Structural Versatility of 3d-Ce III Heterometallic Coordination Polymers Using Co II or Cu II

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ABSTRACT: In the present work, we report the synthesis and characterization of two new heterometallic coordination polymers based on Ce III and containing Co II or Cu II cations, assembled by the bifunctional ligand 1H-imidazole-4,5-dicarboxylic acid, [Ce(H2O)2(HIDC)Co(IDC)]·H2O CoCe and [Ce(H2O)2(H2IDC)Cu(H2O)(IDC)Cu2(H2,IDC)] CuCe. Compound CoCe was obtained under one pot hydrothermal synthesis, while CuCe was synthesized by a step-by-step synthesis using the metalloligand [Cu(H2IDC)2-](H2O)2 Cu1, as precursor. From a structural point of view, CoCe presents an intricately 3D structure, in which alternating Λ-Δ chiral Co II chains can be observed, which are assembled by discrete Ce III fragments, giving rise to the 3D structure. Meanwhile, CuCe presents a structure formed by [Cu3Ce2] heterometallic chains, partially assembled by Cu II cations in a 2D structure. Magnetic properties reveal that both CoCe and CuCe present a global antiferromagnetic behavior, dominated by the interaction between Co II-Co II or Cu II-Cu II entities connected by μ-xN,O-xO″′′,N' bridges, belonging to H1-IDC anionic derivatives. Moreover, a weak ferromagnetic phenomenon was found in compound CoCe, corroborated by hysteresis loops and ac magnetization.

1. INTRODUCTION

In the field of material science, the new technologies drive the innovation in the synthesis and characterization of different kinds of novel materials. In this sense, the coordination polymers (CPs) are one of the most studied materials. The interest in this kind of compounds lies in that a combination of different metal centers with a proper ligand can afford an infinity of new structures, with novel architectures and topologies. Homometallic CPs have been extensively studied in fields such as luminescent sensors,1,2 magnetic materials,3,4 gas separation,5,6 semiconductor materials,7 and heterogeneous catalysts.8 On the other hand, researches on CPs that combine more than one different kind of metal cations are still less exploited. For example, heterometallic coordination polymers (HCP) based on 3d and 4f cations have become attractive in recent years, principally due to the differences on the coordination features which permit obtaining sophisticated structured glasses and novel properties. For example, Jin et al. reported the synthesis of two 3D frameworks [Pr5Cu3I4(IN)2(H2O)2] (solv) and [solv = benzene or toluene] using isonicotinic acid (HIN). These Pr III-Cu I compounds showed a high framework stability and reversible solvent exchange, but the most important feature was that both compounds presented chiral structures, these obtained from a symmetrical ligand.9 On the other hand, using pyrazine-2,3-dicarboxylic acid (H2pzdc), Yang et al. obtained a series of 3d-4f 2D networks [Ln2Co(pzdc)4(H2O)6]·2H2O (Ln = La III, Pr III, Eu III, and Gd III) that were used as catalysts in the synthesis of cyanohydrin. These compounds showed very high conversions for benzaldehyde and high selectivity to cyanohydrin at room temperature in solvent free conditions.10 Zhang et al. presented an excellent example of multifunctional materials in a family of isostructural 3D compounds [LnZnL(CO3)2(H2O)] (Ln = Eu III, Gd III, Dy III, Ho III, Er III, Tm III, Yb III, Lu III; L = 4′-(4-carboxyphenyl)-2,2′,6′,2′′-terpyridine). Structurally, all the compounds presented interpenetrated and chiral structures. Moreover, compound Eu III-Zn II presented potential applications in luminescent sensing of nitrobenzene, while the
Table 1. Crystal Data and Structure Refinement for CoCe and CuCe

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<tr>
<th></th>
<th>CoCe</th>
<th>CuCe</th>
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Gd$^{III}$Zn$^{II}$ framework allowed one to quantify the magnetic interactions between Gd$^{III}$ ions, by the calculation of the coupling constant.$^{11}$

