Polyhedron 61 (2013) 45–55

Contents lists available at SciVerse ScienceDirect

Polyhedron

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

Syntheses, structures and magnetic properties of azido- and phenoxo-bridged complexes of manganese containing tridentate aroylhydrazone based ligands

Hassan Hosseini-Monfared [a,*], Rahman Bikas [a], Joaquín Sanchiz [b,*], Tadeusz Lis [c], Milosz Siczek [c], Jiri Tucek [c], Radek Zboril [d], Peter Mayer [e]

[a] Department of Chemistry, University of Zanjan, 45195-313 Zanjan, Iran
[b] Departamento de Química Inorganíca, Universidad de La Laguna, 38206 La Laguna, Tenerife, Spain
[c] Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, Wroclaw 50-383, Poland
[d] Regional Centre of Advanced Technologies and Materials, Faculty of Science, Department of Physical Chemistry, Faculty of Science, Palacky University, 17. listopadu 1192/12, in Olomouc, 771 46 Olomouc, Czech Republic
[e] Fakultat für Chemie und Pharmazie, Ludwig-Maximilians-Universitat, München, Butenandtstr. 5-13, Haus D, D-81377 München, Germany

ARTICLE INFO

Article history:
Received 14 March 2013
Accepted 19 May 2013
Available online 27 May 2013

Keywords:
Dinuclear Mn complexes
Magnetic behavior
Azide
Coordination polymer
Hydrazones

ABSTRACT

Five new compounds have been prepared by the reaction of $MnCl_2{\cdot}4H_2O$ with aroylhydrazone in the presence of NaN_3: $[Mn(L^1)(N_3)(HOCH_3)]_2$ (**1**), $[Mn(L^2)(N_3)(HOCH_3)]_2$ (**2**), $[Mn(L^3)(N_3)(HOCH_3)_{0.75}(EtOH)_{0.25}]_2$ (**3**), $[Mn(L^4)(N_3)(HOCH_3)]_2$ (**4**) and $[Mn_2(L^2)_2(HOCH_3)_2]_n$ (**5**). (HL^1 = (*E*)-3-hydroxy-N′-(1-(pyridin-2-yl)ethylidene)-2-naphthohydrazide, HL^2 = (*E*)-N′-(phenyl(pyridin-2-yl)methylene)furan-2-carbohydrazide, H_2L^3 = (*Z*)-N′-(4-oxo-4-phenylbut-2-en-2-yl)isonicotinohydrazide, H_2L^4 = (*E*)-N′-(5-bromo-2-hydroxybenzylidene)isonicotinohydrazide). In absence of NaN_3 the mononuclear complex $[Mn(H_2L^5)_2(EtOH)_2Cl_2]$ (**6**) was obtained by the reaction of $MnCl_2{\cdot}4H_2O$ and H_2L^5 ((*E*)-N′-(2-hydroxy-3-methoxybenzylidene)isonicotinohydrazide). All the compounds have been characterized by elemental analyses, IR spectra, single crystal X-ray diffraction and magnetic susceptibility measurements. Compound **6** exhibits mononuclear structure, **1**–**4** dinuclear structure whereas complex **5** yields two-dimensional sheets parallel to the (100) plane in which the deprotonated H_2L^4 act as bridging ligand. The magnetic study reveals dominating antiferromagnetic interactions in **1** and **5** whereas the ferromagnetic coupling dominates in **2**–**4**. The magnetic properties are interpreted in terms of the electronic structure of the Mn ions and structural parameters.

1. Introduction

The study of poly-nuclear manganese complexes is of current interest due to the role they play in several redox systems such as in water oxidation in the active centre of Photosystem II [1] and in other redox-biochemical processes. Additionally, many manganese complexes possess large numbers of unpaired electrons, making them precursors for magnetic materials [2–5]. These findings have triggered the investigation of new molecular complexes based on manganese ions. In this context, dinuclear manganese Schiff base complexes are known to exhibit interesting magnetic properties [6,7] that can further be tailored towards assembly of molecule exhibiting single molecule magnet (SMM) behavior. Due to the presence of energy barrier between spin-up and spin-down states, the SMMs may be potentially used as information storage at the molecular level. Moreover, these might be the unique systems for studying quantum spin tunnelling and quantum phase interference leading to their applications in molecular electronics too [8].

