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A serials of sandwich-like trinuclear and one-dimensional chain cyanide-bridged iron(III)-copper(II) complexes: Syntheses, crystal structures and magnetic properties

Jingwen Shi[a], Wenlong Lan[a], Yanjie Ren[b], Qingyun Liu[c], Hui Liu[a], Yunhui Dong[a], Daopeng Zhang[a,*]

[a] *College of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255049, PR China*
[b] *College of Life Sciences, Shandong University of Technology, Zibo 255049, PR China*
[c] *College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266510, PR China*

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ABSTRACT

Four pyridinecarboxamide *trans*-dicyanideiron(III) building blocks and one macrocyclic copper(II) compound have been employed to assemble cyanide-bridged heterometallic complexes, resulting in a serials of cyanide-bridged Fe^{III}-Cu^{II} complexes with different structure types. The series of complexes can be formulated as: $\{[Cu(Cyclam)][Fe(bpb)(CN)_2]_2\}\cdot 4H_2O$ (**1**), $\{\{[Cu(Cyclam)][Fe(bpb)(CN)_2]\}ClO_4\}_n\cdot nH_2O$ (**2**), and $\{[Cu(Cyclam)][Fe(bpmb)(CN)_2]_2\}\cdot 4H_2O$ (**3**), $\{[Cu(Cyclam)][Fe(bpClb)(CN)_2]_2\}\cdot 4H_2O$ (4) and $\{\{[Cu(Cyclam)][Fe(bpdmb)(CN)_2]\}ClO_4\}_n\cdot 2nCH_3OH$ (**5**) (bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate, $bpmb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4-methyl-benzenate, $bpClb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4-chloro-benzenate, $bpdmb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4,5-dimethyl-benzenate, Cyclam = 1,4,8,11-tetraazacyclotetradecane). All the complexes have been characterized by elemental analysis, IR spectra and structural determination. Single X-ray diffraction analysis shows the similar neutral sandwich-like structures for complexes **1**, **3** and **4**, in which the two cyano precursors acting as monodentate ligand through one of their two cyanide groups were coordinated face to face to central Cu(II) ion. The complexes **2** and **5** can be structurally characterized as one-dimensional cationic single chain consisting of alternating units of $[Cu(Cyclam)]^{2+}$ and $[Fe(bpb/bpdmb)(CN)_2]^{-}$ with free ClO_4^{-} as balanced anion. Investigation over magnetic properties of the whole serials of complexes reveals the antiferromagnetic magnetic coupling between the neighboring cyanide-bridged Fe(III) and Cu(II) ions in complexes **3** and **4** and the ferromagnetic interaction in complexes **1**, **2** and **5**, respectively.

1. Introduction

The research field of the heterometallic function complex has always been given intense attention in the recent history of the coordination chemistry. Among all the fields of the function coordination chemistry, the molecule-based magnetic materials [1–5], including high-T_c magnet [6–8], single molecule magnet (SMMs) [9–13], single chain magnet (SCMs) [14–17], spin crossover (SCO) [18–21], photomagnetic [22–24] and chiral magnetic materials [25–27], continue to attract great interest due not only to fully revealing the magnetic coupling nature between the paramagnetic metal centers, the magneto-structural correlation, and the exotic magnetic phenomena but also to their potential applications in many high-tech fields. Because its well ability of the cyanide bridge to efficiently transfer the magnetic interactions between paramagnetic metal ions, polycyanometallates with or without the peripheral blocking organic ligand(s) have been known to be efficient building blocks to assemble coordination polymers (CPs) with interesting magnetic properties. Up to now, many paramagnetic cyano precursors containing different number of the cyanide groups have been rationally designed and used to prepare the cyanide-bridged homo- or heterometallic magnetic complexes with divers structures and the appealing magnetic properties [28–31].

The *trans*-dicyanometallates can be defined as metal complexes containing either 3d or 4f metal ion usually blocked by two *trans* cyanide groups and an equatorial organic ligand. Due to their distinct structural feature – two *trans* cyanide groups and the big equatorial organic ligand, these types of the cyano precursors have been proven excellent building blocks to construct low-dimensional cyanide-bridged

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[*] Corresponding author.
E-mail address: dpzhang73@126.com (D. Zhang).

