

The [2 × 2] grid tetranuclear Fe(II) and Mn(II) complexes: Structure and magnetic properties



Li Zhang, Juan-Juan Wang, Guan-Cheng Xu *

Key Laboratory of Material and Technology for Clean Energy, Ministry of Education, Key Laboratory of Advanced Functional Materials, Autonomous Region, Institute of Applied Chemistry, Xinjiang University, Urumqi, 830046, Xinjiang, P. R. China

ARTICLE INFO

Article history:

Received 25 September 2013

Accepted 30 October 2013

Available online 7 November 2013

Keywords:

Iron(II)

Manganese(II)

Tetranuclear complexes

Crystal structures

Magnetic properties

ABSTRACT

Tetranuclear complexes, $[\text{Fe}_4(\text{HL})_4](\text{ClO}_4)_4 \cdot 5\text{H}_2\text{O}$ (**1**) and $[\text{Mn}_4(\text{HL})_4](\text{ClO}_4)_4 \cdot 2\text{MeCN} \cdot 2\text{H}_2\text{O}$ (**2**) with [2 × 2] rectangle and square grid structure were self-assembled using the flexible ligand, 1,5-bis(1-(pyridine-2-yl) ethylidene)carbonohydrazide. The structures and magnetic properties were characterized by single crystal X-ray diffraction and variable temperature magnetic susceptibility measurements, respectively. For **1**, the iron(II) centers are in distorted octahedral environment with N_4O_2 or N_5O coordination spheres through two bridging enolyl oxygen atoms and two bridging N–N single bonds. Whereas, for **2**, all four manganese(II) centers are in a distorted octahedral geometry with N_4O_2 coordination spheres through enolyl oxygen atoms connecting two adjacent metal ions. The magnetic properties of **1** and **2** show intramolecular antiferromagnetic exchanges.

© 2013 Elsevier B.V. All rights reserved.

