



Account/Revue

Dinuclear manganese, iron, chromium, and cobalt complexes derived from aroylhydrazone ligands: Synthetic strategies, crystal structures, and magnetic properties

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ARTICLE INFO

Article history:

Received 30 June 2015

Accepted after revision 10 September 2015

Available online 19 November 2015

Keywords:

Coordination chemistry

Transition metals

Ligand design

Crystal structure

Magnetic properties

ABSTRACT

Coordination clusters of 3d metals continue to attract the intense interest of the scientists from the synthetic inorganic chemistry, bioinorganic chemistry and molecular magnetism communities. We review here the synthetic strategies employed in a continuous effort to obtain new and potentially magnetically interesting dinuclear molecules based on iron, manganese, chromium, and cobalt metal ions. The reported systems are pure homometallic 3d materials. We have focused on describing aspects of the synthesis, the crystal structures and the magnetic behaviour of these coordination compounds with low nuclearity. A deep solid-state and magnetic characterization of these systems has allowed us to gain evidence regarding the role played by weak exchange interactions and geometrical factors on the slow dynamics of the magnetization. In addition, the analysis through ab initio calculations has provided a valuable insight into the influence of organic periphery, bridging ligands, and remote substituents on the exchange coupling constant (J). In the case of a dinuclear complex based on manganese, the largest ferromagnetic interaction between two Mn^{III} has been observed ($J = 19.7 \text{ cm}^{-1}$).

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1. General details and prospects

Coordination clusters of paramagnetic 3d metal ions continue to attract significant interest owing to their aesthetically pleasing structures and fascinating physical properties as well as their relevance to metalloenzymes [1]. When the intermetallic bridges of this class of compounds create a superexchange pathway, this often leads to isotropic couplings and, in some cases, slow relaxation of the magnetization to make a so-called single-

molecule magnet (SMM) [2]. Such compounds (SMMs) are promising candidates for applications in molecular spintronics, high-density data storage and quantum information processing [3]. In the molecular magnetism field, compared to those of other transition metals, complexes of manganese are often characterized by large spin ground states, and this, in conjunction with the presence of Jahn–Teller distorted Mn^{III} ions, makes manganese polynuclear complexes ideal candidates for single-molecule magnet behaviour [4], the archetype of SMMs being the $[\text{Mn}_{12}\text{O}_{12}(\text{AcO})_{16}(\text{H}_2\text{O})_4]$ reported in 1993 by Christou, Sessoli, Gatteschi, Hendrickson et al. [5].

The design and synthesis of molecular materials with predictable magnetic properties continues to remain a challenging task because structural factors governing

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exchange coupling between paramagnetic centres are complex and elusive. The use of assisted self-assembly and site-targeted reactions has provided interesting examples of high-nuclearity clusters, mostly characterized by large magnetic moments in the ground state (S). But, to better gain evidence regarding the role played by weak exchange interactions and geometrical factors on the slow dynamics of the magnetization, systems based on small nuclearity are necessary, since they are less complex systems.

In recent decades, a class of complexes characterized by a small number of paramagnetic transition metal ions (<30) connected with each other by simple bridging anions, typically O^{2-} , HO^- or CH_3O^- , i.e. oxo, hydroxo, and methoxo bridges, respectively, has provided valuable insights as simple models of more complex systems [1]. These promising advances in materials science have stimulated us in the research effort on dinuclear complexes, the simplicity of which favours studies of structure-coupling constant relationships and time-consuming theoretical calculations [6].

In the field of coordination chemistry in general and of molecular magnetism in particular, it is noticeable that chemists largely prefer to use either commercially available ligands or those that can be easily synthesized, in order to produce systems based on coordination chemistry. It is worth noting, in passing, that this is unfortunate since it leads to the impression that most compounds resulting from modern coordination chemistry approaches are discovered by luck rather than by an informed knowledge of how a system with a given set of component might behave. In its defence, however, this approach avoids the difficult and often unfruitful step of synthesizing a tailored ligand, which could easily possess coordination properties not predictable from the “paper chemistry” ideas used in its design.

