Heterometallic trinuclear $Cu^{II}M^{III}_2$ (M = Fe or Cr) complexes with novel bridges and unusual magnetic properties†

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Three new trinuclear complexes based on $[Cu(L^n)]^{2+}$ (L^1 = 1,5,8,12-tetramethyl-1,3,6,8,10,13-hexaazacyclotetradecane, L^2 = 1,3-propanediamine (tn)) and $[M(bpb)(CN)_2]^-$ (bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate, M = Fe or Cr) have been synthesized and characterized structurally and magnetically. The Cu(II) ions adopt an axially-elongated octahedron with four N atoms from the L^n ligands occupying the equatorial plane and another two atoms (cyano nitrogen atoms or amide oxygen atoms) from two $[M(bpb)(CN)_2]^-$ moieties at the axial positions, resulting in a neutral linear trinuclear complex. Magnetic studies show that the $CuFe_2$ compound bridged by the amido group exhibits ferromagnetic behaviour. The two cyano-bridged $CuFe_2$ or $CuCr_2$ compounds show unusual magnetic properties: weak antiferromagnetic Cu(II)–Fe(III) coupling and negligible Cu(II)–Cr(III) magnetic exchange, proved by the results of the field dependence of magnetization.

Introduction

As a family of functional materials, ligand-bridged metallic complexes as molecular magnets have received much attention and have been widely investigated for two decades because of their potential applications.[1] The cyanide group has become one of the most attractive ligands for bridged complexes that display rich molecular structures and fascinating magnetic properties.[2–5] Very recently, much attention has been directed to magneto-structural correlation.[3] If the area could be greatly advanced, it is possible to directedly design practical and valuable molecule-based magnetic materials. In this context, a hybrid strategy of synthesizing low-dimensional complexes has been developed.[4]

Until now, there have been many reports on the synthesis of polyaza macrocyclic complexes[5] and application in modern chemical techniques.[6,7] However, investigations concerning C-methyl substituent macrocycle complexes are comparatively rare.[8] Compared with other common pendent macrocyclic complexes, steric C-methyl substituents on the macrocycle framework make the spatial structure more open.[9]

Recently, we have shown that the dicyano-containing building blocks $[M(bpb)(CN)_2]^-$ (M = Fe, Cr)[10] are versatile building blocks for the synthesis of low-dimensional complexes. Based on the magnetic studies on a series of cyanide-bridged Ni_2Fe complexes a rough magneto-structural correlation has been derived.[10] In this work, we prepared three bimetallic trinuclear complexes $[CuL^1][Fe(bpb)(CN)_2]_2 \cdot 4H_2O$ (**2**), $[CuL^1][Cr(bpb)(CN)_2]_2 \cdot 4H_2O$ (**3**) and $[Cu(tn)_2][Fe(bpb)(CN)_2]_2 \cdot 2H_2O$ (**4**), which are suitable candidates for the magneto-structural correlation study. The structures of $[M(bpb)(CN)_2]^-$ and $[CuL^1]^{2+}$ is shown in Scheme 1.

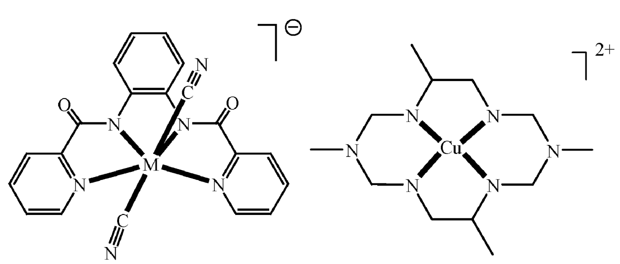
Experimental

Materials

All chemicals and solvent used in the synthesis were of reagent grade. $K[M(bpb)(CN)_2]$ was prepared according to the literature method.[11]

Measurements

Elemental analyses for carbon, hydrogen and nitrogen were carried out with a Elementar Vario EL. Infrared spectroscopy was performed on a Magna-IR 750 spectrophotometer in the 4000–400 cm^{-1} region. Magnetic susceptibility measurements of crystalline samples were carried out on a Quantum Design MPMS SQUID magnetometer. The applied magnetic field was 5000 Oe for **2**, 1000 Oe for **3**, and 10 kOe for **4**, respectively. The experimental susceptibilities were corrected for diamagnetism of the constituent atoms (Pascal's tables).



