



Figure 1. a) Characterizing angles of a typical Cu(POP)(bipyridine)[†] cation. b) Proposed conformers of [Cu(xantphos)(Phbp)][†] and interconversion pathway through inversion of the xanthene unit.

Keywords: Copper(I), Luminescence, Light-emitting electrochemical cells, LECs, bipyridine, bisphosphanes, conformers

MS20-P5 Structure and magnetocaloric properties of Gadolinium borohydrides

Pascal Schouwink¹, Emilie Didelot¹, Yong-Su Lee², Thomas Mazet³, Radovan Cerny[†]

1. University of Geneva
2. Korea Institute of Science and Technology
3. Université de Lorraine

email: pascal.schouwink@gmail.com

Recently, a thorough understanding of the building principles underlying inorganic metal borohydrides has promoted the search for functional materials outside the well-known field of hydrogen storage.¹ In particular, we can follow very simple design strategies based on a close structural relationship to metal oxides and halides. The low molecular mass per unit of the borohydride anion can be seen as a useful property for energy-related applications in general, where light and dense materials are often favoured. Here, we have explored if borohydrides may be potential magnetic coolers. We begin our investigations on these applications with the exploration of Gd-compounds, Gadolinium being the active magnetic ion in many benchmark cryogenic coolers. The results show that, as assumed from previous studies on Mn(BH₄)₂, the exchange interaction is very low across the BH₄ linker, and these materials can hence be considered paramagnetic salts down to very low temperatures. We present an illustrative and purposeful series of novel double-cation metal borohydride salts with a high spin density per unit mass, K_jGd(BH₄)_{4+j} (j = 0, 1, 2, 3), where the molar magnetic entropy change increases with j, while the number of Gd-Gd nearest neighbours decreases simultaneously, from 6 in Gd(BH₄)₃ to 0 in the double perovskites K₃Gd(BH₄)₆, Cs₂Gd(BH₄)₆ as well as in the novel structure type K₂Gd(BH₄)₅. For j = 0,1,3 the coordination polyhedron around Gd is an octahedron, whereas the 5-fold coordination is reported in two different geometries for j = 2 in K₂Gd(BH₄)₅, which results in a remarkable magnetic entropy change -ΔS_m of 54.6 J kg⁻¹K⁻¹ (9T). The differences in j lead to different dimensionalities of the Gd-BH₄ substructure, which comprises 2D and 3D networks as well as isolated polyanions, and are reflected in magnetization measurements. In the currently investigated compounds Potassium is used as a second counter-cation in order to build the double cation salts. There is room to improve the gravimetric magnetic entropy change by substituting K⁺ for molecules lighter in weight such as NH₄⁺. Such cationic substitutions are known to occur readily in complex hydrides¹ and a perspective will be presented on the synthesis and the potential behaviour of such materials.

Keywords: Borohydride, Magnetocaloric effect, Powder Diffraction, DFT