# ABSTRACT

Lanthanide complexes are of great scientific interest because of their potential applications in the area of catalysis, photochemistry, contrast agents, ion exchange, supramolecular chemistry, luminescence and pharmacology. Lanthanides are the hard acids and prefer to combine with hard bases like oxygen. The best suitable ligands are carboxylic acids and aminocarboxylic acids owing to the great variety of binding modes, which satisfy the high coordination number requirements of lanthanides.

In the present study, some new lanthanide complexes of dicarboxylic acids and aminocarboxylic acids were synthesized at atmospheric pressure by using different metal-ligand ratios under various pH conditions. The desired products were crystalline compounds, which were characterized by X-ray crystallography, elemental analysis, infrared spectroscopy, thermal analysis, magnetic susceptibility measurements and vibrating sample magnetometer analysis. The present study includes the following newly synthesized and characterized lanthanide complexes.

Two isostructural one-dimensional coordination polymers of 2-aminobenzoic acid $[Ce(C_7H_6NO_2)_3]_n$ **(I)** and $[Pr(C_7H_6NO_2)_3]_n$ **(II)** were described. The metal ions adopted distorted capped square anti-prismatic $MO_9$ coordination geometries. The anthranilate ligands bridged the metal ions in bridging-bidentate (O, $\mu_2$-O′) mode to generate [010] chains in the crystal and each ligand feature an intramolecular N–H···O hydrogen bond. It was notable that two very similar, but crystallographically distinct chains occur in the unit cell.

Cerium(III) and Ytterbium(III) complexes of nicotinic acid, $Ce_2(C_6H_4NO_2)_6(H_2O)_4$ **(III)** and $Yb_2(C_6H_4NO_2)_6(H_2O)_4$**(IV)** were synthesized. The single crystal analysis revealed that complexes were dinuclear bridged by carboxylate groups of nicotinic acid molecules through quadruple mixed bridging {double bidentate bridging ($\mu_2$-$\eta^1\eta^1$)$_2$ double tridentate bridging ($\mu_2$-$\eta^2\eta^1$)$_2$} in **(III)** and quadruple bridging ($\mu_2$-$\eta^1\eta1$)$_4$ in **(IV)**. Thus the cerium ions were nine coordinated in **(III)**, while the ytterbium ions were eight coordinated in **(IV)**.

Four novel glutarate coordination polymers $Pr(C_5H_6O_4)(C_5H_7O_4)(H_2O)]\cdot H_2O$ **(V)** and $[Nd(C_5H_6O_4)(H_2O)_4]\cdot Cl$, **(VI)**, $[Eu(C_5H_6O_4)(H_2O)_4\cdot Cl]$, **(XV)** and $[Tb(C_5H_6O_4)(C_5H_7O_4)(H_2O)_2]_n$ **(XVI)** were described. Compound **(V)** was a three-dimensional coordination polymer incorporating chains of edge-sharing $PrO_{10}$ polyhedra. Its glutarate ion adopted an extended conformation, whereas its hydrogen glutarate ion takes on a twisted conformation. O–H···O hydrogen bonds are seen in the crystal structure, which features small channels occupied by water molecules. Compound **(VI)** was a one-dimensional coordination polymer containing double chains incorporating pairs of edge-sharing $NdO_9$ polyhedra linked by glutarate dianions. A network of O–H···O and O–H···Cl hydrogen bonds helped to consolidate the structure. Compound **(XV)** was isostructural with compound **(VI)**. Compound **(XVI)** was one dimensional coordination polymer in which the terbium ion was coordinated by three bidentate chelating carboxylate groups, one bridging carboxylate O atom and two water molecules, to generate a $TbO_9$ polyhedron.

Three novel malonate coordination polymers of lanthanide$\{[Nd(C_3H_2O_4)](OH_2)_3Cl](H_2O)_{0.5}\}_n$ **(VII)** and $\{[Ho(C_3H_2O_4)]OH_2)_4[NO_3\}_n$ **(VIII),** and $\{[Gd(C_3H_2O_4)(OH_2)_4][NO_3]\}_n$, **(IX)** were synthesized. Structural analysis revealed that compound **(VII)** had 1D structure forming zigzag chain of Nd(III) atoms which extended into 3D supramolecular network via hydrogen bonds through coordinated non coordinated water molecules and chloride ligands. Compounds **(VIII)** and **(IX)** were isostructural having 2D coordination networks forming six and fourteen membered rings. The 2-dimensional sheet with H-bonding extended the structure into three dimensions via nitrate anions and water molecules.

Two homodinuclear erbium (iii) $[Er(2AMB)_3.(H_2O)_2]_2.3H_2O$ **(X)**, $[Er(4AMB)_3.(H_2O)_2]_2.2H_2O$ **(XI)** and three ytterbium(iii) complexes, $[Yb_2(2AMB)_6(H_2O)_4]\cdot 2C_2H_6O$ ( **XII**) and$Yb_2(3AMB)_6(H_2O)_4]\cdot 3H_2O$ **(XIII)**$[Yb_2(4AMB)_6.4(H_2O)].2(H_2O)$ **(XIV)** (2AMB = 2-amino-benzoate anion, 3AMB = 3-aminobenzoate anion, 4AMB= 4-aminobenzoate anion) have been synthesized. The $Ln^{3+}$ions in these complexes were bridged through double bidentate bridging $(\mu 2\text{-}\eta^1\eta^1)_2$.Thus each metal atom was eight coordinated

adopting $MO_8$ distorted dodecahedral geometry (Where M= Er, Yb) having two O atoms from bridging carboxylate, four O atoms from the chelating carboxylate and two O atoms from aqua ligands. The crystal structures were stabilized by N–H···O, O–H···O, O–H···N, and C–H···O hydrogen bonds, C–H···π interactions and weak π–π stacking interactions.

Thermal analyses were in agreement with the proposed stoichiometry. The magnetic moment of the complexes **III-X** and **XII** were measured at room temperature. The experimentally measured effective magnetic moment values for these complexes showed that the energy level of Ln(III) ions were not disturbed by the ligands and behaved just like free ions. The magnetic hysteresis curves for compounds **III**, **IV, V and VI** were drawn by using vibrating sample magnetometer measurements, which exhibited ferromagnetic behavior with high coercivity.