Synthesis, Crystal Structures, and Magnetic Properties of One-Dimensional Mixed Cyanide- and Phenolate-Bridged Heterotrimetallic Complexes

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ABSTRACT: Two one-dimensional (1D) cyanide- and phenolate-bridged heterotrimetallic complexes $\{[Cu^{II}Mn^{II}(L^1)][Fe^{III}(bpb)(CN)_2]\}_n \cdot (ClO_4)_n \cdot (H_2O)_n$ (**1**) and $\{[Cu^{II}Mn^{II}(L^1)][Cr^{III}(bpb)(CN)_2]\}_n \cdot (ClO_4)_n \cdot (H_2O)_n$ (**2**) (bpb^{2-} = 1,2-Bis(pyridine-2-carboxamido)benzenate) have been designed and prepared based on cyanide-containing building blocks $K[M(bpb)(CN)_2]$ [M = Fe(III) and Cr(III)] together with compartmental macrocyclic Schiff-base complex $[CuMn(L^1)] \cdot (ClO_4)_2$, in which H_2L^1 is derived from 2,6-diformyl-4-methyl-phenol, ethylenediamine, and diethylenetriamine. Investigation of their magnetic properties reveals the overall antiferromagnetic behavior of these two complexes. These results seem to represent the first example of 1D infinite cyanide- and phenolate-bridged single chain-like compounds containing three kinds of spin carriers 3d-3d′-3d″ prepared by a stepwise method.

The design and synthesis of heterometallic complexes have stimulated the interest of chemists in molecular magnetism and bioinspired and/or biomimicry chemistry.[1,2] In particular, the complexes composed of three spin carriers in the form of 2p-3d-3d′,[3] 2p-3d-4f,[4] 3p-3d-4f,[5] 3d-3d′-3d″,[6] 3d-3d′-4d,[7] 3d-4f-3d′,[8] and 3d-4f-5d[9] are expected to exhibit more intriguing magnetic properties arising from third metal ions than those heterobimetallic counterparts. However, to the best of our knowledge, such types of heterotrimetallic complexes have been relatively rarely reported thus far, limited to only about 20 examples prepared using a stepwise method or one-pot procedure probably due to the difficulty in selecting appropriate precursors and crystallizing corresponding complexes. Nevertheless, the majority of heterotrimetallic complexes obtained based on multicyanometallates $[M(CN)_m]^{n-}$ as building blocks were revealed to display relatively complicated magnetic topology,[6−9] which leads to a limitation in clearly elucidating their magneto-structural correlation and preparing interesting heterotrimetallic SMMs and SCMs. In comparison with multicyanometallates, modified species $[ML(CN)_y]^{x-}$ have been employed as good precursors in constructing low-dimensional cyanide-bridged heterobimetallic complexes with two spin carriers such as discrete polymetallic aggeragates,[10] one-dimensional (1D) chains,[11] and two-dimensional (2D) layered networks.[12] As a result, the design and synthesis of 1D cyanide-bridged chain heterotrimetallic complexes with three spin carriers utilizing cyanide-containing building blocks $[M(bpb)(CN)_2]^-$ [M = Fe(II) and Cr(III)] have started to attract our interest.

In the present case, heterotrimetallic complexes were successfully obtained by employing a stepwise procedure. The heterobimetallic precursor $[CuMn(L^1)] \cdot (ClO_4)_2$, Scheme 1, was obtained from the transmetalation reaction of $[CuPb(L^1)] \cdot (ClO_4)_2$ in the presence of manganese sulfate,[6b] which reacts with the modified cyanometallates $[M(bpb)(CN)_2]^-$ [M = Fe(III) and Cr(III)], leading to the isolation of target heterotrimetallic complexes $\{[CuMn(L^1)][Fe(bpb)(CN)_2]\}_n \cdot (ClO_4)_n \cdot (H_2O)_n$ (**1**) and $\{[CuMn(L^1)][Cr(bpb)(CN)_2]\}_n \cdot (ClO_4)_n \cdot (H_2O)_n$ (**2**) with 1D infinite cyanide-bridged single chain-like molecular architecture; for a detailed description of the synthesis, see Supporting Information. It is worth noting that the reaction between other modified building blocks $[M(bpb')(CN)_2]^-$,[11f] in which bpb′ represents bpb^{2-} substituted