Scheme 1 Structures of $[M(bpb)(CN)_2]^-$ (M = Fe, Cr) and $[CuL^1]^{2+}$.

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† Electronic supplementary information (ESI) available: Fig. S1: Temperature dependence of $\chi_m T$ for **3**. The solid line represents the theoretical results based on the parameters J = 0.18(1) cm^{-1} and g = 1.98(1). See DOI: 10.1039/b605521d

Synthesis

CAUTION! Metal macrocyclic ligands containing perchlorate anions may be potentially explosive, so they should be carefully handled.

$[CuL^1](ClO_4)_2$ (1). To a methanol (50 mL) solution of $CuCl_2 \cdot 2H_2O$ (48.4 mmol, 8.5 g) were slowly added pn (98.6 mmol, 8.6 mL) and 40% formaldehyde (20 mL), and 25% methylamine (111 mmol, 13.8 mL). The mixture was refluxed for 24 h and the resultant red–violet solution was cooled to room temperature, then was filtered to remove the insoluble solid. To the filtrate an excess amount of sodium perchlorate dissolved in methanol were added, and the mixture was placed in a refrigerator until a red–violet precipitate was generated. Red crystals suitable for single-crystal structural analysis were obtained by recrystallization of the precipitate from hot water. Yield: ~10%. Anal. Calc. for $C_{12}H_{30}Cl_2CuN_6O_8$: C, 27.67; H, 5.81; N, 16.13. Found: C, 27.84; H, 5.80; N, 16.11%. IR: ν_{max}/cm^{-1} 3420m (ν_{NH}), 3230s (ν_{NH}), 2951m (ν_{NH}), 1102 s (ν_{ClO}).

$[CuL^1][Fe(bpb)(CN)_2]_2 \cdot 4H_2O$ (2). To an MeCN–H_2O (1 : 1) solution (5 mL) of $[CuL^2](ClO_4)_2$ (0.05 mmol, 26 mg) was added dropwise a methanol solution (10 mL) of $K[Fe(bpb)(CN)_2]$ (0.05 mmol, 23 mg). The dark brown crystals were generated by slow evaporation of the black solution. Yield: ~30%. Anal. Calc. for $C_{52}H_{62}CuFe_2N_{18}O_8$: C, 50.27; H, 5.03; N, 20.29. Found: C, 50.13; H, 5.12; N, 20.49%. IR: ν_{max}/cm^{-1} 2130s (ν_{CN}), 2120s (ν_{CN}), 1613s (ν_{CO}).

$[CuL^1][Cr(bpb)(CN)_2]_2 \cdot 4H_2O$ (3). This compound was prepared by a similar method of $[CuL^2][Fe(bpb)(CN)_2]_2$ except that $K[Cr(bpb)(CN)_2]$ (0.05 mmol, 23 mg) was used instead of $K[Fe(bpb)(CN)_2]$. Yield: ~30%. Anal. Calc. for $C_{52}H_{62}CuCr_2N_{18}O_8$: C, 49.86; H, 5.15; N, 20.13. Found: C, 49.83; H, 5.12; N, 20.15%. IR: ν_{max}/cm^{-1} 2133s (ν_{CN}), 1621s (ν_{CO}).

$[Cu(tn)_2][Fe(bpb)(CN)_2]_2 \cdot 2H_2O$ (4). To an aqueous solution of $[Cu(tn)_2](ClO_4)_2$ prepared *in situ* by mixing $Cu(ClO_4)_2$ and tn (molar ratio is 1 : 2) in 10 mL of water was added $K[Fe(bpb)(CN)_2]$ in methanol (15 mL) at room temperature. Slow evaporation of the mixed solution gave rise to red–brown single crystals, which were filtered off, washed with a small amount of water and ethanol, and dried in the air. Yield: ~30%. Anal. Calc. for $C_{46}H_{48}CuFe_2N_{16}O_6$: C, 50.40; H, 4.41; N, 20.44. Found: C, 50.20; H, 4.49; N, 20.54%. IR: ν_{max}/cm^{-1} 2132s (ν_{CN}), 2115s (ν_{CN}), 1615s (ν_{CO}).

