PS08.00.31 SUPRAMOLECULAR OXOMETALATE CHEMISTRY: OCTAMOLYBDATE AS A BUILDING BLOCK, Tomoji Ozeki, Akira Kitamura and Atsushi YAGASAKI *Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152, Japan and **Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662, Japan

β-Octamolybdate has been found to form two kinds of complexes with trivalent lanthanum cations: [La(MoO₄)₂]²⁻ and [La₃ (NO₃)₆ (MoO₄)₂]⁺. In the former, whose analogue can also be prepared for Y, Ce, Pr, Nd, Gd and Yb, the coordination sphere of lanthanum is completed square anti-prismatically by 8 oxometalate oxygen atoms of the two [MoO₄]²⁻ moieties, thus forming a dimeric octamolybdate linked to each other via the La³⁺ cation. In the latter, nitrate anions coordinate to the La³⁺ cation to terminate further polymerization. So far this anion was only synthesized for La, Ce and Pr, indicating that the heavier lanthanide elements with smaller ionic radii cannot accommodate octamolybdate and nitrate anions simultaneously. These two polyoxometalate complexes show the potential to compose supramolecular oxometalate complexes utilizing octamolybdate as building blocks and the lanthanide cations as the glue.

[La(MoO₄)₂]²⁻  [La₃ (NO₃)₆ (MoO₄)₂]⁺

PS08.00.32 CRYSTAL CHEMISTRY OF MERCURIC INORGANIC COMPOUNDS AND MINERALS, N.A.Pal'chik, S.A.Magarill, L.M.Volkova. Institute of Geology Sib. Branch RAS, Novosibirsk, Russia; Institute of Inorganic Chemistry Sib. Branch RAS, Novosibirsk, Russia; Institute of Chemistry FE Branch RAS, Vladivostok, Russia

An unique property of mercury, due to its electron shell structure, is the capacity for forming linear Hgₚ (p=2,3,4,∞) systems with the Hg-Hg distance of 2.46-2.64 Å. The Hg₂⁺ bond lengths were found to be dependent on x: in Hg₂ As₂ (dumbbell) 2.46-2.54, in Hg₂ As₂ (chain) 2.55, for Hg₂ As₂, 2.55-2.62, and in Hg₂ infinite chain 2.64 Å. In these systems, Hg₂⁺ has the formal valency from +1 to +0.3. In tellurium dioxide, tellurates and mercury compounds form planar triangles with the Hg₂ As₂ distances of 2.71-2.72 Å, respectively. In the triangles, the formal valency of Hg₂⁺ is +1.33, suggesting that this structural fragment involves a mixed-valent mercury atom. In tellurium dioxide, however, the Hg₂⁺ is coordinated two oxygen atoms and the Hg₂⁺ As₂ distance to the nearest mercury atom of the triangle is more than 3 Å. Similarly, in the structure of waterstibite, Hg₂⁺ polyhedra and (Hg₂⁺)₂⁻ dumbbells are at a distance of >3 Å. The Hg₂ As₂ structure is also of interest in that a linear (Hg₂⁺)₂⁻ tetrad (with the distances 2.59-2.62 Å) is bonded to the other tetrad at the Hg₂⁺ Hg₂⁺ distance of 2.96 Å to form an infinite polymer with the chain charge +0.5.

A relation between conducting and other physical properties and structural peculiarities of these compounds is discussed in this report. As an example, in the Hg₂As₂ structure, infinite Hg₂⁺ Hg₂⁺ chains (2.64 Å), running in two mutually perpendicular nonintersecting directions, are responsible for anisotropic superconductivity. Crystal chemical properties of these minerals and inorganic compounds will allow an understanding and an explanation for their physical properties, crystallization conditions, as well as modelling the basic skeleton of new minerals and compounds and predicting their physical properties.

Zn₂⁺Mg⁺⁺Se thin layers have been reported to adopt the sphalerite structure type of the substrate for 0<x<0.5 [1]. X-ray studies of bulk Zn₂⁺Mg⁺⁺Se crystals grown from the range 0<x<0.5 by the Bridgman method [2,3] have shown that above x=0.2 the structure is of the wurtzite type rather than of the sphalerite type. Powder X-ray analysis of a new crystal prepared from a mixture of ZnSe, Mg and Se reveals the presence of the 4H polytype. In the Mg⁺⁺-rich end of the crystal (wurtzite type, x=0.25 determined by EMPA) the 4H phase is not detected while at the other end the amount of 4H is considerable. Due to the lack of pure 4H phase, the structural information was obtained by Rietveld refinement of the mixture of wurtzite and 4H. For x=0.21, the lattice constants of 4H are a=4.041, c=13.214. The 4H polytype is known in other II-VI systems, e.g. in (Cd,Zn)S and ZnTe(S) crystals grown by the same method [4]. The polytypism in both (Zn,Mg)Se and ZnSe structures implies the need for studies of the possible polytypes formation in quaternary (Zn,Mg)Se(S), a component of heterostructures considered for use in blue light emitting diodes and lasers, in order to explain the degradation processes in such electroluminescent devices.


Using four-circle diffractometer and Buerger precession camera with an image plate the structure of Bridgman grown single crystals of stoichiometric and nickel rich (x = 0.08) Ni₁₋ₓAlₓ⁺⁺ (Pm-3m) has been refined. Moreover, samples were deformed plastically at 800 - 900 °C.

Lattice parameters obtained from 120 reflections agree with literature values at room temperature [1-3]. In addition data between 120 and 320 K have been obtained for both lattice parameters a and thermal expansion coefficients α. These are for x = 0: a = 2.8872(2) Å at r.t. and a = 1.4(2) • 10⁻⁴ K⁻¹ between 120 and 320 K; for x = 0.08: a = 2.8792(2) Å.

Refinement of size occupancy factors on integrated intensity data leads to Ni on A1 positions for the nickel rich sample (s.o.f. Ni/A₁ = 0.074(10)). This agrees well with results taken from electron beam microanalysis (x = 0.078(23)). Buerger precession exposures were taken from deformed crystals in order to analyze the shape of reciprocal lattice points.