

Cyano-bridged Fe₂Cu clusters: Control of magnetic properties through *cis*–*trans* arrangement



Peng-Fei Zhuang, Lun Luo, Tao Liu*, Yi Luo, Xian-Hui Xie, Hui Zheng, Liang Zhao, Cheng-Qi Jiao, Jun-Li Wang, Ji-Xiang Hu, Cheng He, Chun-Ying Duan

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China

ARTICLE INFO

Article history:

Received 16 July 2014

Received in revised form 31 July 2014

Accepted 6 August 2014

Available online 9 August 2014

Keywords:

Cyano

Trinuclear

Ferromagnetic

Antiferromagnetic

Cis–*trans*

ABSTRACT

It remains a challenge to control the magnetic properties of molecule-based magnetic materials through chemical modification. Utilizing two tricyanometalate precursors with different steric hindrance, the *cis*–*trans* arrangement can be tuned in cyano-bridged {Fe₂Cu} trinuclear complexes. The *cis* trinuclear [Fe^{III}(Tp)(CN)₃]₂Cu^{II}(dpa)₂·2H₂O (**1**) (Tp = hydrotris(pyrazolyl)borate, dpa = 2,2-dipyridylamine) was obtained with tricyanometalate possessing smaller steric hindrance, whereas the *trans* trinuclear [Fe^{III}(pzTp)(CN)₃]₂Cu^{II}(dpa)₂ (**2**) (pzTp = tetrakis(pyrazolyl)borate) was obtained using tricyanometalate with larger steric hindrance. The *cis* and *trans* arrangement leads to ferromagnetic and antiferromagnetic behaviors, respectively. Density functional theory (DFT) calculations were carried out to further substantiate the magnetic behaviors of both complexes. DFT computations show that the calculated magnetic coupling constant *J* was in agreement with the experimental results.

© 2014 Elsevier B.V. All rights reserved.

The design and synthesis of new molecule-based magnetic materials have attracted a great deal of attention due to their unique magnetic properties and potential applications in high-density information storage, quantum computation, and so on [1–3]. A current topic for research in this field is the preparation of magnetic materials whose physical properties can be controlled by external stimuli [4–6]. One more efficient synthetic approach to prepare cyano-bridged molecule-based magnetic materials is to utilize metalocyanates as multidentate ligands and linkers, because the metalocyanate building blocks are good candidates to provide directional assembly with controllable structure and physical properties [7,8]. With a rational design, a series of cyano-bridged molecule-based magnetic complexes have been synthesized and characterized [9–11]. It is well-known that the building blocks play an important role in influencing the structure of the resulting complexes. However, it is challenging to control the magnetic properties of molecule-based magnetic materials via tuning the arrangement of building blocks [12–14]. Based on the mentioned consideration, we aimed at using [Fe^{III}Tp(CN)₃][−] (Tp = hydrotris(pyrazolyl)borate) or [Fe^{III}pzTp(CN)₃][−] (pzTp = tetrakis(pyrazolyl)borate) as the building block to directional assembly with coordination unsaturated metal cation [Cu(dpa)₂]²⁺ (dpa = 2,2-dipyridylamine). The use of pzTp instead of Tp in a tricyanometalate system is supposed to increase the steric effect of the capped ligand, which may lead to the different arrangement. Herein, we have succeeded in constructing two new cyano-bridged

{Fe₂Cu} trinuclear complexes **1** and **2**, wherein ferromagnetic interaction dominates in *cis*-**1**, while *trans*-**2** is antiferromagnetic. DFT calculations have also been performed to determine the coupling constants, which are in good agreement with the experiment values.

Complexes **1** and **2** were synthesized by a diffusion method in a test tube [15]. Single-crystal X-ray diffraction analyses revealed that **1** crystallized in the triclinic space group *P* – 1 [16]. The structure is made up of neutral [Fe^{III}(Tp)(CN)₃]₂Cu^{II}(dpa)₂ and non-coordinated water molecules. Within **1**, [Fe^{III}(Tp)(CN)₃][−] act as a monodentate ligand through one of its three cyano groups toward a central [Cu^{II}(dpa)₂]²⁺ unit, while each [Cu^{II}(dpa)₂]²⁺ unit is linked to two [Fe^{III}(Tp)(CN)₃][−] units, forming a nearly vertical trinuclear [Fe^{III}(Tp)(CN)₃]₂Cu^{II}(dpa)₂, which is shown in Fig. 1a. The two terminal [Fe^{III}(Tp)(CN)₃][−] fragments are bridged by the central [Cu(dpa)₂]²⁺ unit in the *cis*-arrangement. In **1**, there are crystallographically independent Fe1, Fe2 and Cu1 centers. Each Fe1 center is coordinated by three cyano carbon atoms and three nitrogen atoms of Tp, forming a distorted FeC₃N₃ octahedral coordination configuration with a C_{3v} symmetry. The Fe1 – C bond lengths are 1.907–1.934 Å, and the Fe1 – N distances are 1.972–1.991 Å (Table S1). The coordination mode of Fe2 center is similar to that of Fe1 center. The Fe2 – C bond lengths are 1.908–1.924 Å, and the Fe2 – N distances are 1.972–1.987 Å, respectively. The Fe – C≡N linkages are close to linearity with bond angles of 176.9–179.6°. Each Cu1 center is located in a distorted N₆ octahedral coordination environment. The equatorial positions are occupied by one cyano nitrogen atom and three nitrogen atoms from two dpa ligands, while the two axial positions are occupied by one cyano nitrogen atom and one nitrogen atom from dpa ligand.