X-Ray crystallography

The data collections were conducted at 293 K. The structures were solved by the direct method (SHELXS-97) and refined by full-matrix least squares (SHELEXL-97) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined by using a riding model. Weighted R-factors, wR, and all goodness of fits (S) were based on F^2, conventional R-factors are based on F, with F set to zero for negative F^2.

Crystal data for $[CuL^1](ClO_4)_2$ (1). $C_{12}H_{30}Cl_2CuN_6O_8$, M = 520.86, monoclinic, space group $P2_1/n$, a = 8.8437(12), b = 8.7562(11), c = 13.5885(18) Å, β = 102.355(3)°, U = 1027.9(2) Å^3, Z = 2, μ(Mo-Kα) = 1.376 mm^{-1}, 6182 reflections measured ($2.52 \le \theta \le 27.00°$) and 2247 considered unique (R_{int} = 0.0339). The final $wR(F^2)$ was 0.1921 (all data), with conventional R_F 0.0698 for 133 parameters.

Crystal data for $[CuL^1][Fe(bpb)(CN)_2]_2 \cdot 4H_2O$ (2). $C_{52}H_{62}CuFe_2N_{18}O_8$, M = 1242.44, monoclinic, space group $P2_1/c$, a = 15.740(3), b = 13.5539(16), c = 13.4949(14) Å, β = 90.108(10)°, U = 2879.0(7) Å^3, Z = 2, μ(Mo-Kα) = 0.932 mm^{-1}, 5254 reflections measured ($1.98 \le \theta \le 25.00°$) and 5020 considered unique (R_{int} = 0.0429). The final $wR(F^2)$ was 0.1618 (all data), with conventional R_F 0.0626 for 371 parameters.

Crystal data for $[CuL^1][Cr(bpb)(CN)_2]_2 \cdot 4H_2O$ (3). $C_{52}H_{62}CuCr_2N_{18}O_8$, M = 1234.74, monoclinic, space group $P2_1/c$, a = 15.969(4), b = 13.5984(15), c = 13.4235(11) Å, β = 90.115(12)°, U = 2914.9(8) Å^3, Z = 2, μ(Mo-Kα) = 0.795 mm^{-1}, 5363 reflections measured ($1.97 \le \theta \le 25.00°$) and 5123 considered unique (R_{int} = 0.0504). The final $wR(F^2)$ was 0.2004 (all data), with conventional R_F 0.0690 for 367 parameters.

Crystal data for $[Cu(tn)_2][Fe(bpb)(CN)_2]_2 \cdot 2H_2O$ (4). $C_{46}H_{48}CuFe_2N_{16}O_6$, M = 1096.24, monoclinic, space group $P2_1/n$, a = 10.761(2), b = 15.6358(19), c = 14.1161(18) Å, β = 94.630(12)°, U = 2367.3(7) Å^3, Z = 2, μ(Mo-Kα) = 1.118 mm^{-1}, 3484 reflections measured ($1.95 \le \theta \le 25.00°$) and 2568 considered unique (R_{int} = 0.0324). The final $wR(F^2)$ was 0.1178 (all data), with conventional R_F 0.0374 for 322 parameters.

CCDC reference numbers 614387–614390.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605521d

Results and discussion

Syntheses

With the Cu(II) ion as the template, formaldehyde can be very active to condense pn and methylamine to form a new branched hexaaza macrocycle complex $[CuL^1](ClO_4)_2$ in the presence of $NaClO_4$. We have found that the product obtained from the reactions is largely affected by the molar ratio of the reactants. The hexaza macrocycle is best generated by the reaction of Cu(II) ion, pn, CH_2O and CH_3NH_2 in a 1 : 2 : 5.3 : 2.3 molar ratio rather than 1 : 2 : 4 : 2. The reason for this divergence is possibly that CH_2O and CH_3NH_2 could volatilize during the reaction due to their low boiling points.

The cyano ligands $K[M(bpb)(CN)_2]_2$ contain cyano N atoms and amide O atoms. Both could coordinate to the Cu(II) atom in formation of ligand-bridged compounds,[12] however, the cyano group has been usually thought to have stronger coordination ability compared with the amido group. Therefore, the cyanide-containing building block can be effectively employed for the synthesis of ligand-bridged species.

