

New Re(IV)-Ln(III)-based complexes: structural characterization and magnetic properties

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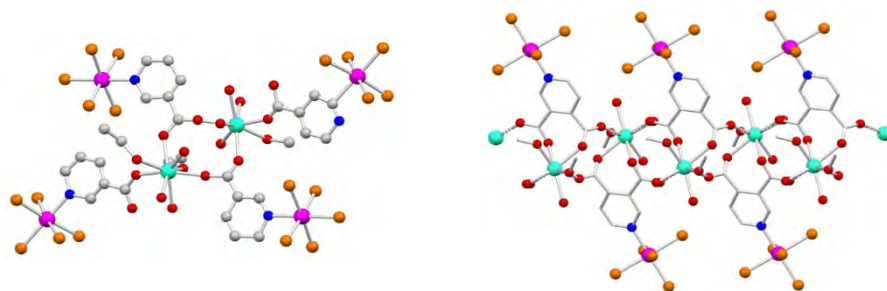
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Molecular magnetism has mostly focused on *3d* and *4f* complexes. Magnetic studies on *4d-4f* or *5d-4f* compounds are comparatively scarce. The interesting results recently reported using heavier transition metal ions as spin carriers have stimulated their use as building blocks to develop new magnetic heterometallic architectures.[1,2] Among them, rhenium(IV) is an interesting choice. It is a $5d^3$ ion with three unpaired electrons in its most common octahedral coordination geometry, and due to its high spin-orbit coupling constant, Re(IV) presents also high magnetic anisotropy of the ground state.[2] Thus, we have designed two suitable metalloligands of formula $[\text{ReBr}_5(\text{Hnic})]^-$ and $[\text{ReBr}_5(3,4\text{-H}_2\text{pydc})]^-$, based on 3-pyridinecarboxylic acid (Hnic) and 3,4-pyridinedicarboxylic acid (3,4-H₂pydc) respectively. The reaction of these metalloligands with Ln(III) ions (Ln= Dy, Tb, Ho, Gd, Eu, Ce) has led to the obtention of a number of Re(IV)-Ln(III) systems presenting two different molecular topologies depending on the metalloligand. Namely, the use of $[\text{ReBr}_5(\text{Hnic})]^-$ allowed the isolation of discrete hexanuclear complexes of general formula $(\text{NBu}_4)_4[\text{ReBr}_5(\text{Hnic})]_2\{\text{Ln}(\text{EtOH})_2(\text{H}_2\text{O})_3\}_2[\text{ReBr}_5(\text{nic})]_4$ (systems *type-1*), while coordination polymers of general formula $[\text{Ln}(\text{DMF})_3(\text{MeOH})][\text{ReBr}_5(3,4\text{-pydc})]_n \cdot \text{DMF}$ (DMF = N,N'-dimethylformamide) were obtained with $[\text{ReBr}_5(3,4\text{-H}_2\text{pydc})]^-$ (systems *type-2*).

Single crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Firstly, the data confirms that complexes belonging to the same type of systems are isostructural among them, independently from the identity of the Ln(III). This is a remarkable feature concerning the further analysis of the magnetic properties. The crystal structure of *type-1* complexes reveals that the asymmetric unit consist of one anionic hexanuclear complex (see figure) together with two units of the anionic Re(IV)-based metalloligand and four tetrabutylammonium cations. The structure of *type-2* compounds can be described as a central-extended linear motif of Ln(III) ions connected by the bridging-rhenium metalloligands peripherally disposed to the motif (see figure).

Magnetic properties of the *type-1* and *type-2* compounds were studied on microcrystalline samples in a temperature range from 2 to 300 K. AC susceptibility measurements in presence of a static magnetic field showed frequency-dependent out-of-phase signals at the lowest temperatures for both *type-1* and *type-2* Dy-based compounds.

Figure 1. Molecular structure of the hexanuclear species (left); Molecular structure of the linear compounds (right). Color code: Re



(pink); Ln (light green); Br (orange); N (blue); O (red); C (grey). Hydrogen atoms and DMF molecules have been omitted for a better view.

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[2] C. Pejo, G. P., M. G. F. Vaz, R. González, et al, *Chem. Eur. J.*, 21, 8696-8700.

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