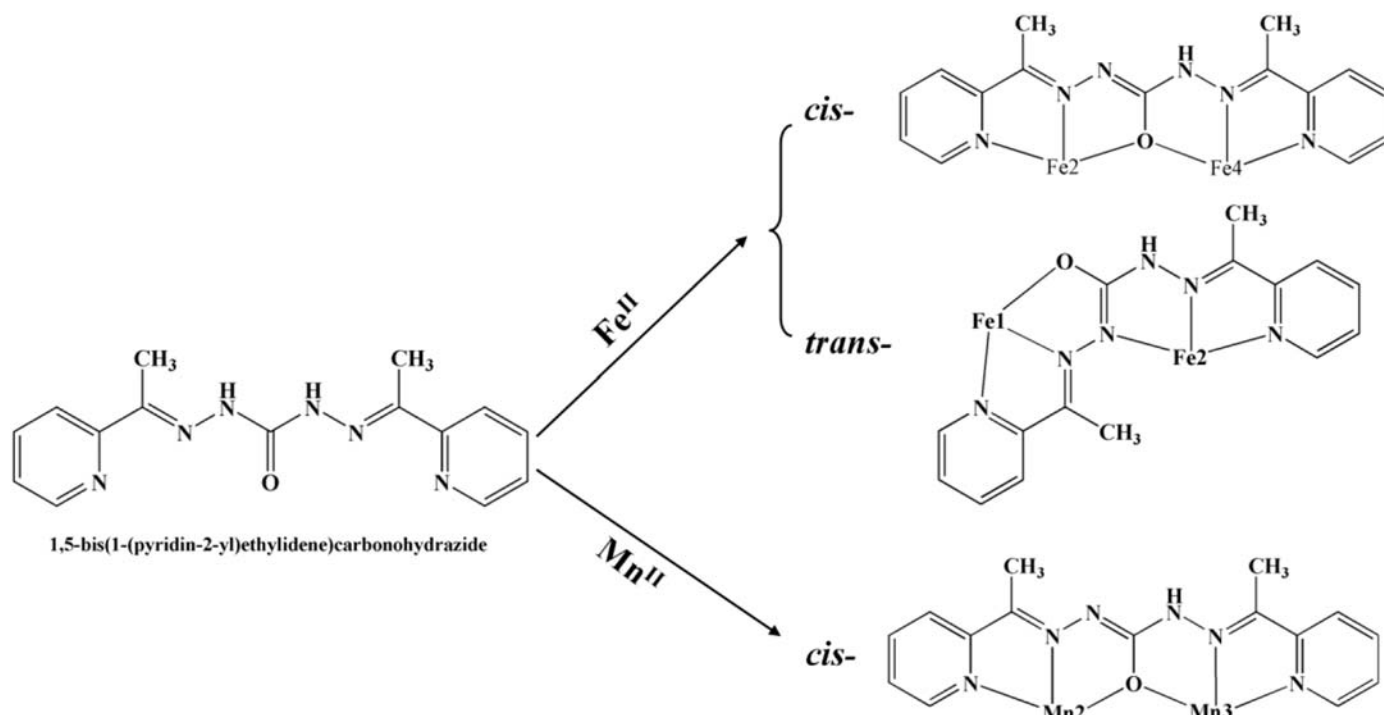
Self-assembly of transition metal ions with multifunctional organic ligands, especially the metallosupramolecular square and rectangle grids, has attracted continuous scientific interest in recent years, owing to their potential applications, such as information storage, molecular devices and processing technology. The [2 × 2] grid tetranuclear complexes [1–7], [3 × 3] square grid complexes and [4 × 4], [5 × 5] grid-type supra-molecular architectures [8–14], have been prepared and structurally characterized. In these studies, the picolyl hydrazone ligands, ditopic carbonylhydrazide and thiocarbonylhydrazide based ligands as paradigms were widely used in the self-assembly of [2 × 2] grid tetranuclear complexes [1–4,7]. As for the presence of different kinds of potential donor sites: enolyl oxygen atom, pyridine and azomethine nitrogen atoms, various derivatives of carbonylhydrazide based ligands are prone to produce [2 × 2] grid complexes. However, only a few studies concern the preparation, structural characterization and magnetic properties of transitional metal complexes of this type of carbonylhydrazide based ligands.

A square grid $[\text{Zn}(\text{HL})_4](\text{BF}_4)_4 \cdot 10\text{H}_2\text{O}$ ($\text{H}_2\text{L} = \text{bis}(2\text{-benzoylpyridine ketone}) \text{ carbonylhydrazide}$) was firstly reported by E. P. Manoj et al., in which all four Zn(II) centers are bridged by enolyl oxygen atoms [1]. And then several other [2 × 2] rectangle and square grids were successively achieved through this kind of flexible ligands and metal ions, including Ni(II), Co(II) and Fe(II) [2–4]. The resulting compounds exhibit interesting structures and magnetic properties. For example, the complex $[\text{Co}_4(\text{HL}1\text{a})_2(\text{L}1\text{a})_2](\text{CF}_3\text{SO}_3)_2 \cdot (\text{CH}_3\text{OH})_4 \cdot (\text{H}_2\text{O})_3$ ($\text{H}_2\text{L}1\text{a} = 1,5\text{-bis}(1\text{-pyridine-2-yl}) \text{ ethylidene carbonylhydrazide}$) possesses [2 × 2] rectangle grid structure and all cobalt centers are bridged by two N–N

