

**PS08.01.41 A NEW LOOK AT SIMPLE STRUCTURES: THE ALKALINE EARTHS CHALCOGENIDES.** A. Vegas and D. Tranqui. Instituto Rocasolano, CSIC, Serrano 119, E-28006 Madrid, Spain and Laboratoire de Cristallographie, CNRS, F-38042 Grenoble, France

The structures of the NaCl-type alkaline earths chalcogenides are analyzed on the basis of their fcc cation array which are compared with the structure of their parent metals as it has been reported for other compounds (1). The results are that, in most cases, the M-M distances in the compounds, reproduce the values observed in the pure metals.

In some cases, as in the sulfides and selenides of Ca and Sr, the coincidence is also in topology in such a way that the metal net is almost unaltered by the inclusion of the S or Se atoms. Thus, CaS, CaSe, SrS and SrSe can be described as S- and Se-stuffed elements as it was reported for CaF<sub>2</sub> (2).

In the case of MTe (M=Ca, Sr, Ba), the cation fcc-array is formed by (002) planes of the respective bcc-metal, in such a way that second-nearest neighbors distances of the metal are reproduced in the compounds. The general trend is that small anions as O<sup>2-</sup> tend to reproduce distances of the high pressure metallic phases and that greater anions as Te<sup>2-</sup> tend to reproduce distances of the high temperature metallic phases.

(1) A. Vegas, A. Romero & M. Martínez-Ripoll. *J. Solid State Chem.* (1990), 88, 594-596. *Acta Cryst.* (1991), B47, 17-23.

(2) M. O'Keeffe & B. G. Hyde. *Structure and Bonding* (1985), 61, 77-144.

**PS08.01.42 SPECIFIC FEATURES OF RARE-EARTH POLYHEDRA IN ALKALI LANTHANIDE NITRATES.** A.G. Vigdorichik, Institute of Crystallography, Russian Acad. of Sci., Leninsky pr. 59, Moscow, 117333, Russia

This research was performed in the framework of a systematic study undertaken to explain the structure and properties of compounds of alkali rare-earth nitrates with common formula of  $(n-3m)A[(m)Ln(n)(NO_3)(k)(H_2O)](l)(H_2O)$ , where A=alkali cations; n,m,k,l=stoichiometric coeff. The analysis of crystal-chemical characteristics of Ln coordination polyhedra was carried out on the basis of our own experimental data (about 50 crystal compounds) and the data reported in literature. Their shape, symmetry and other properties were analyzed. In all compounds reviewed, the coordination numbers (CN) of the Ln atoms are 10 or 12. CN=12 is characteristic only of the elements of the cerium subgroup. Three types of coordination of the Ln-atoms by nitrate group were found: monodentate, bidentate and bridging bidentate. While reviewing structural data on the compounds in question, we face an exceedingly limited assortment of coordination polyhedra for high coordination numbers - there are only three types: icosahedron, tetracapped trigonal prism, and bicapped tetragonal antiprism. All 12-vertex polyhedra appear as slightly distorted icosahedra. An atom of Ln tends to form a symmetrical coordination arrangement even in the case when it occupies a position without any symmetry elements. It should also be noticed that complexes with the different composition and stoichiometries may correspond to identical coordination polyhedra.

**PS08.01.43 STRUCTURE OF [Sn(2-Se-C<sub>5</sub>H<sub>4</sub>N)<sub>2.15</sub>(SPh)<sub>1.85</sub>]: AN X-RAY CRYSTALLOGRAPHIC STUDY SUPPORTED BY CHEMICAL AND <sup>119</sup>Sn NMR SPECTROSCOPIC DATA.** Jagadees J. Vittal, Philip A. W. Dean, Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada

