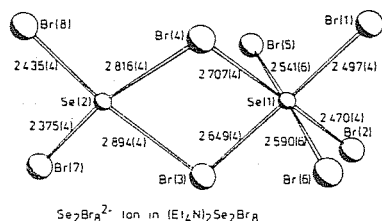


08.2-5 STRUCTURAL CHEMISTRY OF SELENIUM(II) COMPOUNDS: CRYSTAL AND MOLECULAR STRUCTURES OF NOVEL HALOGENOSELENATES(II). By B. Krebs, E. Lührs, L. Stork and R. Willmer, Institute of Inorganic Chemistry, University of Münster, D-4400 Münster, Federal Republic of Germany

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 SeCl_4^{2-} , SeBr_4^{2-} , and 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°C , $Z = 4$) is the first mixed-valence chalcogen halogen compound. It consists of an octahedral SeBr_6 group and a square-planar 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°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°C), $Z = 2$. The centrosymmetric Se_{11}^{2-} anion consists of two 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 SeBr_4 units with two triply bridging Br), $\text{Se}_5\text{Br}_{12}^{2-}$ (five linked planar SeBr_4 groups with four tr. br. Br) and the mixed-valence $\text{Se}_4\text{Br}_{12}^{2-}$ anion (SeBr_6 octahedron and two SeBr_4 squares linked through edges + one associated 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 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 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
KNaO	P4/m	400.2	----	621.4	2
RbNaO	P4/m	409.3	----	653.1	2
KLiO	Omca	861.8	640.3	641.7	8
RbLiO	Prma	656.8	351.8	888.8	4
NaLiS	P4/m	402.6	----	649.5	2
KLiS	P4/m	431.8	----	696.2	2
RbLiS	P4/m	442.9	----	723.6	2
RbNaS	P4/m	471.1	----	756.0	2
KNaS	Prma	781.5	459.7	832.9	4
RbKS	Prma	822.2	504.3	945.2	4
KNaSe	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 $Fm\bar{3}m$ showing anti- CaF_2 -type geometry, the resulting ternary chalcogenides are largely different in structure:

- KNaO (1), RbNaO (3), NaLiS (4), KLiS (5,6), RbLiS and RbNaS have the tetragonal anti- PbCl_2 -structure (space group $P4/m$, $Z=2$).
- KNaS (7), orthorhombic (space group $Prma$, $Z=8$), shows a very individual structure with the exceptional C.N. 3 observed for Li surrounded by O.
- KNaS (8) and RbKS crystallize with the anti- PbCl_2 -structure (space group $Prma$, $Z=4$).
- RbLiO shows a structure related to the 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 CaF_2 -structures.

Recently, we characterized KNaSe (orthorhombic, probably of PbCl_2 -type structure) as the first inter-alkali metal selenide.

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