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, JOC - University of Zürich, CH-8093 Zürich, Switzerland; Bruce James, John Liesegang, Vikma Zuzlich, Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

The structures of several thallolathate (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 TlCl₃⁻ species, a dimer and a variety of anionic chain forming species. The role of the cation and the oxidation 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 Ho₅C₅S, U₅C₆ or U₃C₅C₆. In others the carbon atoms form pairs as, for instance, in Gd₅Mn₆C₆, La₅FeC₅, Ce₄CoC₅. SoC₅C₅ and U₂NiC₅. Carbon pairs are found together with isolated carbon atoms. Some carbon pairs corresponding to double bonds, however, the hydroxyls usually result in saturated and unsaturated hydrocarbons ranging from methane to the various isomers of hexane and hexone. The positions of the metal atoms in the carbides UCoC₂, LaMn₁₋₁C₂, PrMn₁₋₁C₂, TbMn₁₋₁C₂, PbReC₂, and La₃O₄C₂ correspond to those of the binary structure types MoN₁₋₁BaC₁₋₁, Th₂Ni₁₋₁Zn₁₋₁, Co₂Si₁₋₁, and Mn₂Si₁₋₁. Most of these carbides are metallic conductors, others (LaRhC₂, Ce₂RhC₂, Sc₂ReC₂, and Sc₂CoC₂) are semiconductors. Y₃FeCo is a superconducting below 3.6 K. The tetragonal structure of YCo₃Co is most simple with one variable positional parameter. It contains a linear (Y-Co-Y)₃₃ polyhedral. In the carbides PbReC₂, Gd₅Re₃C₅, Th₂NiC₂, and Tb₂NiC₂ 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 polyhedrons, 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 (A₉₋₅Cu₂₀(II)H₂O(NO₃)₃ • 3H₂O • Al-Kapör, 1. Šabik, N. Furmanova, Institute of Physics, Faculty of Sciences, University of Novi Sad, Yugoslavia, Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia

Starting from the isostructural compounds hexaquaoluminium (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 the 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, Dcal = 3.174 g/cm³ and the space group P2₁/c indicate to isomorphism and probably isostructuralism with component compounds. The structure was refined starting from the coordinates of hexaquaoluminium(III) nitrate trihydrate using the program SHELXL-93 with the variable value of the occupancy 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, 3245 Fo > 4σ(Fo), np = 279, wR2 = 0.117, S = 0.947, Δσ = 0.002, Δρmax = 0.33 e/Å³) confirm the isostructuralism. The distribution of the cations Al⁺³ and Cr⁺³ in the special position (0.0, 0.12, 0.12) shows from the final values of occupation factors Kt(AI) = 0.381(18), Kt(Cr) = 0.115(9), (Kt(AI) - 0.222(19), Kt(Cr) = 0.256(10) that the total relative abundance of AI 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 Ag₃PbBr₇ and Ag₅PbBr₁₃ in the system AgBr-PbBr₃ [1]. AgPbBr₃ melts congruously 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 Ag₅PbBr₇-layers are formed parallel to the [010]-plane. The octahedra within the layers are arranged in a way that lead to 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- 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 position in the original space group 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 Stummayr, Dept. of Inorg. Chemistry, Kepler University, Altenberg; G.-A. 4040 Linz, Austria

An investigation of the sections TIX₃MX₄T₅X₇ (M = Ca, Cu; T = W, Nb, Ta; X = S, Se) led among others [1], to the pseudo two-dimensional compounds TIX₃CuTaS₈ and TIX₅AgTaS₈. In the former CuS₂ and T₄S₄ 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 TIX₃AgTaS₈. Almost planar layers, built up by double tetrahedra [S₄Ag₂S₄TaS₄] sharing their free corners, run through the structure parallel to (101).

The complex anions in the isostructural series TIX₃Cu₄TaS₉ consist of corrugated layers which are built up by edge and corner sharing TXY₆ octahedra which run parallel to (101). Corrugation of these layers leads to the formation of distorted tetrahedral niches which are occupied by Cu. The Ti-ions between the layers are in a bicipapped trigonal prismatic chalcogen coordination. Homologous layers are found in Rb₃Cu₂HfS₆, however here their stack-