The presence of two different metal cations in this type of 3d-4f materials adds structural complexity and gives the possibility of obtaining new functionalities. As the hardness of both cations is different, the use of an N$_2$O-bifunctional ligand seems to be the most reasonable strategy for the rational design of heterometallic CPs,$^{12-14}$ since 3d cations can bind either N or O atoms, while 4f centers are strongly oxophilic according to the Pearson HSAB theory.$^{15}$ For this reason, the 1H-imidazole-4,5-dicarboxylic acid attracted our attention, due to (a) the existence of both a N-heterocyclic ring from imidazole and carboxylate functionalities, (b) the ability to generate different anionic species, in order to balance the positive charge, and (c) the existence of multiple coordination modes, among others.$^{16,17}$ Although H$_2$IDC has been previously used as a building block for the 3d-4f,$^{18-21}$ its rich coordination chemistry still makes this organic linker an exceptional candidate to be used in the construction of new 3d-4f HCPs. In the present work, we report the synthesis, structural and magnetic characterization of two new 3d Ce$^{III}$ HCPs (3d = Co$^{III}$ or Cu$^{II}$), [Ce(H$_2$O)$_2$(HIDC)Co(IDC)]; H$_2$O CoCe and [Ce(H$_2$O)$_2$(HIDC)Cu(H$_2$O)(IDC)] CuCe, which were obtained under hydrothermal conditions using one pot and step-by-step synthesis for CoCe and CuCe, respectively.

### 2. Experimental Section

#### 2.1. Synthesis of [Ce(H$_2$O)$_2$(HIDC)Co(IDC)]·H$_2$O (CoCe). A suspension of H$_2$IDC (0.3 mmol), Co(NO$_3$)$_2$·6H$_2$O (0.3 mmol), and Ce(acac)$_3$ (0.3 mmol) (acac = acetylacetonate) was placed in a 23 mL Teflon-lined stainless-steel autoclave vessel with 10 mL of water and heated at 150 ℃ for 5 days, under self-generated pressure. The reaction mixture was cooled down to room temperature. Fuchs prismatic crystals of CoCe, stable and suitable for X-ray diffraction, were separated by filtration. MW: 560.28 g/mol. Yield of 50%, based on the lanthanide salt. Analysis calculated for CoCe$_{10}$H$_{14}$N$_{14}$O$_{11}$ (%): C, 21.44; H, 1.62; N, 10.00. (%) Found: C, 21.28; H, 1.73; N, 9.65. A suspension of [Ce(H$_2$O)$_2$(H$_2$IDC)·Cu(H$_2$O)(IDC)]·Cu$_2$(H$_2$IDC) (CuCe). Compound CuCe was obtained in a two-step reaction, using [Cu(H$_2$IDC)$_2$(H$_2$O)$_2$] (CuI), as metallograph. CuI was synthesized by a 2 h reflux of a solution of Cu(NO$_3$)$_2$·3H$_2$O (5 mmol) and H$_2$IDC (10 mol) in 30 mL of water. (MW: 409.79 g/mol. Yield of 89%, based on the copper salt). Analysis calculated for Cu$_{12}$Ce$_{10}$H$_{14}$N$_{14}$O$_{11}$ (%): C, 29.32; H, 2.44; N, 13.67. (%) Found: C, 30.15; H, 2.46; N, 13.77. A suspension of CuI (0.15 mmol), Ce(NO$_3$)$_3$·3H$_2$O (0.10 mmol) and K$_2$CO$_3$·H$_2$O (0.10 mmol) was placed in a 23 mL Teflon-lined stainless-steel autoclave vessel with 10 mL of water and heated at 120 ℃ under self-generated pressure for 5 days. The reaction mixture was cooled down to room temperature in 16 h. Light blue stick crystals of CuCe, stable and suitable for X-ray diffraction, were separated by filtration. MW: 735.959 g/mol. Yield of 51%, based on lanthanide salt. Analysis calculated for Cu$_{12}$Ce$_{10}$H$_{14}$N$_{14}$O$_{11}$ (%): C, 23.96; H, 1.74; N, 11.42. (%) Found: C, 23.47; H, 1.78; N, 10.66.

#### 2.2. X-ray Data Collection and Structure Determination. A single crystal of CoCe was directly picked up and glued on a glass capillary using epoxy resin. Scans on a Bruker AXS diffraction meter confirmed enough crystal quality to perform full recording data at room temperature. X-ray radiation of Mo–Kα ($\lambda = 0.71073$ Å) was
used. Data were reduced by SAINT,22 and empirical absorption corrections were applied using SADABS.23 Single-crystal X-ray diffraction data of CuCe were collected at 150 K on a D8 VENTURE Bruker AXS diffractometer and processed with the APEX3 program suite,24 also using Mo-Kα as X-ray wavelength. Frame integration and data reduction were carried out with the program SAINT,22 and SADABS was employed for multiscan-type absorption corrections.23

Using the Olex225 package, the crystal structures were solved with the ShelXT26 structure solution program using Dual Methods, and refined with the ShelXL27 package using least-squares minimization based on $F^2$. Crystallographic data details on data collections and refinement parameters of the crystal structure are summarized in Table 1. Structure drawings have been made with TOPOS software.28 Additional data concerning the crystals and the refinement parameters are detailed in the Supporting Information (Table S1 for CoCe and Table S2 for CuCe).

