

The application of coordination chemistry principles to material synthesis

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Extensive studies of single-molecule magnets (SMMs) have evoked the emergence of a new research field: molecular spintronics, where SMMs are used as the core building blocks for recording, transport and sensing devices [1 - 3]. Typical SMMs comprise of organic molecules and 3d transition metal (TM) cores (especially Mn, Fe, and Co) and their electronic and magnetic properties can be conveniently tuned by selecting appropriate molecules or TM atoms [2, 3]. Coordination complexes of paramagnetic metal ions of the second and third transition series have attracted considerable interest due to strong spin - orbital interactions giving rise to a significant magnetic anisotropy. The study of paramagnetic compounds based on 4d and 5d transition metals is an emerging research topic in the field of molecular magnetism. An essential driving force for the interest in this area is the fact that heavier metal ions introduce important attributes to the physical properties of paramagnetic compounds.

The magnetic properties of the lanthanides are due to the electrons in the partial filled 4f shell. The magnetic properties of the first-row transition metals are due to the electrons in the partial filled 3d shell. There are two important differences between the 3d shell and the 4f shell. The first difference is that d electrons have much greater overlap with their neighboring atoms than f electrons do. This means that d bands are not as localized as f bands are. The second difference is that the spin-orbit coupling is much stronger in the lanthanides than in the 3d transition metals.

The possibility of constructing single molecule magnets (SMMs) using a single lanthanide ion was first demonstrated experimentally on phthalocyaninato-lanthanide complexes having a double-decker structure [4]. The lanthanide complexes showing SMM behavior have significantly large axial magnetic anisotropy, which is given to the complexes by essentially different mechanism than those of the well-established 3d metal-cluster SMMs. In the 3d cluster SMM cases, the easy-axis-type magnetic anisotropy, which is represented by the negative zero-field-splitting constant D , is caused by the magnetic interactions among high-spin 3d metal ions in a molecule. In the lanthanide single-ionic SMM cases, on the other hand, such anisotropy is given by the ligand field (LF) in which the lanthanide ion is placed.

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