

08.2-25 CRYSTAL STRUCTURE OF THE PHASE IV

OF RbLiSO_4 . By W. Steurer, H. Wittmann and H. Jagodzinski, Inst.f.Kristallographie und Mineralogie d.Universität, Theresienstr. 41, D-8000 München 2, FRG and A.Pietraszko, Inst. of Low Temperatures and Structure Research of the Polish Academy of Sciences, POB 937, 50-950, Wrocław, Poland. The structure of the commensurate modulated phase IV was determined by single crystal X-ray diffractometry at 446 K. Space group: $P11n(\text{No.7})$, $Z=20$, $a=9.157(1)$, $b=5.316(1)$, $c=43.654(3)$ Å, $\beta=89.97(1)^\circ$, $U=2125$ Å³, $D_x=2.95$ Mg m⁻³, $R=0.073$, $R_w=0.047$ for 1862 reflexions ($I>0$). The fivefold superstructure parallel c is caused by the ordering of the SO_4 tetrahedra.

If we designate a right(left)-hand rotation around c by $+(-)$ then the sequence of the SO_4 groups in one unit cell can be described by: $++++-----$ (phase I: $++$, phase III: $---+$, phase V_{442k} : $+-$, phase V_{rt} : $-+$ (A.Pietraszko and H. Jagodzinski(1984). Submitted to Z.Kristallogr.)).

To facilitate the comparison of the different phases, refinements of the high temperature phase I and the average structures of the phases III and IV were performed using split positions or anharmonic temperature factors, and the probability density functions of all atoms were calculated (program Prometheus. U.H.Zucker, E.Perenthaler, W.F.Kuhs, R.Bachmann and H.Schulz(1983). J.Applied Cryst. 16, 358). The structural relationships between the different phases will be discussed.

08.2-26 STRUCTURAL CHEMISTRY OF TERNARY THALLIUM CHALCOGENIDES: THE CRYSTAL STRUCTURES OF $\text{Tl}_4\text{Si}_4\text{S}_4$, $\text{Tl}_4\text{Si}_4\text{Se}_4$, $\text{Tl}_2\text{Ge}_2\text{S}_4$, AND $\text{Tl}_2\text{Ge}_2\text{Te}_4$.

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The title compounds were prepared from the elements by thermal synthesis. The determination of the crystal structures was based on single crystal intensity measurements carried out on a four-circle diffractometer (experimental absorption corrections by ψ scans).

$\text{Tl}_4\text{Si}_4\text{S}_4$ is monoclinic, space group Cc with $a = 12.518(3)$, $b = 11.241(2)$, $c = 7.567(2)$ Å, $\beta = 112.80(2)^\circ$, and $Z = 4$. The structure is composed of tetrahedral $[\text{Si}_4\text{S}_4]^{4-}$ anions (mean distance Si-S: 2.130 Å) and Tl^+ cations, each surrounded by six S atoms. The compound is isostructural with $\text{Tl}_4\text{Ge}_2\text{S}_4$ (G. Eulenberger, Z. Kristallogr. (1977), 145, 427). New structural aspects will be discussed.

$\text{Tl}_4\text{Si}_4\text{Se}_4$ crystallizes in the monoclinic system as well, space group $C 2/c$ with $a = 11.664(9)$, $b = 7.277(4)$, $c = 24.903(12)$ Å, $\beta = 99.93(5)^\circ$, and $Z = 8$. In analogy to $\text{Tl}_4\text{Si}_4\text{S}_4$, the structure is characterized by tetrahedral $[\text{Si}_4\text{Se}_4]^{4-}$ anions (mean distance Si-Se: 2.272 Å) connected by Tl^+ cations at five sets of positions. The SiSe_4 tetrahedra build up slabs composed of two layers of SiSe_4 tetrahedra parallel (001). The central plane between them is occupied by Tl atoms. These SiSe_4 double layers are again linked by the remaining Tl atoms arranged in parallel slabs. Each of three Tl atoms is coordinated to six Se atoms. The two further Tl atoms are in (5+1)- and 4-coordination, respectively, and exhibit strong stereochemical activity of the lone 6s electron pair of univalent thallium.