One of the coordination water molecules linked to CeIII cations presents disorder (O2WA and O2WB with occupancy of 0.46 and 0.64, respectively). In addition, the solvate H2O molecules O3W and O4W present fractional occupancy (0.3 and 0.7, respectively) and were counted as one H2O molecule in the final formula. Finally, some hydrogen atoms in CoCe belonging to O2W, O3W, and O4W were not located, but were included in the reported formula of the compound.

2.4. Magnetic Measurement. Magnetic measurements were carried out using a Quantum Design Dynacool Physical Properties Measurement System (PPMS), equipped with a Vibrating Sample Magnetometer (VSM). The dc data were collected under external applied fields of 1–15 kOe in the 1.8–300 K temperature range.

Isothermal magnetization measurements were performed between 0 and ±90 kOe at temperatures varying from 1.8 to 8 K. Diamagnetic corrections (estimated from Pascal constants) were considered.29 ac susceptibility was performed at several frequencies, with a 500 Oe dc field and 1 Oe ac oscillating field.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure of [Ce(H2O)2(HIDC)Co(IDC)]·H2O (CoCe) and [Ce(H2O)2(H2IDC)Cu(H2O)(IDC)Cu0.2(H1.6IDC)]2 (CuCe). CoCe crystallizes in a monoclinic $P_{2_1}/n$ space group and presents an extended framework. The asymmetric unit contains one CoII, one CeIII with one HIDC2− and IDC3− anions, and three H2O molecules. The different protonation degrees observed in the imidazole ligand can be related to the two particular coordination modes, $\eta^3$-$\kappa O$-$\kappa O'$-$O''$-$N$ and $\eta^3$-$\kappa N$-$O$-$\kappa O'$-$O''$-$O'''$-$N'$, observed for HIDC2− and IDC3−, respectively (Figure 1a,b). The CoII centers present a...
distorted octahedral geometry (CoN$_2$O$_3$) with a mer configuration formed by two $\kappa$N$_{3}$O-IDC$^{2-}$ and one $\kappa$N$_{3}$O-HIDC$^{2-}$ (Figure 2a) with $d_{Co-N}$ and $d_{Co-O}$ in the ranges of 2.060(5)–2.140(5) Å and 2.130(4)–2.190(4) Å, respectively (Table S1). The Ce$^{III}$ cations present nonacoordination, forming exclusively by oxygen atoms, with $d_{Ce-O}$ between 2.385(5) and 2.682(4) Å (Figure 2b). The geometry of the CeO$_9$ moiety was calculated with the SHAPE software, giving a capped square antiprism ($C_4$ symmetry, $J_{10}$ of Johnson polyhedra$^{31}$), where the uncapped square base of the prism generates a chain along the $\alpha$ axis. One of the water molecules linked to the Ce$^{III}$ cations presents an occupational disorder (O2W).

The Co$^{II}$ chains are connected by Ce$^{III}$ dinuclear discrete moieties [Ce(H$_2$O)$_2$(HIDC)]$^{2+}$, generating three different Ce–Co interactions by means of anti-anti carbamate (Ce1–Co1$^{2+}$ = 6.326(3) Å; Ce1–Co1$^{2+}$ = 6.218(2) Å; Ce1–Co1$^{2+}$ = 6.268(3) Å) and an oxocarboxylate (Ce1–Ce1$^{2+}$ = 4.741(2) Å) bridge. The isolated [Ce(H$_2$O)$_2$(HIDC)]$^{2+}$ moiety presents an internal Ce-Ce syn-anti carbamate bridge, with a Ce1–Ce1$^{2+}$ distance of 5.870(4) Å. Furthermore, CoCe presents a small interstitial space filled with H$_2$O molecules along the $b$ axis (Figure S2).