Scheme 1. Schematic Molecular Structures of Building Blocks $[CuMn(L^1)]^{2+}$ and $[M(bpb)(CN)_2]^-$ [M = Fe(III) and Cr(III)]

$[CuMnL^1]^{2+}$ $\qquad$ $[M(bpb)(CN)_2]^-$ (R$_1$ = R$_2$ = H)

M = Fe(III) and Cr(III)
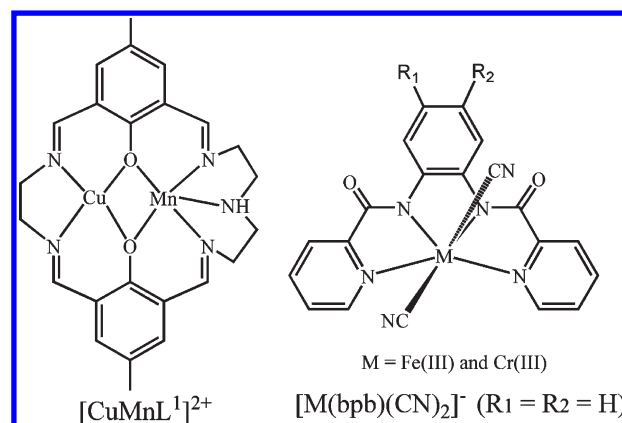
macrocyclic ligand bpmb^{2-} (R$_1$ = CH$_3$, R$_2$ = H), bpClb^{2-} (R$_1$ = Cl, R$_2$ = H) and bpdmb^{2-} (R$_1$ = R$_2$ = CH$_3$) as shown in Scheme 1, and $[CuMn(L^1)] \cdot (ClO_4)_2$ failed to give perfect single crystals to determine their molecular structure, indicating the disturbance effect of bpb substituent groups on the crystallization of complexes obtained. In the IR spectra of the two heterotrimetallic complexes **1** and **2**, the absorption bands at 2132 and 1650 cm^{-1} for **1** and 2146 and 1651 cm^{-1} for **2** are attributed to the stretching vibrations of bridging C≡N groups and C=N groups of Schiff-base ligand, respectively. Observation of a strong peak centered at 1087 cm^{-1} for **1** and **2** suggests the presence of ClO$_4^-$ anion.[11a]

Crystallographic data and other pertinent information for these two complexes are summarized in Table S1 (Supporting Information). Selected bond distances and bond angles with the estimated standard deviations are listed in Table S2 (Supporting Information). X-ray crystallography shows the isomorphic nature of compounds **1** and **2**, both of which crystallize in space group of $P2_1/c$, exhibiting a 1D infinite single chain molecular structure composed of repeated [NC-M(bpb)-CN−Mn-Cu(L^1)] [M = Fe(III) and Cr(III)] units, Figure 1. The detailed molecular structures for these two compounds are elucidated by taking **1** as a representative. The asymmetric unit of **1** consists of a [Fe(bpb)(CN)$_2$]$^-$ anion, a [CuMn(L^1)]$^{2+}$ ion, a perchloric anion

