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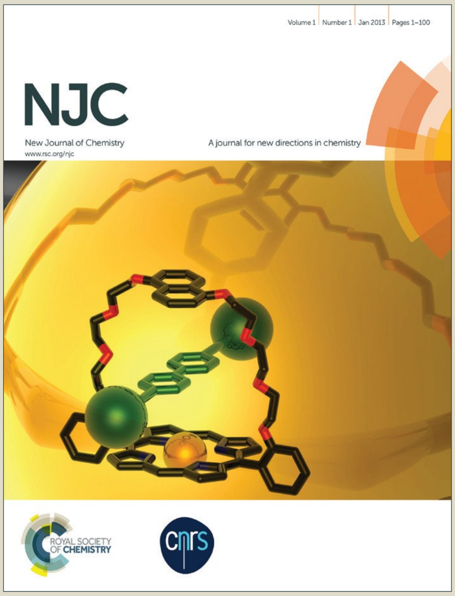

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ARTICLE

Ligand-directed assembly of trinuclear and one-dimensional heterotrimetallic $Cu^{II}Ln^{III}Fe^{III}$ complexes. Unusual antiferromagnetic $Cu^{II}Fe^{III}$ coupling via cyano bridges

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New heterotrimetallic complexes $[Cu(vapln)(H_2O)Ln(H_2O)_3Fe(CN)_6]\cdot xH_2O$ (Ln = Gd, x = 3 for complex **1**; Ln = Tb, x = 3 for complex **2**; Ln = Dy, x = 1.75 for complex **3**; H_2valpn = *N*,*N* '-bis(3-methoxysalicylidene)-1,3-diaminopropane), $\{[Cu(Me_2vapln)]_2Ln(H_2O)Fe(CN)_6\cdot xH_2O\cdot yCH_3CN\}_n$ (Ln = Gd, x = 5, y= 2.5 for complex **4**; Ln = Tb, x = 4.5, y = 1.5 for complex **5**; Ln = Dy, x = 5.5, y = 2.5 for complex **6**; Ln = Y, x = 6, y = 4 for complex **7**; H_2Me_2vapln = *N*,*N* '-bis(3-methoxysalicylidene)-2,2-dimethyl-1,3-diaminopropane) have been synthesised by the reaction of Cu(valpn) (or $Cu(Me_2vapln)$), Ln^{3+} and $[Fe(CN)_6]^{3-}$ in a molar ratio of 2:1:1. Complexes **1-3** have a CuLnFe trinuclear structure, consisting of phenoxo-bridged Cu-Gd and cyano-bridged Gd-Fe moieties. Complexes **4-7** contain the phenoxo-bridged Cu_2Ln units that are connected by $[Fe(CN)_6]^{3-}$ to form a one-dimensional (1D) zig-zag structure. In the trinuclear complexes **1-3**, the $[Fe(CN)_6]^{3-}$ anion coordinates to Ln^{3+}, whereas to Cu^{2+} in complexes **4-7**. Magnetic studies demonstrate that there exists the ferromagnetic interaction between Cu(II) and Gd(III) ions via the phenoxo bridges, while the cyano-bridges transit antiferromagnetic coupling between low-spin Fe(III) and Cu(II) or Gd(III). The fitting to the magnetic susceptibilities of complexes **1** and **4** gave the parameters of J_{CuGd} = 2.392 and 2.945 cm^{-1}, J_{FeGd} = -0.341 cm^{-1} and J_{FeCu} = -0.378 cm^{-1}. The ac magnetic measurements reveal that complex **6** shows slow magnetization relaxation with energy barrier of 12.3 K and the relaxation time $\tau_0 = 1.65\times10^{-6}$ s, typical of a single-chain magnet.