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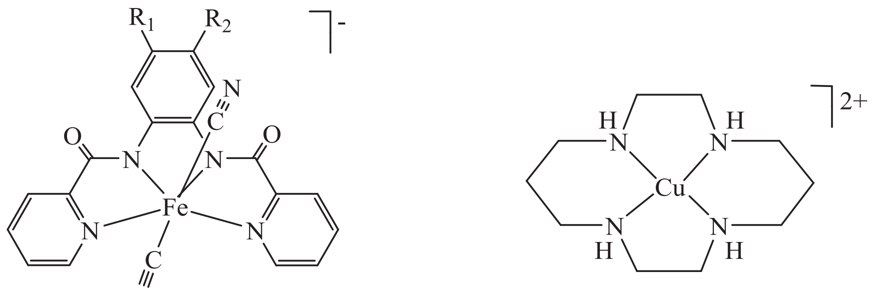

trans-$[Fe(L)(CN)_2]^-$($R_1 = R_2$ = H, L = bpb^{2-}; R_1 = H, R_2 = Me, L = $bpmb^{2-}$; R_1 = H, R_2 = Cl, L = $bpClb^{2-}$; $R_1 = R_2$ = Me, L = $bpdmb^{2-}$)

$[Cu(Cyclam)]^{2+}$

Scheme 1. The starting materials used to prepare the complexes **1**–**5**.

magnetic complexes, especially for polynuclear entities and one-dimensional chains [29,32]. Based-on the rigid in-plane tetradentate pyridinecarboxamide ligands L (L =1,2-bis(pyridine-2-carboxamido) benzenate), a series of Fe(III), Cr(III), Co(III) *trans*-dicyanometallates have been successfully employed to synthesize cyanide-bridged complexes with many kinds of paramagnetic compounds as assemble segments, such as Schiff-base manganese(III) [33–35], porphyrin manganese(III) [36], macrocyclic nickel(II) [37], manganese(II) [38] and chiral amine copper(II) compounds [39]. To throw further light on the magnetism system of these types of building blocks(Scheme 1), the reactions of four *trans*-dicyanoiron(III) precursors with the macrocyclic copper(II) compound $[Cu(Cyclam)][ClO_4]_2$ (Cyclam = 1,4,8,11-tetraazacyclotetradecane) have been investigated. Three cyanide-bridged Fe_2Cu trinuclear complexes, $\{[Cu(Cyclam)][Fe(bpb)(CN)_2]_2\}\cdot4H_2O$ (**1**), $\{[Cu(Cyclam)][Fe(bpmb)(CN)_2]_2\}\cdot4H_2O$ (**3**), $\{[Cu(Cyclam)][Fe(bpClb)(CN)_2]_2\}\cdot4H_2O$ (4) and two one-dimensional cyanide-bridged Fe-Cu complexes, $\{\{[Cu(Cyclam)][Fe(bpb)(CN)_2]\}ClO_4\}_n\cdot nH_2O$ (**2**), $\{\{[Cu(Cyclam)][Fe(bpdmb)(CN)_2]\}ClO_4\}_n\cdot2nCH_3OH$ (**5**), (bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate, $bpmb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4-methyl-benzenate, $bpClb^{2-}$ = 1,2-bis(-pyridine-2-carboxamido)-4-chloro-benzenate, $bpdmb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4,5-dimethyl-benzenate) were obtained. In this paper, the syntheses, crystal structures, and magnetic properties of the above five complexes will be detailed described.

2. Experimental section

Elemental analyses for the C, H and N have been performed on Elementary Vario El. The infrared spectroscopy (KBr) was carried out within the range of 4000–400 cm^{-1} with Magna-IR 750 spectrophotometer. The temperature dependent magnetic susceptibilities and the field dependence magnetization were measured on a Quantum Design MPMS SQUID magnetometer, and the experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

2.1. General procedures and materials

The four dicyanometallates were synthesized according to the methods described in literature [40]. All the preparation reactions were carried out under an air atmosphere without the protection of nitrogen. All the used chemicals and solvents were commercial with reagent grade without further purification.

