

Cyanide-Bridged Tetranuclear $RE^{III}_2Fe^{III}_2$ ($RE = Y, Tb, Dy$) Molecular Squares with 2,2':6',2''-Terpyridine as a Capping Ligand

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Abstract. Self-assembly reaction between hydrated rare-earth (RE) nitrates $RE(NO_3)_3 \cdot 6H_2O$ with $K_3Fe(CN)_6$ in H_2O/DMF solution by employing the tridentate ligand 2,2':6',2''-terpyridine (terpy) as a capping ligand has yielded three cyanide-bridged compounds $[RE(terpy)(DMF)(H_2O)_2][Fe(CN)_6] \cdot 6H_2O$ [$RE = Y$ (**1**), Tb (**2**), Dy (**3**)]. FT-IR spectra confirmed the presence of terpy ligands and cyanide groups in compounds **1–3**. Single-crystal X-ray structural analysis

indicated that these compounds are isomorphous and adopt neutral $[RE_2Fe_2]$ molecular squares, which are further linked through hydrogen bonding interactions to generate a three-dimensional supramolecular network. Magnetic susceptibility measurements revealed that significant single ion magnetic anisotropy dominates the properties of these compounds.

Introduction

In the past few decades, considerable efforts have been focused on the design and elaboration of functional coordination compounds.^[1] Among these materials, cyanide-bearing assemblies have grown rapidly because of their intriguing architectures and promising potential applications in many fields.^[2–7] In particular, cyanide-bridged molecular squares offered a unique opportunity for further investigation, because they represent one of the simplest type of molecular structure and have exhibited a wide range of physical properties such as rich electrochemistry, valence- and spin-state control, and spin-crossover phenomenon.^[8] Generally, capping ligands were usually employed to control the number and relative position of available coordinated sites on the cyanometallates during the synthesis process of these molecular squares.^[9–17] In contrast to this approach, there are rare examples of $[M(CN)_6]$ ($M = Fe, Co, Cr$) based squares reported previously by employing uncapped cyanometallates and limiting the coordination number on solvated metal cations.^[18–20] In principle, the rigid polydentate ligands with appropriately oriented chelating sites can clip the metal cations at the corners and thus may result in squares with perfect co-planarity. However, the suc-

cessful assembly of molecular squares from polydentate ligands is rare and still remains a great challenge.

As a result of our ongoing study of the syntheses and functionalities of low-dimensional cyanide-bridged coordination compounds,^[21–23] the tridentate ligand 2,2':6',2''-terpyridine (terpy) was used in our laboratory as a capping ligand to react with rare-earth (RE) ions and $[Fe(CN)_6]^{3-}$ precursor, isolating three heterometallic compounds $[RE(terpy)(DMF)(H_2O)_2][Fe(CN)_6] \cdot 6H_2O$ [$RE = Y$ (**1**), Tb (**2**), Dy (**3**)] with molecular squares. Herein, we reported their syntheses, crystal structures, infrared spectra, and magnetic properties.

Results and Discussion

Single-crystal X-ray diffraction analysis revealed that compounds **1–3** are isomorphous and crystallize in the triclinic space group $P\bar{1}$ (Table 1). Herein only the structure of compound **1** is depicted in detail (Figure 1), and the molecular structures of compounds **2** and **3** are shown in Figure S1 and Figure S2 (Supporting Information), respectively. The structure of compound **1** can be described as a centro-symmetric tetranuclear $[Y_2Fe_2]$ molecular square. The asymmetric unit of compound **1** consists of one $[Y(terpy)(DMF)(H_2O)_2]^{3+}$ cation, one $[Fe(CN)_6]^{3-}$ anion, and six crystallized water molecules. Each Fe atom is in a slightly distorted octahedral arrangement with six cyanide ligands, where two *cis* cyanide groups acting as a μ -linker bridged to adjacent Y^{III} sites and the remaining ones are terminal. There are no dimensional differences between the mean values for the bridging and terminal cyanide ligands. The Fe1–C and C–N bond lengths range from 1.930(5) to 1.951(5) Å, and 1.135(7) to 1.152(6) Å, respectively, whereas the Fe1–CN bonds remain almost linear with the maximum deviation from linearity of 3.2°. The Y^{III} atom adopts a distorted decahedral environment, filled by two

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Table 1. Crystallographic data and structural refinement for compounds **1–3**.

