Syntheses, structures, and magnetic properties of heterometallic coordination polymers with carboxyphosphonate linkers[†]

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Five heterometallic coordination polymers were synthesized utilizing the multifunctional carboxyphosphonate ligand N-(phosphonomethyl)iminodiacetic acid (H₄PMIDA), N(CH₂PO(OH)₂)(CH₂COOH)₂, with a coordinating nitrogen atom and two carboxylate and one phosphonate groups. The compounds were characterized structurally and magnetically. $[Cu_2M_2(PMIDA)_2(H_2O)_6]\cdot 3H_2O$ for M = Mn (1-CuMn), Co (2-CuCo), and Cd (3-CuCd) are isostructural (space group *P*2₁/n) and made of honeycomb-like 2D layers which, in turn, are made of unusual double-stranded *meso*-helices. $[Cu_2Ln_2(PMIDA)_2(C_2O_4)(H_2O)_6]\cdot 3.5H_2O$ for Ln = La (4-CuLa) and Nd (5-CuNd)) are also isostructural (*P*2₁/c) but with open 3D framework structures. They contain dinuclear CuLn(PMIDA) secondary building units that are bridged by phosphonate tetrahedra and form infinite chains along the *c* axis. The chains are interconnected *via* carboxylic groups and form double-decker layers which, in turn, are connected by the oxalate linkers to form the open three-dimensional framework. The magnetic properties of the compounds were measured and analyzed in detail.

Introduction

The design and synthesis of metal–organic coordination polymers attracts much attention for many reasons, not the least of which are their intriguing variety of architectures and topologies and their potential for applications in a wide range of fields.^{1,2} However, while homometallic systems have been extensively explored, not much has been done with heterometallic systems.³ Yet, heterometallic coordination polymers could potentially be very beneficial for two major reasons: one, the introduction of a second metal center may allow for the construction of appealing new topologies, and two, the incorporation of unusual metal coordination environments may influence the physical properties of the materials, especially their catalytic, photoluminescent, and magnetic properties.⁴

There are two main approaches toward the construction of heterometallic coordination polymers. One is to use preformed metal complexes as linkers for the interconnection of the second metal centers by coordinating to them.⁵ Such a "complex as a ligand" approach was first applied successfully by Kahn *et al.* in the oxamato-bridged manganese(II)–copper(II) chain [MnCu(pbaOH)(H₂O)₃] (pbaOH = 2-hydroxy-1,3-propylenebi-s(oxamate)),⁶ and then extended to other 3d-3d heterobimetallic systems with interesting magnetic properties (long-range 3D magnetic order and single-chain magnets).⁷ The second and more general strategy for the synthesis of heterometallic coordination frameworks relies on: a) the self-assembly of the different metal

ions with organic linkers with different donor atoms and b) the different preference of the metal atoms towards different functional groups of a linker. A number of 3d-4f frameworks have been synthesized by the latter approach using multidentate multifunctional ligands such as pyridinecarboxylate, amino acids, imidazoledicarboxylic acid, and iminodiacetic acid.8,9 The selection of the two or more different metals in these cases goes hand in hand with the choice and design of the interconnecting ligands so that the coordination sites of the latter are appropriate for each of the metals. While much attention has been focused on structures with nitrogen-containing carboxylate linkers, only very few reports have dealt with heterometallic compounds with phosphonate linkers.¹⁰ At the same time, functionalized phosphonates such as carboxyphosphonates and nitrogen-containing phosphonates and carboxyphosphonates could be the best choice for the construction of heterometallic extended structures because of their variety of diverse coordinating sites and modes with different affinities towards different metal centers.

With the above considerations in mind, we explored heterometallic coordination polymers with ligands with three different functional groups that can potentially coordinate to metals, namely a nitrogen site and carboxylic and phosphonic groups. Here we report the synthesis and structural and magnetic characterization of five heterometallic compounds with N-(phosphonomethyl)iminodiacetic acid (H₄PMIDA), N(CH₂PO₃H₂)(CH₂COOH)₂: [Cu₂M₂(PMIDA)₂(H₂O)₆]·3H₂O for M = Mn (1-CuMn), Co (2-CuCo), Cd (3-CuCd), and [Cu₂Ln₂(PMIDA)₂(C₂O₄) (H₂O)₃]·3.5H₂O for Ln = La (4-CuLa), Nd (5-CuNd).