Introduction

Since the single-molecule magnets (SMMs) and single-chain magnets (SCMs) were reported, the researches of SMMs and SCMs have been attracted a wide attention for their potential applications in information storage.[1,2] In the early years, the most reported SMMs just contained one kind of metallic ions of 3d.[3] Considering the large magnetic momentum and high magnetic anisotropy of 4f metallic ions, 4f metals were used for synthesizing SMMs.[4] For improving the ground spin values and magnetic anisotropy of complexes, the d and f metallic ions were combined together and some of these complexes behaved as SMMs.[4d-g] Therefore, d-f heherobimetallic complexes became good candidates for SMMs or SCMs.[5] With the study of magnetic interactions between metallic ions, cyano-, oxamidato- and phenoxo-bridged trimetallic complexes have been reported.[6] Because heterotrimetallic complexes probably show improved magnetic properties, the study on trimetallic complexes is significant.[7-11] According to the previous reports, trimetallic SMMs or SCMs mainly include cyano- and phenoxo-bridged 3d-4f-3d', 3d-4f-4d and 3d-4f-5d complexes,[7,8] and Ni(SB), Zn(SB) and Cu(SB) (SB^{2-} = Schiff base ligands) are the main Schiff base metallic complexes available to obtain trimetallic complexes.[7-9] By using different Schiff base metallic complexes, obtained trimetallic complexes show diverse crystal structures. Under a similar reaction condition, complex $[Cu(valpn)LnFe(CN)_6]$ shows a one-dimensional structure, while the Ni(II) analog $[Ni(valpn)LnFe(CN)_6]$ has a two-dimensional (2D) layered structure.[9b] Similarly, complex $[Ni(valpn)Ln(NO_3)(H_2O)W^{IV}(bpy)(CN)_6]$ has a 2D structure.[10] Interestingly, octanuclear cyclic hetero-trimetallic complexes $[(LnNi_2)\{Fe(CN)_6\}]_2$, $[(LnZn_2)\{Fe(CN)_6\}]_2$ and $[(LnNi_2)\{W(CN)_8\}]_2$ based on the Schiff ligand Me_2valpn^{2-} have been reported very recently.[8b,9a,11] Although a number of heterotrimetallic complexes based on Cu(SB) reported[7a,8a,12] possess 1D chain, trinuclear structure and decanuclear square molecular structures,[8c,12,13,14] no similar cyclic octanuclear $[(LnCu_2)\{Fe(CN)_6\}]_2$ complexes have been found.

Considering the Jahn-Teller effect of Cu(II) ion, we expect to synthesize trimetallic complexes based on Cu(II), Ln(III) and $[Fe(CN)_6]^{3-}$. We choose bimetallic complexes $\{[Cu(valpn)]_2Ln\}^{3+}$ and $\{[Cu(Me_2valpn)]_2Ln\}^{3+}$ (Ln^{3+} = Gd, Tb, Dy) as precursors to react with $K_3[Fe(CN)_6]$, respectively. Three trinuclear complexes $[Cu(vapln)(H_2O)Ln(H_2O)_3Fe(CN)_6]\cdot xH_2O$ (L = Gd, x = 3 for complex **1**; Ln = Tb, x = 2 for complex **2**; Ln = Dy, x = 1.75 for complex **3**) and four 1D chain complexes $\{[Cu(Me_2vapln)]_2Ln(H_2O)Fe(CN)_6\cdot xH_2O\cdot yCH_3CN\}_n$ (Ln = Gd, x = 5, y= 2.5 for complex **4**; Ln = Tb, x = 4.5, y = 1.5 for complex **5**; Ln = Dy, x = 5.5, y = 2.5 for complex **6**; Ln = Y, x = 6, y = 4 for

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complex **7**) have been synthesized. Here, we present the synthesis, structures and magnetic properties of these complexes.

Results and discussion

Synthesis and characterizations

Three trinuclear and three 1D Cu(II)-Ln(III)-Fe(III) complexes have been prepared by the reaction of Cu(II) Schiff bases, the Ln(III) salts and $K_3[Fe(CN)_6]$ in the molar ratio of 2:1:1 in a MeCN-H_2O mixture. Unexpectedly, complexes **1-3** of the valpn^{2-} Schiff base ligand have the metallic molar ratio of 1:1:1 instead of 2:1:1. This phenomenon indicates that the $\{[Cu(valpn)]_2Ln\}^{3+}$ precursor is not stable, and decomposes to form $\{[Cu(valpn)]Ln\}^{3+}$ when reacting with hexacyanoferrite(III). It is worth mentioning that the reaction of $[Cu(valpn)]Gd(NO_3)_3$ with $K_3[Fe(CN)_6]$ in water gave rise to a 1D double chain complex $[Cu(valpn)Gd(H_2O)_3Fe(CN)_6]\cdot 4H_2O$, where the Gd^{3+} ion is coordinated by two $[Fe(CN)_6]^{3-}$ anions.[6b] The formation of trinuclear complexes instead of the 1D double chain might be due to the presence of excess [Cu(valpn)] that hamper the coordination of additional $[Fe(CN)_6]^{3-}$ to Gd^{3+}. Previous studies on the Ni(II)-H_2Me_2valpn-Ln(III)-Fe(III)$(CN)_6$ system have led to the isolation of cyclic octanuclear $Ni_4Ln_2Fe_2$ complexes.[11] However, for the Cu(II)-H_2Me_2valpn system, 1D complexes **4-7** have been obtained. The present result shows that the metallic ions and the Schiff base ligands can modulate the molecular structure of the trimetallic complexes.

