirm the isorstructuralism. The distribution of the cations Al³+ and Cr³+ in the special position (0,0.0,1/2) shows from the final values of occupation factors K₁(Al)=0.381(18), K₂(Al)=0.619(9), (K₁(Cr)=0.222(19), K₂(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 bellow the point of statistical ordering.


PS08.01.20 SUB- AND SUPERSTRUCTURE OF AgPbBr₃. H.-L. Keller, H.Ullmann, Chemistry Department/Inorganic Chemistry, University of Dortmund, Germany.

Substructure and superstructure of AgPbBr₃ are discussed.

The compound AgPbBr₃ exists beside the compounds AgPbBr₅ and AgPb₃Br₇ in the system AgBr-PbBr₃ [1]. AgPbBr₃ melts congruently at 282°C. The crystal structure was determined from a single crystal with X-ray methods. AgPbBr₃ 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 AgBr₅ 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 PbBr₂-superstructuretype.

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 crystal system as before, but with the short axis three times enlarged. The superstructure is refined with data received from powder diffraction using Rietveld-methods in the original spacegroup type Cmcm (a' = 3a).


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

An investigation of the sections TIX₃ (X=Mo, W) shows that among others [1], to the pseudo two-dimensional compounds TIX₃Cu₂Ta₂S₈ and TIX₃Ag₂Ta₂S₈. In the former Cu₂S₄ and Ta₄ 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 TIX₃Ag₂Ta₂S₈. Almost planar layers, built up by double tetrahedra [S₄AglTa₂S₄] sharing their free corners, run through the structure parallel to (101).

The complex anions in the isostructural series TIX₃Cu₂Ta₂S₈ consist of corrugated layers which are built up by edge and corner sharing TIX₃ octahedra which run parallel to (101). 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 bisected trigonal prismatic coordination. Homologous layers are found in Rb₃Cu₂Hf₅Se₈ however here their stack-
ing leads to two entirely different chalcogen configurations for the two independent Rb+ ions; one of them occupies a split position and shows drastically enhanced thermal displacements.

In contrast to the Ce-doped sample, no anomalous changes were observed in the undoped sample with temperature going down.

The new Li-Ge-S compound, Li₄GeS₄, has been successfully grown as the main product in the Li₅S-La₅S₃-Ge-S system at temperature under 973K. The clear white to light yellow moisture-sensitive crystals are grown by heating the above reagents in 2:1:2:6 proportions at 973K for 200hrs and slowly cooling to 773K. The reagents were mixed and put in a carbon tube which was sealed inside an evacuated quartz tube (~10⁻³ Torr). The well-developed single crystals had pillar-shaped habits.

An X-ray single crystal intensity data collection has been carried out for Li₄GeS₄ using a four-circle RIGAKU AFC6S diffractometer with MoKα radiation at room temperature. The crystal was mounted inside of a capillary with mineral oil. The space group was found to be Pnma, and the cell dimensions are a=14.107(6), b=7.707(3) and c=6.162(2)Å estimated from 18 well-centered reflections in the range of 55° < 2θ < 60° using MoKα. The intensity data were collected up to 60° in 2θ. The crystal structure including the lithium-sites has been solved by direct-methods using SHELXS-86 and successive Difference-Fourier synthesis. The final R and wR-values are 1.85 and 1.65% for 866 observed reflections, respectively.

The Li₄GeS₄ structure has three lithium-sites and one germanium-site. The lithium sites have two different coordination types. The Li₁-site is coordinated to five sulfurs in a square pyramidal geometry and can be viewed as a remarkably distorted NaCl-like framework. The other lithium sites, the Li₂ and Li₃ have distorted tetrahedral coordination types connected in a three dimensional framework. The germanium atom is also tetrahedrally coordinated by four sulfur atoms and is found as an isolated GeS₄⁻ unit.

The crystal structure of Li₄GeS₄ is similar to the K₃SnSe₄ [1] structure type, but has slight differences caused by the differences in ionic radii of the alkali metals and the chalcogenides. The Li₄GeS₄ structure exhibits disorder at the Li₁-site which is not found for K₁ in K₃SnSe₄.

PS08.01.24 CRYSTAL STRUCTURE OF A NEW Li-Ge-S COMPOUND, Li₄GeS₄. Yoshitaka Matsuishi1, Mercouri G. Kanatzidis, Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322 USA

The new Li-Ge-S compound, Li₄GeS₄, has been successfully grown as the main product in the Li₅S-La₅S₃-Ge-S system at temperature under 973K. The clear white to light yellow moisture-sensitive crystals are grown by heating the above reagents in 2:1:2:6 proportions at 973K for 200hrs and slowly cooling to 773K. The reagents were mixed and put in a carbon tube which was sealed inside an evacuated quartz tube (~10⁻³ Torr). The well-developed single crystals had pillar-shaped habits.

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