Experimental

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification.

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[†] Electronic supplementary information (ESI) available: Bond lengths and angles; FTIR data; PXRD patterns; polyhedral representations of layer structures; ZFC and FC magnetization vs. temperature. CCDC reference numbers 742512–742516. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b915459k

Cu(CH₃COO)₂·4H₂O (100 mg, 0.5 mmol), H₄PMIDA (114 mg, 0.5 mmol), and 0.5 mmol of either Mn(CH₃COO)₂·4H₂O, Co(CH₃COO)₂·4H₂O or Cd(CH₃COO)₂·2H₂O were dissolved in 6 mL of H₂O and heated at 100 °C for 2 days in stainless steel reactors with Teflon liners. After cooling to room temperature, crystals of single-phase products were collected, washed with H₂O, and dried in air. Yields (based on Cu): 63% for **1-CuMn**, 75% for **2-CuCo**, 56% for **3-CuCd**.

Synthesis of 4-CuLa and 5-CuNd

Cu(CH₃COO)₂·4H₂O (100 mg, 0.50 mmol), H₄PMIDA (114 mg, 0.5 mmol), H₂C₂O₄ (23 mg, 0.25 mmol), and 0.5 mmol of La(NO₃)₃·6H₂O or Nd(NO₃)₃·6H₂O were dissolved in 6 mL of H₂O and heated at 100 °C for 2 days in stainless steel reactors with Teflon liners. After cooling to room temperature, crystals of single-phase products were collected, washed with H₂O, and dried in air. Yields (based on Cu): 61% for **4-CuLa** and 50% for **5-CuNd**.

Structure determination

Data sets were collected on a Bruker APEX-II diffractometer with a CCD area detector at 100 K with Mo K α radiation ($\lambda = 0.71073$ Å). Raw data collection and processing were done with the SMART software, SAINT was used for the data reduction and for correction for Lorentz and polarization effects,¹¹ and the absorption corrections were applied using the SADABS routine. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the SHELXTL software package.¹² All nonhydrogen atoms were refined with anisotropic displacement parameters during the final cycles, while the hydrogen atoms were calculated in ideal positions at the carbon atoms. More details of the data collections and structure refinements are presented in Table 1.

Physical measurements

Infrared spectra were collected over the range 650-4000 cm⁻¹ using a SensIR IlluminatIR spectrometer with a diamond ATR fitted to an Olympus microscope. The spectra are the average of 128 scans each. Powder X-ray diffraction (PXRD) was carried out with a Scintag XDS 2000 powder diffractometer using Cu Ka radiation ($\lambda = 1.5418$ Å), solid state detector, scan range of 5° to 50° (2 θ), step size 0.05° and scan rate 5.0°/min. Magnetic measurements were performed on polycrystalline samples with Quantum Design MPMS-XL SQUID magnetometer. а Magnetic susceptibilities were measured over the temperature range 2-300 K with an applied magnetic field of 2 kOe. Field dependences of the magnetizations were measured using a flux magnetometer in applied fields of up to 70 kOe generated by a conventional pulsed technique. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