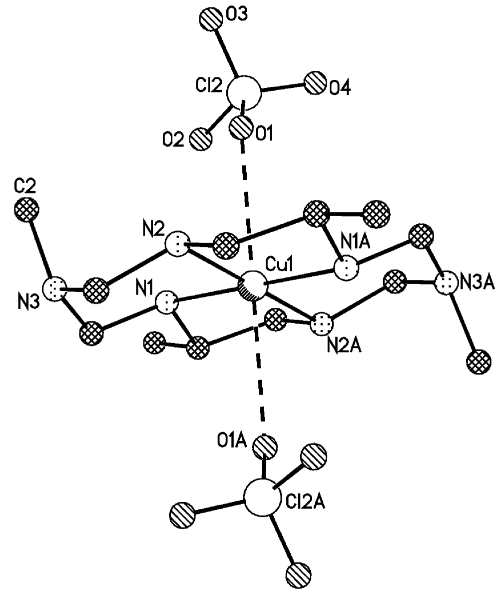

Fig. 1 The structure of $[CuL^1](ClO_4)_2$ (**1**). Symmetry operation: A $1-x, -y, -z$.

Single crystals of the bridged trinuclear Cu^{II}–M^{III} complexes were similarly synthesized by slow evaporation of equimolar mixtures of the Cu(II) precursors and $K[M(bpb)(CN)_2]_2$. The possibility that homometallic compounds form during the reaction was excluded based on the crystal data and the charge equilibrium. The crystals of the cyanide-bridged Ni_2Fe analogues have been reported to be synthesized by diffusing the Ni(II)-macrocycle into the solution of $K[Fe(bpb)(CN)_2]$ because directly mixing the two reactants only gives precipitates.[10] These different phenomena can be attributed to the different reaction properties of the metal ions. First, due to the Jahn–Teller effect of the Cu(II) ion, the axial coordination attack of the cyano nitrogen atoms is weak. Second, two methyl groups of the macrocycle occupying equatorial sites results in a degree of steric hindrance. Therefore the reaction speed is distinctly slower, resulting in the formation of single crystals by direct mixing.

The IR spectra of the cyano-bridged complexes are similar and exhibit several cyano stretching absorptions in the range 2000–2200 cm^{-1}, suggestive of the presence of both bridged and nonbridged CN^- ligands in $[M(bpb)(CN)_2]^-$. The peak at 1613–1621 cm^{-1} can be reasonably ascribed to $\nu_{C=O}$ of $[M(bpb)(CN)_2]^-$. The strong broad peak centered at 1102 cm^{-1} indicate the presence of free ClO_4^- anions in $[CuL^1](ClO_4)_2$.

Table 1 Selected bond distances (Å) and angles (°) for $[CuL^1](ClO_4)$ (**1**)

Cu(1)–N(1)	2.001(4)	Cu(1)–N(2)	2.020(5)
Cu(1)–O(1)	2.690(9)		
N(1A)–Cu(1)–N(2)	85.81(17)	N(1)–Cu(1)–N(2)	94.19(17)

Symmetry transformations used to generate equivalent atoms: A $1-x, -y, -z$.

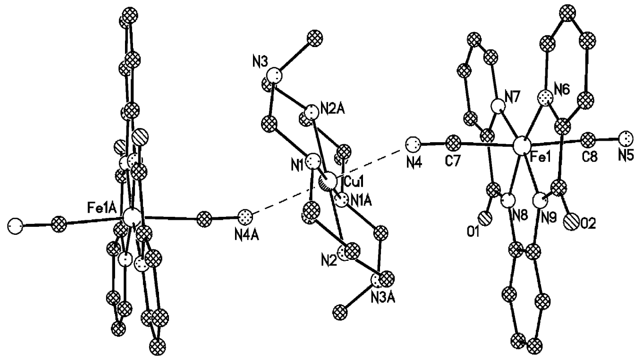

Fig. 2 Trinuclear structure of complex $[CuL^1][Fe(bpb)(CN)_2]_2\cdot 4H_2O$ (**2**). For the $CuCr_2$ complex (**3**) the Fe ions are replaced by Cr. Symmetry operation: A $1-x, 1-y, -z$.