On the other hand, CuCe crystallizes in a monoclinic P$2_1/n$ space group and presents an extended structure with an asymmetrical unit that consists of one Ce$^{III}$, two different Cu$^{II}$ cations, Cu1 and Cu2 (the latter with a fractional occupancy of 0.2), three coordination water molecules, and different deprotonated species of H$_2$IDC. A diprotonated H$_2$IDC$^{2-}$ and a totally deprotonated IDC$^{3-}$ species can be easily identified, presenting a coordination fashion of $\kappa$N$_{3}$O and $\eta^3$-$\kappa$O-$\kappa$O$^*$$^-$ of 2.000(2) Å (Table S2). Moreover, Cu2 presents a CuN$_2$O$_3$ square plane environment, reached by two trans $\kappa$N$_{3}$O-IDC$^{3-}$ anions with $d_{Cu-N}$ of 1.942(3) Å and $d_{Cu-O}$ of 2.000(2) Å (Table S2). Moreover, the Cu2 centers are interacting weakly in the equatorial positions with two carboxylates groups from two additional IDC$^{3-}$ anions with a $d_{Cu-O}$ of 2.765(2) Å (O10$^{II}$), giving a (4 + 2) pseudo-octahedral geometry (Figure 4b). On the other hand, Ce$^{III}$ cations present a nonacoordination with a CeO$_8$ environment, with a $d_{Ce-O}$ in the range of 2.4645(19)–2.6825(18) Å (average 2.54 Å) and with a $d_{Ce-N}$ of 2.640(2) Å (Table S2). The calculated geometry with SHAPE$^{30}$ is the same to that obtained for CoCe, capped square antiprism ($C_4$ symmetry, $J_{10}$ of Johnson polyhedra$^{31}$), with the uncapped face of the prism occupied by $\kappa$O$^*$$^-$HIDC$^{2-}$ and $\kappa$O$^*$$^-$HIDC$^{3-}$, while the capped face is formed by two trans H$_2$O molecules and two HIDC$^{2-}$ anions with two coordination modes, $\kappa$O$^*$$^-$ and $\kappa$N$_{3}$O-IDC$_3$$^-$. Similar to CoCe, one of the oxygen belonging to the carboxylate groups of $\kappa$N$_{3}$O-IDC$_3$$^-$ occupies the capped position (Figure 4c and Figure S1b). In addition,
CuCe presents a complex extended structure depicted in Figure 5, which can be described in terms of heterometallic tetranuclear rings $[\text{Ce}(\text{H}_2\text{O})_2(\text{H}_2\text{IDC})(\text{H}_2\text{O})(\text{H}_1.6\text{IDC})(\text{IDC})]^{0.4-}$ labeled as $[\text{Ce}_2\text{Cu}_2]$, having a Cu1-Ce1-Cu1-Ce1 arrangement. The Cu-Ce connectivity of the ring is produced by two anti-anti-carboxylate bridges ($\text{Cu}_1\cdots\text{Ce} = 6.0128(4)$ Å and $\text{Cu}_2\cdots\text{Ce} = 6.4998(4)$ Å). Furthermore, these $[\text{Ce}_2\text{Cu}_2]$ cyclic fragments are self-assembled through an anti/anti-carboxylate bridge between Ce-Ce cations ($\text{Ce}_1\cdots\text{Ce} = 6.9284(2)$ Å), forming a 1D substructure along the $b$ axis (Figure 5). The $[\text{Ce}(\text{H}_2\text{O})_2(\text{H}_2\text{IDC})(\text{H}_2\text{O})(\text{H}_1.6\text{IDC})(\text{IDC})]^{0.4-}$ anionic 1D substructures are also partially assembled by Cu2 cations localized just between one $\text{H}_1.6\text{IDC}^{1.4-}$ and one $\text{IDC}^{3-}$ anions belonging from two adjacent $[\text{Ce}_2\text{Cu}_2]$ fragments, thus reaching a 2D arrangement. This final assembly generates a Cu2–Ce bridge by means of the anti-anti carboxylate ($\text{Cu}_2\cdots\text{Ce} = 6.12309(18)$ Å) and a Cu1–Cu2 bridge through $\mu^2-\kappa\text{N},\text{O}-\kappa\text{O}^{'},\text{N}^{'},\text{IDC}^{2-}$ ($\text{Cu}_1\cdots\text{Cu}_2 = 5.9445(3)$ Å).

