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Structural variations in terbium(III) complexes with 1,3-adamantanedicarboxylate and diverse co-ligands

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ABSTRACT

Terbium nitrate was reacted with 1,3-adamantanedicarboxylic acid (LH₂) under solvo-hydrothermal conditions with either *N,N*-dimethylformamide (DMF) or *N,N*-dimethylacetamide (DMA) as organic solvents. Hydrolysis of the latter co-solvents resulted in the formation of formate or acetate ions, respectively, which are present as co-ligands in the 1D coordination polymer [Tb(L)(HCOO)(H₂O)₂] (**1**) and the 2D assembly [Tb(L)(CH₃COO)(H₂O)] (**2**). The increase in dimensionality in the latter arises from the higher connectivity provided by acetate versus formate, the L²⁻ ligand being bis-chelating in both cases. The complex [Tb₂(L)₃(H₂O)₅][Tb₂(L)₃(H₂O)₄].3H₂O (**3**), another 1D species, crystallizes alongside crystals of **2**. Further addition of cucurbit[6]uril (CB6), with DMF as co-solvent, gave the two complexes [Tb₂(L)₂(CB6)(H₂O)₆](NO₃)₂.6H₂O (**4**) and [H₂NMe₂]₂[Tb(L)(HCOO)₂]₂.CB6.3H₂O (**5**). Complex **4** crystallizes as a 3D framework in which Tb(L)⁺ chains are connected by tetradentate CB6 molecules, while **5** unites a carboxylate-bridged anionic 2D planar assembly and layers of CB6 molecules with counter-cations held at both portals.

Keywords: Terbium(III); Coordination polymers; Structure elucidation; Carboxylate ligands

1. Introduction

The use of hydrothermal methods for the synthesis of hybrid metal–organic polymeric species is widespread, in particular in the case of those based on trivalent lanthanide cations, which elicit much interest, mostly for their distinctive optical properties.¹ However, an interesting modification of the synthesis conditions consists in using mixtures of water and organic solvents.

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