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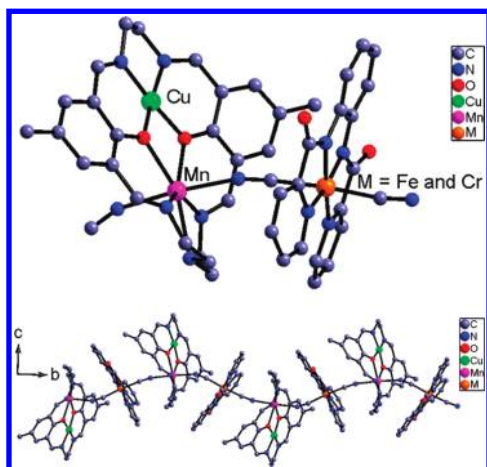
Figure 1. The coordination drawing of heterotrimetallic compounds **1** and **2** (top) with a perchloric anion and a water molecule omitted for clarity as well as a 1D infinite single chain structure (bottom).

as balance ion, and a crystalline water molecule. The Cu(II), Fe(III), and Mn(II) ions are tetra-, hexa-, and hepta-coordinated with square planar, octahedral, and distorted pentagonal-bipyrimidal coordination geometry, respectively. For Cu(II) ion, the coordination sphere consists of two nitrogen atoms and two oxygen atoms of the Schiff-base ligand L^1. In addition, it is worth noting that there is weak interaction between the oxygen atom of water molecules and the copper(II) atom because of the long distance of O---Cu = 3.013 and 3.046 Å for **1** and **2**, respectively. The coordination sphere of Fe(III) ions is formed by four nitrogen atoms of the bpb ligand and two carbon atoms from the cyanogen groups. For Mn(II) ion, the coordination geometry is composed of three nitrogen atoms and two oxygen atoms of L^1 ligand to form the equatorial plane, and two nitrogen atoms of cyanogen groups occupying the axis positions. In the [Fe(bpb)(CN)$_2$]$^-$ block, the Fe−N bond length is in the normal range of 1.9134(10)−1.966(6) Å. As listed in Table S2 (Supporting Information), the bond angle of Fe−C≡N amounts to 170.7(8) and 175.6(7)°, clearly indicating the presence of a good linear configuration for three atoms. In the [CuMn(L^1)]$^{2+}$ block, the average distance of Cu−N and Cu−O bonds are 1.914(8) and 1.920(6) Å, respectively, which is consistent with those of related complexes containing the N−Cu−O segment.[6b,8b] This is also true for the average bond length of Mn−O and Mn−N in a distance of 2.324(3) and 2.203(6) Å. The neighboring Cu(II) and Mn(II) ions are bridged by two oxygen atoms with the average bond angle of Cu−O−Mn 114.3(3)° and separated with the average distance of 3.293(6) Å. The two blocks [Fe(bpb)(CN)$_2$]$^-$ and [CuMn(L^1)]$^{2+}$ are connected by the cyano-group binding to the Mn(II) ion. Despite the linear conformation for the three corresponding atoms as suggested by the bond angle of N6−Mn−N7#2 = 174.5(3)° (symmetry code: #2 −x + 3/2, y − 1/2, −z + 3/2), the Mn−N−C bonds are slightly more bent with the angle amounting to 165.6(7) and 157.2(8)°, in line with that in heterobimetallic Mn(II)−Fe(II) counterparts.[11b] The Mn(II) and Fe(III) ions are separated with the average distance of 5.235(8) Å. The repeated [NC-M(bpb)-CN-Mn-Cu(L^1)] units extend along the *b* axis, forming a 1D infinite single chain framework structure. The neighboring chains are connected with the ClO$_4^-$ anions to form a 2D supramolecular structure via weak intermolecular hydrogen bonding interactions, Figure 2.

