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 Nb6L12O6 units (L = Cl, O) wherein oxygen and chlorine are perfectly ordered. Oxygen favours the interconnection of clusters via double Oi–a/Oa–i bridges in a similar way to the double S i–a/Sa–i bridges found in Chevrel phases based on face capped Mo6L12O6 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 A2Nb6Cl12O2 (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 [(M6Li)xL12]z− and [(M6Li)xL12]z− units (a = apical, i = inner).2 As sketched in Fig. 1, M6 clusters are bonded to six terminal ligands (L1) in both kinds of units but they are edge-bridged by twelve inner ligands (L2) in the [(M6Li)xL12]z− unit (M = Nb, Ta, W) and face-capped by eight inner ligands (L2) in the [(M6Li)xL12]z− 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 nature of the metal and the ligands. The solubilisation of M6 solid state compounds provides [(M6Li)xL12]z− or [(M6Li)xL12]z− 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 crystals9,10 or coordination polymeric framework11−13 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 L2−a apical ligands (1-D: Cs2Nb6Br6F12.16 (Cs2Nb6Br6F12.16 according to the Schafer notation),2 2-D: Li2Nb6Cl16 (Li2Nb6Cl12(Cl42C12)2),17 3-D: Nb6F15 (Nb6F12F6.2)18 and Na2NbF6–Nb6F12−XnF6 (X = Cl, Br)19,20 series). In the Nb6L13 3-D compounds (Nb6L13L18),