In 2006, we reported the $[Mn_2]$ system $[Mn_2(HL_A)_4(\mu-OCH_3)_2]$ **C1** ($H_2L_A = 2$ -salicyloylhydrazono-1,3-dithiolane or N' -(1,3-dithiolan-2-ylidene)-2-hydroxybenzohydrazide), the core of which consists of two trivalent manganese ions that are connected via two methoxo bridging co-ligands (originating from MeOH solvent). The

two Mn^{III} centres are ferromagnetically coupled, with a spin ground state of $S = 8/2$, which was corroborated by EPR spectroscopy and DFT calculations that confirm also the negative sign of the $D_{S=4}$ parameter [7]. This system is especially appealing since it displays the largest coupling constant so far reported for a Mn^{III} – Mn^{III} intramolecular interaction: $J = 19.7 \text{ cm}^{-1}$ (for the spin Hamiltonian used see section 3.2 below and ref.[7] as well). The strength of this interaction is associated with the peculiar unsymmetrical arrangement of the ligands driven by (the) two non-classical CH– π hydrogen bonds imposed by the dithiolane ligand (see its molecular structure in the solid state, Fig. 1).

With all this in mind, we nonetheless felt it worthwhile to explore ways using designed ligands and in which we could prepare 3d-based isostructural analogues of pioneer $[Mn_2]$ system, to better understand the roles played by the organic periphery, the bridging ligands, and the remote substituents on the exchange coupling constants between the two coordinated metal centres.

It is shown that the $[Mn_2]$ system framework is both magnetically and structurally robust in the solid state, indicating that the $[Mn_2]$ system is an excellent platform for peripheral chemical engineering in the development of magnetic materials and devices. We have therefore embarked on a program of exploring the coordination chemistry of various novel aroylhydrazone ligands (representative examples are given in Fig. 2), so far with a range of functional groups, aiming at accessing new dinuclear compounds with a strong ferromagnetic exchange coupling scenario, with, expectedly, the preparation of a compound with two transition metals showing a SMM behaviour and/or an intramolecular coupling constant larger than the record value $J = 19.7 \text{ cm}^{-1}$ (so far held by our $[Mn_2]$ system **C1**). Such ferromagnetically coupled systems could therefore be incorporated into crystal lattices along with conducting molecules, and be addressed on a variety of surfaces including biological molecules, which may lead to the formation of innovative magnetic/conducting bifunctional materials [8]. One should note, however, that to better get insights in the coordination chemistry of magnetic materials, synthetic strategies must

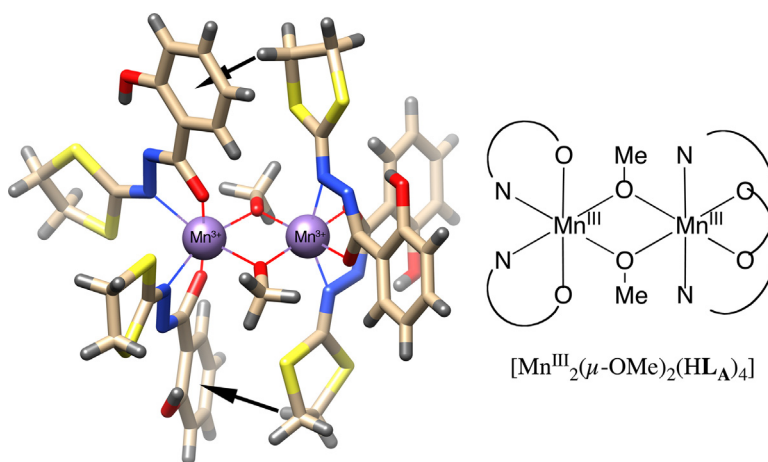


Fig. 1. (Colour online.) Left: Molecular structure of the $[Mn^{III}$ – $Mn^{III}]$ system framework **C1**. Ligand = HL_A^- ($H_2L_A = 2$ -salicyloylhydrazono-1,3-dithiolane). Solvent molecules have been omitted for clarity. The black arrows represent the CH– π hydrogen bonds. Right: ChemDraw representation of the complex **C1**.

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