MS07.06.02 SOLID STATE CONVERSION IN SINGLE CRYSTALS OF A COORDINATION COMPOUND. Ulli Englert, Beate Ganter, and Trixie Wagner, Institut f. Anorg. Chemie, RWTH Aachen, 52056 Aachen, Germany; Wolfgang Kläui, Institut f. Anorg. Chemie, Heinrich-Heine-Universität, 40225 Düsseldorf, Germany.

Topotactic elimination of an aqua ligand in [Eu<sub>2</sub>Cl<sub>6</sub>(H<sub>2</sub>O)]BF<sub>4</sub> (cation in fig 1, <sup>1</sup>LOEt = [Co(Cp)(P<sub>2</sub>Et<sub>2</sub>O)]<sup>2+</sup>) may be achieved in single crystals under very mild conditions, i.e. simply in a stream of dry nitrogen for ca. 2 hrs at room temperature. Color and morphology of the crystals do not change, but the half-width of the reflections increases. The molecular and crystal structures of both the diqua complex in fig 1 and the monoaqua reaction product (showing shorter Co-Eu distances and a larger Co-Eu-Co angle) are closely related: The space group at 113 K is resulted to be monoclinic P2<sub>1</sub>/n [Z = 4, a= 5.7289(6), b= 7.5373(5), c= 5.3480(3), â= 90°] which is close to that in 9R BaRuO<sub>3</sub> (2.55 Å). The structure consists of an open framework of BaO<sub>6</sub> octahedra and ZrO<sub>6</sub> octahedra held together by corner sharing. The cubic phase transition is suggested to be due to a high oxygen ion mobility in the structure. The mechanism for negative thermal expansion in other oxide materials is generally restricted to much narrower temperature ranges and is anisotropic. This material therefore has potential applications in the electronics and ceramic industries as a constituent of composites with overall zero expansion.

The structure has been solved using powder X-ray and neutron diffraction data and refined at 14 temperatures from 0.3 to 693 K. The low temperature structure consists of an open framework of corner sharing ZrO<sub>6</sub> octahedra and WO<sub>4</sub> tetrahedra. Around 430 K the structure undergoes a phase transition from monoclinic P2<sub>1</sub>/n to the centric spacegroup Pm. Above the phase transition the structure can be described in terms of the same ZrO<sub>6</sub> units as at low temperature, but with a disordered arrangement of WO<sub>4</sub> tetrahedra.

The nature of this phase transition suggests a high oxygen ion mobility in the structure. The mechanism for negative thermal expansion in this material will be discussed in light of the structural results.