The IR spectra of complexes **1-3** show strong absorption peaks at 2095, 2099 and 2090 cm^{-1}, respectively, which are due to cyanides in $Fe[(CN)_6]^{3-}$. Complexes **4-6** all have two strong absorption peaks in the cyanide region, 2114, 2146 cm^{-1} for complex **4**, 2116, 2145 cm^{-1} for complex **5**, 2114, 2148 cm^{-1} for complex **6** and 2025, 2110 cm^{-1} for complex **7**. The splitting of the C≡N stretching vibration suggests the formation of Fe-C≡N-Cu bridges in complexes **4-7**. The strong peaks at 1626-1635 cm^{-1} should be assigned to the C=N stretching of the Schiff base ligands in complexes **1-7**.

Crystal structure

Crystal data and structural details for complexes **1**–**7** are listed in Table 1 and Table 2, and important bond distances and angles are collected in Table S1† and Table S2†, respectively.

Because complexes **1** and **2** are isomorphous, the structures of complexes **1** and **3** are described in detail as examples. Complexes **4-7** are isostructural, and crystallize in the orthorhombic space group, *P*bca. The structure for complex **5** is described here as a representative.

The crystal structure of complex **1** is shown in Fig. 1 (left). $[Fe(CN)_6]^{3-}$ is connected with $(CuGd)^{3+}$ by a cyanide, affording a trinuclear structure. The Cu^{II} ion is penta-coordinated by the N_2O_2 of the Schiff base valpn^{2-} occupying the basal plane, and the water oxygen atom O1W or O1W' at the apical position. O1W and O1W' are crystallographically disordered, and the occupancies have been refined to be 0.35 and 0.65, respectively. Interestingly, O1W' involves in the weak coordination of Cu1 and Gd1 with the Cu1-O1W' bond length of 2.714(7) Å and Gd1-O1W' bond length of 2.753(10) Å. The O1W'-Cu1-Gd1 angle is 51.8(2)°, indicating that O1W' severely deviates from the apical position of square pyramidal of Cu1. Thus, Cu1 has a distorted square pyramidal coordination geometry. However, the O1W-Cu1-Gd1 angle of 72.4(7)° suggests that O1W is situated at the comparatively proper axial position, and in this case the Cu1 coordination sphere is close to regular square pyramidal. Besides O1W and four oxygen atoms from vapln^{2-}, the other four coordination sites around Gd1 are occupied by three water oxygen atoms and a cyanide nitrogen atom. The Gd-O/N bond lengths are in the range of 2.330(3)-2.591(3) Å for Gd-O, 2.371(3)-2.753(10) Å for Gd-O$_{water}$ and 2.473(4) Å for Gd-N$_{cyano}$. The Gd^{III} ion exhibits a GdO_8N coordination sphere, and the coordination sphere is close to the Muffin structure of C_s calculated by the SHAPE software.[15] The structure of complex **2** is similar to that of complex **1**, and the disorder of O1W and O1W' similarly exists with the occupancies of 0.46 and 0.54, respectively (Fig. S1, ESI).

Complex **3** has a trinuclear molecular structure (Fig. 1, right), slightly different from that of complexes **1** and **2**. The apparent difference is that the bridging water oxygen atom solely coordinates to Cu1, and the Dy(III) ion becomes octa-coordination. Therefore, the O3W-Cu1-Dy1 angle is 87.6°, normal for apical coordination of O3W towards Cu1. The coordinate environment of Dy1 is square antiprism (D_{4d}).

Table 1 Crystal data for complexes **1-3**

complex	**1**	**2**	**3**
Formula	$C_{25}H_{34}GdFeN_8CuO_{11}$	$C_{25}H_{34}TbFeN_8CuO_{11}$	$C_{25}H_{31.5}DyFeN_8CuO_{9.75}$
Formula weight	899.24	900.91	881.97
T (K)	293	293	293
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	12.923(3)	12.889(3)	8.5391(2)
b (Å)	12.032(2)	12.035(2)	24.9879(8)
c (Å)	22.590(8)	22.242(8)	15.7226(5)
β (º)	108.13(3)	105.12(3)	92.0769(12)
V (Å^3)	3338.1(16)	3330.6(15)	3352.59(17)
Z	4	4	4
D_{calcd} (g·cm^{-3})	1.789	1.797	1.747
μ (mm^{-1})	3.091	3.230	3.323
Reflections [$I > 2\sigma$]	6137	6148	6368
GOF	1.038	1.035	1.021
*R*1 [$I > 2\sigma(I)$]	0.0352	0.0383	0.0346
*wR*2 (all data)	0.0912	0.1037	0.0883