	1	2	3
Formula	C ₂₄ H ₃₄ FeN ₁₀ O ₉ Y	C ₂₄ H ₃₄ FeN ₁₀ O ₉ Tb	C ₂₄ H ₃₄ FeN ₁₀ O ₉ Dy
<i>M_r</i>	751.37	821.38	826.93
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	10.3421(14)	10.3023(19)	10.2860(12)
<i>b</i> /Å	13.3574(18)	13.260(3)	13.3393(15)
<i>c</i> /Å	13.5460(19)	13.473(3)	13.5685(16)
<i>a</i> /°	94.019(2)	93.400(2)	94.1350(10)
<i>β</i> /°	110.667(2)	110.788(2)	110.8500(10)
<i>γ</i> /°	102.652(2)	103.647(2)	101.3120(10)
<i>V</i> /Å ³	1685.9(4)	1651.3(6)	1685.4(3)
<i>Z</i>	2	2	2
<i>ρ_c</i> /g·cm ⁻³	1.480	1.652	1.622
<i>μ</i> /mm ⁻¹	2.204	2.625	2.691
Total, unique	13624, 6801	13942, 7413	12927, 6296
Observed [<i>I</i> > 2σ(<i>I</i>)]	4765	6534	5519
GOF on <i>F</i> ²	1.028	1.063	1.037
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0528, 0.1355	0.0338, 0.0954	0.0323, 0.0834
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0874, 0.1573	0.0411, 0.1011	0.0392, 0.0874

bridged cyanide groups, three nitrogen atoms from one terpy ligand, two water molecules, and one DMF ligand. The average distance for Y1–N bonds is 2.463 Å, slightly larger than 2.334 Å for Y1–O bonds. Meanwhile, the Y1–NC bonds are bent significantly [161.3(4)° for Y1–N1C1 and 163.3(4)° for Y1–N6C6; symmetric code: (i) $-x + 2, -y + 2, -z$], opposition to the linear Fe1–CN units. The geometrical data of the Y1–N_{terpy} and Y1–O bonds are identical to those reported for [M^{III}(CN)₄] (*M* = Ni, Pd, Pt), [M^{III}(CN)₆] (*M* = Fe, Co), and [W^V(CN)₈] based metal-terpy compounds.^[18,24,25]

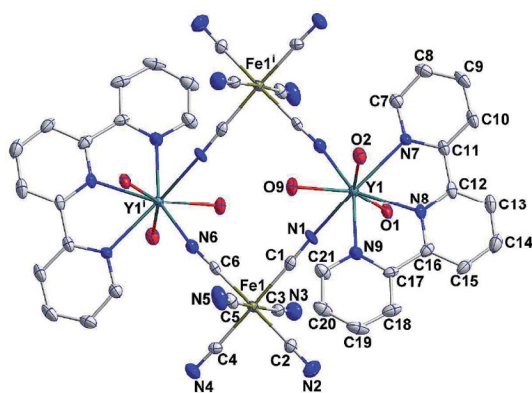


Figure 1. The neutral [Y₂Fe₂] molecular square of compound **1**. All hydrogen atoms, crystallized water molecules, and carbon and nitrogen atoms from DMF molecules are omitted for clarity. Symmetric code: (i) $-x + 2, -y + 2, -z$.

As a result, two [Y(terpy)(DMF)(H₂O)₂]³⁺ units and two [Fe(CN)₆]³⁻ anions are linked alternatively through the –Y–N≡C–Fe– linkages to generate a neutral tetranuclear [2 × 2] molecular square. The square resides on an inversion center and hence the four metal atoms are exactly coplanar. Two Fe^{III} and two Y^{III} atoms are located on the vertexes, whereas bridged cyanide groups form the sides. The intramolecular Y^{III}–Fe contacts of the square are about 5.420 and 5.469 Å, the diagonal Y^{III}–Y^{III} and Fe^{III}–Fe distances are 7.906 and 7.488 Å, respectively, and the vertex angles are 93.11° for

