

ABSTRACT

The aim of this study was to explore the coordination chemistry of lanthanide with multidentate oxygen donor ligands at different reaction conditions like ligand-metal ratio, solvent system, pH of the solution and temperature. The primary focus was to obtain the novel coordination complexes in crystalline form. The good quality crystals and non reported structures thus obtained were characterized by using single crystal Bruker Kappa APEX II CCD Diffractometer at Materials Chemistry Laboratory, GC University, Lahore and Nonius Kappa-CCD Diffractometer equipped with Oxford Cryosystem at Chemical Crystallographic laboratory, University of Oxford. The complexes were also characterized by FTIR Spectroscopy, Elemental Analysis, Thermal Analysis and SQUID Analysis.

Pyridine-2,4,6-tricarboxylate (PTA) and Pyridine-2,6-dicarboxylate (PDA) owing to their variable coordination modes as well variable coordination number of Lanthanides are responsible for formation of variety of coordination complexes. Due to greater coordination modes, it is obvious that PTAH_3 are very useful means to design novel coordination polymers. Moreover, appropriate metal to ligand ratio, use of co-ligand, solvent polarity, hydrothermal conditions and longer time of reaction are requisite for generation of coordination polymers. Several Lanthanides complexes such as Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, Holmium, Erbium, and Ytterbium with PTAH_3 and PDAH_2 are synthesized and investigated. Crystal lattice constants of Isomorphous coordination polymers 16-18, 20-23 and 25-29 clearly exhibit the lanthanide contraction effect as the average Ln-O and Ln-N bond distances decrease with the series of Lanthanum to Erbium.

In novel Ce(III) 1-D and 2-D polymers of (PTA), $[\text{Ce}_2(\text{PTAH})_4(\text{OXA})(\text{H}_2\text{O})_7\text{Na}_2]_n \cdot (\text{H}_2\text{O})_4$ (1) and $[\text{Ce}(\text{PTA})(\text{H}_2\text{O})_3]_n \cdot (\text{H}_2\text{O})$ (2), PTA ligand is ten-coordinated in 1 to generate bicapped square antiprismatic CeO_8N_2 while nine coordinated in 2 to trigonal prismatic, square face bicapped geometry. The oxalate ligand in both polymers $[\text{Ce}_{1.3}(\text{PTAH})_2(\text{OXA})_2(\text{Gly})(\text{H}_2\text{O})_2]_n \cdot (\text{Gly}) \cdot (\text{H}_2\text{O})_4$ (3), $[\text{Ce}_{2.6}(\text{PTAH})_4(\text{OXA})_2(\text{H}_2\text{O})_{10}]_n \cdot (\text{MeOH}) \cdot (\text{H}_2\text{O})_7$ (4) is generated *in situ* from the cleavage and chemical rearrangement of the PTAH_3 ligand. Ce(III) ions show three different coordination numbers of seven and ten in 3 to generate pentagonal bipyramidal CeO_7 and bicapped square antiprismatic CeO_8N_2 coordination geometry while eight and ten in 4 to generate trigonal prismatic, square face bicapped CeO_8 and bicapped square antiprismatic CeO_8N_2 coordination geometry. Lanthanum(III), $[\text{La}(\text{PDA})(\text{PDAH})_2(\text{H}_2\text{O})_2]_n \cdot (\text{H}_2\text{O})_4$ (5) is 1-D polymer while Cerium(III), $[\{\text{Ce}(\text{PDAH})_3\}\{\text{Ce}(\text{PDA})(\text{ETG})(\text{H}_2\text{O})_3\}]_n \cdot (6\text{H}_2\text{O})$ (6) is a mixed-ligand binuclear Complex of pyridine-2,6-dicarboxylate (PDA) exhibiting tricapped trigonal prismatic CeO_6N_3 and Square-face monocapped antiprism CeO_8N coordination geometries. Five (7-11) novel heteronuclear M(I)-Ln(III) (M = Na; Ln = Nd, Pr, Ce, Ho and Yb) 3-D coordination polymers based on PDA are synthesized by using sodium azide as a source