Table 2 Crystal data for complexes **4-7**

Complex	**4**	**5**	**6**	**7**
Formula	$C_{53}H_{67.5}GdFeN_{12.5}Cu_2O_{14}$	$C_{51}H_{63.5}TbFeN_{11.5}Cu_2O_{13.5}$	$C_{53}H_{65.5}DyFeN_{12.5}Cu_2O_{12.5}$	$C_{56}H_{74}YFeN_{14}Cu_2O_{15}$
Formula weight	1443.87	1395.48	1423.11	1455.13
T (K)	173	293	293	100
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P*bca	*P*bca	*P*bca	*P*bca
a (Å)	21.1918(9)	21.134(11)	21.085(4)	21.0615(9)
b (Å)	23.3200(8)	23.479(12)	23.379(5)	23.2526(9)
c (Å)	26.6459(12)	26.843(14)	26.922(5)	26.6468(9)
V (Å^3)	13168.2(9)	13319(12)	13271(5)	13049.9(9)
Z	8	8	8	8
D_{calcd} (g·cm^{-3})	1.457	1.392	1.424	1.481
μ (mm^{-1})	1.914	1.955	2.023	1.815
GOF	1.131	1.022	1.039	1.052
*R*1 [$I > 2\sigma(I)$]	0.0920	0.0683	0.0758	0.0596

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*wR*2 (all data)	0.2307	0.2171	0.1842	0.1302

The crystal structure of complex **5** is exhibited in Fig. 2. The structure of **5** consists of two crystallographically independent $\{[Cu(Me_2vapln)]_2Tb(H_2O)\}^{3+}$ and one $[Fe(CN)_6]^{3-}$ anion. The Cu-N$_{cyano}$ coordination bonds alternatively link $\{[Cu(Me_2vapln)]_2Tb(H_2O)\}^{3+}$ with $[Fe(CN)_6]^{3-}$, which leads to a 1D zig-zag chain. Each $[Fe(CN)_6]^{3-}$ is connected with two $\{[Cu(Me_2vapln)]_2Tb(H_2O)\}^{3+}$ fragments through two *trans*-cyanides. Both Cu(II) ions are penta-coordinate with a square pyramidal coordination environment. The coordination sites of N_2O_2 from $(Me_2vapln)^{2-}$ are situated in the basal plane, and the apical position is occupied by the nitrogen atom from $[Fe(CN)_6]^{3-}$ with corresponding Cu-N$_{cyano}$ bond distances of 2.201(7) Å and 2.163(8) Å, respectively. These apical Cu-N$_{cyano}$ bond distances are slightly longer than the basal Cu-N/O bond distances (1.977(6)-1.993(6) Å / 1.962(4)-1.994(5) Å) in the basal plane. The bridging bond angles of C≡N-Cu are in the range of 149.2(7)-151.3(7)°. Two crossing Cu(Me$_2$valpn) moieties chelate the Tb(III) ion with eight oxygen atoms from the two $(Me_2vapln)^{2-}$ ligands, and one oxygen from a water molecule coordinates to the Tb(III) ion to complete the nine-coordination sphere. The Tb(III)-O bond lengths are in the range of 2.338(4)-2.624(5) Å. The coordinate environment of Tb(III) is near to Muffin or spherical capped square antiprism calculated by using the SHAPE software.[15] The coordination modes of $\{[Cu(Me_2vapln)]_2Ln(H_2O)\}^{3+}$ in complexes **5** - **7** are similar to that of cyclic octanuclear complexes $[Ni_2(Me_2vapln)_2Ln(H_2O)Fe(CN)_6]_2$.[11] The 1D chain structure of complexes **5** - **7** can be regarded as the open mode of the cyclic octanuclare $[Ni_2(Me_2vapln)_2Ln(H_2O)Fe(CN)_6]_2$.[11] It is noteworthy that the bridging modes of $[Fe(CN)_6]^{3-}$ should be responsible for the formation of 1D or octanuclear structure, *trans* for the former and *cis* for the latter.