Table 1 Summary of crysta	llographic data for the complexes 1	-CuMin, 2-CuCo, 3-CuCd, 4-CuLa a	nd 5-CuNd		
	1-CuMn	2-CuCo	3-CuCd	4-CuLa	5-CuNd
formula	$C_{10}H_{32}Cu_{5}Mn_{2}N_{2}O_{24}P_{2}$	$C_{10}H_{3},C_{0},C_{1},N,O_{24}P,$	$C_{10}H_{32}Cd_2Cu_5N_2O_{24}P_2$	$\mathrm{C}_{24}\mathrm{H_{62}Cu_4La_4N_4O_{55}P_4}$	$C_{24}H_{62}Cu_4Nd_4N_4O_{55}P_4$
fw	863.28	871.26	978.20	2220.46	2241.78
T, \mathbf{K}	100(2)	100(2)	100(2)	100(2)	100(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
$a, \check{\mathrm{A}}$	10.133(6)	10.010(5)	10.217(6)	8.302(8)	8.236(8)
$b, \check{\mathbf{A}}$	16.757(2)	16.705(7)	16.788(1)	20.639(8)	20.366(5)
$c, { m \AA}$	16.207(8)	15.976(2)	16.244(2)	9.463(4)	9.406(3)
β , deg	95.402(2)	95.628(2)	95.647(2)	109.876(2)	110.286(1)
$V, \AA^{\overline{3}}$	2739.9(2)	2658.7(5)	2772.9(1)	1525.1(4)	1480.0(4)
Z	4	4	4	1	1
$D_{ m c},~{ m g}~{ m cm}^{-3}$	2.093	2.177	2.343	2.418	2.515
μ, mm^{-1}	2.653	3.032	3.245	4.337	5.090
θ , deg	2.28 - 28.41	1.77 - 28.36	1.75 - 28.33	1.97 - 28.31	2.00-28.42
$\operatorname{GOF}(F)$	1.035	1.172	1.165	1.159	1.076
$R_I^{a/W} R_2^{b}$ (I>2 σ (I))	0.0360/0.0925	0.0405/0.1066	0.0446/0.1169	0.0290/0.0656	0.0235/0.0576
R_I^a/wR_2^{-b} (all data)	0.0389/0.0944	0.0430/0.1080	0.0481/0.1188	0.0313/0.0664	0.0253/0.0584
$^{a} R_{I} = \Sigma \ F_{\mathrm{o}} - F_{\mathrm{c}} /\Sigma F_{\mathrm{o}} .$	${}^{\gamma}R_{2} = [\Sigma w(F_{0}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{0}^{2})]^{1/2}.$				

Results and discussion

Crystallographic studies

Since compounds 1-CuMn, 2-CuCo, 3-CuCd are isostructural, the structure will be described for 1-CuMn. The asymmetric unit contains two copper and two manganese atoms (the equimolar ratio was confirmed by ICP analysis). Each Cu(II) center is in a square pyramidal coordination formed by one PMIDA ligand in a tetradentate coordination (N1, O1, O3 and O7 for Cu1, and N2, O8, O10 and O12 for Cu2) and a single phosphonate oxygen atom from a second PMIDA unit (Fig. 1). The Cu-Oapical bond lengths, 2.281(2) Å for Cu1–O7 and 2.317(2) Å for Cu2–O12, are much longer than the Cu–O/N_{basal} distances of 1.894(2)–2.021(2) and 1.914(2)-2.015(3) Å for Cu1 and Cu2, respectively. The manganese atoms are octahedrally coordinated: Mn1 by three water molecules, two phosphonate oxygen atoms (O7, O13A), and one carboxylic oxygen atom (O11B) from three different PMIDA ligands; Mn2 by four water molecules and two phosphonate oxygen atoms from two different PMIDA ligands. The Mn–O distances are normal and within the range 2.049(2)– 2.270(3) Å.

The most interesting feature in **1-CuMn** is the specific way in which the metal centers are linked by phosphonate tetrahedra to form a double-stranded *meso*-helical motif with a pitch of 19.906 Å (Fig. 2). Thus, the Cu centers, interconnected by the phosphonate groups, and the Mn centers, interconnected by the

$\begin{array}{c} C4 \\ C4 \\ 02 \\ 013 \\ 013 \\ 0118 \\ 016 \\ 018 \end{array} \xrightarrow{0}{0}{0}{0}{0}{1}{0}{0}{0}{1}{0}{0}{0}{1}{0}{0}{1}{0}{0}{1}{0}{0}{1}{0}{0}{1}{0}{1}{0}{0}{1}{0}{0}{1}$

Fig. 1 The coordination environment of Cu^{2+} and Mn^{2+} ions in 1-CuMn (thermal ellipsoids at 30% probability level).