Simplification of both structures of CoCe and CuCe using TOPOs$^{28}$ (considering the metal centers as nodes and the contraction of ligands to their centroids as linkers) allows a better visualization of the topologies of the framework. In CoCe (Figure 6a), it is possible to observe the parallel helical $[\text{Co}^{+}\text{IDC}]^{-}$ substructures (blue sticks) that are related to each other by an inversion center. Meanwhile, in green, the $[\text{Ce}(\text{H}_2\text{O})_2(\text{HIDC})]^{2-}$ moieties are connecting the Co-chains, to achieve the 3D extended structure, in which
HIDC$^{2-}$ and IDC$^{3-}$ are behaving as tritopic and tetratopic linkers. On the other hand, Figure 6b shows the [Ce$_2$Cu$_2$] moieties (blue-green sticks) forming the 1D heterometallic substructure connected by the Cu2 nodes (light blue sticks). In CuCe, both H$_{1.6}$IDC$_{1.4}^-$ and IDC$_{3}^-$ species are behaving as tritopic linkers, and the diprotonated H$_2$IDC$_{2}^-$ act as the blocking ligand of the Ce$^{III}$ cations, thus preventing the growth of the structure in this direction.

Remarkably, herein we report the synthesis of two new 3$d$-4$f$ heterometallic coordination polymers (HCP) based on Ce$^{III}$ and two different 3$d$ cations, Co$^{II}$ or Cu$^{II}$, by using a single organic linker, the bifunctional ligand 1H-imidazole-4,5-dicarboxylic acid (H$_3$IDC). H$_3$IDC has proven to be an excellent ligand to construct coordination polymers with intricate and beautiful structures, using different metals cations such as from ns block$^{31-35}$ 3$d$$^{36-39}$ and 4$d$ transition cations$^{40,41,42}$ and with lanthanide cations.$^{35,44}$ The versatility of this ligand also relies on the multiple anionic species that can be generated: H$_2$IDC$^-$, HIDC$^{2-}$, and IDC$^{3-}$, which not only allows the balance of charges of the cations but also gives multiple coordination sites with different coordination capabilities. Nevertheless, 3$d$-4$f$ HCPs using this ligand as organic linker are still scarce. In our previous work, we used H$_3$IDC$_{-}$ in addition with oxalate as coligand, to create intricate 3D Co$^{II}$-Gd$^{III}$ and 2D Cu$^{II}$-Gd$^{III}$ networks.$^{35}$ In this work, CoCe and CuCe were constructed only by H$_3$IDC anionic derivatives. From a synthetic point of view, compound CoCe was obtained in a one pot hydrothermal synthesis, whereas CuCe was obtained in a two-step synthesis using Cu1 as metalloligand. The one pot synthesis dominates the preparation of 3$d$-4$f$ HCP, while assembly of complexes using solvo/hydrothermal synthesis to obtain HCP has not been frequently

