

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.Kapor¹, S.Rakic¹, N.Furmanova², Institute of Physics, Faculty of Sciences, University of Novi Sad, Yugoslavia¹, Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia²

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.Meszaros: 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-

ing leads to two entirely different chalcogen coordinations for the two independent Rb^+ ions; one of them occupies a split position and shows drastically enhanced thermal displacements.

[1] K.O. Klepp, D. Mayr & H. Boller, *IVth European Conference on Solid State Chemistry*, Dresden 1992, Book of Abstracts, p.363.

Compound	a (Å)	b (Å)	c (Å)	β (°)	s.g.
$Tl_2Cu_4V_2S_8$	7.262(3)	17.63(1)	5.337(2)		Pna2 ₁
$Tl_2Cu_4Nb_2S_8$	7.351 (4)	18.045(8)	5.517(1)		Pna2 ₁
$Tl_2Cu_4Ta_2S_8$	7.395(2)	18.051(6)	5.525(1)		Pna2 ₁
$Tl_4Ag_2Ta_2S_8$	7.932(9)	10.395(6)	10.025(5)	90.61(0)	P2 ₁ /n
$Tl_2Cu_2Hf_3Se_8$	14.392(3)	3.828(1)	14.387(3)	113.69(2)	C2/m
$Tl_2Cu_2Zr_3S_8$	14.328(2)	3.787(0)	14.250(2)	113.59(2)	C2/m
$Tl_2Cu_2Zr_3Se_8$	14.033(2)	3.7008(6)	13.874(3)	113.93(1)	C2/m
$Rb_2Cu_2Hf_3Se_8$	25.15(1)	3.783(3)	9.409(5)	105.37(5)	C2/m

PS08.01.22 COMPOSITION, CRYSTAL STRUCTURES, THERMAL STABILITY OF NEW TERNARY POTASSIUM-CONTAINING MOLYBDATES. R.F.Klevtsova, L.A. Glinskaya, Zh.G. Bazarova, P.V. Klevtsov, Institute of Inorganic Chemistry, Novosibirsk, Russia

The $K_2MoO_4 - AMoO_4 - Zr(MoO_4)_2$ (A=Mg,Mn) systems were investigated by using quasibinary sections and new phases, ternary molybdates of different compositions (I - $K(Mg_{0.5}Zr_{0.5})(MoO_4)_2$; II - $K_{0.6}(Mn_{0.9}Zr_{0.9})(MoO_4)_3$ III - $K_5(A_{0.5}Zr_{1.5})(MoO_4)_6$), were established to exist there. Single crystals were prepared by spontaneous flux crystallization and studied by an X-ray structure analysis (KUMA and CAD 4 diffractometers, Mo K radiation). Some crystallographic data are given in the table.

	Sp.gr	a	c	Z	dx	R
I	P3(-)m1	5.763	7.187	1	3.348	0.022
II	R3(-)c	9.474	24.371	6	3.336	0.046
III-Mg	R3c	10.576	37.511	6	3.576	0.026
III-Mn	R3c	10.584	37.576	6	3.606	0.027

The compounds were shown to fall into three different structure types: (a) glaserite (I); (b) NASICON (II); (c) $-Ca_3(PO_4)_2$ (III). These are built up on the base of three-dimensional frameworks of MoO_4 tetrahedra and MO_6 octahedra with the potassium atoms in the voids. All structures investigated have the following characteristic: a statistic filling of M octahedral positions by the Mg(or Mn) and Zr atoms. Structural peculiarities (size, shape, site occupancy and modes of joint of the coordination polyhedra) were used to interpret physical properties. The comparative crystal chemical analysis of the investigated and related compounds has been carried out. The thermal analysis showed that all compounds melt incongruently at 550-700°C. Polymorphism has not been revealed in the crystals.

PS08.01.23 X-RAY DIFFRACTION STUDY OF $Nd_{2-x}Ce_xCuO_{4-y}$. I.P. Makarova¹, A. Bram², H. Burzlaff³. ¹Institute of Crystallography, Russian Academy of Sciences, 117333, Moscow, Russia; ²ESRF, BP220, 38043 Grenoble, France, ³Lehrstuhl für Kristallographie, Institut für Angewandte Physik der Universität Erlangen-Nürnberg, 91054 Erlangen, Germany.

Changes in the atomic structure and the electron density distribution in single crystals of $Nd_{2-x}Ce_xCuO_{4-y}$ caused by Ce-doping have been studied using X-ray diffraction data. Four samples of $Nd_{2-x}Ce_xCuO_{4-y}$ have been investigated:
 Nd_2CuO_4 , 293 K, 20 K [1];
 $Nd_{2-x}Ce_xCuO_{4-y}$ (I), x=16%, 293 K [2];
 $Nd_{2-x}Ce_xCuO_{4-y}$ (II), x=13%, 293 K [2], 296 K, 150 K, 25 K;
 $Nd_{2-x}Ce_xCuO_{4-y}$ (III), x=15%, HTSC, 293 K.

The main change on the electron density maps is the rearrangement of the charge density at the Cu position with Ce-doping, that indicates the change of the valence state of the Cu atom. At room temperature the formation of a density maximum at the

Nd/Ce position was observed. As the temperature and the displacement parameters decrease, the maximum is split into six separated maxima, that may indicate the disordering at the Nd/Ce position. In contrast to the Ce-doped sample, no anomalous changes were observed in the undoped sample with temperature going down.

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1. I.P. Makarova, V.I. Simonov, M. Blomberg, M. Merisalo, accepted for publication in Acta Cryst.
2. I.P. Makarova, A. Bram, et al. (1994). Physica C, 223, 1.

PS08.01.24 CRYSTAL STRUCTURE OF A NEW Li-Ge-S COMPOUND, Li_4GeS_4 . Yoshitaka Matsushita, Mercuri G. Kanatzidis, Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322 USA

The new Li-Ge-S compound, Li_4GeS_4 , has been successfully grown as the main product in the $Li_2S-La_2S_3-Ge-S$ 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 ($\sim 10^{-5}$ Torr). The well-developed single crystals had pillar-shaped habits.

An X-ray single crystal intensity data collection has been carried out for Li_4GeS_4 using a four-circle RIGAKU AFC6S diffractometer with $MoK\alpha$ 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 $a=14.107(6)$, $b=7.770(3)$ and $c=6.162(2)$ Å estimated from 18 well-centered reflections in the range of $55^\circ < 2\theta < 60^\circ$ using $MoK\alpha 1$. 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 Li_4GeS_4 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 GeS_4^{4-} unit. The crystal structure of Li_4GeS_4 is similar to the K_4SnSe_4 [1] structure type, but has slight differences caused by the differences in ionic radii of the alkali metals and the chalcogenides. The Li_4GeS_4 structure exhibits disorder at the Li1-site which is not found for K1 in K_4SnSe_4 .

- [1] K. O. Klepp; Z. Naturforsch. 47b (1992) 411