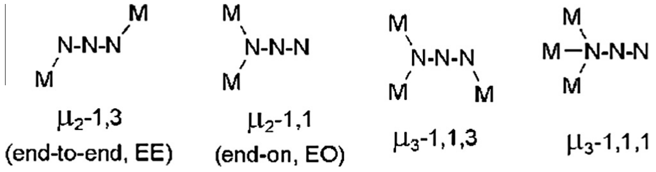
Among the bridging pseudohalide ions (N_3^-, NCS^-, NCO^-), the azide has been widely utilized not only as a versatile bridging ligand, but also as an excellent magnetic coupler [9]. When the azide anion acts as bridging ligand [10], it can bind metal ions in different coordination modes. The most common are the end-to-end (μ_2-1,3-N_3, EE) [11], and end-on (μ_2-1,1-N_3, EO) [12] modes, whereas triply μ_3-1,1,1-N_3 [13], μ_3-1,1,3-N_3 [14] quadruply μ_4-1,1,1,1-N_3 [10] and μ_4-1,1,3,3-N_3 [15] coordinated modes remain relatively rare (Scheme 1). In most cases the end-to-end ($\mu_{1,3}$) and end-on ($\mu_{1,1}$) coordination modes mediate antiferromagnetic and ferromagnetic interaction, respectively, but an increasing number of exceptions have been recently observed [16]. Hence, the

---

* Corresponding authors. Tel.: +98 241 5152576; fax: +98 241 5283203 (H. Hosseini-Monfared).

E-mail addresses: monfared@znu.ac.ir (H. Hosseini-Monfared), jsanchiz@ull.es (J. Sanchiz), milosz.siczek@chem.uni.wroc.pl (M. Siczek), radek.zboril@upol.cz (R. Zboril), pemay@cup.uni-muenchen.de (P. Mayer).

0277-5387/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2013.05.033



Scheme 1. The common metal ion bridging modes for azide ion illustrated by double-bridged μ_2-1,3 (EE), μ_2-1,1 (end-on), triple-bridged μ_3-1,1,3 and μ_3-1,1,1.

synthesis, the structural characterization and the study of the magnetic properties of azide-containing complexes with different magnetic features is an emerging and substantial subject of scientific researches.

Acyl and aroyl hydrazones are a multipurpose class of ligands (Scheme 2) which have a range of biological and chemical activities. Hydrazones exhibit physiological and biological activities in the treatment of several diseases such as tuberculosis [17], Fe overload [18,19], and also as inhibitors for many enzymes [20]. Their metal complexes have also found applications in various physical and chemical processes e.g. non-linear optics, sensors, medicine [21] and, as well as non-symmetrical salens, can act as effective catalysts towards alkene epoxidation [22]. Moreover, they are of interest in the field of electrochromism where a change in the oxidation state of the metal is possible [23]. Acyl and aroyl hydrazones contain trigonal N- and O-donor atoms that can coordinate to metal ions [24] acting as bidentate [25], tridentate, tetradentate [26], or pentadentate ligands [27] depending on the nature of heterocyclic ring-substituents attached to the hydrazone unit. These ligands exhibit a facile keto–enol tautomerization which can modulate the coordination to the metal as a mono-negative or di-negative ligand in the keto or enol form, respectively.

