Lanthanide complexes with 5,5'-Azobistetrazolate as ligand - astounding effects influencing the coordination behavior

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Different series of lanthanide complexes with 5,5'-azobistetrazolate ($C_2N_{10}^{2-}$; ZT) as a ligand were synthesized. An astounding effect for the Tb(III) complexes with ZT is the alteration of crystallization behavior due to only picomolar amounts of Am(III).[1] Usually, the early Ln elements form complexes with a coordinative bond between the metal center and the ZT ligand, whereas the later Ln elements form salt-like compounds.[2] In contrast, the Am-doped heavy $[Tb(Am)(H_2O)_7ZT]_2ZT\cdot10H_2O$ is isostructural to the light lanthanide (Ce-Gd) ZT compounds forming a coordinate bond. (figure 1) Another surprising effect was as example that super critical CO_2 proved to be a suitable desiccant enabling the synthesis of an unusually water-poor complex of Dy(III) under aqueous conditions.[3] Usually, the ZT moiety is stabilized by H-bonds to lattice H_2O or coordination of an N-atom of the ZT to the lanthanide ion. The salt-like compound, $[Dy(H_2O)_8]_2ZT_3$, constitutes a unique exception to the above rule. (figure 2) Finally, based on the results from the series of aqueous Ln complexes with ZT as ligand,[2] the formation of the corresponding carbonates was investigated. The carbonate ZT series of the lanthanides does not show any structural changes from coordinative to salt-like behavior, like the original complexes.[4]

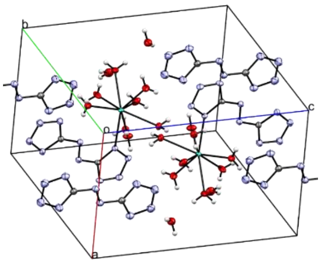

Figure 1 $[Tb(Am)(H_2O)_7ZT]_2\ ZT\cdot10H_2O$

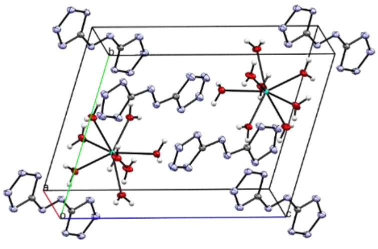

Figure 2 $[Dy(H_2O)_8]_2ZT_3$

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