* Corresponding author.

E-mail address: liutao@dlut.edu.cn (T. Liu).

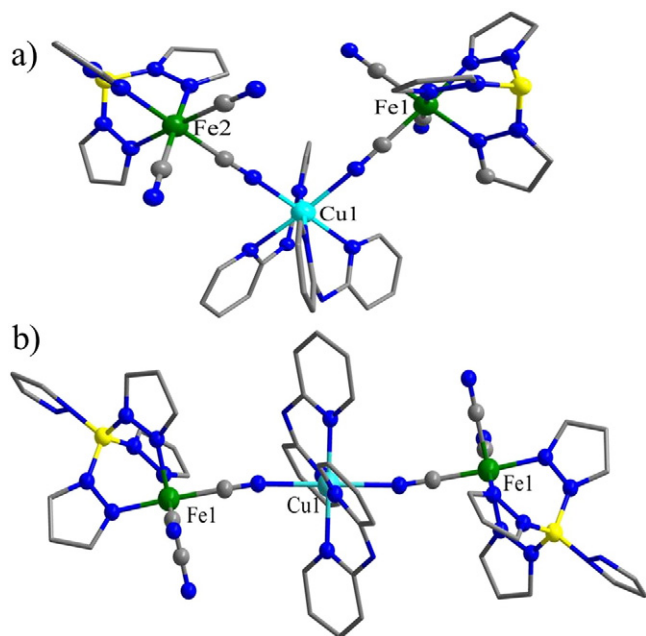


Fig. 1. a) Crystal structure of **1**; b) crystal structure of **2**, H and O atoms have been omitted for clarity (Fe, green, Cu, aqua, C, gray, N, blue, B, yellow).

The Cu1–N_{equatorial} bond lengths are 2.017–2.068 Å, and the Cu1–N_{axial} distances are 2.269–2.343 Å. Such structural characteristics indicated that the Fe1 center was low-spin Fe^{III}. Three metal centers were in a nearly perpendicular array with a Fe1–Cu1–Fe2 angle of 91.73°. The C≡N–Cu1 bond angles are slightly deviate from linearity with bond angles of 164.6 and 170.3°. The intramolecular Fe1–Cu1, Fe2–Cu1, and Fe1–Fe2 distances are 5.267, 5.061 and 7.414 Å, respectively, while the closest intermolecular Fe–Cu, Cu–Cu, and Fe–Fe distances are 8.462, 10.267 and 7.853 Å, respectively, indicating that the intermolecular magnetic interaction is very weak.

Complex **2** also crystallized in the triclinic space group *P* – 1 [16]. The composition of **2** is very similar to **1** except using [Fe(pzTp)(CN)₃][–] to replace [Fe(Tp)(CN)₃][–]. The change increases the steric exclusion between the dpa ligands and adjacent building blocks, leading to three metal centers in a linear array with a Fe1–Cu1–Fe1 (symmetry codes: –*x* + 2, –*y*, –*z* + 1) angle of 180.0°, forming a linear centrosymmetrical trinuclear. The crystal structure comprises one [Cu(dpa)₂]²⁺ and two terminal [Fe^{III}(pzTp)(CN)₃][–] units. The two [Fe^{III}(pzTp)(CN)₃][–] fragments are bridged by the central [Cu(dpa)₂]²⁺ unit in the *trans*-arrangement, which is depicted in Fig. 1b. Three nitrogen atoms from pzTp and three cyano carbon atoms are coordinated to each Fe1 center. The Fe1–C bond lengths are 1.923–1.932 Å and the Fe1–N distances are 1.969–1.979 Å, respectively (Table S2). The Fe–C≡N linkages are almost linear with bond angles of 177.2–180.0°. The equatorial plane of the Cu1 center is occupied by four nitrogen atoms from two dpa ligands, and two nitrogen atoms from the cyano occupy its axial positions, leading to a severely axially elongated N₆ octahedral coordination configuration. The Cu1–N_{equatorial} bond lengths are 2.016–2.021 Å, and the Cu1–N_{axial} distance is 2.416 Å. The structural parameters indicate that the Fe1 center was low-spin Fe^{III}. The C≡N–Cu1 bond angle is somewhat deviate from linearity with bond angle of 167.7°, which is comparable to that found in **1**. The intramolecular Fe1–Cu1, and Fe1–Fe1 distances are 5.451 and 10.902 Å, respectively, while the closest intermolecular Fe–Cu, Cu–Cu, and Fe–Fe distances are 8.313, 8.044 and 7.717 Å, respectively.