Y1–Fe1–Y1 and 86.89° for Fe1–Y1–Fe1, indicating slight deviations from the ideal square arrangement. The structural parameters of molecular squares for compounds **1–3** are summarized in Table S1 (Supporting Information). The similar square core environment has also been observed in [M^{III}(CN)₆] based (*M* = Fe, Co, Cr) bimetallic compounds with the same or different capping ligands.^[18–20] Terminal cyanide ligands, coordinated and uncoordinated water molecules are all involved in the formation of hydrogen bonding network for compounds **1–3**. Coordinated and uncoordinated water molecules interact with four terminal cyanide ligands through O–H⁺–N hydrogen bonds. Simultaneously, coordinated water molecules interact with uncoordinated ones by O–H⁺–O hydrogen bonds. Furthermore, the lattice water molecules are also interlinked by O–H⁺–O hydrogen bonds. As a consequence, the adjacent squares are held together by above hydrogen bonding interactions, forming a three-dimensional supramolecular network (Figure S3, Supporting Information). The shortest intermolecular Fe^{III}–Fe, Y^{III}–Y and Fe^{III}–Y distances are 9.865, 8.876, and 7.660 Å, respectively, indicating that the intermolecular magnetic interaction is very weak. The structural parameters of intra- and intermolecular distances for all compounds are summarized in Table S2 (Supporting Information).

IR spectra of compounds **1–3** exhibit similar bands because of their isomorphous feature (Figure 2). For the free terpy ligand, two strong absorption bands at 1600–1538 and 1486–1392 cm⁻¹ can be assigned to the ν(CN) and ν(CC) bonds stretching, respectively. These two bands in IR spectra of compounds **1–3** show 11–15 cm⁻¹ shift to lower wavenumbers due to the coordination of metal ions. The bands in the low energy region of 800–400 cm⁻¹ from free terpy were also observed in compounds **1–3**, indicating the presence and coordination of terpy ligands. The peaks at about 2127 and 2148 cm⁻¹ are ascribed to the stretching vibrations of terminal and bridging cyano groups, respectively. In general, the bridged cyanide frequencies in cyanide compounds are observed at higher frequencies due to the kinematic coupling. The board peaks at

3400–3200 cm^{-1} are related to the stretching vibration of hydroxyl groups from lattice water molecules, while the presence of the bound water molecules was observed at 3601 cm^{-1} . The strong stretching frequencies of C=O bonds are located at 1660 cm^{-1} , which are related to the coordinated DMF molecules. The results from IR spectra of compounds 1–3 agree well with those from single-crystal X-ray structural analysis.

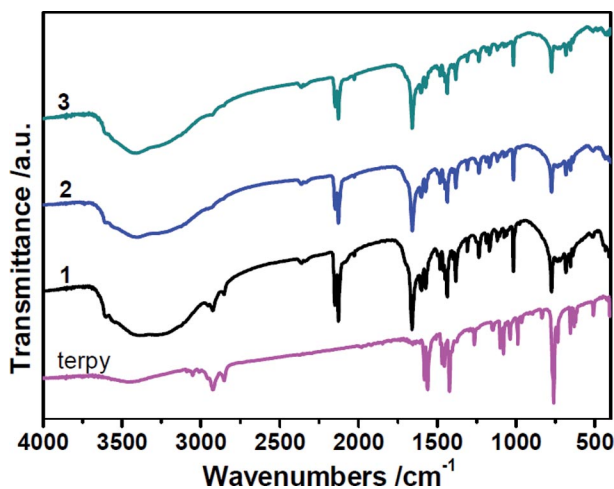


Figure 2. IR spectra of the free terpy ligand and compounds 1–3.

Magnetic Properties

Magnetic susceptibility measurements for compounds 1–3 were performed on polycrystalline samples at 1 kOe over the temperature range 1.8–300 K (Figure 3a). Due to the diamagnetism of the Y^{III} ion, compound 1 can be considered as an isolated low-spin Fe^{III} ion system. The observed $\chi_{\text{M}}T$ value at 300 K is $0.88 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is significantly higher than the spin only one ($0.375 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$) for an isolated Fe^{III} ($S = 1/2$) ion, suggesting the presence of significant orbital contributions to the magnetic moment. Upon cooling, the $\chi_{\text{M}}T$ value decreases until reaches the value of $0.51 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 1.8 K. The magnetic thermal behavior of compound 1 is typical for a magnetically isolated low-spin distorted octahedral Fe^{III} system with spin-orbital coupling of the ${}^2\text{T}_{2\text{g}}$ ground term.^[26] The magnetic nature of compound 1 can be further confirmed by the field-dependent magnetization measured up to 70 kOe at 1.8 K, as shown in Figure 3b. As the external field increases, the magnetization of compound 1 continuously increases and reaches a value of $1.2 N_{\mu_{\text{B}}}$ at 70 kOe, which is in agreement with the theoretical saturation value ($1 N_{\mu_{\text{B}}}$) for the single Fe^{III} ion (calculated from $M_{\text{S}} = gS_{\text{Fe}}$ with $g = 2$).