The magnetic properties of complexes **1** and **2** were investigated on a SQUID magnetometer in the temperature range of 2.0−300.0 K under an outer field of 2000 Oe. As shown in Figure 3, the changing tendency for temperature dependence of magnetic susceptibility for **1** and **2** is similar. The room temperature value
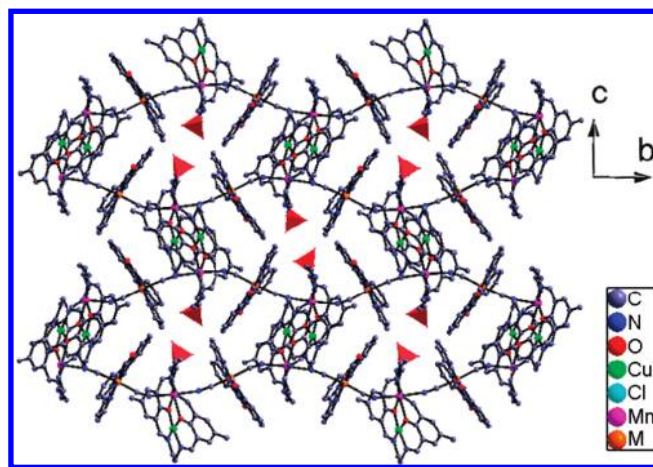
Figure 2. The 2D packing diagram of compounds **1** and **2** along the *a* axis (red polyhedron being perchloric anion).
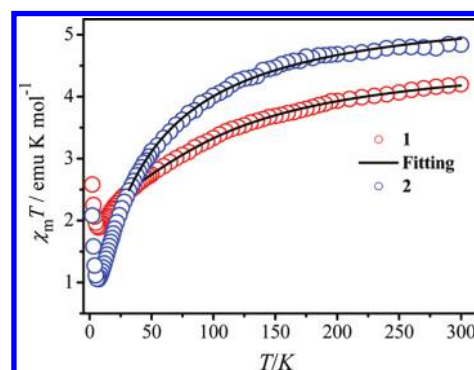
Figure 3. Temperature dependence of $\chi_m T$ for **1** and **2** (the blue solid lines represent the best fitting for these two complexes).

of $\chi_m T$ 4.198 emu K mol^{-1} for **1** and 4.838 emu K mol^{-1} for **2** is slightly smaller than the expected value of 5.125 emu K mol^{-1} [one Cu(II) ion $S = 1/2$, one Mn(II) ion $S = 5/2$, and one Fe(III) ion $S = 1/2$] for **1** and 6.625 emu K mol^{-1} [one Cu(II) ion $S = 1/2$, one Mn(II) ion $S = 5/2$, and one Cr(III) ion $S = 3/2$] for **2** with $g = 2.00$, respectively. When the temperature is lowered, the $\chi_m T$ value decreases slowly until about 150 K for these two complexes, then decreases quickly to a minimum value of 1.887 emu K mol^{-1} for **1** and 1.053 emu K mol^{-1} for **2** at 7.0 K. Upon the further decrease of temperature, the magnetic susceptibility of **1** and **2** increases to 2.580 emu K mol^{-1} and 2.080 emu K mol^{-1} at 2.0 K, respectively. These results indicate the presence of an overall antiferromagnetic interaction in these two complexes. The magnetic susceptibilities obey Curie−Weiss law in the temperature range above 30 K for **1** and **2**, giving a negative Weiss constant $\theta = -35.99$ K and Curie constant $C = 4.46$ emu K mol^{-1} for **1**, as well as Weiss constant $\theta = -41.26$ K and Curie constant $C = 5.76$ emu K mol^{-1} for **2**. The negative Weiss constant confirms the strong antiferromagnetic interaction exhibited by these two complexes in high temperature.

On the basis of crystal structure and magnetic data for these two complexes as well as the previous magnetic properties of the 1D cyanide-bridged Fe(III)−Mn(II) compounds, the cyanide- and phenolate-bridged heterotrimetallic single chains of **1** and **2** containing repeated units composed of [CuMn(L^1)]$^{2+}$ and [M(bpb)CN$_2$]$^-$ blocks exhibit mainly the characteristic antiferromagnetic behavior of the phenoxo-bridged [CuMn(L^1)]$^{2+}$ building block. In comparison with the magnetic coupling J_{CuMn} ($-11 \sim -39$ cm^{-1}) through the phenolate-bridge,[6b,14] the relatively weaker antiferromagnetic interaction (J_{MnM}) between Mn(II) and M(III) [M = Fe and Cr] ions is regarded as intramolecular