of sodium metal. PDA adopts four kinds of coordination modes while Ln(III) is nine coordinated to generate tricapped trigonal prismatic LnO_6N_3 geometry. Sodium metal show five and six coordination numbers to generate square pyramidal NaO_5 , trigonal prismatic NaO_6 and octahedral NaO_6 geometries. Each Ho(III) ion is nine-coordinated (12). Praseodymium binuclear $[\text{Pr}_2(\text{PDA})_3(\text{PDAH})(\text{H}_2\text{O})_4]_n \cdot (\text{PYDH})(\text{H}_2\text{O})_8$, 1-D coordination polymer derived from PDA is obtained by hydrothermal synthesis (13). Each Pr(III) ion is nine coordinated to tri-capped trigonal prism PrO_6N_3 and PrO_8N Square-face monocapped antiprismatic geometries. Praseodymium complex $[\text{Pr}(\text{PTAH})(\text{H}_2\text{O})_3] \cdot (\text{H}_2\text{O})_2$ was synthesized using (1:1) ligand-metal ratio (14). Cerium 1-D polymer $[\text{Ce}(\text{PTA})(\text{H}_2\text{O})_5]_n \cdot (\text{H}_2\text{O})_4$ was synthesized by using (4:1) ligand-metal ratio (15). Ce(III) ion is nine coordinated with tricapped trigonal prism geometry. 3-D (16-18) coordination polymers $[\text{Ln}_4(\text{PTAH})_6(\text{H}_2\text{O})_9(\text{NH}_3)]_n \cdot (\text{H}_2\text{O})_6$; where (Ln(III) = Ce, Nd, and La) are derived heating in an autoclave under autogenous pressure. Two types of coordination modes, with one novel mode, to generate trigonal prismatic, square face bicapped CeO_7N_2 and monocapped tetragonal prismatic CeO_9N geometries are observed for each of three polymers. 17 % void volume (solvent molecule) is calculated by using Platon. Four complexes $[\text{Ln}(\text{PDA})_2(\text{PDAH}_2)] \cdot (\text{DMA})$; where (Ln(III) = Ce, Ho, Sm and Nd) (20-23) and a ytterbium complex $[\text{Yb}(\text{PDA})_3]_n \cdot (\text{DMA})_3(\text{H}_2\text{O})_4$ (19) are obtained under solvothermal condition. The dimethylamine was generated in situ from the cleavage and chemical rearrangement of dimethylformamide. Dimethylamine and water molecules link neighbouring polymeric chains via $\text{N-H} \cdots \text{O}$ and $\text{O-H} \cdots \text{O}$ hydrogen bonds into a two-dimensional framework for 19. In (24) Erbium complex $[\text{Er}(\text{PDAH})_3] \cdot (\text{H}_2\text{O})_{10}$ having ten non-coordinated water molecules are responsible for strong Hydrogen bonding between oxygen atoms of carboxyl groups to generate 3-D layer filled packing diagram with crystal water molecules. Each metal is nine coordinated to generate most common tricapped trigonal prismatic LnO_6N_3 geometry for conventional tridentate O, N, O coordination mode. Five (25-29) 2-D coordination polymers $[\text{Ln}(\text{PDA})(\text{PDAH})]_n$; where (Ln(III) = Er, Gd, Tb, Eu and Pr) are obtained by hydrothermal synthesis. Each metal is eight coordinated to trigonal prismatic, square face bicapped LnO_6N_2 geometry. Adjacent 2-D chains are further extended to a 3-D hydrogen-bonded layered network through the intermolecular π - π interactions and $\text{C-H} \cdots \text{O}$ hydrogen bonds.

TGA analyses are consistent with the proposed stoichiometry. Most of the complexes showed significant thermal stability. Superconducting Quantum Interference Device (SQUID) analysis has revealed that Curie-Weiss law behavior is observed at different temperature ranges with negative value of Weiss constant θ . In the high temperature end (300 K) $\chi_m T \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ provides an effective magnetic moment μ_{eff} in (μ_B) Bohr magneton which are slightly larger or smaller than the expected value of per formula for lanthanide ions in the ground state. The overall behavior of $\chi_m T$ with temperature and negative value of Weiss constant is typical for the presence of antiferromagnetic exchange coupling interactions.