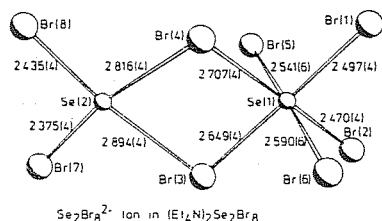


08.2-5 STRUCTURAL CHEMISTRY OF SELENIUM(II) COMPOUNDS: CRYSTAL AND MOLECULAR STRUCTURES OF NOVEL HALOGENOSELENATES(II). By B. Krebs, E. Lührs, L. Stork and R. Willmer, Institute of Inorganic Chemistry, University of Münster, D-4400 Münster, Federal Republic of Germany

Compounds with selenium and tellurium in the oxidation state +2 are only moderately stable, in contrast to tetravalent systems. Recently, we reported crystal structures of the first solid halogenoselenates(II) and -tellurates(II) which were obtained as salts with large organic cations. They contain square-planar  $\text{SeCl}_4^{2-}$ ,  $\text{SeBr}_4^{2-}$ , and  $\text{TeX}_4^{2-}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) or planar  $\text{Se}_2\text{Br}_6^{2-}$  ions (S. Pohl, A. Schäffer, B. Krebs, Z. Krist., 1983, 162, 180; B. Krebs, A. Schäffer, S. Pohl, Z. Naturforsch., 1984, 39b, 1633). Here we report crystal structure investigations on a number of novel oligomeric halogenoselenates(II) which are of special interest with respect to the role of the inert electron pairs at selenium for the structural chemistry of these systems. General structural and bonding relationships can be derived from the results.

The novel  $\text{Se}_2\text{Br}_8^{2-}$  ion (Fig.) which was obtained in the black tetraethylammonium salt (orthorhombic,  $Pnn2$ ,  $a = 13.235$ ,  $b = 24.822$ ,  $c = 9.353$  Å at  $-130^\circ\text{C}$ ,  $Z = 4$ ) is the first mixed-valence chalcogen halogen compound. It consists of an octahedral  $\text{SeBr}_6$  group and a square-planar  $\text{SeBr}_4$  unit linked through edges with no apparent electronic exchange between the Se atoms ( $\text{Se}\dots\text{Se}$  4.043 Å). The tetraethylammonium salt of the dimeric mixed-ligand complex  $[\text{Se}_2\text{Br}_4(\text{SCN})_2]^{2-}$  crystallizes in space group  $P2_1/n$  with  $a = 8.598$ ,  $b = 12.250$ ,  $c = 14.431$  Å,  $\beta = 102.41^\circ$  at  $-130^\circ\text{C}$ ,  $Z = 2$ . Similar to  $\text{Se}_2\text{Br}_6^{2-}$  the



$\text{Se}_2\text{Br}_4\text{S}_2$  frame of the anion is planar with the linear SCN groups standing perpendicular to this plane. The strong trans influence of the SCN ligands makes the central four-membered ring highly asymmetric.

$\text{Se}(\text{Se}_5)_2^{2-}$  is a new type of a mixed-valence polyselenide. The red tetraphenylphosphonium salt  $(\text{Ph}_4\text{P})_2\text{Se}_{11}$  is monoclinic, space group  $P2_1/n$ ,  $a = 12.748$ ,  $b = 14.659$ ,  $c = 14.037$  Å,  $\beta = 108.53^\circ$  ( $-130^\circ\text{C}$ ),  $Z = 2$ . The centrosymmetric  $\text{Se}_{11}^{2-}$  anion consists of two  $\text{Se}_6$  rings in chair configuration which are linked in a spirocyclic manner through the central  $\text{Se}(\text{II})$  being in a square-planar coordination.