interaction (zJ'). As a consequence, the 1D infinite heterotrimetallic single chain can be regarded as a model consisting of alternating $[CuMn(L^1)]^{2+}$ and isolated spin $[M(bpb)CN_2]^-$ [M = Fe(III) and Cr(III)] units.[8d] Equations I and II deduced from this rough model were used to evaluate the coupling strength between Cu(II) and Mn(II) ions bridged by phenoxo atoms as well as the intermolecular interaction between $[CuMn(L^1)]^{2+}$ and $[M(bpb)CN_2]^-$ units.[8d]

$$\chi = \chi_{CuMn} + \chi_{Fe} = \frac{Ng^2\beta^2}{3KT}\left(\left(84\exp\left(\frac{5}{2}J_{CuMn}/KT\right)\right.\right.$$
$$+30\exp\left(-\frac{7}{2}J_{CuMn}/KT\right)\bigg/7\exp\left(\frac{5}{2}J_{CuMn}/KT\right)$$
$$\left.\left.+5\exp\left(-\frac{7}{2}J_{CuMn}/KT\right)\right)+\frac{1}{2}\times\frac{3}{2}\right) \qquad (I)$$

$$\chi = \chi_{CuMn} + \chi_{Cr} = \frac{Ng^2\beta^2}{3KT}\left(\left(84\exp\left(\frac{5}{2}J_{CuMn}/KT\right)\right.\right.$$
$$+30\exp\left(-\frac{7}{2}J_{CuMn}/KT\right)\bigg/7\exp\left(\frac{5}{2}J_{CuMn}/KT\right)$$
$$\left.\left.+5\exp\left(-\frac{7}{2}J_{CuMn}/KT\right)\right)+\frac{3}{2}\times\frac{5}{2}\right) \qquad (II)$$

$$\chi_m = \frac{\chi}{1-(2zJ'/Ng^2\beta^2)\chi} \qquad (III)$$

The best fit of the experimental data in the range above 30 K gives $J_{CuMn} = -20.06$ cm^{-1}, $zJ' = -1.22$ cm^{-1}, and $g = 1.97$ for **1** as well as $J_{CuMn} = -6.92$ cm^{-1}, $zJ' = J_{CrMn} = -2.91$ cm^{-1}, and $g = 2.03$ for **2**, further confirming the presence of characteristic antiferromagnetic interaction in these two compounds. The coupling constant J_{CuMn} is consistent with that of heterobimetallic Cu(II)–Mn(II) complexes reported previously.[6b,13,14] The magnetic coupling between neighboring Mn(II) and Fe(III) ions bridged by cyanogen groups is responsible for the big intramolecular constant, and the zJ' value is therefore approximately regarded as the corresponding J_{MnM} value, namely, $zJ' = J_{MnM}$ [M = Fe and Cr]. J_{FeMn} value is consistent with the intermolecular coupling constant in the heterobimetallic Fe(III)–Mn(II) complexes.[11] J_{CrMn} value is in line with those reported for cyanide-bridged Cr(III)–Mn(II) compounds.[15] The field-dependent magnetizations measured up to 50 kOe at 2 K for **1** and **2** are shown in the inset of Figure S1 (Supporting Information). Both curves have a similar changing tendency. The magnetization increases with a relatively fast speed with increasing field until 15 kOe, then increases smoothly up to about 3.05 $N\beta$ for **1** and 1.04 $N\beta$ for **2** until 50 kOe. These data are very close to the saturated value of 3.0 $N\beta$ for **1** and 1.0 $N\beta$ for **2** but obviously lower than the value of uncoupled Mn(II), Cu(II), and low spin Fe(III) ions based on $g = 2.00$, confirming again the overall antiferromagnetic coupling interaction in these two complexes.[11a] Similar to other reported heterotrimetallic systems, the final overall magnetic properties of heterotrimetallic are determined by the competition of magnetic coupling between different binuclear subunits.[3–9] Therefore, it may be one of the most effective strategies for the assembly of interesting molecular magnetic materials based on some well-known suitable ferromagnetic binuclear and multinuclear building blocks. For example, the first heterotrimetallic compounds which show slow relaxation behaviors was reported recently based on this consideration.[9c]