Crystal structures

The ORTEP drawing of $[CuL^1](ClO_4)_2$ with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles of $[CuL^1](ClO_4)_2$ are listed in Table 1. The copper atom occupies the inversion centre site, and is in a distorted octahedral environment coordinated by the four secondary nitrogen donors of the macrocycle in the equatorial plane and two oxygen atoms of two perchlorate anions in the axial positions. The Cu–N bond distances to the secondary N(1), N(2), N(1A) and N(2A) atoms of the aza macrocycle are in the range of 2.001(4)–2.020(5) Å. The Cu–O bond length (2.690(9) Å) is longer than the equatorial Cu–N bond distance due to the presence of the Jahn–Teller effect for Cu(II) ion.

Complexes $[CuL^1][Fe(bpb)(CN)_2]_2\cdot 4H_2O$ (**2**) and $[CuL^1][Cr(bpb)(CN)_2]_2\cdot 4H_2O$ (**3**) are isostructural, with the structure of the former shown in Fig. 2. Selected bond distances and angles of those compounds are listed in Table 2. The two complexes have centrosymmetric trinuclear structures with the copper ion situated at the inversion centre. The coordination geometry about Cu(II) is an axially-elongated octahedron with four secondary N atoms from the hexazamacrocycle occupying the equatorial plane. The two axial sites are occupied by two cyano atoms of $[M(bpb)(CN)_2]^-$, yielding a sandwich-like structure. For **2**, the Cu–N_{axial} bond distances are 2.531(6) Å, while for **3** the bond distances are 2.514(6) Å.

Table 2 Selected bond distances (Å) and angles (°) for $(CuL^1)[M(bpb)(CN)_2]\cdot 4H_2O$

	2 (M = Fe)	**3** (M = Cr)
Cu(1)–N(1)	2.032(6)	2.031(6)
Cu(1)–N(2)	1.982(5)	1.992(6)
Cu(1)–N(4)	2.531(6)	2.514(6)
M(1)–C(7)	1.970(7)	2.080(7)
M(1)–C(8)	1.965(8)	2.091(8)
M(1)–N(6)	2.007(6)	2.082(6)
M(1)–N(7)	2.006(5)	2.077(6)
M(1)–N(8)	1.879(6)	1.955(5)
M(1)–N(9)	1.885(5)	1.963(5)
Cu(1)···M(1)	5.386(1)	5.485(2)
Cu(1)–N(4)–C(7)	146.9(6)	148.9(6)
N(4)–C(7)–M(1)	176.1(6)	173.8(6)
N(5)–C(8)–M(1)	177.3(6)	177.6(6)

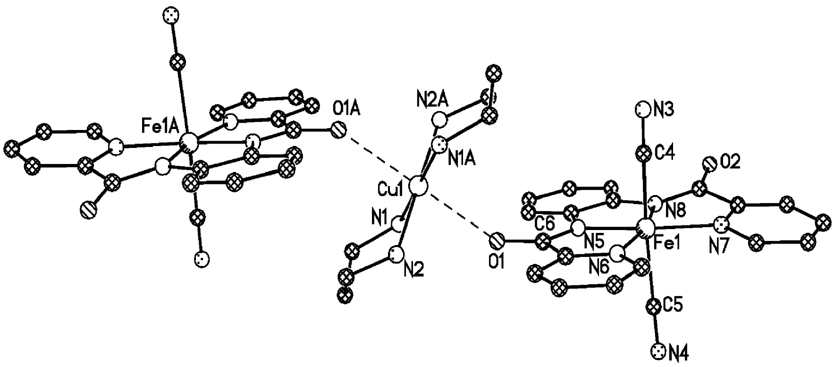

Fig. 3 Structure of the complex $[Cu(tn)_2][Fe(bpb)(CN)_2]_2 \cdot 2H_2O$ (**4**). Symmetry operation: A $-x, -y, 1 - z$.

The cyanide bridges are bent with Cu–N≡C bond angles of 146.9(6) and 148.9(6)°, respectively. The adjacent M···Cu distances are 5.386(1) Å for Fe(1)···Cu(1) and 5.485(2) Å for Cr(1)···Cu(1). The nearest intermolecular metal···metal distances are 6.565 and 6.479 Å, respectively (M(1)···M(1)#1, #1: $2 - x$, $1 - y$, $-z$, M = Fe or Cr).

