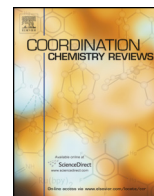




Contents lists available at ScienceDirect

# Coordination Chemistry Reviews

journal homepage: [www.elsevier.com/locate/ccr](http://www.elsevier.com/locate/ccr)



## Review

# A review of manganese-based molecular magnets and supramolecular architectures from phenolic oximes

Chen-I Yang\*, Zu-Zhen Zhang, Sheng-Bo Lin

Department of Chemistry, Tunghai University, Taichung, Taiwan

## Contents

1. Introduction .....	00
2. Zero-dimensional systems .....	00
2.1. Mn <sub>2</sub> .....	00
2.2. Mn <sub>3</sub> .....	00
2.3. Mn <sub>4</sub> .....	00
2.4. Mn <sub>5</sub> .....	00
2.5. Mn <sub>6</sub> .....	00
2.6. Mn <sub>7</sub> .....	00
2.7. Mn <sub>8</sub> .....	00
2.8. Mn <sub>9</sub> .....	00
2.9. Mn <sub>12</sub> .....	00
2.10. Mn <sub>32</sub> .....	00
3. One-dimensional systems .....	00
3.1. [Mn <sub>3</sub> ] <sub>n</sub> .....	00
3.2. [Mn <sub>4</sub> ] <sub>n</sub> .....	00
3.3. [Mn <sub>6</sub> ] <sub>n</sub> .....	00
3.4. [Mn <sub>8</sub> ] <sub>n</sub> .....	00
3.5. [Mn <sub>21</sub> ] <sub>n</sub> .....	00
3.6. [Mn <sub>2</sub> Cu] <sub>n</sub> .....	00
4. Two- and three-dimensional compounds .....	00
4.1. Mn <sub>3</sub> -based two-dimensional compounds .....	00
4.2. Mn <sub>4</sub> -based three-dimensional compound .....	00
5. Conclusions .....	00
Acknowledgments .....	00
References .....	00

## ARTICLE INFO

### Article history:

Received 14 July 2014

Accepted 21 December 2014

Available online xxx

## ABSTRACT

Phenolic oximes, which are frequently used as bridging ligands in the construction of molecule-based magnets, have stimulated considerable interest in magnetochemistry. This *tutorial review* is concentrated on manganese-based phenolic oximes systems and related magnetochemistry and consists of five main sections. The first section offers an introduction to Mn-based phenolic oxime complexes and some

*Abbreviations:* ac, alternating current;  $U_{\text{eff}}$ , anisotropy barrier;  $H$ , applied magnetic field;  $D$ , axial anisotropy; HO<sub>2</sub>CPh, benzoic acid;  $J$ , coupling constant; dc, direct current; JT, Jahn–Teller;  $g$ , Landé  $g$ -value;  $\chi''$ , out-of-phase susceptibility; SMM, single-molecule magnet;  $\chi_M$ , susceptibility;  $\chi_M T$ , susceptibility temperature product; ZFS, zero-field splitting; Hhmp, 2-(hydroxymethyl)pyridine; tmtacn, 1,4,7-trimethyl-1,4,7-triazacyclononane; Et<sub>3</sub>N, triethylamine; Naphth-saoH, 2-hydroxy-1-naphthaldoxime; tpa, tris(2-pyridylmethyl)amine; TBC[8], *p*-tert-butylcalix[8]arenes; HO<sub>2</sub>CPh(Me)<sub>4</sub>, 3,5-dimethylbenzoic acid; HO<sub>2</sub>Ph(CF<sub>3</sub>)<sub>2</sub>, 3,5-diflorobenzoic acid; HO<sub>2</sub>CPh(Cl)<sub>2</sub>, 3,5-dichlorobenzoic acid; 2,4'-bpy, 2,4'-bipyridine; <sup>t</sup>BuSaoH<sub>2</sub>, 3,5-di-tert-butyl-salicylaldoxime; Val, DL-valine; 4,4'-bpy, 4,4'-bipyridine; dpe, 1,2-di(4-pyridyl)ethylene; dpp, 1,3-di-4-pyridylpropane; O<sub>2</sub>C-Ph-CO<sub>2</sub>, isophthalate; O<sub>2</sub>C-CH<sub>2</sub>CH<sub>2</sub>-CO<sub>2</sub>, succinate; H<sub>2</sub>bd, 1,3-butanediol; Ph-saoH<sub>2</sub>, phenyl salicylaldoxime; Et-saoH<sub>2</sub>, 2-hydroxypropiophenone oxime; Me-saoH<sub>2</sub>, 2-hydroxyphenylethanone oxime; 4-MeO-H<sub>2</sub>salox, 2-hydroxy-4-methoxy-benzaldehyde oxime; Cl-saoH<sub>2</sub>, 5-chlorosalicylaldoxime.