Figure 6. Simplified structural schemes of (a) CoCe and (b) CuCe using TOPOs.
used. For instance, using a cobalt 0D binuclear building block [Co$_2$($H_2$TTHA)($H_2$O)$_2$] or 1D [Co(Pzdc)$_2$] precursor, the syntheses of two different 3D HCPs [Ce$_2$Co(Pzdc)$_4$($H_2$O)$_6$]·2H$_2$O and [Ce($H_2$O)$_4$Co$_2$(TTHA)(SCN)$_4$]·H$_3$O$^+$ (H$_6$TTHA = triethylenetetraaminehexaacetic) were reported. Additionally, Gao et al. reported the synthesis of the 2D HCPs [Ce$_2$Co$_3$(EDTA)$_3$·($H_2$O)$_{11}$]·12H$_2$O, using in this case a 4f metalloligand Na[Ce(EDTA)$_4$]·2H$_2$O (EDTA = ethylenediamine-N$_2$N$_2$N$'$,N$'$-tetaacetate). Regarding the one pot methodology, Lio et al. reported the synthesis of [Ce$_2$Co(tia)$_4$($H_2$O)$_4$]$_3$D HCPs ($H_2$tia = 5-(1H-1,2,3-triazol-1-yl)isophthalic acid) by the hydrothermal route. Furthermore, several HCPs based on Cu$^{II}$ and Ce$^{III}$, using a wide variety of organic acids, such as nicotinic, iminodiacetic, oxidiacetic, and 1,2,4,5-benzetetracarboxylic acids, or some bifunctional ligands, such as piridin-2,6-dicarboxylic acid and pirazin-2,3-dicarboxylic acid, have been reported. However, to the best of our knowledge, Cu$^{II}$-Ce$^{III}$ or Co$^{II}$-Ce$^{III}$ HCP, using H$_3$IDC as an organic linker, has not been yet reported. Additionally, one of the most interesting features of the structure of CoCe is the presence of chiral Co$^{III}$-based chains within the 3D structure. The three
chelating rings generated by the $\kappa N_2O$ coordination of the IDC$^{3-}$ and HIDC$^{2-}$ species give rise to either the $\Lambda$ or $\Delta$ arrangement, which produces chirality in the chains. Thus, imidazole-dicarboxylic acid derivatives are well-known to generate chiral structures like Mn$^{1+}$, Cd$^{1+}$, and Zn$^{1+}$ coordination polymers.$^{6,57}$ Nevertheless, achiral coordination polymers with chiral substructures are not easy to find. Li et al. reported $\Lambda$ and $\Delta$ helical Co$^{II}$-based chains in the [Co(HPPhIDC)-(CH$_3$OH)]$_n$ framework, using the H$_2$IDC homologous ligand 2-(p-isopropylphenyl)-1H-imidazole-4,5-dicarboxylic acid (H$_2$PPhIDC).$^{38}$ Moreover, the two 3D 3d-4f HCP based on Co$^{II}$ and Gd$^{III}$ that we previously reported present the same Co$^{II}$ chiral chain arrangement, as that observed in CoCo$_{51}$. As far as we know, the two previously reported Co$^{II}$-Gd$^{III}$ 3D frameworks,$^{52}$ together with CoCo$_{51}$ reported in this work, are the unique examples of 3d-4f heterometallic coordination polymer containing this kind of homometallic chiral substructures as part of a 3D heterometallic network.

3.2. Magnetic Properties. Figure 7a and Figure S4a show the $\chi_M$ vs $T$ and $\chi_M \times 10^{-1}$ vs $T$ plots for CoCo$_{53}$ between 300 and 1.8 K at 1 kOe. Compound CoCo$_{53}$ follows the Curie–Weiss law between 300 and 50 K, with $C = 4.11$ emu·mol$^{-1}$·K and $\theta = -31.8$ K. A $\chi_M$ vs $T$ product of 3.70 emu·K·mol$^{-1}$ is observed at room temperature, which is higher than 2.68 emu·K·mol$^{-1}$, expected for a noninteracting Co$^{II}$ ($S = 3/2; g = 2.0$) and Ce$^{III}$ ($L = 3; g = 6/7$). This higher value is attributed to the strong anisotropy present in the Co$^{II}$ cation with a high-spin configuration and a distorted $O_h$ geometry. As the temperature is lowered from 300 K, the $\chi_M$ vs $T$ values decrease monotonously to a minimum value of 1.37 emu·K·mol$^{-1}$ at 7.5 K. Clearly, the negative value of the Weiss constant and the decrease of $\chi_M$ vs $T$ with the lowering of temperature suggest that an overall antiferromagnetic behavior is present in CoCo$_{53}$. Nevertheless, from 7.5 K, an increase of $\chi_M$ vs $T$ can be observed as the temperature is decreased, reaching a maximum value of 3.70 emu·K·mol$^{-1}$ at 2 K, suggesting a ferromagnetic behavior below 7.5 K. Furthermore, Figure 7b shows $\chi_M$ vs $T$ plots at several applied fields (0.25–15 kOe) in a temperature range of 1.8–8 K, showing that the ferromagnetic behavior becomes more evident at lower applied fields. The ac susceptibility (Figure 7c,d) is in agreement with the dc measurement, showing a well-defined frequency independent maximum near 2.4 K for $\chi_M'$ and $\chi_M''$ components. ZFC and FC measurements at 50 Oe (Figure S4b) show a complete reversibility until 2 K. However, a small difference in the $\chi_M$ vs $T$ value was observed at 1.8 K, being 9.87 and 10.5 emu·K·mol$^{-1}$ for ZFC and FC, respectively. Additionally, isothermal field dependent magnetization measurements were performed for CoCo$_{53}$. The curves of $N_\beta$ vs $H/\chi_M$ measured at 1.8, 3, 5, and 8 K are not superimposed in a master curve (Figure 7e), confirming that the higher value of $\chi_M$ at room temperature for CoCo$_{53}$ is due to the presence of the anisotropy typical of the paramagnetic centers. Furthermore, $N_\beta$ vs $H$ hysteresis loop (Figure 7f, Figure S4c) show an S-shaped plot for CoCo$_{53}$, thus indicating that the saturation was not reached, giving a maximum value of 2.3 $N_\beta$ at 90 kOe, which is less than the expected value for four electrons belonging to one Co$^{II}$ and one Ce$^{III}$ ($d^5$ high spin and $f^6$ electrons). The isothermal magnetization plots permit one to infer that the observed decrease of the $\chi_M$ vs $T$ values can be attributed to the antiferromagnetic coupling between the paramagnetic centers and also by the strong spin–orbit contribution belonging mainly from the high-spin Co$^{II}$ cation in a distorted $O_h$ geometry.$^{59}$ On the other hand, the frequency independent maximum of the in-phase ($\chi_M'$) and out-of-phase ($\chi_M''$) signals, together with the irreversibility in the ZFC-FC measurements and the S shape of the hysteresis loop, can be associated with a weak ferromagnetic behavior as the product of noncompensated antiferromagnetic coupling.