Fig. 3 Polyhedral representation of the honeycomb-like layer in 1-CuMn along the *b*-axis.

same phosphonate groups, form single-stranded helices that turn in different directions and generate a double-stranded *meso*helical chain. Although single-stranded helices have been observed in some coordination polymers,¹³ the occurrence of a double-stranded or a multiple *meso*-helix is very rare.¹⁴

The double-stranded helices are in turn connected *via* carboxylic groups and form honeycomb-like layers parallel to the *ac* plane (Fig. 3). The layers are stacked in …ABAB… sequence and are held together by numerous interlayer hydrogen-bonds that involve coordinated and uncoordinated water as well as uncoordinated carboxylic oxygen atoms (O2, O4, O9).

4-CuLa and 5-CuNd are also isostructural and crystallize in the monoclinic $P2_1/c$ space group. Taking **4-CuLa** as an example, the asymmetric unit of the structure contains one Cu and one La atoms (Fig. 4). The Cu^{II} ion has an elongated octahedral geometry with one PMIDA ligand coordinated in a tetradentate fashion (N1, O1, O3 and O7) exactly as in 1-CuMn, one phosphonate oxygen atom from another PMIDA (O6), and one water molecule (O13). The Cu-O axial distances, 2.637(3) and 2.530(3) Å, are much longer than the Cu–O/N basal distances of 1.934(3)-2.019(3) Å as expected due to Jahn-Teller distortion. The La^{III} center is nine-coordinate in a distorted tricapped trigonal prism where O3, O5, and O10 are the capping atoms. The nine coordinated oxygen atoms are provided by two phosphonate groups, three carboxylic groups from two PMIDA ligands, one bidentate oxalic anion, and two water molecules. The La-O distances are in the range 2.450(3)-2.765(3) Å and



Fig. 4 The coordination environment of Cu^{2+} and La^{3+} ions in **4-CuLa** (thermal ellipsoids at 30% probability level).



Fig. 5 Polyhedral representation of the double layers in **4-CuLa** along the *b*-axis.

compare well with the distances reported for other La^{III} phosphonates.¹⁵

The alternation of Cu^{II} and La^{III} ions in **4-CuLa** bridged by carboxylate and phosphonate groups results in the formation of double-layer slabs parallel to the *ac* plane (Fig. 5). Each metal atom is connected to five other metal atoms, two of the same and three of different type. The linkages of Ln atoms between adjacent double layers through the oxalic bridges give rise to a threedimensional sandwich framework with channels filled by water molecules (Fig. 6).

One common feature in the two structure types is the tetradentate coordination of the Cu centers by PMIDA ligands as shown in Chart 1. This suggests that the initial step in the formation of the compounds is most likely the coordination of PMIDA to copper ions to form Cu(PMIDA)^{2–}. The latter should be, therefore, considered the building unit of the extended structure. The PMIDA ligand, however, has additional sites that are available for further coordination, and this allows the unit Cu(PMIDA)^{2–} to act as a linker between the second metal centers, either Mn or La. The two structure types differ only because of the different coordination requirements and oxidation states of the secondary metals. Thus, in **1-CuMn** the PMIDA molecules coordinate to two or three Mn- atoms (Chart 1, b and



Chart 1 The ligand H_4PMIDA (a) and its coordination modes in 1-CuMn (b and c) and in 4-CuLa (d).

c) while in **4-CuLa** they interact with four La centers (Chart 1, d). It should be pointed out that such coordination modes are not found for PMIDA in homometallic compounds.¹⁶

