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

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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 5d³ 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 [ReBr₅(Hnic)]⁻ and [ReBr₅(3,4-H₂pydc)]⁻, based on 3-pyridinecarboxilic acid (Hnic) and 3,4-pyridinedicarboxilic acid (3,4-H₂pydc) respectively. The reaction of these metaloligands 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 metaloligand. Namely, the use of [ReBr₅(Hnic)]⁻ allowed the isolation of discrete hexanuclear complexes of general formula (NBu₄)₄[ReBr₅(Hnic)]₂{[Ln(EtOH)₂(H₂O)]₂[ReBr₅(nic)]₄} (systems type-1), while coordination polymers of general formula [Ln(DMF)₃(MeOH)][ReBr₅(3,4-pydc)]ₖ·DMF (DMF = N,N’-dimethylformamide) were obtained with [ReBr₅(3,4-H₂pydc)]⁻ (systems type-2).

Single crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). 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 tetrabutylamonium 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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