Figure 8a and Figure S4d depict $\chi_M$ vs $T$ and $\chi_M^{-1}$ vs $T$ plots between 300 and 1.8 K for CuCu$_{53}$ at 1 kOe. Compound CuCu$_{53}$ follows the Curie–Weiss law between 300 and 100 K, with $C = 1.42$ emu·K·mol$^{-1}$ and $\theta = -45.7$ K. The $\chi_M$ vs $T$ value at 300 K for this compound is 1.21 emu·K·mol$^{-1}$, which is very near to the expected $\chi_M$ vs $T$ value for noninteracting Ce$^{III}$ and 1.2 Cu$^{II}$ cations (1.24 emu·K·mol$^{-1}$ considering $J_{Cu} = S/2; g_{Cu} = 6/7; S_{Cu} = 1/2; g_{Cu} = 2.00$), confirming the Cu$_{0.7}$Ce ratio discussed in the structural section. As the temperature is lowered from 300 K, $\chi_M$ vs $T$ also decreases sharply to a minimum value of 0.59 emu·K·mol$^{-1}$ at 1.8 K. This decrease of $\chi_M$ vs $T$ in the whole temperature range, in addition to the negative value of $\theta$ in $\chi_M^{-1}$ vs $T$ plot, can be associated with antiferromagnetic interactions between the paramagnetic centers in CuCu$_{53}$. On the other hand, $N_\beta$ vs $H/\chi_M$ plot at 1.8 K (Figure 8b) shows that saturation is not reached, giving a value of 1.76 $N_\beta$ at 90 kOe, which is rather far from the expected value for...
noninteracting CeIII and 1.2 CuII cations (2.2 Np considering gCu = 6/7 and gCo = 2.00). In addition, the field dependent magnetization of CuCe obtained at different temperatures shows a very low orbital contribution attributed to the presence of CeIII cations, since CuII is magnetically isotropic.

Remarkably, the inclusion of 3d and 4f cations into intricated frameworks presents a challenge in the rational correlation between structures and magnetic phenomena. In this sense, the chemical connectivity between the paramagnetic ions is an important feature for the analysis of the magnetic properties in 3d-4f HCPs. Since 4f orbitals are shielded by more external orbitals, the superexchange coupling through organic bridges between 3d-4f is expected to be less in magnitude than the interaction between 3d-3d spin carriers. Consequently, the interaction between 3d/3d orbitals is expected to be stronger than that of 3d/4f or 4f/4f orbitals. As stated in the structural description section, CoCe and CuCe exhibit a wide variety of chemical bridges (Figure S5a,b) between the paramagnetic centers, making possible the interaction between Ce-Ce and Ce-3d cations by means of carboxylate groups belonging to H3IDC anionic species. However, the more important interactions should be expected between 3d-3d cations through the \( \mu^2-\kappa N_{\text{O}}-\kappa O^\prime/N' \) bridge, which are known as mediators of antiferromagnetic interactions.