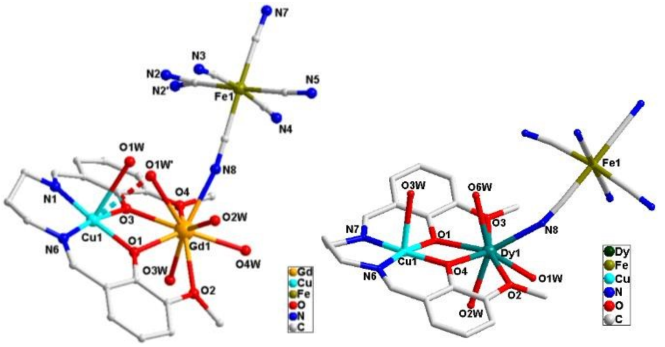
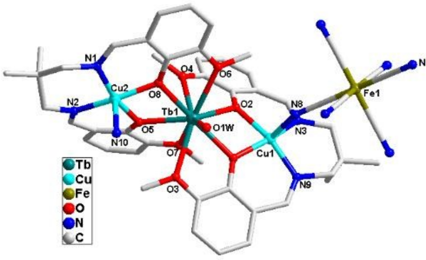


Fig. 1 Crystal structure of complexes **1** (left) and **3** (right). In complex **1**, O1W and O1W' are disordered. Hydrogen atoms and solvent molecules have been omitted for clarity.



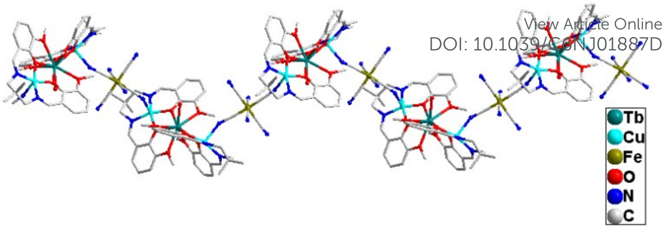


Fig. 2 Crystal structure of complex **5** (above) and 1D zig-zag chain structure along the *b* axis (below). Hydrogen atoms and solvent molecules have been omitted for clarity.

Magnetic properties

Static magnetic susceptibility. The variable-temperature magnetic susceptibilities of complexes **1-6** were measured under an external magnetic field of 1000 Oe. The magnetic date was collected in the range 2.0-300 K. The measured results are shown in Fig. 3.

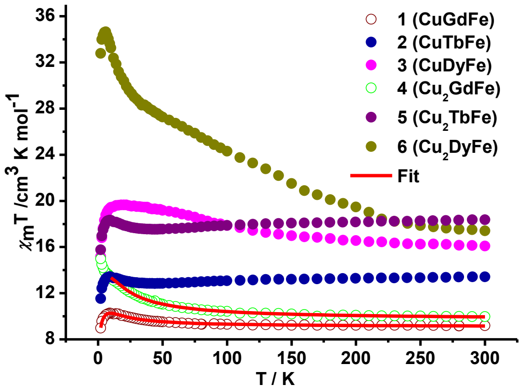


Fig. 3 Temperature dependence of $\chi_m T$ for complexes **1-6**. The solid lines indicate the best fitting results for complexes **1** and **4**.

As shown in Fig. 3, the $\chi_m T$ values are 9.19 cm^3 K·mol^{-1} (**1**), 12.81 cm^3 K·mol^{-1} (**2**) and 16.09 cm^3 K·mol^{-1} (**3**), at room temperature, close to the theoretical values for a non-coupling CuLnFe system (Table S3 assuming g = 2.00 for Cu(II) and low-spin Fe(III)). The slight difference in $\chi_m T$ values should be due to the presence of Cu(II) and low-spin Fe(III) that usually have a g factor higher than 2.0, and similar situation occurs to complexes **4-6** (vide infra). When the temperature decreases, the $\chi_m T$ value of complex **1** remains constant down to 100 K, and rapidly increases to a maximum of 10.28 cm^3 K mol^{-1} at 9 K. Then, $\chi_m T$ shows a sharp decrease until 2 K. This behaviour suggests the presence of a predominant ferromagnetic interaction in complex **1**, which is supported by the positive Curie-Weiss constant (1.465 K). The decrease of $\chi_m T$ below 9 K should be due to the presence of intramolecular Fe-Gd and intermolecular antiferromagnetic interaction. Complex **3** shows a magnetic property similar to that of complex **1**, with a maximum of $\chi_m T$ at 18 K. For complex **2**, the $\chi_m T$ value decreases with the lowered temperature and reaches a minimum value at 40 K. Below 40 K, $\chi_m T$ increases reaching a maximum value at 9 K. The high temperature decrease of $\chi_m T$ from 300 K to 40 K might be due to the thermal depopulation of the excited Stark sub-levels for Tb(III) that suppress the Cu(II)-Tb(III) ferromagnetic interaction and the Fe-Tb negligible or weak

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ferromagnetic coupling.[16] The χ_mT values of complexes **2** and **3** decrease at lower temperature (9-18 K) upon cooling, which may be due to the depopulation of Stark sub-levels of Ln(III) ions and/or the intermolecular antiferromagnetic interaction.

