

ABSTRACT

Multinuclear coordination aggregates (CAs) consisting of different spin carriers led to a wide variety of structural topology and interesting properties, such as single molecule magnet, magnetic cooler, photophysical, catalytic and biomedical application. The 3d-4f heterometallic aggregates are gaining importance during the last two decades due to their fascinating coordination behaviour, interesting molecular structures and potential for molecular magnet behaviour. The complexes bearing 4f ions show stimulating magnetic properties due to the presence of a high ground state spin (S), and high magnetic anisotropy (D), while coupling with adjacent 3d ions for ferromagnetic interactions. Compartmentalized ligands holding specific coordination pockets with the ability of selective binding of 3d and 4f ions are the preferred choice for the synthesis of new family of 3d-4f complexes. In this regard, phenol based flexible organic side arm bearing Schiff bases are of great choice to stabilize hitherto unknown structures. Ancillary bridges like hydroxido, alkoxido, oxido, carboxylato etc. either *in situ* generated or externally added can further stabilize the multinuclear end products. The X-ray quality single crystal growth technique also play a crucial role after the solution state synthesis using selected ligands and metal ion salts in definite molar ratio. Other parameters such as solvent, temperature, pH, and reaction time also play a significant role in achieving the reaction products. In this thesis, three phenol-based ligands with two dedicated coordination pockets bearing N and O donors have been examined in the presence of available ancillary ligands. The simplest complex consisting Co and Ln ions side by side in a single entity have been synthesized from semicarbazide arm bearing Schiff base ligand. Remaining coordination sites were captured by the 3d ion salt derived carboxylate groups. Stabilization of these smaller entities inhibited further aggregation pathway and showed both ferro and antiferromagnetic interactions within the binuclear Co-Ln site. Hydroxido-bridged cubic Ni_2Ln_2 family of complexes have been synthesized from the same semicarbazide arm bearing ligand and characterized by X-ray structure determination and variable temperature magnetic susceptibility measurement. Amino alcohol arm bearing ligand was scrutinized for the synthesis of a series of Ni_4Ln_4 aggregates from the bridging connections of carboxylate and hydroxide groups dangling from two cuboidal units. The magnetic property was comparable with the Ni_2Ln_2 type due to the presence of nearly similar bond distance and angles. Novel octanuclear Co_4Ln_4 and heptanuclear Ni_3Ln_4 complexes have been synthesized from the same ligand system having carboxy side arm. The multiple number of hydroxy and carboxylate groups along with ligand carboxy arms concomitantly acted for the stabilization of this series. All these complexes have been characterized from X-ray structure determinations and variable temperature magnetic susceptibility measurements. SMM behaviour was observed only for anisotropic Dy^{III} analogue in complex Co_4Dy_4 due to collinear arrangement of the anisotropy axes.

Keywords: Multinuclear aggregate; Schiff base; Self-aggregation; Ancillary ligand; X-ray structure; Variable temperature; Magnetic susceptibility.