The temperature-dependent magnetic susceptibilities (χ) of **1** were performed under 1000 Oe in the temperature range of 2–300 K (Fig. 2). At 300 K, the χT value was 1.76 cm³ mol^{–1} K per Fe₂Cu unit, which is

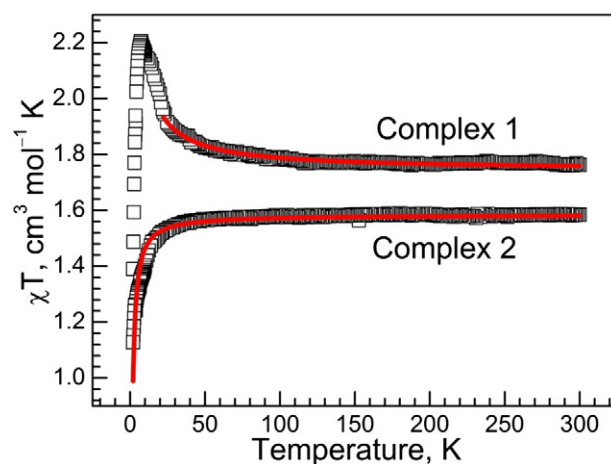


Fig. 2. Temperature-dependent magnetic susceptibilities of **1** and **2** in the temperature range of 2–300 K under an applied field of 1000 Oe. The solid line are the best fit with the model described in text.

larger than the spin-only value for two uncoupled low-spin Fe^{III} atoms ($S = 1/2$, $g = 2.0$) and one high-spin Cu^{II} atom ($S = 1/2$, $g = 2.0$). The larger value is probably owing to the underestimated g value for Fe and Cu, which is often larger than 2.0 [17]. As the temperature decreased, the χT value gradually increased to a maximum value of 2.21 cm³ mol^{–1} K at 7.5 K. This curve is in agreement with a ferromagnetic coupling between the Fe^{III} and Cu^{II}. According to the structure, the data was simulated with the Magpack program based on an exchange Hamiltonian $H = -2J(S_{\text{Fe1}} \cdot S_{\text{Cu1}} + S_{\text{Fe2}} \cdot S_{\text{Cu1}})$, where J is the exchange magnetic coupling constant [18]. The best fitting results were obtained from 300 to 25 K, gives $g = 2.5$ and $J = 3.79$ cm^{–1} with the agreement factor $R = 1.16 \times 10^{-5}$. The magnitude of the exchange coupling constant is somewhat lower than those observed for other molecules with Fe^{III}–CN–Cu^{II} linkages [19]. Below 7.5 K, the χT value drops sharply, reaching 1.39 cm³ mol^{–1} K at 2 K, which could be attributed to the zero-field splitting and/or weak intermolecular antiferromagnetic interactions [20]. In the temperature range of 2–300 K, the magnetic susceptibility data is the fitting to the Curie–Weiss law with a Curie constant C of 1.75 cm³ mol^{–1} K and a Weiss constant θ of 2.14 K. The positive Weiss constant further confirms that the ferromagnetic coupling takes place between Fe^{III} and Cu^{II} centers through the cyano-bridged. These magnetic behaviors were consistent with an intramolecular Fe^{III}–Cu^{II} ferromagnetic interaction, which can be rationalized in terms of the strict orthogonality of the magnetic orbitals of the low-spin Fe^{III} [d^5 , $t_{2g}^5 e_g^0$] and high-spin Cu^{II} [d^9 , $t_{2g}^6 e_g^3$] centers, an arrangement that normally gives rise to ferromagnetic coupling [21]. Field dependence of magnetization of **1** at 1.8 K is displayed in Fig. S1. The isothermal magnetization nearly linear with the field in low field region and reaches a saturated value of 3.6 N β at 50 kOe, is close to the theoretical value for two magnetically isolated low-spin Fe^{III} ions and one magnetically isolated high-spin Cu^{II} ion, which further confirms the presence of ferromagnetic coupling between the Fe^{III} and Cu^{II} ions.

The magnetic centers in **2** have the same and similar linkages to that in **1**, but they show very different magnetic behaviors due to *cis*–*trans* arrangement of the building block (Fig. 2). The χT product was 1.58 cm³ mol^{–1} K at 300 K, upon cooling, the χT product still remains quasi-constant down to 25 K and then rapidly decreased to a minimum value of 1.13 cm³ mol^{–1} K at 2 K. Such a magnetic behavior indicates the presence of a weak antiferromagnetic coupling between the Fe^{III} and Cu^{II} ions. A similar antiferromagnetic behavior has also been observed in other complexes [22]. The same fitting method was applied to **2** in the whole temperature to give values of $J = -1.12$ cm^{–1} and $g = 2.37$ with the agreement factor $R = 1.97 \times 10^{-4}$. The negative J value indicates that there is a weak antiferromagnetic coupling between Fe^{III} and Cu^{II} ions, the J values are similar to those reported for

Download English Version:

<https://daneshyari.com/en/article/1303662>

Download Persian Version:

<https://daneshyari.com/article/1303662>

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