In addition to the experimental investigation over the magnetic property of heterotrimetallic complexes **1** and **2** with magnetic topology possessing three different metal ions, it is also worth exploring the mechanism of antiferromagnetic interaction between Cu(II) and Mn(II) ions as well as between Mn(II) and

M(III) [M = Fe and Cr] ions in these two compounds on the basis of a simple metal orbital theory. The magnetic orbital for the square planar Cu(II) (d^9), octahedral low-spin Fe(III) (d^5), octahedral Cr(III) (d^3), and pentagonal-bipyramidal Mn(II) (d^5) ion is $(d_{x^2-y^2})^1$ for Cu(II) ion, $(d_{xy})^1$, $(d_{xz})^1(d_{yz})^1(d_{xy})^1$, and $(d_{xz})^1(d_{yz})^1(d_{xy})^1(d_z^2)^1(d_{x^2-y^2})^1$, respectively. Among which, (d_{xz}), (d_{yz}), and (d_{xy}) orbitals belong to π-type (t$_{2g}$), while (d_z^2) and $(d_{x^2-y^2})$ are σ-character (e$_g$) ones.[13] In compounds **1** and **2**, the magnetic orbital $(d_{x^2-y^2})^1$ of Cu(II) ion points from the metal to the four coordinated atoms, inducing the overlap (superexchange) with the magnetic orbitals $(d_{xz})^1(d_{yz})^1(d_{xy})^1(d_z^2)^1(d_{x^2-y^2})^1$ of Mn(II) ion.[13] Nevertheless, for the purpose of making largest degree of overlapping between the orbitals of metal ion and coordinating atoms, the two σ-typed magnetic orbitals of pentagonal-bipyramidal coordinated Mn(II) ion is also adjusted to point to the seven coordinating atoms, leading to σ-type superexchange pathway [(d$_{x^2-y^2}$)-e$_g$]. This contributes mainly to the antiferromagnetic coupling (J_1) between Cu(II) and Mn(II) ions in **1** and **2**.[13] Similar to the 1D cyanide-bridged heterobimetallic Fe(III)–Mn(II) complexes reported previously by this group,[11b] the overall antiferromagnetic coupling between Mn(II) and low spin Fe(III) (t$_{2g}^5$e$_g^0$) ions through the cyanide bridge is determined by the overlap of magnetic orbitals through the π(t$_{2g}$-t$_{2g}$) pathways. This is also true for the antiferromagnetic coupling between Mn(II) and Cr(III) (t$_{2g}^3$e$_g^0$) ions. At the end of this section, it is worth noting that the increase of $\chi_m T$ below 7 K is observed, indicating the presence of ferromagnetic interaction. According to the previous result, this behavior is related to the fact that the easy axes of each Mn(II) ion possess different directions.[14]

In summary, two new 1D cyanide-bridged heterotrimetallic single chain complexes with three different 3d spin carriers exhibiting antiferromagnetic behavior have been designed and prepared by a stepwise method. Magnetic investigation reveals a different anti-ferromagnetic coupling character between different neighboring metal ions such as Cu(II) and Mn(II) as well as Mn(II) and M(III) [M = Fe and Cr] due to the different characteristic magnetic orbital overlaps.

Supporting Information Available: X-ray crystallographic files (CIF), file of check-cif, diagrams of the structures, selected bond distances, and angles of compounds **1** and **2**. This information is available free of charge via the Internet at http://pubs.acs.org/.

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