For compounds 2 and 3, the room-temperature $\chi_{\text{M}}T$ values are 13.14 and $15.32 \text{ cm}^3 \text{ K mol}^{-1}$, respectively, which are slightly higher than the theoretical ones (compound 2: $12.20 \text{ cm}^3 \text{ K mol}^{-1}$; compound 3: $14.55 \text{ cm}^3 \text{ K mol}^{-1}$) for two uncoupled RE^{III} and low-spin Fe^{III} ions. As the temperature is lowered, the $\chi_{\text{M}}T$ values of both compounds remain almost constant before 50 K and then decrease rapidly to minimum values of 8.85 and $12.36 \text{ cm}^3 \text{ K mol}^{-1}$ for compounds 2 and 3 at

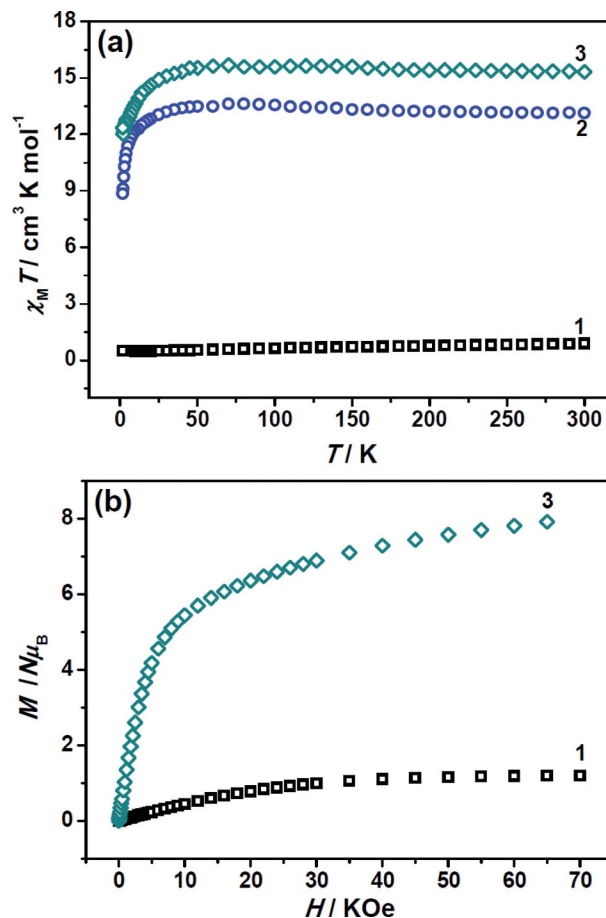


Figure 3. (a) Temperature dependence of $\chi_{\text{M}}T$ for compounds 1–3 measured at 1 kOe; (b) Field dependence of the magnetization for compounds 1 and 3 at 1.8 K.

1.8 K, respectively. The curves suggest that the couplings within compounds 2 and 3 might be difficult to be clarified because the superexchange interactions (ferro- or antiferromagnetic) and single ion anisotropy of RE^{III} ions (thermal depopulation of the Stark levels) are intertwined together. The field-dependent magnetization measurement of compound 3 was further carried out (Figure 3b). The magnetization increases continuously and reaches the maximum value ($7.92 N_{\mu_{\text{B}}}$) at 65 kOe without saturation, which is lower than the theoretical one on the basis of the noninteracting ions of the $[\text{Dy}_2\text{Fe}_2]$ unit. The magnetic behavior for compounds 2 and 3 was also observed in the polymeric chains $[\text{Tb}(\text{tptz})(\text{H}_2\text{O})_4\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ [tptz = 2,4,6-tri(2-pyridyl)-1,3,5-triazine] and $\text{RE}(\text{DMF})_6\text{Fe}(\text{CN})_6$ ($\text{RE} = \text{Tb}, \text{Dy}$),^[27,28] in which no significant magnetic interactions between the RE^{III} and Fe^{III} ions. Similarly, the magnetic interactions between the RE^{III} and Fe^{III} ions in compounds 2 and 3 are also negligible, due to the significant magnetic anisotropy and/or the population of low-lying excited states. Trying to further make magneto-structural correlations for both compounds has proved impossible until now because of the complexity of the 3d-4f magnetic interactions and the few complexes reported in the literature with similar RE-CN-Fe core. Work is underway in our