\* Corresponding author. Tel.: +886423590121x32237.

E-mail address: [ciyang@thu.edu.tw](mailto:ciyang@thu.edu.tw) (C.-I. Yang).

<http://dx.doi.org/10.1016/j.ccr.2014.12.011>

0010-8545/© 2015 Elsevier B.V. All rights reserved.

**Keywords:**Phenolic oxime  
Molecule-based magnet  
Single-molecule magnet  
Single-chain magnet  
Slow magnetic relaxation  
Supramolecular architecture

important results obtained from magneto-structural correlations in phenolic oximes compounds which will be discussed in the following sections. The next three sections provide overviews of phenolic oxime-mediated Mn compounds from zero-dimension to one-, two- and three-dimensional supramolecular architectures and their unusual magnetic properties including SMM and SCM behavior. The last section contains concluding remarks and provides perspectives for the future of phenolic oxime-mediated compounds.

© 2015 Elsevier B.V. All rights reserved.

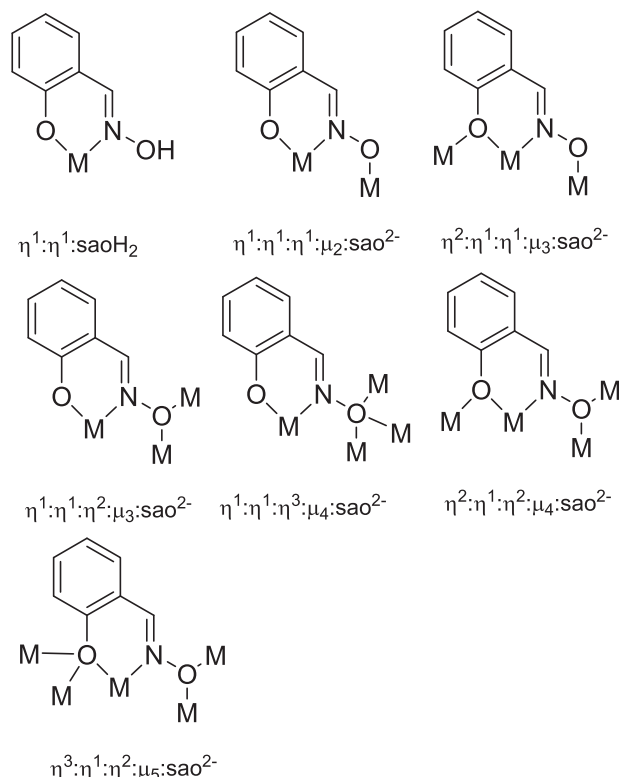
**1. Introduction**

The preparation and study of molecular magnetism is one of the leading topics in the field of coordination chemistry [1]. Among these compounds, single-molecule magnets (SMMs) and single-chain magnets (SCMs) have been the subjects of a great deal of attention because of their unique magnetic properties based on a slow relaxation of magnetization and their potential applications in information storage and quantum computation at the molecular level [2–13]. It opens up a popular avenue to nanoscale electronic devices, sensors and high-density data storage media at the molecular level [14–16]. For a SMM, sluggish magnetization relaxation phenomena such as magnetization hysteresis loops and frequency-dependent out-of-phase alternating current (ac) magnetic susceptibility arise from its high-spin ground state ( $S$ ), which is split by a large negative axial zero-field splitting (ZFS,  $D$ ), leading to a spin-reversal barrier ( $U_{\text{eff}}$ ) to the slow relaxation of magnetization,  $U_{\text{eff}} = |D|S^2$  and  $|D|(S^2 - 1/4)$  for a transition metal SMM with integer and half integer spins, respectively [17,18]. The large  $S$  values arise from ferromagnetic or competing antiferromagnetic exchange. The first reported SMM was  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ , with  $S = 10$  and  $D = -0.50 \text{ cm}^{-1} = -0.72 \text{ K}$  [19–23]. Since then, a number of SMMs have been reported with  $S$  values ranging from  $3/2$  to  $83/2$  and nuclearity from 1 to 84 [5–12,24,13,25–38]. For a SCM, it must possess a large uniaxial anisotropy, participate in strong intrachain exchange interactions without spin compensation between the magnetic units, and the chains should be well isolated, in order to avoid two- (2D) and three-dimensional (3D) ordering. Gatteschi et al. reported on the first such compound with an isolated spiral chain structure, which has been described as an Ising chain because of the presence of anisotropic  $\text{Co}^{\text{II}}$  metal ions and the high ratio between intra- ( $J$ ) and inter-chain ( $J'$ ) magnetic interactions [39]. Glauber's model for Ising spin chains explained the slow dynamics of their