Magnetic properties

Magnetic measurements were performed on polycrystalline samples of complexes 1-CuMn, 2-CuCo, 3-CuCd, 4-CuLa and 5-CuNd. The magnetic susceptibility of 1-CuMn was measured in the range 2–300 K (Fig. 7). The $\chi_M T$ value of 9.25 $emu \cdot K \cdot mol^{-1}$ at room temperature is slightly lower than the spin-only value of 9.50 $emu \cdot K \cdot mol^{-1}$ expected for two highspin Mn^{II} (S = 5/2 and g = 2) and two Cu^{II} (S = 1/2 and assuming g = 2 ions. Upon lowering the temperature $\gamma_M T$ decreases continuously to reach 7.90 emu·K·mol⁻¹ at 10 K. This is then followed by an abrupt increase and a maximum of 9.65 $emu \cdot K \cdot mol^{-1}$ at 2 K. This behavior is indicative of antiferromagnetic coupling between the magnetic centers Cu^{II} and Mn^{II}. The observed field-dependent magnetization of ca. M = 7.93 $N\beta \cdot mol^{-1}$ at 7 T is as expected for antiferromagnetically coupled Cu^{II}₂Mn^{II}₂ unit. The magnetizations after zero-field-cooling (ZFC) and field-cooling (FC) in the temperature range of 2-15 K and at low applied field of 50 Oe coincide with each other and indicate the absence of long-range magnetic ordering above 2 K. This confirms that the compound should be viewed as a 2D network made of dinuclear Cu^{II}Mn^{II} units that are interconnected by carboxylate and phosphonate bridges but are magnetically isolated. As such, the hightemperature magnetic data can be fitted by a model of Cu^{II}Mn^{II} units and their Hamiltonian $H = -2JS_{Cu} \cdot S_{Mn}$ as follows:



Fig. 6 View of the 3D framework of 4-CuLa showing channels filled by non-coordinated water molecules.



Fig. 7 Plots of $\chi_{\rm M}T$ versus *T* for **1-CuMn** at a field of 2 KOe. Solid lines represent the best fitting of the data. The inserts show magnetization versus field up to H = 70 kOe at 2 K for **1-CuMn**.



Fig. 8 Plots of $\chi_M T$ versus *T* for **2-CuCo** at a field of 2 KOe. Solid lines represent the best fitting of the data. The inserts show magnetization versus field up to H = 70 kOe at 2 K for **2-CuCo**.

$$\chi = \frac{2Ng^2\beta^2}{kT} \frac{5 + 14\exp(3J/kT)}{5 + 7\exp(3J/kT)}$$
(1)

$$\chi_{\rm M} = \frac{\chi}{1 - \chi \left(2zJ'/Ng^2\beta^2\right)} \tag{2}$$

This model and equations (1) and (2) allow for simulation of the temperature dependence of $\chi_M T$ above 10 K (Fig. 7, and this gives best fit parameters of g = 1.98, J = -8.42 cm⁻¹, and zJ' = -0.20 cm⁻¹ ($R = 9.20 \times 10^{-4}$). The signs and relative magnitudes of the exchange parameters compare well with those in other oxygen-bridged compounds containing high-spin Mn^{II} and Cu^{II} ions.¹⁷

The temperature dependence of the magnetic susceptibility for 2-**CuCo** is displayed in Fig. 8. The room temperature $\chi_{\rm M}T$ value of 6.75 emu \cdot K \cdot mol⁻¹ is much higher than the expected spin-only value for two Cu^{II} and two high-spin Co^{II} ions, and this is indicative of significant orbital contributions from the Co^{II} ions. Upon lowering the temperature, $\chi_{\rm M}T$ decreases continuously to 3.83 $emu \cdot K \cdot mol^{-1}$ at 7 K, then goes up slightly to 3.92 $emu \cdot K \cdot mol^{-1}$ at 5 K, and finally drops to 3.54 emu \cdot K \cdot mol⁻¹ at 2 K. All this suggests antiferromagnetic coupling between the Cu^{II} and Co^{II} centers. This is supported further by the apparently unsaturated magnetization value of 4.61 $N\beta \cdot mol^{-1}$ at 7 T and temperature of 2 K (insert in Fig. 8). The ZFC and FC magnetizations carried out in the 2-15 K range at 50 Oe showed no evidence of magnetic ordering. The magnetic exchange interactions and the spin-orbit coupling for the compound were estimated based on the simple phenomenological equation $\chi_M T = A \exp(-E_1/kT) + B \exp(-E_2/kT)$ where A + B is equal to the Curie constant and E_1 and E_2 are the "activation energies" of the spin-orbit coupling and the magnetic interaction, respectively.¹⁸ The best parameters obtained after least-squares fitting are $A + B = 7.30 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$, and $E_1 = 55.01$ and $E_2 = 1.01 \text{ cm}^{-1}$. E_1 is consistent with the values reported for other Co^{II} systems.^{18,19} The positive activation energy E_2 confirms that antiferromagnetic interactions are operative in 2-CuCo.