lab on the preparation and magnetic investigation of high-spin cyanide-bridged 3d-4f systems by varying the types of rare-earth ions or capping ligands.

Conclusions

We have demonstrated a facile approach to synthesize cyanide-bridged bimetallic compounds with molecular square structure, although negligible magnetic interactions between rare earth(III) and low-spin iron(III) ions were found in these materials. The presence of tridentate capping ligands during the synthesis process is practically responsible for the formation of low-dimensional architectures. Studies on tuning the magnetism of $\text{Fe}(\text{CN})_6$ based bimetallic system by varying rare-earth ions are in progress in our laboratory.

Experimental Section

Materials and General Methods: All chemicals and solvents were purchased from commercial sources and used without further purification. FT-IR spectra were measured with a Nicolet FT 1703X spectrophotometer in the form of KBr pellets in the 4000–400 cm^{-1} region. All magnetic measurements on microcrystalline sample were conducted on a Quantum Design MPMP-XL7 superconducting quantum interference device (SQUID) magnetometer. Corrections of measured susceptibilities were carried out considering both the sample holder as the background and the diamagnetism of the constituent atoms according to Pascal's tables.^[29]

Syntheses of $[\text{RE}(\text{terpy})(\text{DMF})(\text{H}_2\text{O})_2][\text{Fe}(\text{CN})_6]\cdot 6\text{H}_2\text{O}$ [$\text{RE} = \text{Y}$ (1**), **Tb** (**2**), **Dy** (**3**)]:** Single crystals of compounds **1–3** were prepared at room temperature by the slow diffusion of a DMF solution (3 mL) containing $\text{RE}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.10 mmol) and terpy (0.20 mmol) into a water solution (15 mL) of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.10 mmol). After about 2–3 weeks, yellow rod-shaped crystals were obtained. Yield for compound **1**: ca. 37% based on the RE salt. Compounds **2** and **3** have similar mass yields. $\text{C}_{24}\text{H}_{34}\text{FeN}_{10}\text{O}_9\text{Y}$ (**1**): calcd. C 38.37; H 4.56; N 18.64%; found: C 37.96; H 4.51; N 18.82%. $\text{C}_{24}\text{H}_{34}\text{FeN}_{10}\text{O}_9\text{Tb}$ (**2**): calcd. C 35.10; H 4.17; N 17.05%; found: C 34.98; H 4.25; N 17.19%. $\text{C}_{24}\text{H}_{34}\text{FeN}_{10}\text{O}_9\text{Dy}$ (**3**): calcd. C 34.94; H 4.15; N 16.98%; found: C 34.77; H 4.33; N 17.12%.

X-ray Crystallographic Analysis: Single-crystal X-ray diffraction data for compounds **1–3** were collected with a Bruker Smart Apex II diffractometer equipped with $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Diffraction data analysis and reduction were performed within SMART and SAINT.^[30] Correction for Lorentz, polarization, and absorption effects were performed within SADABS.^[31] Structures were solved using Patterson method within SHELXS-97 and refined using SHELXL-97.^[32–34] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of terpy and DMF ligands were calculated at idealized positions and included in the refinement in a riding mode with U_{iso} for H assigned as 1.2 or 1.5 times U_{eq} of the attached atoms. The hydrogen atoms bound to water molecules were located from difference Fourier maps and refined as riding with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting

the depository numbers CCDC-1027871 (**1**), CCDC-1027872 (**2**), and CCDC-1027873 (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): The molecular squares of compounds **2** and **3**; selected bond lengths and angles of compounds **1–3**; the intra- and intermolecular distances of compounds **1–3**.

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