Yellow crystalline Sn(2-Se-C<sub>5</sub>H<sub>4</sub>N)<sub>2.15</sub>(SPh)<sub>1.85</sub> (1) has been shown by <sup>119</sup>Sn NMR spectroscopy to contain both Sn(2-Se-C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>(SPh)<sub>2</sub> and Sn(2-Se-C<sub>5</sub>H<sub>4</sub>N)<sub>3</sub>(SPh). The crystal and molecular structure of 1 has been determined by single crystal X-ray diffraction techniques. Crystal data: monoclinic, space group P2<sub>1</sub>/n,  $a = 9.795(2)$  Å,  $b = 22.355(4)$  Å,  $c = 11.362(2)$  Å,  $\beta = 108.873^\circ$ ,  $V = 2354.2(8)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.837$  g cm<sup>-3</sup>,  $d_{\text{obs}} = 1.87(5)$  g cm<sup>-3</sup>,  $Z = 4$ ,  $R1 = 0.0306$ ,  $wR2 = 0.0651$  for 2756 data ( $I \geq 2\sigma(I)$ ) and 258 parameters. Crystallographic evidence for the presence of co-crystallized Sn(2-Se-C<sub>5</sub>H<sub>4</sub>N)<sub>3</sub>(SPh) occurs only in a minor lengthening of one of the two Sn-S bonds, Sn(1)-S(1) (compared with expectation for pure Sn(2-Se-C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>(SPh)<sub>2</sub>), and an excess of electron density at S(1) when the data are modelled as Sn(2Se-C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>(SPh)<sub>2</sub>. These effects are attributed to a crystallographic disorder of SPh and  $\eta^1\{-2\text{-Se-C}_5\text{H}_4\text{N}\}$  at the S(1)Ph site, involving isostructural Sn( $\eta^2\{-2\text{-SeC}_5\text{H}_4\text{N}\}$ )<sub>2</sub>( $\{\eta^1\{-2\text{-Se-C}_5\text{H}_4\text{N}\}\}$ (SPh) and Sn( $\eta^2\{-2\text{-Se-C}_5\text{H}_4\text{N}\}$ )<sub>2</sub>(SPh)<sub>2</sub>.

**PS08.01.44 NEW POLYANIONIC SELENOAURATES: THE CRYSTAL STRUCTURES OF Cs<sub>2</sub>Au<sub>2</sub>Se<sub>3</sub>, CsAuSe<sub>3</sub> AND Na<sub>5</sub>AuSe<sub>12</sub>.** Claudia Weithaler, Kurt O. Klepp, Dept. Of Inorg. Chemistry, Kepler University, Altenbergerstr. 69, A-4040 Linz, Austria

Cs<sub>2</sub>Au<sub>2</sub>Se<sub>3</sub> (1) and CsAuSe<sub>3</sub> (2) are characterized by pseudo-one dimensional structures. The seleno anions are helical chains with the sequence ...Au-Se-Au-Se<sub>2</sub>-Au... and ...Au-Se<sub>3</sub>-Au..., resp. Au is in almost linear chalcogen coordination characteristic for Au(I). Se-Au-Se bond angles are 175.4(1)° (1) and 173.3(4)° (2), the bond angles on the Se atoms vary between 83.6(1)° and 103.5(4)°. Au-Se bond lengths are close to 2.40 Å.

In contrast to (1) and (2) the coordination of gold in Na<sub>5</sub>AuSe<sub>12</sub> (3) is almost square planar, in accord of an oxidation state of +3 for the gold atoms. The compound is characterized by discrete anionic species where four triselenido chains act as monodentate ligands on the central Au atom. Au-Se bond lengths are close to 2.50 Å, Se-Se bonds vary between 2.346(2) Å and 2.362(2) Å, the bond angles on the central selenium atoms of the four crystallographically different chains are close to 102°.

The crystal structures were determined from CAD4-data obtained with MoK $\alpha$  radiation. All atoms were refined anisotropically to conventional R- values of 0.042 (1), 0.079 (2) and 0.032 (3), respectively. The crystal structures will be published in *J. Alloys Comp.*

Crystal Data:

Formula	s.g.	a (Å)	b (Å)	c (Å)	$\beta$ (°)	Z
Cs <sub>2</sub> Au <sub>2</sub> Se <sub>3</sub>	C2/c	9.769(5)	13.44(1)	7.178(3)	90.69(2)	4
CsAuSe <sub>3</sub>	C2/c	6.466(3)	13.75(1)	7.624(5)	112.16(2)	4
Na <sub>5</sub> AuSe <sub>12</sub>	P21	7.145(1)	16.790(6)	8.291(1)	107.13(1)	2