The ball-and-stick drawing of $[Cu(tn)_2][Fe(bpb)(CN)_2]_2 \cdot 2H_2O$ (**4**) is presented in Fig. 3. Selected bond distances and angles are listed in Table 3. Although this complex also has a centrosymmetric trinuclear conformation with the copper ion situated at the inversion centre, it has a molecular structure different from complexes **2** and **3**. The coordination polyhedron of the copper atom is also an elongated octahedron. The equatorial positions are occupied by four nitrogen atoms from two tn ligands with the corresponding bond distances of 2.018(4) Å for Cu(1)–N(1) and 2.016(4) Å for Cu(1)–N(2), and two amido oxygen atoms are situated at the axial positions with a Cu–O bond length of 2.547(3) Å. Interestingly, the strong coordination donors, the cyanide nitrogen atoms, are not involved in bridging. This situation has been seldom observed although amido oxygen atoms have been employed for coordination.[12] The dihedral angle between the CuN_4 plane and the bpb^{2-} plane is 63.2°. The intramolecular Fe(1)···Cu(1) separation is 6.216(1) Å through the amido bridges and is thus more remote compared to the former two complexes.

For $[M(bpb)(CN)_2]^-$ with two types of bridges, either cyano or amido bridges can possibly form although the cyano-bridged compounds are more frequently obtained. The final product will depend on its stability and solubility in the reaction solvent. When $[Cu(tn)_2]^{2+}$ is used to react with $[Fe(bpb)(CN)_2]^-$, the amido-bridged $CuFe_2$ species forms in preference to the cyano-bridged $CuFe_2$ complex.

Table 3 Selected bond distances (Å) and angles (°) for $[Cu(tn)_2][Fe(bpb)(CN)_2] \cdot 2H_2O$ (**4**)

Cu(1)–N(1)	2.018(4)	Fe(1)–N(5)	1.901(3)
Cu(1)–N(2)	2.016(4)	Fe(1)–N(6)	1.987(3)
Cu(1)–O(1)	2.547(3)	Fe(1)–N(7)	2.010(4)
Fe(1)–C(4)	1.958(9)	Fe(1)–N(8)	1.884(3)
Fe(1)–C(5)	1.990(10)	Fe(1)···Cu(1)	6.216(1)
C(6)–O(1)–Cu(1)	167.7(5)	Fe(1)–C(5)–N(4)	178.1(5)
Fe(1)–C(4)–N(3)	178.1(7)		

Magnetic properties

The magnetic susceptibilities of three trinuclear complexes have been measured, as shown in Fig. 4–6 in the form of $\chi_M T$ *vs.* T. High-temperature magnetic data for complexes $[CuL^1][M(bpb)(CN)_2]_2 \cdot 4H_2O$ (M = Fe (**2**); M = Cr (**3**)) are similar, both remaining unchanged with a decrease of the temperature. The room temperature $\chi_M T$ values for **2** and **3** are 1.24 and 4.05 emu K mol^{-1}, respectively, in good agreement with the expected spin-only values of 1.12 for one Cu^{2+} ($S = 1/2$) and two low-spin Fe^{3+} ($S = 1/2$) ions and 4.125 emu K mol^{-1} for one Cu^{2+} ($S = 1/2$) and two Cr^{3+} ($S = 3/2$) ions. The low-temperature magnetic susceptibilities are different: for **2**, a sharp decrease in $\chi_M T$ occurs below 50 K, while for **3** a rapid decrease occurs below 20 K. This behaviour seems to imply the presence of antiferromagnetic coupling in both compounds.

