PS08.01.17 STRUCTURAL DIVERSITY IN THALLIUM CHEMISTRY. Margaret James, Department of Chemistry, Mount Saint Vincent University, Halifax, Nova Scotia, Canada  E3M 2K6; Anthony Linden, IOC - University of Zurich, CH-8093 Zurich, Switzerland; Bruce James, John Liesegang, Vilma Zuzich, Department of Chemistry, La Trobe University, Bendora, Victoria 3083, Australia

The structures of several chloroaluminate (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 TICl 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 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, UW4C4, or U3Re5C8. In others the carbon atoms form pairs as, for instance, in Gd3Mn2C6, Lu3FeC4, CeCoC2, CeNiC2, and in the many carbides with CeNiC2-, CeCoC2-, and UCoC2-type structures. In Dy3Na3C12, La13Re9C12, ErRu2C11, Cu3NiC2, Yb4NiC2, and U2NiC3 carbon pairs are found together with isolated carbon atoms. Sc2ReC7 contains C3 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 UCoC2, LaNi1-xC2, PrMnxC2, TbMnxC2, Pr2ReC5, and La3O6C2 correspond to those of the binary structure types MoNi2, BaCd1, ThZn17, ThNi17, CoSi1, and MnSi1. Most of these carbides are metallic conductors, others (LaRhC2, CeRhC2, CeReC2, and Sc2ReC7) are semiconductors; Y2FeC4 is superconducting below 3.6 K. The structure types for the transition metals are also derived from propadiene. In the carbides Pr2ReC5, Gd3Ru2C5, ThNi12C2, and TbNi12C2 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 (Al1-xTc2x0.5(2)H2O)0.5(NO3) x • 3H2O. A.Kapor1, S.Rakic1, N.Furmanova2, Institute of Physics, Faculty of Science, University of Novi Sad, Yugoslavia1, Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia2

Starting from the isostructural compounds hexaaqualuminium (chromium)(III) nitrate trihydrate [1,2], a saturated aqueous solution was prepared with mass ratio of the components 75:25. Highly higrosopic 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: \(a = 13.882(9) \text{Å}, b = 9.612(4) \text{Å}, c = 10.918(5) \text{Å}, \beta = 95.43(4) \text{°} \), \(V = 14506(6) \text{Å}^3, M_r = 381.39, D_r = 1.746 \text{Mg} \text{m}^{-3} \) 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 hexaaqualuminium (chromium)(III) nitrate trihydrate using the program SHELXL XL 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 (R=0.038, 3245F_0 > 4σ(F_0), np= 279, wR2=0.117, \(S = 0.947, \Delta<0.002, \Delta p_{\text{max}} = 0.33 \text{ e/Å}^3 \) confirm the isostructurality. The distribution of the cations Al3+ and Cr3+ in the special position (0,0,0,1/2,0,1/2) shows from the final values of occupation factors \(K_1(Al)=0.381(18), K_1(Cr)=0.615(10), K_2(Al)=0.222(19), K_2(Cr)=0.256(10) \) 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 bellow the point of statistical ordering.


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

Substructure and superstructure of AgPbBr3 are discussed. The compound AgPbBr3 exists beside the compounds AgPbBr3 and AgPbBr 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 AgBr-poly-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 PbCl2-structure.

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 leads to a number of additional weak reflections. Indexing of X-ray powder diffractions shows a new material 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).


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

An investigation of the sections TIX-MxTV2X4 (M = Ca,Ag; T=V,Nb,Ta, X= S,Se) led among others [1], to the pseudo two-dimensional compounds TIX-CuxTS4 and TIX-Ag2TS4. In the former CuS4 and TS4 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 TIX-Ag2TS4. Almost planar layers, built up by double tetrahedra [S2Ag2TSn2] sharing their free corners, run through the structure parallel to (101).

The complex anions in the isostructural series TIX-CuTV2X4 consist of corrugated layers which are built up by edge and corner sharing TVX6 octahedra which run parallel to (101). Corrugation of these layers leads to the formation of distorted tetrahedral niches which are occupied by Ca. The Tl-ions between the layers are in a bicipated trigonal prismatic coordination. Homologous layers are found in RbCuHfH5Se8, however here their stack-