$\text{Tl}_2\text{Ge}_2\text{S}_4$ is orthorhombic, space group $Pnma$ with $a =$

$8.824(2)$, $b = 6.633(2)$, $c = 13.977(4)$ Å, and $Z = 4$. The structure is characterized by infinite double chains

$[\text{Ge}_2^{\text{II}}\text{Ge}_2^{\text{IV}}\text{S}_8]^{4-}$ held together by Tl^+ cations. The double chains are composed of Ge-S single chains containing alternately divalent and tetravalent Ge atoms. These single chains are linked in pairs by S bridges between the Ge(II) and Ge(IV) atoms. As in typical thiogermanates(IV), the tetravalent Ge atoms are tetrahedrally coordinated to four S atoms (mean distance Ge(IV)-S: 2.224 Å). The divalent Ge atoms are bonded to three atoms forming with them ψ -tetrahedral arrangements (mean distance Ge(II)-S: 2.355 Å). The lone electron pair of the GeS_3E tetrahedron is directed towards a Tl atom at a distance of 3.106 Å only. The nine S atoms around Tl(2) form a distorted tricapped trigonal prism. With Tl(1), one of the S atoms is replaced by a Ge(II) atom (mean distance Tl-S: 3.437 Å).

$\text{Tl}_2\text{Ge}_2\text{Te}_4$ is triclinic, space group $P\bar{1}$, with $a = 9.471(2)$, $b = 9.714(2)$, $c = 10.389(2)$ Å, $\alpha = 89.39(1)$, $\beta = 97.27(1)^\circ$, $\gamma = 100.79(1)^\circ$, and $Z = 2$. The structure is built from Ge_2Te_4 units with Ge-Ge bonds which are linked in a three-dimensional structure by Tl atoms coordinated to essentially six Te atoms. The Ge atoms are tetrahedrally bonded to three Te atoms and one further Ge atom. The most important mean distances are: $d(\text{Ge-Ge}) = 2.456$ Å, $d(\text{Ge-Te}) = 2.573$ Å, and $d(\text{Tl-Te}) = 3.511$ Å. The lone 6s electron pairs of Tl(I) display significant stereochemical activity.

08.2-27 STRUCTURE AND BONDING IN URANIUM(IV) COMPLEXES CONTAINING THE UO_2X_4 (X = Cl, Br) CHROMOPHORE

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In octahedrally co-ordinated complexes of uranium containing the UO_2X_4 (X = Cl, Br) chromophore the bonding distances involving uranium have been observed to display a complementary axial-equatorial relationship (J.F. de Wet and J.G.H. du Preez, *J.C.S. (Dalton)*, 1978, 592-596). Specifically, the shorter the (axial) U-O bonds, the longer the (equatorial) U-X bonds, which adopt a more-or-less square planar configuration, and *vice versa*. These effects may be interpreted in terms of the predominantly ionic character of uranium in such complexes, and of the resulting ligand-ligand repulsions; the effects are, however small, and require accurate structure determinations.

We report here on the structural data obtained on six further U(IV) complexes of the type UX_4L_2 (Table 1), where L is an oxygen donor ligand terminating in R=O (R = C, S, P, As). The structure determinations were based on data in which errors due to absorption were eliminated as far as possible.

The U-X and U-O bond lengths observed in these structures confirm and extend the evidence found previously for axial-equatorial relationships (*loc.cit.*), with mean values (in Å) for U-X and U-O in each structure, respectively: 1: 2.605(3), 2.248(6); 2: 2.604(8), 2.249(12); 3: 2.607(8), 2.268(17); 4: 2.770(1), 2.218(8); 5: 2.619(3), 2.231(7); 6: 2.804(7), 2.145(34).