For Gd(III) with the fairly small zero-field splitting of the ground state (less than 1 cm^{-1}),[17] dc magnetic susceptibility of complex **3** can be described by the spin Hamiltonian operator eq. (1).

$$\hat{H} = -2J_{\mathrm{CuGd}}\hat{S}_{\mathrm{Cu}}\hat{S}_{\mathrm{Gd}} - 2J_{\mathrm{FeGd}}\hat{S}_{\mathrm{Fe}}\hat{S}_{\mathrm{Gd}} \quad (1)$$

The data in the whole temperature range of 2-300 K were fitted by using the MagPack software,[18] and the best results are: J_{FeGd} = -0.341 cm^{-1}, J_{CuGd} = 2.392 cm^{-1}, g = 2.052. This result indicates the existence of weak antiferromagnetic Fe-Gd interaction ($2J_{\mathrm{FeGd}}$ = -0.49 – -0.84 cm^{-1})[9b,16,19] and moderate ferromagnetic Cu-Gd interaction,[6b,8a,8c,12c,17,20,21] as usual.

Complexes **4–6** have, at room temperature, χ_mT values of 9.96 cm^3 K·mol^{-1} (**4**), 13.97 cm^3 K·mol^{-1} (**5**) and 16.97 cm^3 K·mol^{-1} (**6**), close to the theoretical values for a non-coupled Cu_2LnFe system (Table S3). When the temperature is lowered, χ_mT value of complex **4** remains constant down to 100 K and then increases rapidly to a maximum at 2 K. This behaviour is associated with the overall ferromagnetic interaction in complex **4**. For complexes **5** and **6**, the χ_mT values increase gradually with cooling and reach the maximum values at about 6 K before decreasing. In the temperature range of 150-300 K, the dc magnetic susceptibilities are consistent with the Curie-Weiss law and give positive Curie-Weiss constants, indicating the presence of predominant ferromagnetic interactions at high temperatures. Below 6 K, the rapid decrease of χ_mT for complexes **5** and **6** might be due to the depopulation of the Stark sublevels in the Ln(III) ions.

We have approximately fitted the magnetic properties of complex **4** to a cyclic octanuclear model (Fig. 4) using the MagPack software[18] and the Hamiltonian operator of this model is described as eq. (2).

$$\begin{aligned}\hat{H} = &-2J_1(\hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{Gd1}} + \hat{S}_{\mathrm{Cu2}}\hat{S}_{\mathrm{Gd1}} + \hat{S}_{\mathrm{Cu3}}\hat{S}_{\mathrm{Gd2}} + \hat{S}_{\mathrm{Cu4}}\hat{S}_{\mathrm{Gd2}}) \\ &-2J_2(\hat{S}_{\mathrm{Fe1}}\hat{S}_{\mathrm{Cu2}} + \hat{S}_{\mathrm{Fe1}}\hat{S}_{\mathrm{Cu3}} + \hat{S}_{\mathrm{Fe2}}\hat{S}_{\mathrm{Cu1}} + \hat{S}_{\mathrm{Fe2}}\hat{S}_{\mathrm{Cu4}})\end{aligned} \qquad (2)$$

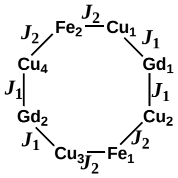

Fig. 4 The fitting model of magnetic susceptibility for complex **4**.

