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PAPER

Octahedral niobium cluster-based solid state halides and oxyhalides: effects of the cluster condensation *via* an oxygen ligand on electronic and magnetic properties†

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The influences of an oxygen ligand on the structural, magnetic and electronic properties of octahedral niobium cluster-based oxides and oxychlorides are reported. The Nb₆ metal cluster is edge-bridged by twelve inner ligands and additionally bonded to six apical ligands to form Nb₆L₁₂L₆^a units (L = Cl, O) wherein oxygen and chlorine are perfectly ordered. Oxygen favours the interconnection of clusters *via* double O^{i-a}/O^{a-i} bridges in a similar way to the double S^{i-a}/S^{a-i} bridges found in Chevrel phases based on face capped Mo₆L₈L₆^a units. Periodic density functional theory (DFT) calculations confirm that increasing the number of inner oxygen ligands at the expense of chlorine atoms favours the 14 metal-electron (ME) count per octahedral cluster unit. It is also shown that weak interactions occur between neighbouring clusters. Indeed, magnetic measurements performed on A_xNb₆Cl₁₂O₂ (A = Rb, x = 0.816(8); A = Cs, x = 1) series containing 15-ME species evidence antiferromagnetic interactions at low temperatures. Broken-symmetry DFT calculations of exchange parameters within spin dimer analysis confirm the experimental results.

Introduction

The term *metal atom cluster*, introduced by F. A. Cotton in the early 1960's, defines a finite group of metal atoms held together *via* metal–metal bonds.¹ Typical examples are found for octahedral nano-sized metallic clusters of transition elements which are easily obtained by solid state synthesis at high temperatures. They are associated with halogen or chalcogen ligands to form [(M₆L₁₂)L₆^a]ⁿ⁻ and [(M₆L₈)L₆^a]ⁿ⁻ units (a = apical, i = inner).² As sketched in Fig. 1, M₆ clusters are bonded to six terminal ligands (L^a) in both kinds of units but they are edge-bridged by twelve inner ligands (Lⁱ) in the [(M₆L₁₂)L₆^a]ⁿ⁻ unit (M = Nb, Ta, W) and face-capped by eight inner ligands (Lⁱ) in the [(M₆L₈)L₆^a]ⁿ⁻ unit (M = Mo, W, Re). The intrinsic properties of M₆ cluster units—one- or two-electron reversible redox process, magnetism and luminescence—depend on the

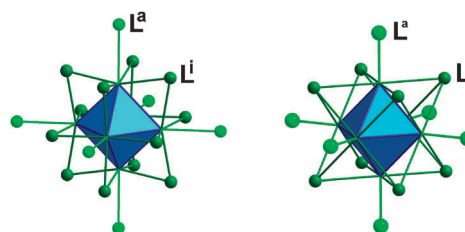


Fig. 1 Representation of edge-bridged (M₆L₁₂)L₆^a (left) and face-capped (M₆L₈)L₆^a (right) units.

nature of the metal and the ligands. The solubilisation of M₆ solid state compounds provides [(M₆L₁₂)L₆^a]ⁿ⁻ or [(M₆L₈)L₆^a]ⁿ⁻ discrete building blocks in solution with specific physico-structural properties that can be used, *via* soft chemistry routes, in the design of hybrid organic/inorganic assemblies,³ organometallic stars and dendrimers,^{4,6} luminescent nanoparticles,^{7,8} liquid crystals^{9,10} or coordination polymeric framework^{11–13} as well as molecular junctions.^{14,15}

The structures of niobium octahedral cluster halides are built up from either discrete or interconnected units in one, two or three directions of space (noted 1-, 2- and 3D respectively) by common L^{a-a} apical ligands (1-D: Cs₂Nb₆Br₅F₁₂¹⁶ (Cs₂Nb₆Br₅F₇F_{2/2}^{a-a}F₄ according to the Schäfer notation),² 2-D: Li₂Nb₆Cl₁₆ (Li₂Nb₆Cl₁₂Cl_{4/2}^{a-a}Cl₂),¹⁷ 3-D: Nb₆F₁₅ (Nb₆F₁₂F_{6/2}^{a-a})¹⁸ and Na₂NbF₆–Nb₆F_{12-x}X_xF₆ (X = Cl, Br)^{19,20} series). In the Nb₆L₁₅ 3-D compounds (Nb₆L₁₂L_{6/2}^{a-a}),

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† We dedicate this work to Didier Astruc on the occasion of his 65th birthday.