Cao et al.\(^6\) and Li et al.\(^6\) reported the magnetic properties of 3D networks having Co\(^{II}\) and the \( \mu^2-\kappa N_{\text{O}}-\kappa O^\prime/N' \) bridge, but belonging to p-methoxyphenyl-1H-imidazole-4,5-dicarboxylate\(^6\) or 2-p-isopropylphenyl-imidazolodiacarboxylate\(^6\) organic ligands, respectively. In both cases, antiferromagnetic interactions were established between these transition metal cations. Furthermore, Massoud et al. found the same type of magnetic interaction between CuII cations linked by \( \mu^2-\kappa N_{\text{O}}-\kappa O^\prime/N' \) bridges belonging to the H3IDC ligand, but now being part of a binuclear compound.\(^6\) These facts permit us to assess that the predominant magnetic behavior in CoCe and CuCe is produced mainly by the superexchange interactions between the 3d cations. Nevertheless, Kahn et al. reported the magnetic coupling between CuII-4f ions in a 1D isosctructural CuII-LnIII series.\(^6\) The author found that magnetic interactions between CuII and LnIII depend on the electronic configuration of the 4f cations, being antiferromagnetic for CeIII to EuIII and ferromagnetic for GdIII to LuIII.\(^6\) Therefore, in our case, the Cu-Ce interactions through carboxylate bridges can be expected to contribute to the bulk antiferromagnetic behavior observed for CuCe. In contrast, the nonisotropic character of the CuII cations produces difficulties in the correlation of the corresponding magnetic properties, especially if 4f cations are present. However, taking into account the information reported for CoII cations, both the antiferromagnetic behavior at high temperature and the weak ferromagnetism below 7.5 K observed for CoCe can be mainly attributed to interactions of the CoII cations. It is important to note that a weak ferromagnetism emerging from an antiferromagnetic coupled system can be originated by the nonperfect antiparallel arrangement between spins carriers,\(^6\) as stated by Shao et al., for \( \left[ \text{Fe(LN})_{3},(\text{CN})_2 \right] \) (LN = 2,13-dimethyl-3,6,9,12-tetraaza-1(2,6)pyridinacycloctadecaphane-2,12-diene). In this 1D compound, the iron pentagonal bipyramids are tilted to each other in the cyano-FeII chains, which leads to a weak ferromagnetism at low temperatures.\(^6\) In the case of CoCe, the subtle deviations observed in the cobalt octahedra along the CoII-chains (Figure S6a,b), can be responsible for the weak ferromagnetic behavior mentioned above.

4. CONCLUSIONS

Two new heterometallic coordination polymers based on CeIII and two different 3d cations, CoII and CuII, and the bifunctional ligand 1H-imidazole-4,5-dicarboxylic acid (H3IDC) were successfully synthesized by two different synthetic approaches. The anionic species derived from the H3IDC ligand probed to be excellent organic linkers to prepare heterometallic 3d-4f coordination polymers, with interesting structural features. CoCe presents a 3D coordination network, with alternated Δ-Δ chiral CoII-chains substructures, generated from an achiral synthetic medium. Meanwhile, the 2D CuCe contains [CuII CeII] heterometallic moieties assembled by partially occupied CuII cations. On the other hand, magnetic properties of CoCe and CuCe reveal antiferromagnetic behavior in both cases, but with the presence of a weak ferromagnetic behavior in CoCe. Considering the reported magnetic data, it is possible to infer that the role of the CeIII cation is rather innocent from a magnetic point of view, being the magnetic properties dominated by the 3d cations. However, the lanthanide cations are essential for the construction of these two heterometallic networks. Remarkably, the inclusion of 3d cations and lanthanide cations using the versatile linker 1H-imidazole-4,5-dicarboxylic acid offers a new potential via to the rational design of 3d-4f HCPs with novel architectures and interesting properties.

## ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.8b00590.

Description of the polyhedra around CeIII centers in CoCe and CuCe (Figure S1); view along ac plane of CoCe (Figure S2); SEM image and EDX analysis of CoCe (Figure S3); \( \chi_M \) vs T, ZFC-FC measurements and inset hysteresis loop for CoCe, \( \chi_M \) vs T measurements for CuCe (Figure S4); magnetic pathways for CoCe and CuCe (Figure S5); scheme of spins arrangement in the CoII-based chains in CoCe and CoII-imidazole-CoII moiety (Figure S6); experimental and simulated single crystal PXRD for CuCe and CoCe (Figure S7) (PDF)

Accession Codes

CCDC 1832094–1832095 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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■ REFERENCES


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