



Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Review Articles

Low-dimensional heterometallic assemblies involving orbitally degenerate cyanometallate and displaying slow magnetic dynamics

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ARTICLE INFO

Article history:

Received 5 July 2017

Received in revised form 19 November 2017

Accepted 5 December 2017

Available online xxx

Keywords:

Molecular magnetism

Single-molecule magnets

Single-chain magnets

Magnetic anisotropy

Cyanometallates

Orbitally degenerate complexes

ABSTRACT

Low-dimensional (0D and 1D) molecular nanomagnets involving homoleptic cyanometallates as orbitally degenerate causing highly anisotropic magnetic exchange interactions are considered. Special attention is paid to the origins of the magnetic anisotropy for two groups of metallogligands. The first includes hexacyanometallates of Fe, Ru and Os having octahedral geometry of coordination polyhedron, while the second integrates the heptacyano complexes of Mo and Re in pentagonal bipyramid coordination environment.

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Contents

1. Introduction	00
2. Hexacyanometallate based assemblies	00
2.1. SMMs incorporating $[M(CN)_6]^{3-}$	00
2.2. SCMs incorporating $[M(CN)_6]^{3-}$	00
3. Heptacyanometallate based assemblies	00
3.1. LD magnets involving heptacyanomolibdate $[Mo(CN)_7]^{4-}$	00
3.2. LD magnets involving heptacyanorhenate $[Re(CN)_7]^{3-}$	00
4. Conclusion	00
Acknowledgment	00
Appendix A. Supplementary data	00
References	00

1. Introduction

The synthesis and study of molecular magnetic materials has attracted much attention over the past few decades [1–7]. It is closely related to the extraordinary possibilities of organic and supramolecular coordination chemistry for design of different heterometallic assemblies with remarkable magnetic properties, opening a wide scope to develop the polyfunctional materials pos-

sessing both magnetic and other functionalities (electrical, non-linear optical, luminescence etc.) [7–11]. Low-dimensional (LD) molecular nano-magnets occupy a special niche in the field of molecular magnetism due to their potential IT-applications: information storage at the molecular level, quantum computing, or spintronics devices [12–14]. LD systems known as single-molecule magnets (SMMs) [15–17] for the 0D objects, and single-chain magnets (SCMs) [18–20] for 1D ones, are the molecular metal organic polynuclear coordination compounds with a high-spin ground state and showing slow magnetization relaxation rate, together

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<https://doi.org/10.1016/j.jmmm.2017.12.022>
0304-8853/© 2017 Published by Elsevier B.V.

with magnetic hysteresis below a characteristic blocking temperature (T_B).

For the SMMs, this phenomenon occurs due to a magnetic bistability. The spin–spin interaction is described by the spin Hamiltonian $H = D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2)$, where D and E are the zero field splitting (ZFS) parameters [21,22]. D is the axial parameter, which can be both positive and negative, the latter situation leads to a double-well potential, in which two lowest quantum states $+M_S$ and $-M_S$ are divided by an energy barrier U_{eff} to be surmounted for magnetization reversal. The rhombic parameter E is related to axial distortion. Hence, the height of the barrier is determined by a large ground-state spin S and magnetic anisotropy D : $U_{\text{eff}} = |D|S^2$ and $|D|(S^2 - 1/4)$ for integer and half-integer spin, respectively [15]. ZFS is the most common source of magnetic anisotropy in first-row transition metal complexes. These parameters play an essential role for blocking of magnetization in LD magnets [6]. This situation applies to systems with uniaxial anisotropy (or Ising-type anisotropy), for which D should be negative and large, whereas E must be as small as possible to avoid coupling among m_S components, leading to tunneling between them.

Slow magnetic relaxation has also been found for 1D coordination polymers [23]. In terms of greater relaxation barriers, SCMs possess an advantage over SMMs. This benefit originates from an additional contribution in U_{eff} , named correlation energy Δ_ξ , which is provided by an exchange coupling (J) between the paramagnetic centers. Taking into account that an interaction between adjacent spin carriers is $-2J_1 \cdot S_2$, $\Delta_\xi = 4|J|S^2$ for an isotropic model when $|D/J| > 4/3$ (Ising limit), while if $|D| \ll |J|$, $\Delta_\xi = 4S^2|D|^{1/2}$ (Heisenberg limit) [24,25]. Therefore, for an infinite magnetic chain the total spin reversal barrier can be written as $U_{\text{eff}} = \Delta_A + 2\Delta_\xi$ [26–28]. However, in a finite-length spin chain, the contribution of the correlation energy to the U_{eff} is twice as small ($U_{\text{eff}} = \Delta_A + \Delta_\xi$) due to a nucleation effect of the chain ends. Indeed, at low temperatures the relaxation dynamics of SCMs are typically described by the finite-length model [18].

Despite a lack of the long-range magnetic order, at a finite temperature the LD molecular materials can fix their magnetization in the absence of an applied magnetic field due to slow magnetic relaxation below T_B . Anisotropy plays a key role for slow magnetic dynamics. The main problem in regulation of the magnetic anisotropy is a clear preference of transition metal ions for octahedral coordination having no anisotropy with ideal O_h symmetry, in which anisotropy is due to a symmetry lowering in distorted octahedron, but it is hard to tune finely such a deformation purposefully in the complexes of Co^{2+} , Mn^{3+} , and Ni^{2+} displaying anisotropy with $|D| < 10 \text{ cm}^{-1}$ [21].