We attempted to fit the magnetism using a trinuclear model on the basis of the isotropic Hamiltonian $\hat{H} = -2J\hat{S}_{Cu}(\hat{S}_{M1} + \hat{S}_{M2})$ for the two cyanide-bridged complexes. The M^{III}–M^{III} magnetic coupling has been neglected due to the long distances (*ca.* 10.8 Å). The best fit gave the parameters of $g = 2.09(1)$, $J = -0.59(1)$ cm^{-1} for **2**, and $g = 1.98(1)$, $J = -0.18(1)$ cm^{-1}

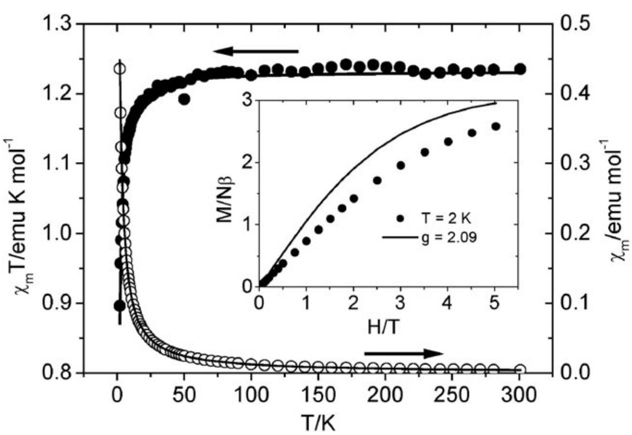

Fig. 4 Temperature dependence of $\chi_m T$ and χ_m for $[CuL^1][Fe(bpb)(CN)_2]_2 \cdot 4H_2O$ (**2**). The solid line represents the theoretical results based on the parameters described in the text. Inset: field dependence of magnetization at 2 K. The solid line represents the theoretical data based on the Brillouin function for nonexchanging S_{Cu} and two S_{Fe} ions with $g = 2.09$.

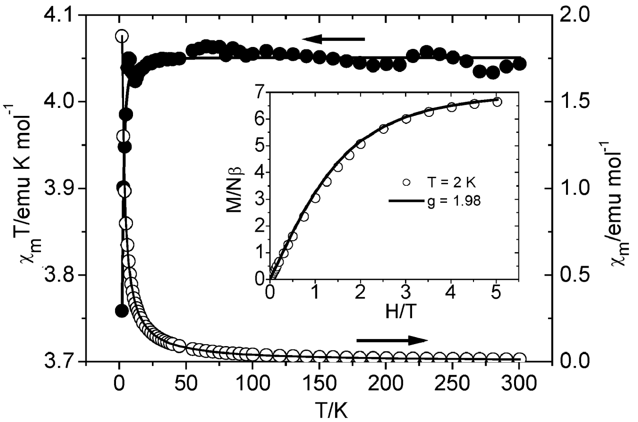

Fig. 5 Temperature dependence of $\chi_m T$ and χ_m for $[CuL^1][Cr(bpb)(CN)_2]_2 \cdot 4H_2O$ (**3**). The solid line represents the theoretical results based on the parameters described in the text. Inset: field dependence of magnetization at 2 K. The solid line represents the theoretical data based on the Brillouin function for nonexchanging S_{Cu} and two S_{Cr} ions with $g = 1.98$.

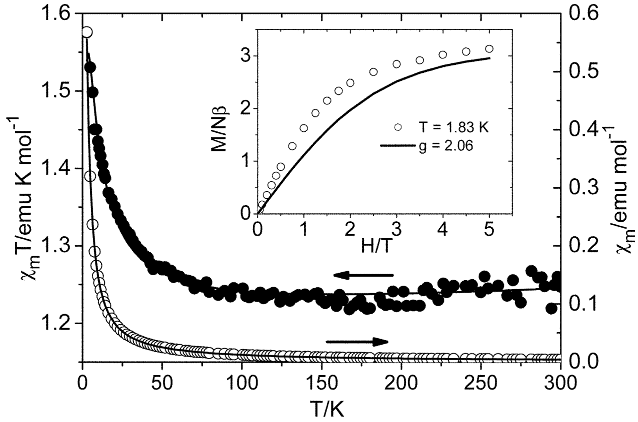

Fig. 6 Temperature dependence of $\chi_m T$ and χ_m for $[Cu(tn)_2][Fe(bpb)(CN)_2]_2 \cdot 2H_2O$ (**4**). The solid line represents the theoretical results based on the parameters described in the text. Inset: field dependence of magnetization at 2 K. The solid line represents the theoretical data based on the Brillouin function for nonexchanging S_{Cu} and two S_{Fe} ions with $g = 2.06$.

for **3**. From Fig. 4, we can see that the calculated values are in good agreement with the experimental data for complex **2**, though for **3** there is a minor divergence at low temperatures (Fig. S1, ESI†). Considering that such bimetallic complexes involve weak cyanide bridging as the cyano nitrogen atoms usually take up the axial positions of the elongated octahedral Cu(II) surroundings, weak magnetic coupling should be expected.