The magnetizations of **3-CuCd** and **4-CuLa** are very similar because Cd^{II} and La^{III} ions are diamagnetic and the magnetic behavior is due only to the Cu^{II} ions (Fig. 9). The $\chi_M T$ values for **3-CuCd** and **4-CuLa** at room temperature are very similar, 0.85 and 0.80 emu·K·mol⁻¹, respectively, and fall in the range expected for two isolated Cu^{II} ions (S = 1/2). As the temperature decreases $\chi_M T$



Fig. 9 Plots of $\chi_M T$ versus *T* for **3-CuCd** and **4-CuLa** (insert) at a field of 2 kOe. Solid lines represent the best fitting of the data.

decreases very slowly and then abruptly falls at low temperatures reaching values of 0.59 and 0.39 emu · K · mol⁻¹ at 2 K for **3-CuCd** and **4-CuLa**, respectively. A closer inspection of the structure of the two compounds aimed at finding possible magnetic interactions revealed that it can be approximated simply with a uniform chain of copper(II) ions connected by -O-P-O- bridges. The data were analysed using the expression derived from the isotropic spin-exchange Hamiltonian $H = -J\sum S_i \cdot S_{i+1}$ where S = 1/2. The best fitting results with intermolecular interactions (zJ') were obtained for g = 2.10 and 2.08, J = -2.01 and -0.94 cm⁻¹, zJ' = -0.05 and -0.07 cm⁻¹, temperature-independent paramagnetism (TIP) = 0.013 and 0.021 emu/mol, and $R = 2.5 \times 10^{-3}$ and 5.7×10^{-4} for **3-CuCd** and **4-CuLa**, respectively. The negative J values confirm the presence of antiferromagnetic exchange transmitted by the phosphonate groups.

Lastly, the magnetization of **5-CuNd** (Fig. 10) shows a room temperature value of 4.37 emu · K · mol⁻¹ for $\chi_M T$. This is very close to the calculated value expected for two isolated Cu^{II} ($S_{Cu} = 1/2$) and two isolated Nd^{III} ions (J = 9/2, $g_J = 8/11$). Upon lowering the temperature $\chi_M T$ marginally decreases until 50 K below which it decreases more rapidly reaching its lowest value of 2.40 emu · K · mol⁻¹ at 2 K. The data above 100 K obey the Curie–Weiss law with C = 4.74 emu · K · mol⁻¹ and $\theta = -26.79$ K (Fig. 10). Further interpretation and simulation of the magnetic properties of this compound, however, are very difficult due to: a) first-order orbital momentum and the resulting spin–orbital couplings of the single lanthanide ions,²⁰ and b) the complicated nature of the structure with many Nd^{III}–Cu^{II}, Nd^{III}–Nd^{III}, and Cu^{II}–Cu^{II} interactions mediated through μ_2 -O, O–P–O, and oxalic bridges.



Fig. 10 Plots of $\chi_M T$ and $1/\chi_M$ versus T for **5-CuNd** at a field of 2 kOe. Solid lines represent the best fitting of the data using the Curie–Weiss law.

Conclusions

In summary, we have successfully synthesized a series of heterometallic d-d and d-f coordination polymers utilizing a multifunctional nitrogen-containing carboxyphosphonate ligand. Although many heterometallic complexes have been reported, examples of phosphonate-bridged heterometallic frameworks are still quite rare. Compounds **1-CuMn**, **2-CuCo** and **3-CuCd** are rare examples of heterometallic two-dimensional polymers containing double-stranded *meso*-helices, while compounds **4-CuLa** and **5-CuNd** are three-dimensional 3d-4f open-framework structures with interesting double layers. Further exploration for phosphonate-bridged heterometallic materials combining openframework structures and interesting magnetic properties is currently under way in our laboratory.

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