single bonds and two enolyl oxygen atoms. As a result, two cobalt centers are in the N_4O_2 type while the other cobalt centers are in the N_5O coordination environment. The complex contains two high-spin (HS) and two low-spin (LS) Co(II) ions, which is a rather unusual observation in polynuclear cobalt cluster chemistry [3]. However, in the reported tetranuclear Fe(II) [2 × 2] square complex, $\text{Fe}_4(\text{HL}1\text{a})_4(\text{CF}_3\text{SO}_3)_4 \cdot (\text{CH}_3\text{OH})_2 \cdot (\text{H}_2\text{O})_2$, all four iron centers are in the N_4O_2 coordination mode and only bridged by enolyl oxygen atoms. The tetranuclear Fe(II) complex exhibits interesting spin crossover phenomenon which occurred on one site of the Fe(II) below 130 K [3]. In contrast, $[\text{Fe}_4(\text{HL}^1)_4](\text{BF}_4)_4 \cdot (\text{H}_2\text{O})_2 \cdot \text{CH}_3\text{OH}$ and $[\text{Fe}_4(\text{HL}^1)_4](\text{PF}_6)_4 \cdot (\text{H}_2\text{O})_2 \cdot \text{CH}_3\text{OH}$ ($\text{H}_2\text{L}^1 = 1,5\text{-bis}(1\text{-pyridine-2-yl}) \text{ methylene carbonylhydrazide}$), have similar structure with $\text{Fe}_4(\text{HL}1\text{a})_4(\text{CF}_3\text{SO}_3)_4 \cdot (\text{CH}_3\text{OH})_2 \cdot (\text{H}_2\text{O})_2$, but exhibit different magnetic properties: $[\text{Fe}_4(\text{HL}^1)_4](\text{BF}_4)_4 \cdot (\text{H}_2\text{O})_2 \cdot \text{CH}_3\text{OH}$ undergoes a spin transition occurring on the two Fe^{II} on the same side of the Fe^{II} square, whereas no spin transition was observed in $[\text{Fe}_4(\text{HL}^1)_4](\text{PF}_6)_4 \cdot (\text{H}_2\text{O})_2 \cdot \text{CH}_3\text{OH}$ within the whole temperature range [4]. Compared the structures and magnetic properties of these reported transitional metal complexes with different carbonylhydrazide based ligands, we can see that different anions might give rise to the changes of magnetic properties. Moreover, the central metal ions and different substitutions on the ligands might also have effects on the structure and magnetic property of the complexes.

Inspired by these investigations, we select 1,5-bis(1-(pyridine-2-yl) ethylidene)-carbonohydrazide here as building block for self-assembly of new transitional metal [2 × 2] grids (Scheme 1). Treated with iron(II) and manganese(II) perchlorate, Fe₄ rectangle grid $[\text{Fe}_4(\text{HL})_4](\text{ClO}_4)_4 \cdot 5\text{H}_2\text{O}$ (**1**) and Mn₄ square grid $[\text{Mn}_4(\text{HL})_4](\text{ClO}_4)_4 \cdot 2\text{MeCN} \cdot 2\text{H}_2\text{O}$ (**2**) were obtained, respectively. The experimental details are presented in the supplementary information. The IR spectrum of the complex **1**

* Corresponding author. Tel./fax: +86 991 8580586.
E-mail address: xuguancheng@163.com (G.-C. Xu).



Scheme 1. Representation of the ligand used in this work and coordination modes of ligand in the complexes.

shows strong peaks at 3385, 1548 and 1374 cm^{-1} , which are assigned to $\nu(\text{N-H})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C-O}^-)$ of HL^- , respectively [5,7]. In complex **2**, these bands appear at 3374, 1571 and 1363 cm^{-1} , respectively. It is inferred that the ligand reacted in the enol form in stead of keto form by deprotonation of N-H proton and coordinated to the metal ions Fe^{II} and Mn^{II} . Moreover, the bands at around 3400 and 1086 cm^{-1} in IR spectra of **1** and **2** are the characteristic absorption peaks of H_2O and ClO_4^- , respectively. From these observations, it is concluded that ClO_4^- are present in two complexes for charge balance. The two compounds were also characterized by elemental analysis and single-crystal X-ray diffraction, which confirm that the four ligands bond to iron(II) and manganese(II) ions as monodeprotonated HL^- and tetranuclear complexes were formed.

