m41.p42

Crystal engineering of chiral porous lanthanide tartrates

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Keywords: crystal engineering, polymorphic, hydrothermal synthesis, porosity

The hydrothermal stability of L-tartaric acid was established by solution CD spectrometry. Neutral tartrate solutions are stable for several days at temperatures up to 160°C, allowing exploration of hydrothermal coordination chemistry of the ligand. With lanthanide ions the chiral porous phases 1 $[Ln_2(L-TAR)_3(H_2O)_2]3H_2O$ are formed in good yield and purity for all Ln except Lu, [1]. These compounds are interesting in that two of the three tartrates have similar μ_{2} , κ^{4} binding mode in which the OH groups are chelated, whilst the third tartrate has a simpler $\mu_{2,\kappa}{}^{4}$ binding involving just carboxylate. We have shown that this can also be replaced by addition of succinate to the reaction, affording 2 [Ln₂(L-TAR)₂(SUC)(H₂O)₂]5.5H₂O. These compounds have modified channel structure and larger cavity size with almost twice as much channel water per formula unit. The open frameworks of 1 retain crystalline structure up to 250°C, although they undergo two phase transitions which involve loss of aqua ligands from the framework, [2]. The first of these steps proceeds with a change of the $\mu_{2,\kappa}^{4}$ ligand, to a more complex binding. The process appears reversible over several months at room temperature.



Packing diagrams for a) $1 [Ln_2(L-TAR)_3(H_2O)_2]3H_2O$



b) 2 [Ln₂(L-TAR)₂(SUC)(H₂O)₂]5.5H₂O

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J.A-K. Cha, J. W-H. Kan, S. Thushari, H. H-Y. Sung, I.D. Williams, *Polyhedron*, 2006, in press.