2.2. Preparation of complexes 1, 3, and 4

These three complexes were prepared by the similar slow evaporation procedure, therefore only the synthesis of **1** was detailed as a typical representative. $K[Fe(bpb)(CN)_2]$ (46.5 mg, 0.10 mmol) dissolved in methanol/water (4:1, v-v) (10 mL) was added to a solution of $[Cu(Cyclam)][ClO_4]_2$ (46.3 mg, 0.10 mmol) formed *in-situ* by mixing equivalent mole of Cyclam and $[Cu(ClO_4)_2]\cdot6H_2O$ in CH_3CN. The mixture was stirred at room temperature for several minutes before the tiny insoluble material was filtered out. The filtrate was allowed to slowly evaporate in the dark at room temperature, and the single crystals suitable for X-ray diffraction obtained after about two weeks were collected with the yield about 55–60% (Based-on the cyanide precursor).

Complex **1**: Anal. Calcd. for $C_{50}H_{56}CuFe_2N_{16}O_8$: C, 50.71; H, 4.77; N, 18.92. Found: C, 50.64; H, 4.66; N, 19.04. Main IR bands (cm^{-1}): 2160, 2125 (s, νC≡N), 1615, 1628 (vs, νC═N).

Complex **3**: Anal. Calcd. For $C_{52}H_{60}CuFe_2N_{16}O_8$: C, 51.52; H, 4.99; N, 18.49. Found: C, 51.42; H, 4.85; N, 18.58. Main IR bands (cm^{-1}): 2160, 2126 (s, νC≡N), 1618, 1630 (vs, νC═N).

Complex **4**: Anal. Calcd. for $C_{50}H_{54}Cl_2CuFe_2N_{16}O_8$: C, 47.92; H, 4.34; N, 17.88. Found: C, 47.84; H, 4.18; N, 18.01. Main IR bands (cm^{-1}): 2158, 2125 (s, νC≡N), 1615, 1625 (vs, νC═N).

2.3. Preparation of complexes 2 and 5

These two complexes were prepared by using three layers diffusion method. $K[Fe(bpb)(CN)_2]$ (46.5 mg, 0.10 mmol) or $K[Fe(bpdmb)(CN)_2]$ (49.3 mg, 0.10 mmol) was dissolved in a mixture solvent of H_2O/CH_3OH (1:1, v-v) 5 mL, and the solution was laid in the bottom of a tube. The buffer solution composed by H_2O, CH_3OH and CH_3CN with a ratio of 1:1:1 was carefully added to the above layer. Then, a solution of $[Cu(Cyclam)][ClO_4]_2$ (46.3 mg, 0.10 mmol) formed *in-situ* by mixing equivalent mole of Cyclam and $[Cu(ClO_4)_2]\cdot6H_2O$ in CH_3CN was carefully added to the top of buffer layer. About two-three weeks later, single crystals suitable for X-ray diffraction were obtained, collected by filtration and dried in air.

Complex **2**: Yield: 42.9 mg, 53.3% (Based-on the cyanide precursor). Anal. Calcd. for $C_{30}H_{38}ClCuFeN_{10}O_7$: C, 44.73; H, 4.76; N, 17.39. Found: C, 44.64; H, 4.66; N, 17.48. Main IR bands (cm^{-1}): 2125 (s, νC≡N), 1620, 1626 (vs, νC═N), 1100 (vs, νCl═O).

Complex **5**: Yield: 45.2 mg, 51.4% (Based-on the cyanide precursor). Anal. Calcd. for $C_{34}H_{48}ClCuFeN_{10}O_8$: C, 46.42; H, 5.50; N, 15.92. Found: C, 46.31; H, 5.40; N, 15.13. Main IR bands (cm^{-1}): 2125 (s, νC≡N), 1622, 1630 (vs, νC═N), 1100 (vs, νCl═O).

2.4. X-ray data collection and structure refinement

Single crystals of the complexes **1**–**5** for X-ray diffraction analysis with suitable size were mounted on the glass rod and the crystal data were collected on a Bruker SMART CCD diffractometer with a MoKα sealed tube (λ = 0.71073 Å) at the room temperature, using a ω scan