For cyanide-bridged Cu(II)Fe(III) complexes, most exhibit ferromagnetic behaviour[13,14] although a few have very weak magnetic coupling in which antiferromagnetic or ferromagnetic coupling cannot be distinctly distinguished.[15] For cyanide-bridged Cu(II)Cr(III) complexes, all show ferromagnetic properties.[14,16,17] The ferromagnetic Cu(II)–M(III) (M = Fe or Cr) interaction can be easily understood based on the strict orbital orthogonality.[18,19]

Hence, the magnetic behaviour for **3** is difficult to interpret. Considering the poor fit in the low temperature range and its unusual magnetic behaviour we presume that the decrease of $\chi_M T$ at low temperatures is due to the contribution of a zero-field splitting (zfs) effect for Cr(III).[20] The intermetallic magnetic coupling has been therefore considered as negligible. The best fit to the experimental observations gave satisfactory results: $g = 1.98(1)$, $D = 1.22(2)$ cm^{-1} (see Fig. 5). The field dependence of magnetization measured at 2 K agrees well with the calculated Brillouin curve for noncoupling $2S_{Cr}$ and S_{Cu} spins with $g = 1.98$, suggesting the presence of negligibly small magnetic exchange (inset of Fig. 5).

For complex **2**, the existence of antiferromagnetic coupling is further supported by the isothermal magnetization measurements at 2 K, as shown in the inset of Fig. 4. The calculated curve lies above the experimental data, indicating the presence of appreciable antiferromagnetic interaction.

It should be mentioned that the magnetic measurements have been performed several times, and the magnetic behavior is always the same. However, this antiferromagnetic coupling is unusual because most cyano-bridged Cu(II)M(III) (M = Cr, or Fe) complexes exhibit ferromagnetic interaction. Unfortunately, no further examples could be used for comparison, therefore this is still an open question at present.

Different from the cyano-bridged complexes, the amido-bridged Cu(II)Fe(III) complex (**4**) displays the usual ferromagnetic interaction. The room-temperature $\chi_M T$ value is 1.2 emu K mol^{-1}, slightly higher than the calculated spin-only value of 1.125 emu K mol^{-1}. The $\chi_M T$ value regularly increases with temperature reaching a value of 1.53 emu K mol^{-1} at 5 K.

To evaluate the strength of the magnetic coupling, we tried to fit the magnetic susceptibilities using the isotropic Hamiltonian $H = -2J_{CuFe}S_{Cu}(S_{Fe(1)} + S_{Fe(2)})$ for a $CuFe_2$ species including the zJ' term to account for the intermolecular magnetic interaction. The obtained parameters are $J_{CuFe} = 3.1(1)$ cm^{-1}, $g = 2.06(1)$, and $zJ' = -0.17(1)$ cm^{-1}. As shown in Fig. 6, the fit (solid line) is satisfactory. The positive J_{CuFe} value supports the ferromagnetic nature of intermetallic coupling. This ferromagnetic coupling can be explained in terms of orbital orthogonality of 3d magnetic orbitals between Cu(II) and low-spin Fe(III).[18,19] The present complex is, to our knowledge, the first amido-bridged Cu(II)Fe(III) complex.

In conclusion, the versatile dicyano-containing building blocks $[M(bpb)(CN)_2]^-$ have been used for the synthesis of heterometalllic complexes. Interestingly, amido bridges have been found with the cyano group nonbridging in one of the complexes. Weak antiferromagnetic or negligible magnetic coupling is present in the cyanide-bridged complexes, while ferromagnetic coupling is present in the amido-bridged compound. Future work will involve the preparation of strongly magnetically coupled heterometallic Cu(II)M(III) complexes using the $[M(bpb)(CN)_2]^-$ precusors. To attain this, two- or three-coordinate Cu(II) complexes should be employed.[17,19]

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