

Chiral heterometallic Cu/Ln complexes from enantiopure Schiff base ligands

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Chirality is an intrinsic property of the matter and is important in chemistry, biology, and physics, because it can affect the properties and reactivity of molecules. Coordination metal complexes which combine chirality with magnetic, optical, and electrical properties, have found great attention in recent years and constitute a new and fast-growing class of multifunctional molecular materials for applications in enantioselective synthesis, pharmaceutical development and productions, sensors and devices, spintronics, and environmental pollutants. Metal complexes are prepared by a bottom-up approach based on coordination chemistry methods. The heterometallic 3d/4f complexes combine the electronic properties of the 3d ions with the anisotropy of the lanthanides and by the proper use of chiral ligands constitute new multifunctional materials for potential applications.

We have used enantiopure Schiff base ligands, based on aromatic aldehydes and chiral primary amines, in Cu/Ln chemistry and have isolated families of chiral heterometallic complexes, $[\text{Cu}_8\text{Ln}_4(\text{OH})_8(\text{OMe})_4(\text{O}_2\text{CBut})_8(\text{L1-S or L1-R})_4(\text{H}_2\text{O})_4]$ with $\text{Ln}^{\text{III}}=\text{Gd}$, Tb, Dy, Ho, Er, and Y [1], $[\text{Cu}_4\text{Ln}_2(\text{OH})_2(\text{O}_2\text{CBut})_{6+x}(\text{NO}_3)_{2-x}(\text{L1-S or L1-R})_2(\text{H}_2\text{O})_2]$ with $\text{Ln}^{\text{III}} = \text{Dy}$, $x = 0, 1$, and $[\text{Cu}_2\text{Ln}_4(\text{OH})_4(\text{O}_2\text{CPh})_4(\text{NO}_3)_2(\text{L2-S or L2-R})_2(\text{L}')_2(\text{H}_2\text{O})(\text{MeOH})]$ with $\text{Ln}^{\text{III}} = \text{Gd}$, Tb, Dy, Ho. The complexes of each family are isomorphous, and crystallize in non-centrosymmetric space groups in enantiomeric conformation. The complexes were characterized by single-crystal and powder X-ray diffraction studies. The CD spectroscopic measurements in solution confirmed that the complexes retain their structure and chirality. The magnetic study of the complexes reveals that their properties are determined by the nature of the lanthanide ion and the type of interaction between the Cu^{II} and Ln^{III} ions.

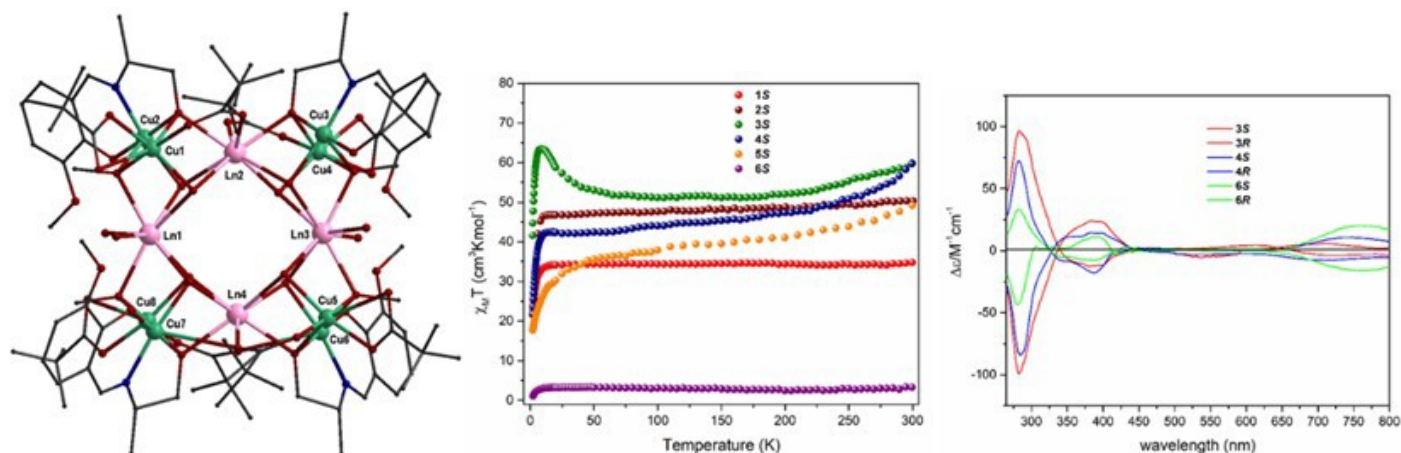


Figure 1. Partially labelled plot of the molecular structure of $[\text{Cu}_8\text{Ln}_4(\text{OH})_8(\text{OMe})_4(\text{O}_2\text{CBut})_8(\text{L1-S or L1-R})_4(\text{H}_2\text{O})_4]$ complexes (left), their magnetic susceptibility measurements in the form of $\chi_M T$ vs T plots (middle), and the solution CD spectra of enantiomeric pairs of complexes (right).

[1] Dermitzaki, D., Panagiotopoulou, A., Pissas, M., Psycharis, V., Raptopoulou, C.P. (2024) *ChemPlusChem* e202400123 (10 pages).