magnetization [40]. The near-octahedral  $\text{Mn}^{\text{III}}$  ion exhibits Jahn–Teller (JT) distortion in the form of an axial elongation that plays an important role in the presence of SMMs and SCMs properties, and the anisotropy energy barriers show a significant dependence on the orientations of JT elongation [41]. Thus, many current routes to molecule-based magnets culminate in  $\text{Mn}^{\text{III}}$  containing complexes, and the associated large single-ion anisotropy has been exploited [42,43].

Phenolic oxime ligands (abbrev as R-saoH<sub>2</sub> or R-H<sub>2</sub>salox) have been explored as chelating ligands in Mn cluster chemistry for applications for molecule-based magnets. They have been observed in their singly-deprotonated form as bidentate chelate compounds with the protonated N-OH not bound, and the doubly deprotonated form as a tridentate chelate [44,45]. These chelating forms can provide a variety of possible binding modes (Scheme 1) to yield polynuclear metal clusters. Molecules containing the triangular  $[\text{Mn}^{\text{III}}_3\text{O}(\text{R-sao})_3]^+$  building block are generally produced in basic alcoholic solutions of  $\text{Mn}^{\text{III}}/\text{R-saoH}_2$  reaction mixtures, where the JT axes of three Mn ions are nearly parallel, resulting in a significant anisotropy [46,47]. Magnetic exchange between Mn ions is dominated by the twisting of the  $-(\text{N}-\text{O})-$  moiety of the

phenolic oxime and the substituent at the oximic C-atom can control the sign and magnitude of the pairwise exchange [48–50]. The  $\text{Mn}/\text{R-sao}^{2-}$  ( $\text{Mn}-\text{O}-\text{N}-\text{Mn}$ ) moiety therefore represents an interesting building block for use in preparing molecule-based magnetic materials.

This review article examines the synthesis, structure and magnetic properties of manganese compounds with phenolic oxime ligands from discrete molecules to multi-dimensional supramolecular architectures and their magnetic properties. The focus here is on Mn compounds that are prepared with phenolic oxime ligands, as shown in Fig. 1. The aim is not to be comprehensive discussion of every known Mn complex containing a phenolic oxime ligand but, rather, to provide the reader with an overview of the range of magnetochemistry and supramolecular architecture that has been achieved with these ligands. Reviewing phenolic oxime ligands illustrates how magnetic interactions changed from anti-ferromagnetically to ferromagnetically and the relations between the structural factors and uniaxial anisotropy for SMM (Table 1). Moreover, this review also provides information regarding the selection of linkage ligands that enhances uniaxial anisotropy into SCM behavior in its supramolecular architectures (Table 2). Further, it is hoped that this might be used as a predictive tool to elucidate the molecule-based magnet properties of these ligands.

**Scheme 1.** Various bridging modes of phenolic oximes reported in this article.

Download English Version:

<https://daneshyari.com/en/article/7748045>

Download Persian Version:

<https://daneshyari.com/article/7748045>

[Daneshyari.com](https://daneshyari.com)