Namely, the spin orbit coupling (SOC) acting on the crystal field terms is a source of magnetic anisotropy. In coordination compounds, the spin–orbit operator, $\hat{H}_{\text{LS}} = \zeta \mathbf{L} \cdot \hat{\mathbf{S}}$, is regulated by a crystal field so that $\zeta < \Delta$ (ζ and Δ is the SOC and the ligand field constants respectively, Δ being $10 Dq$), which is in the order of 100 cm^{-1} for first row transition metals [29–31]. SOC may operate as either a first or second order perturbation. First-order perturbation mixes the spin and orbital components for orbitally degenerate ground state terms. For a complex with a real geometry, the crystal field and JT effects may lift the degeneracy. This is associated with the symmetry considerations given by group theory. However, the orbital momentum is quenched for E and A terms, but unquenched for T terms.

Second-order perturbation may occur even though a ground term is orbitally nondegenerate. It happens due to a spin–orbit mixing of the ground state with orbitally degenerate excited states promoting a splitting of the crystal field ground term. Thus, the spin S associated with the latter is split into $2S+1$ multiplets, which correspond to the m_S states. This is usually called as ZFS [21]. Magneto-structural statistics confirms that the magnitude and sign

of D can be controlled by chemical design manipulating with coordination characteristics of a metal complex.

Cyano-bridged heterometallic complexes have provided a large number of compounds with SMM [5,17,32–34] and SCM [35,36] behaviors. The large part of them comprises 3d cyanides as the core magnetic modules. The use of 4- and 5d cyanometallates in design of LD nanomagnets has a few advantages. First of all, compared to their 3d congeners, they possess higher anisotropy and more diffuse valence orbitals, the latter can offer stronger magnetic exchange interactions [31]. Secondly, these ions exist in a variety of oxidation states. The facile changes in oxidation states and an ability to promote these changes via external stimuli, e.g. by light, to trigger charge transfer reactions, has attracted attention of researchers in the area of multifunctional materials and has produced numerous compounds with several intriguing physical properties, such as photomagnetism [8,9,37].

In this report we briefly review cyanometallate based low-dimensional assemblies displaying slow magnetic dynamics, they having been limited mainly by the heterometallic complexes involving homoleptic cyanides as orbitally degenerate metalloligands and complexes of Mn^{II} and Mn^{III} . Particular attention will be focused on the aspects of chemical design of low-dimensional systems.

2. Hexacyanometallate based assemblies

2.1. SMMs incorporating $[\text{M}(\text{CN})_6]^{3-}$

After recent theoretical prediction about the presumable using of the orbitally degenerate 4d/5d homoleptic cyanometallates with a strong SOC as highly anisotropic synthons in design of molecular nanomagnets [38–41], a series of SMMs [17,33,34,42] and SCMs [20,29,35,36] with such building blocks were obtained. As it was mentioned supra, due to a stereochemical nonrigidity of octahedral coordination polyhedron, magnetic anisotropy in $[\text{Fe}(\text{CN})_6]^{3-}$ based compounds is sensitive even to a tiny coordination octahedron distortion, which split the ${}^2T_{2g}^5$ triplet (O_h) into individual orbital components and, thus, tend to reduce angular orbital momentum L . This was confirmed by a study of the isostructural series of trinuclear SMMs $\{\text{Mn}^{\text{III}}\text{M}^{\text{III}}\text{Mn}^{\text{III}}\}^-$, in which two $\text{Mn}^{\text{III}}(\text{SB})$

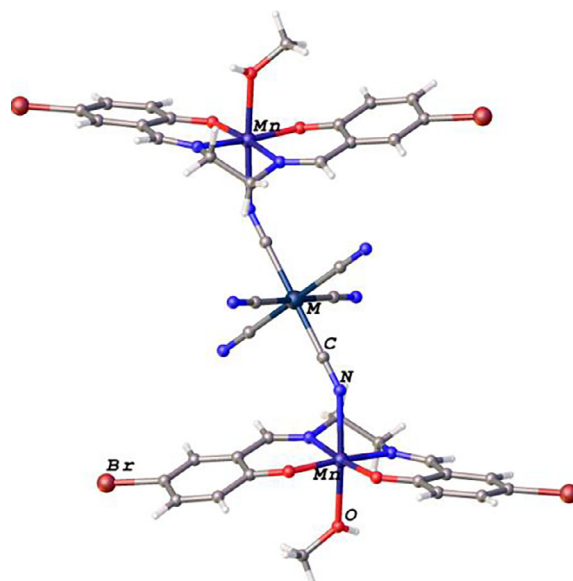


Fig. 1. The trinuclear SMMs, $\text{Et}_4\text{N}[\text{Mn}^{\text{III}}(\text{SB})\text{MeOH}]_2[\text{M}^{\text{III}}(\text{CN})_6]$, $M = \text{Fe}, \text{Ru}, \text{Os}$: compounds 1–3.

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