The structure of the tetranuclear cationic part $[\text{Fe}_4(\text{HL})_4]^{4+}$ in **1** is shown in Fig. 1a and the core structure fragment is shown in Fig. 1b.

Four pseudo-octahedral $\text{Fe}(\text{II})$ centers are assembled into a rectangle with a pair of $\mu\text{-O}$ bridging ligands and a pair of $\mu\text{-N-N}$ bridging ligands. The four $\text{Fe}(\text{II})$ ions adopt two different coordination types: $\text{Fe}(1) / \text{Fe}(3)$ is in the N_4O_2 coordination sphere, while $\text{Fe}(2) / \text{Fe}(4)$ is in the N_5O type. $\text{Fe}(1) / \text{Fe}(3)$ is coordinated by two pyridyl nitrogen atoms, two azomethine nitrogen atoms and two enolyl oxygen atoms from different perpendicular HL^- ligands and $\text{Fe}(2) / \text{Fe}(4)$ binds to two pyridyl nitrogen atoms, three azomethine nitrogen atoms and one enolyl oxygen atom. The bond lengths around $\text{Fe}(2)$, $\text{Fe}(3)$ and $\text{Fe}(4)$ are quite long (average distances of Fe-N and Fe-O are 2.170, 2.158, 2.177 Å and 2.144, 2.079, 2.119 Å, respectively), while the distances around $\text{Fe}(1)$ are shorter (average distances of Fe-N and Fe-O are 1.907 and 1.990 Å, respectively). On the other hand, each ligand bridges two adjacent $\text{Fe}(\text{II})$ ions, which comprises the edges of the rectangle. Two HL^- ligands bind two $\text{Fe}(\text{II})$ ions with a *trans*-conformation, forming the long edges

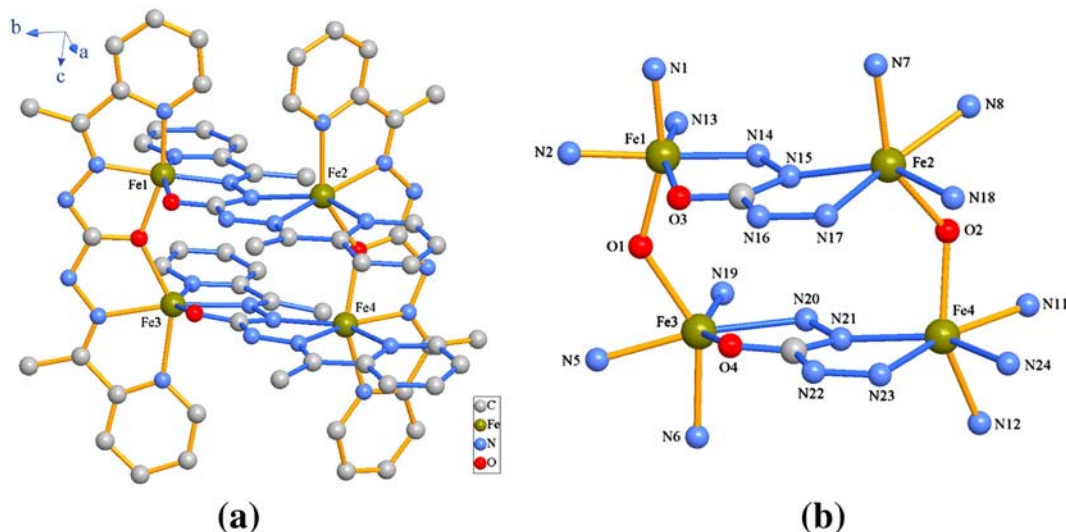


Fig. 1. (a) Structural representation of cationic complex **1**. (b) Structural representation with atom numbering scheme of the tetranuclear core in **1**.

Download English Version:

<https://daneshyari.com/en/article/1301686>

Download Persian Version:

<https://daneshyari.com/article/1301686>

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