In the range of 10-300 K, the best fitting results for complex **4** are: $J_{\mathrm{GdCu}} = J_1$ = 2.945 cm^{-1}, $J_{\mathrm{FeCu}} = J_2$ = -0.378 cm^{-1}, g = 2.078. This result suggests that a weak antiferromagnetic interaction is present between Fe(III) and Cu(II). The Fe(III)-Cu(II) ferromagnetic interaction has been reported with few exceptions.[22] To definitely determine the character of Fe(III)-Cu(II) magnetic coupling in complex **4**, we have studied the magnetic properties of the isostructural complex [Cu_2YFe] (**7**) that contains diamagnetic Y(III). The χ_mT vs. T curve of complex **7** (Fig. S5†) indicates the presence of antiferromagnetic interaction between Cu(II) and Fe(III). The linear Cu-Fe-Cu trinuclear model with the spin Hamiltonian operator $\hat{H} = -2J_{\mathrm{FeCu}}(\hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{Fe}} + \hat{S}_{\mathrm{Fe}}\hat{S}_{\mathrm{Cu2}})$ has been used for the fitting to give the fitting parameters of J_{FeCu} = -0.35(1) cm^{-1}, g = 2.24(1). The J_{FeCu} value is very close to that of complex **4**. The field dependence of the magnetization for complex **7** shows that the experimental data are below the calculated Brillouin curve for noncoupling S_{Fe} and $2S_{\mathrm{Cu}}$ spins with g = 2.24 (Inset of Fig. S5†). This result further verifies the presence of intrachain Fe(III)-Cu(II) antiferromagnetic interaction. For complexes **4** - **7**, the Cu(II) ions are in a square pyramidal configuration, where the unpaired electron lies in the d_{x2-y2} orbital. The abnormal Fe(III)-Cu(II) antiferromagnetic interaction may be related to the bent C≡N-Cu bridging mode, which makes the orbital overlap between $d_{x^2-y^2}$ of Cu(II) and d_{xy} of low-spin Fe(III) possible.[22] Similarly, some cyano-bridged Cu-W/Mo complexes display abnormal Cu-W/Mo antiferromagnetic interaction due to the presence of bent Cu-N≡C bridging linkages (138.4-154.7°).[8c,12c,23] It is noteworthy that the above-mentioned abnormal Cu-Fe/Cr/W/Mo antiferromagnetic interaction occurs to the metal ions where the bridging cyano nitrogen atom is situated at the axial positions of coordination polyhedral of Cu(II).

The fitting result shows that the phenoxo-bridged Cu(II)-Gd(III) interaction for complexes **1** and **4** is ferromagnetic and moderate in magnitude, with the J_{CuGd} values falling in the range of 1.22-7.38 cm^{-1} for available phenoxo-bridged Cu(II)-Gd(III) complexes.[20,21] For comparison, structural data and magnetic properties of phenoxo-bridged CuGd complexes are collected in Table S4†.[6b,12c,20,24] On the basis of the data, we conclude that the smaller of the dihedral angle of CuO_2 and GdO_2 planes, the greater is J_{CuGd} (Fig. S6†, ESI). Moreover, the increase of Gu-Gd bond distance and the Gd-O-Cu angle would simultaneously results in the increase of J_{CuGd}. This conclusion is consistent with the results based on DFT calculation.[25]

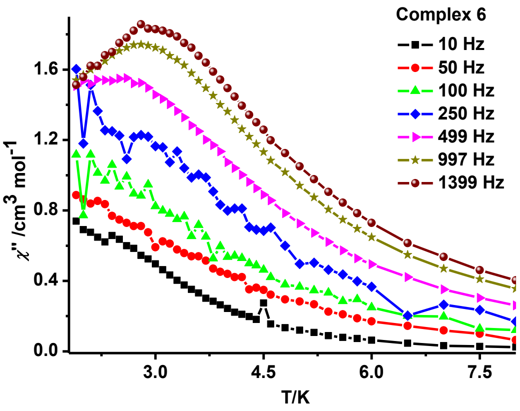

Fig. 5 Temperature dependence of the out-of-phase (χ''_m) ac magnetic susceptibilities for complex **6**.

Dynamic magnetic susceptibility. The ac magnetic susceptibility of complexes **2, 3, 5** and **6** were measured in zero

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and 2000 Oe dc field (measured frequency was 997 Hz). As shown in Figs. S7 and S8†, complexes **2**, **3** and **5** show no peaks above 2 K under zero or 2000 Oe dc field. However, the out-of-phase magnetic susceptibility (χ_m'') of complex **6** under 2000 Oe exhibit broad frequency-dependent peaks below 3 K (Fig. 5). The parameter $\Phi = (\Delta T_p/T_p)/\Delta(\log f) = 0.46$ is within the range of normal super paramagnets, precluding the possibility of a spin glass ($0.01 < \Phi < 0.08$). The Arrhenius equation of $\tau = \tau_0\exp(U_{eff}/kT)$ was employed to extract parameters that relevant to slow relaxation of magnetism. The best fitting result is shown in Fig. S9† with $\tau_0 = 1.65\times10^{-6}$ s and $U_{eff} = 12.3$ K, typical of an SCM.

Conclusions

Seven new heterotrimetallic complexes have been synthesized. The 1D zig-zag chain complexes **4-7** can be regarded as a deformation of octanuclear cyclic structure. Complex **6** (Cu_2DyFe) is a single chain magnet and displays field-induced slow magnetization relaxation. The absence of an single-molecule magnet property in CuDyFe and CuTbFe trinuclear complexes would be related to the presence of Fe-Dy/Tb antiferromagnetic interaction via the cyano bridge,[27,28] which is consistent with the previous assumption that the presence of cyano-bridged Fe(III)-Ln(III) linkages has a negative effect on single-molecule magnets.[11] Unusual intrachain Cu(II)-Fe(III) antiferromagnetic interaction is unambiguously present in the 1D complexes, which is likely to originate from the magnetic orbital overlap via the bent cyanide bridging.

