**Abstract**

Two new related families of formula (GunH)3[Ln(tda)3] I and (AgunH)3[Ln(oda)3]·H2O II (Ln = La, Ce, Pr, Nd & Sm, H2tda = thiodiacetic acid, H2oda = oxydiacetic acid, GunH = guanidinium, AgunH = aminoguanidinium) have been successfully synthesized using a controlled process under oil-bath conditions (at 120 °C for a day) and characterized by various physico-chemical techniques. The structures have been solved for praseodymium and neodymium in I and for lanthanum in II, respectively, from X-ray diffraction data of single crystals. The isostructural complexes of (GunH)3[Pr(tda)3] and (GunH)3[Nd(tda)3] crystallize in the hexagonal crystal system with space group P[6 with combining macron]2c, while (AgunH)3[La(oda)3]·H2O has a triclinic symmetry with the P[1 with combining macron] space group. Generally, coordination number 6 (octahedral) and 4 (tetrahedral) structures are very rare except when bulky ligands are present. Typically, the thiodiacetate (O, S, O) and oxydiacetate (O, O, O) anions act as tridentate ligands to create monomeric structures. Surprisingly, for the first time, the thiodiacetate anion takes a somewhat rare bi-dentate (O, O) mode, leading to trigonal prismatic geometry around the metal ion even for a flexible ligand, whereas the oxydiacetate dianion (oda2−) acquires the usual nine coordinated distorted monocapped square anti-prismatic (MSAP) geometry. The simultaneous TG-DTA of type I complexes could not be recorded due to spurting, while the type II compounds show smooth and similar thermal behaviour on heating. The photo-luminescent properties of I and II have also been investigated at room temperature, which indicate that the emissions come from intra-ligand π–π\* transitions.