Metal complexes with mixed ligands of hydrazone Schiff base and azide are rare [28], although combination of different properties of azide and hydrazone Schiff base as ligands could be interesting. In this sense, there are only a few studies on azide as bridging [29] and non-bridging ligands between two Mn(III) ions [30,31]. And to the best of our knowledge, there is no report on the structure of Mn(II) hydrazone complexes with azide bridging ligands. Thus in order to improve the knowledge in this kind of compounds we report herein the structures, thermal stability and magnetic properties of mononuclear, dinuclear and polymeric Mn(II,III) complexes with mixed azide and aroyl hydrazone ligands (Scheme 2).

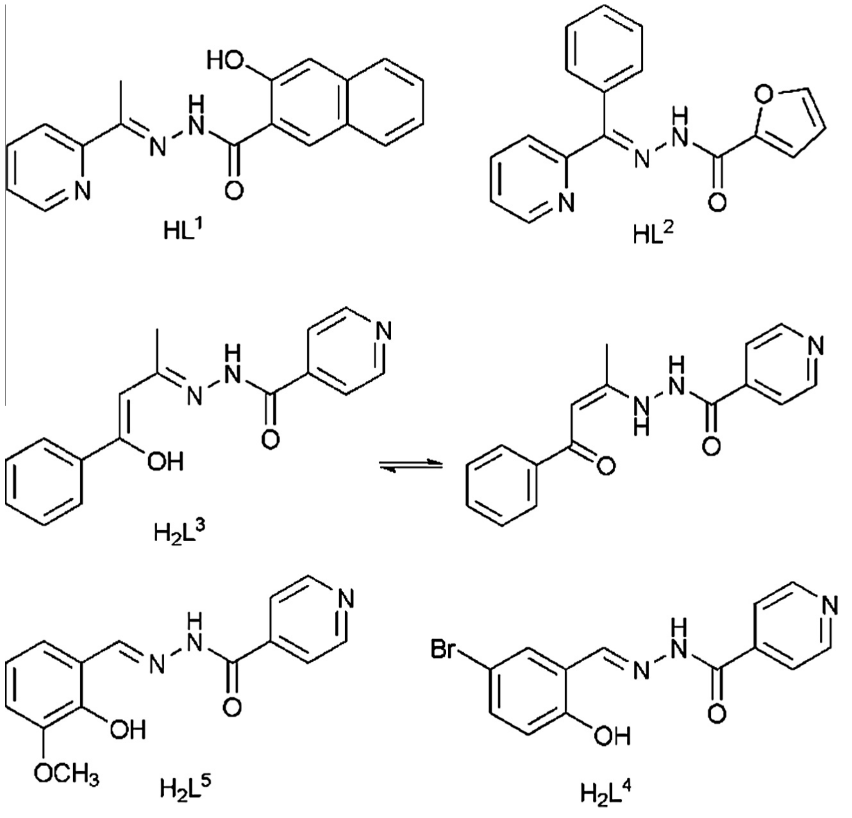
2. Experimental

2.1. Materials and instrumentations

Manganese(II) chloride tetrahydrate, sodium azide, 4-pyridinecarboxylic acid hydrazide, furane-2-carboxylic acid hydrazide, 3-hydroxy-2-naphthoic acid hydrazide, 5-bromo-2-hydroxybenzaldehyde, 2-hydroxy-3-methoxybenzaldehyde, 2-acethylpyridine, 2-benzoyilpyridine, benzoylacetone and solvents were purchased from Merck and used as received. IR spectra were recorded in KBr disks with a Bruker FT-IR spectrophotometer. UV–Vis spectra of solutions were recorded on a thermo spectronic, Helios Alpha spectrometer. Elemental analyses were determined on a CHN Perkin–Elmer 2400 analyzer. The manganese content of the final material was determined by a Varian spectrometer AAS-110.

2.2. Synthesis of the ligands

General procedure: the ligands were prepared in a similar manner by refluxing a mixture of acid hydrazide (1.0 mmol) and appropriate aldehyde or ketone with equivalent molar ratio in 20 ml methanol for 6 h. The solution volume was decreased to 5 ml by removing the solvent and cooled to room temperature. The



Scheme 2. The aroylhydrazone ligands which used in the synthesis of complexes.