Experimental

Materials. All agents were commercially available and used without further purification.

Synthesis. The precursor Cu(valpn) and Cu(Me_2valpn) were prepared similarly. The 1,3-diamopropane (1.48 g, 20 mmol) was dropped into a methanol solution (100 mL) of o-vanillin (6.08 g, 40 mmol) under stirring. After the stirring continued for 10 minutes, acetate copper monohydrate (4.00 g, 20 mmol) was added into the above solution. After the mixture was refluxed for 2 hours, dark green microcrystals were collected by filtration, washed and dried in the air.

Complexes **1-6** were similarly synthesized. Cu(valpn) (40.4 mg, 0.2 mmol) or Cu(Me_2valpn) (43.2 mg, 0.2 mmol) was dissolved in acetonitrile (20 mL), then $Ln(NO_3)_3\cdot6H_2O$ (0.1 mmol) was added. Under stirring, an aqueous solution (5 mL) of $K_3[Fe(CN)_6]$ (32.9 mg, 0.1 mmol) was slowly added to the above dark green solution. After a few minutes, the mixture was filtered and the filtrate was set undisturbed at room temperature. Green block crystals (**1-3**) and deep green block crystals (**4-7**) for X-ray structural analysis were obtained after a few days. Yield: 40%, 43%, 45%, 60%, 72%, 73% and 55%, respectively. The crystals of complex **7** are efflorescent and lose acetonitrile molecules upon exposure to the air. Anal. calcd (%) for $C_{25}H_{34}GdFeN_8CuO_{11}$ (**1**): C, 33.39; H, 3.81; N, 12.46. Found: C, 33.27; H, 3.75; N, 12.56. $C_{25}H_{34}TbFeN_8CuO_{11}$ (**2**): C, 33.33; H, 3.80; N, 12.44. Found: C, 33.51; H, 3.94; N, 12.61. $C_{25}H_{31.5}DyFeN_8CuO_{9.75}$ (**3**): C, 34.05; H, 3.60; N, 12.70. Found: C, 33.58; H, 3.76; N, 12.93. $C_{53}H_{67.5}GdFeN_{12.5}Cu_2O_{14}$ (**4**): C, 44.09; H, 4.71; N, 12.13. Found: C, 43.65; H, 4.83; N, 11.95. $C_{51}H_{63.5}TbFeN_{11.5}Cu_2O_{13.5}$ (**5**): C, 43.89; H, 4.59; N, 11.54. Found: C, 43.81; H, 4.64; N, 11.71. $C_{53}H_{65.5}DyFeN_{12.5}Cu_2O_{12.5}$ (**6**): C, 44.73; H, 4.64; N, 12.30. Found: C, 44.61; H, 4.59; N, 12.58. $C_{48}H_{62}YFeN_{10}Cu_2O_{15}$ (**7**-4MeCN): C, 44.66; H, 4.84; N, 10.85. Found: C, 44.70; H, 4.70; N, 10.80.

Physical measurements. Elemental analyses (C, H, N) were performed on an Elementar Vario Cario Erballo analyzer. Temperature and field-dependent magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL5 SQUID magnetometer. And the experimental susceptibilities were corrected for diamagnetism of Pascal constants. Single-crystal X-ray data were collected on a Rigaku RAXIS RAPID IP, Bruker SMART 1000 CCD or SuperNova four-circle diffractometer. The structure was solved by the direct method (Olex2 1.2 or SHELXS-2014) and refined by a full matrix least-squares method based on F^2 using SHELXL-2014 program.[26] Hydrogen atoms were added geometrically and refined using a riding model. For complex 7, the hydrogen atoms of the coordinating water were found from the E-map, and refined isotropically.

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Graphic abstract

Ligand-directed assembly of trinuclear and one-dimensional heterotrimetallic $Cu^{II}Ln^{III}Fe^{III}$ complexes. Unusual antiferromagnetic $Cu^{II}Fe^{III}$ coupling via cyano bridges

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Rare phenoxo- and cyano-bridged CuLnFe trinuclear complexes have been prepared. The 1D Cu_2DyFe complex displays both single-chain magnetic property and the intrachain Cu(II)---Fe(III) antiferromagnetic coupling. The presence of Fe-C≡N-Ln bridging linkages goes against the single-molecule/chain magnetic property of the complexes.