Further new halogenoselenates(II) which were characterized structurally as the tetraalkylammonium or tetraphenylphosphonium salts include the pure  $\text{Se}(\text{II})$  species  $\text{Se}_3\text{Br}_8^{2-}$  (star-like arrangement of three planar  $\text{SeBr}_4$  units with two triply bridging Br),  $\text{Se}_5\text{Br}_{12}^{2-}$  (five linked planar  $\text{SeBr}_4$  groups with four tr. br. Br) and the mixed-valence  $\text{Se}_4\text{Br}_{12}^{2-}$  anion ( $\text{SeBr}_6$  octahedron and two  $\text{SeBr}_4$  squares linked through edges + one associated  $\text{SeBr}_2$  molecule).

08.2-6 PREPARATION AND STRUCTURES OF INTER-ALKALI METAL CHALCOGENIDES. By Horst Sabrowsky, Petra Vogt and Alfred Thimm, Lehrstuhl für Anorganische Chemie I, Ruhr-Universität Bochum, Germany (F.R.G.).

Inter-alkali metal chalcogenides have been totally unknown until 1982. Our investigation of the phase diagram  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  lead to the compound  $\text{KNaO}$  (1) as first specimen of that new class of compounds, whereas calculations of BEREZNOJ (2) showed no compounds being possible in this system.

Apart of  $\text{KNaO}$ , many new inter-alkali metal chalcogenides have been obtained (Tab. 1) and their structures have been solved by means of X-ray studies.

Table 1: Crystallographic Data of the Inter-alkali Metal Chalcogenides (lattice constants in pm).

Name	S.G.	a	b	c	Z
$\text{KNaO}$	$P4/m$	400.2	----	621.4	2
$\text{RbNaO}$	$P4/m$	409.3	----	653.1	2
$\text{KLiO}$	$\text{Cmca}$	861.8	640.3	641.7	8
$\text{RbLiO}$	$\text{Prma}$	656.8	351.8	888.8	4
$\text{NaLiS}$	$P4/m$	402.6	----	649.5	2
$\text{KLiS}$	$P4/m$	431.8	----	696.2	2
$\text{RbLiS}$	$P4/m$	442.9	----	723.6	2
$\text{RbNaS}$	$P4/m$	471.1	----	756.0	2
$\text{KNaS}$	$\text{Prma}$	781.5	459.7	832.9	4
$\text{RbKS}$	$\text{Prma}$	822.2	504.3	945.2	4
$\text{KNaSe}$	$\text{Prma}$	788.4	470.6	870.4	4

These salt-like, very hygroscopic compounds have been obtained by heating stoichiometric mixtures of the binary chalcogenides corresponding to the final composition in sealed ampoules containing vessels of alumina and silver.

Although the binary chalcogenides all crystallize in space group  $\text{Fm}\bar{3}\text{m}$  showing anti- $\text{CaF}_2$ -type geometry, the resulting ternary chalcogenides are largely different in structure:

- $\text{KNaO}$  (1),  $\text{RbNaO}$  (3),  $\text{NaLiS}$  (4),  $\text{KLiS}$  (5,6),  $\text{RbLiS}$  and  $\text{RbNaS}$  have the tetragonal anti- $\text{PbCl}_2$ -structure (space group  $P4/m$ ,  $Z=2$ ).
- $\text{KNaS}$  (7), orthorhombic (space group  $\text{Prma}$ ,  $Z=8$ ), shows a very individual structure with the exceptional C.N. 3 observed for Li surrounded by O.
- $\text{KNaS}$  (8) and  $\text{RbKS}$  crystallize with the anti- $\text{PbCl}_2$ -structure (space group  $\text{Prma}$ ,  $Z=4$ ).
- $\text{RbLiO}$  shows a structure related to the  $\text{KNaS}$ -type, but the coordination number of lithium against oxygen is 3.
- Investigations of the system  $\text{Rb}_2\text{O}/\text{K}_2\text{O}$  only lead to a phase of mixed crystals  $\text{Rb}_{1-x}\text{K}_x\text{O}$  adopting the  $\text{CaF}_2$ -structures.

Recently, we characterized  $\text{KNaSe}$  (orthorhombic, probably of  $\text{PbCl}_2$ -type structure) as the first inter-alkali metal selenide.

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