

**PS08.01.13 SOLID STATE EMISSION: COPPER(I) HALIDE COMPLEXES WITH PHOSPHINE LIGANDS.** Elizabeth M. Holt, Paul B. Durand and Gilbert Mains, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

Crystalline complexes of types;  $\text{Cu}_4\text{X}_4(\text{PR}_3)_4$ ,  $\text{Cu}_2\text{X}_2(\text{PR}_3)_3$  and  $\text{CuX}(\text{PR}_3)_2$  have been observed to display cubic, rhombohedral and monomeric motifs, respectively, in which copper(I) displays three and four coordination. The stoichiometry of the complexes observed with various  $\text{PR}_3$  ligands may be understood in terms of the cone angle subtended by the  $\text{PR}_3$  group. When excited in the UV, these complexes may show emission in the visible range. For  $\text{Cu}_4\text{X}_4(\text{PR}_3)_4$  complexes, a change from X=iodide to X=bromide leads to quenching of the visible emission. Those complexes (X=I) crystallizing with an internal three fold symmetry element emit in the 470-520 nm range whereas those with an internal two-fold axis emit at lower energy (575-615 nm) when excited at 300 nm. The presence of an aromatic ring in the phosphine ligand leads to quenching of the visible emission for complexes of the type:  $\text{Cu}_2\text{X}_2(\text{PR}_3)_3$ . Two allotropes of formula  $\text{CuBr}[\text{P}(\text{cyclohexane})_3]_2$  crystallize in different space groups depending upon the solvent. The form crystallized from hexane is found in space group  $\text{C2/c}$  with a 2-fold symmetry axis within the monomeric unit. When crystallized from benzene, space group  $\text{P2}_1/\text{n}$  is adopted and there is no internal symmetry element. The two forms display maximum emission at 460 and 400 nm, respectively. Packing differences are also noted. *ab initio* calculations lead to an understanding of the emission behavior of these complexes.

**PS08.01.14 ON STRUCTURES OF  $4\text{X}\cdot 5\text{X}'\cdot 4\text{Y}\cdot \text{Y}'\cdot 80\text{H}_2\text{O}$  AND  $4\text{X}\cdot \text{X}'\cdot 2\text{Y}\cdot \text{Y}'\cdot 46\text{H}_2\text{O}$  CLATHRATE HYDRATES.** E.A. Il'inchik, T.M. Polyanskaya, Institute of Inorganic Chemistry Sib. Branch RAS, Novosibirsk, Russia

In this work, we propose two possible structures with 3-dimensional polyhedral host hydrate frames possessing cage-like voids which are occupied by guest molecules  $4\text{X}\cdot 5\text{X}'\cdot 4\text{Y}\cdot \text{Y}'\cdot 80\text{H}_2\text{O}$  (I) and  $4\text{X}\cdot \text{X}'\cdot 2\text{Y}\cdot \text{Y}'\cdot 46\text{H}_2\text{O}$  (II). Both frames are built of 4 cage types. In I, these are Pd [5<sup>12</sup>6<sup>3</sup>], Td [5<sup>12</sup>6<sup>2</sup>], Dd [5<sup>12</sup>], and D [4<sup>25</sup>8]. Frame II involves Dd' [4<sup>25</sup>8<sup>62</sup>] along with Pd, Td, D cages. X and X' guests occupy Pd and Td cages in both structures. Y and Y' occupy Dd and D in I and Dd' and D cages in II. When filling only large Pd and Td cages by the guests of one sort, I and II are simplified to X·8,89H<sub>2</sub>O and X·9,2H<sub>2</sub>O, respectively.

Both structures are four-storey when viewed along the c axis. In I, the storeys on the levels Z=0 and 1/2 are built of the immediately connected Pd, Td, and Dd cages in the 8Pd:8Td:4Dd ratio; in II, they are built of the Pd and Dd' cages in the 8Pd:4Dd' ratio. A three-dimensional frame is obtained from a successive superposition of the same storey which is rotated through 90° relative to the preceding one. Thus, 6-, 5-, 4- and 6-, 4-angle windows are located over each other and as a result, infinite columns of the Td, Dd, D and Td, D cages with their centers on the Z=1/4 and 3/4 levels are formed in I and II, respectively. In the intermediate storeys, the cages on these levels are not connected immediately. They have the 2Td:4Dd:2D ratio in I and 2Td:2D in II.

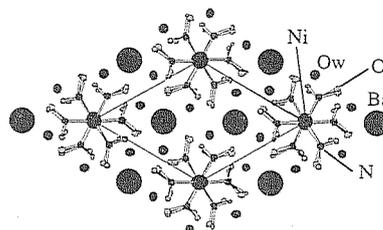
In both structures, there are combined voids (4Td and 2Td·2Pd in I and 2Td·2Pd in II) suitable for the arrangement of the cations of quaternary alkyl salts. Crystal data for I: tetragonal I4(-)c2, a=31,1, c=12.0 Å, Z=4, 59 positional parameters of 21 symmetrically inequivalent oxygens of H<sub>2</sub>O molecules; for II: I4/mcm, a=23,3, c=12.0 Å, Z=4, 19 positional parameters of 9 oxygens. The unit cell parameters are given in this work for corresponding clathrasiles, silicides, germanides and stannides isotypic with the gas hydrate frame.

**PS08.01.15 CRYSTAL STRUCTURE AND THERMAL DECOMPOSITION STUDY OF THE  $[\text{Ba}_2\text{Ni}(\text{NO}_2)_6]\cdot 4\text{H}_2\text{O}$  COMPOUND.** M. Insausti, A. Bolibar, L. Lorente, J.L. Pizarro\* Depts. de Química Inorgánica y Mineralogía-Petrología\*. Universidad del País Vasco. Aptdo 644. 48080 Bilbao. Spain.

In order to get mixed metal oxides, the use of thermal decomposition of molecular precursors has proved to be often a more advantageous way than the ceramic method, involving lower temperatures and shorter reaction times. In this way, we have synthesized and characterized some new nitrite derivatives, and the structure of one of them,  $[\text{Ba}_2\text{Ni}(\text{NO}_2)_6]\cdot 4\text{H}_2\text{O}$ , has been determined by X-ray diffraction methods

The compound crystallizes in the hexagonal space group,  $\text{P6}_3$ , with a = 7.525(1)Å, c = 14.516(1)Å, V = 711.8(1)Å<sup>3</sup>, Z = 2, R = 0.054, R<sub>w</sub> = 0.066. The complex contains a three dimensional arrangement of  $\text{Ni}(\text{NO}_2)_6$  entities, which are placed in the corners of the unit cell, and Ba atoms coordinated to twelve oxygens.

In order to obtain detailed information about the decomposition process, thermogravimetry and differential scanning calorimetry measurements have been performed.



**PS08.01.16 STRUCTURE ANALYSIS OF  $\text{CaYAlO}_4$  UNDER EXTINCTION FREE CONDITION USING SR.** N. Ishizawa, K. Morita, Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta Yokohama 226 and N. Kodama, Tosoh Cooperation, Hayakawa, Ayase 252, Japan

Structure of the  $\text{K}_2\text{NiF}_4$ -type  $\text{CaYAlO}_4$  single crystal has been determined at the beam line 14A of the Photon Factory, KEK, by using a small specimen of  $12 \times 12 \times 6 \mu\text{m}^3$  to reduce the extinction effect. The wavelength of 0.75 Å, which is 508 eV below the Y K edge, was selected to avoid the contamination due to the fluorescence of yttrium in the compound and to reduce the absorption effect. The least-squares refinement gave a final R value of 0.011 for 426 independent reflections in the range  $2\theta \leq 138^\circ$ . The minimum value of the secondary extinction transmission factor was 0.996 for the 200 strongest reflection when the extinction correction was included in the least-squares refinement, suggesting that the secondary extinction was practically negligible. Presence of excess Ca and deficient Y atoms from the nominal composition and associated oxygen vacancies at the apical O(2) site of the  $\text{AlO}_6$  octahedron were detected. The Ca atoms are supposed to be displaced along the c axis to accommodate the oxygen vacancy at O(2) site. Apparent large anisotropy of the thermal parameters of oxygen atoms seems to be due to the variation of possible orientations of oxygen octahedra caused by the distribution of neighboring Ca and Y atoms and oxygen vacancies. This result explains the inhomogeneously broadened line width of the R line fluorescence spectrum created by the variation of the crystal field of  $\text{Cr}^{3+}$  in Cr-doped  $\text{CaYAlO}_4$ . The SR results are compared with the Ag-K $\alpha$  rotating anode experiment. Crystal data are: tetragonal I4/mmm, a=3.6437(1) Å, c=11.8682(3) Å, Z=2, m=53.6 cm<sup>-1</sup>.