

Series of novel 3D microporous heterometallic 3d–4f coordination frameworks with (5,6)-connected topology: synthesis, crystal structure and magnetic properties†

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The hydrothermal reaction of rare earth nitrates, CuCN, 1*H*-1,2,3-triazole-4,5-dicarboxylic acid (H₃tda), and isonicotinic acid (Hina) resulted in the formation of a new series of 3d–4f heterometallic coordination polymers [LnCu(tda)(ina)₂(H₂O)]·3H₂O (Ln = Eu (1), Tb (2), Gd (3), Dy (4), Ho (5)), H₃tda = 1*H*-1,2,3-triazole-4,5-dicarboxylic acid, Hina = isonicotinic acid). Complexes 1–5 are isostructural and structurally characterized by elemental analysis, FT-IR spectroscopy, thermogravimetric analysis (TGA), and single-crystal powder X-ray diffraction (PXRD). Single-crystal X-ray diffraction analysis reveals that the metal cations in these compounds are firstly interconnected by H₃tda ligands to produce a carpet-shaped heterometallic ring [Ln₂(tda)₂Cu₄], and then pillared by bridging Hina molecules to form the 3D layer-pillared porous Ln(III)–Cu(II) heterometallic coordination polymers. In addition, the magnetic properties of 1–5 were also investigated in detail.

Introduction

The rational design and synthesis of lanthanide-transition 3d–4f heterometallic coordination polymers are currently drawing a mass of interest because of the potential synergic effects of different metals within one assembly, fascinating structural topologies and a variety of advanced applications in molecular magnets,^{1,2} molecular recognition,³ luminescent materials,⁴ molecular adsorption,⁵ and semiconductors.⁶

Considering the fact that multidentate ligands of N and O atoms have different affinities to transition and lanthanide metal ions, a typical approach to the construction of 3d–4f hetero-

metallic frameworks can be the reaction of a mixture of 3d and 4f metallic ions with a multidentate bridging ligand containing both N- and O-donor atoms. Additionally, to construct new 3d–4f heterometallic complexes with miscellaneous structural types, the auxiliary multidentate ligands embracing either N- or O-donor atoms are introduced to the reaction system and further behave as a proper bridge between 3d and 4f metal ions. So far, a variety of organic ligands with hybrid nitrogen and oxygen donor atoms have been employed and nicotinic acid,⁷ isonicotinic acid,⁸ imidazolecarboxylate⁹ and pyridinecarboxylate¹⁰ are several typical examples.

However, due to the flexible geometries and high coordination numbers of lanthanide ions, as well as the struggle between lanthanide and transition ions, the preparation of novel 3d–4f coordination frameworks is still a challenging task.¹¹ The key to constructing desirable frameworks of 3d–4f heterometallic complexes is the selection of organic building blocks and central metal cations.

H₃tda can be used to construct 3d–4f heterometallic coordination frameworks because of the following reasons: (1) it is very soluble in water; (2) it is a semirigid and multidentate ligand that contains nitrogen and oxygen donors, where the nitrogen atoms of the triazole possess a strong tendency to coordinate with the transition metal ions, while the oxygen atoms of the carboxyl group prefer to bond to the lanthanide metal ions according to the hard-soft acid-base model.

However, up to now, we find that the H₃tda has been used to construct ordinary monometallic 3d, 4f or heterometallic 3d–3d complexes,¹² whereas a 3d–4f heterometallic framework has never been reported. Inspired by the above-mentioned aspects and our previous work on d–f heterometallic coordination polymers,¹³ herein, we report the synthesis, structure and magnetic properties of the first examples of Ln(III)–Cu(II) layer-pillared 3d–4f heterometallic compounds based on H₃tda, namely, [LnCu(tda)(ina)₂(H₂O)]·3H₂O [Ln = Eu (1), Tb (2), Gd (3), Dy (4), Ho (5); H₃tda = 1*H*-1,2,3-triazole-4,5-dicarboxylic acid, Hina = isonicotinic acid].

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† Electronic supplementary information (ESI) available: TG curves, PXRD patterns, X-ray crystallographic data in CIF format and tables of selected bond distances and angles for 1–5, and the FTIR spectra figures for 1–5. CCDC 888436–888440. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce40346g

Experimental section

Material and methods

All reagents needed for the experiments were commercially available and used as received without further purification. The C, H, and N elemental analysis was carried out with a Perkin-Elmer 2400 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the 4000–400 cm^{-1} ranges on a Nicolet 5DX spectrometer. Thermogravimetric analyses were performed on a Perkin-Elmer TGA7 analyzer with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ in flowing air atmosphere. The magnetic susceptibility data were collected from polycrystalline samples at an external field of 0.1 T on a MPMS XL-7 magnetometer (Quantum Design) in the temperature range 2–300 K. The output data were corrected for the diamagnetism of the sample holder and of the samples calculated from their Pascal constants. Powder X-ray diffraction (PXRD) patterns were recorded on a X-pert diffractometer or Rigaku D/M-2200T automated diffractometer for Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), with a scan speed of 4 $^{\circ} \text{min}^{-1}$ and a step size of 0.02 $^{\circ}$ in a 2θ range of 5–50 $^{\circ}$.

Syntheses of complexes 1–5

Complexes 1–5 were prepared under hydrothermal conditions. A mixture of isonicotinic acid (0.0616 g, 0.5 mmol), H₃tda (0.157 g, 1 mmol), Eu(NO₃)₃·6H₂O for 1 (0.223 g, 0.5 mmol), Tb(NO₃)₃·6H₂O for 2 (0.2265 g, 0.5 mmol), Gd(NO₃)₃·6H₂O for 3 (0.2255 g, 0.5 mmol), Dy(NO₃)₃·6H₂O for 4 (0.2283 g, 0.5 mmol), Ho(NO₃)₃·6H₂O for 5 (0.2295 g, 0.5 mmol), CuCN (0.0448 g, 0.5 mmol) and H₂O (10 mL) was heated to 160 $^{\circ}\text{C}$ for 72 h in a 23 mL Teflon-lined stainless-steel autoclave and then cooled to room temperature at a rate of 5 $^{\circ}\text{C h}^{-1}$. The resulting crystals with purple prism were isolated after washing with distilled water and ethanol, and allowed to dry in air.

[EuCu(tda)(ina)₂(H₂O)]·3H₂O (1). Yield: 53% based on Eu. Anal. calcd for C₁₆H₁₆CuEuN₅O₁₂: C, 28.02; H, 2.35; N, 10.21%. Found: C, 28.00; H, 2.31; N, 10.18%. IR frequencies (KBr, cm^{-1}): 3527w, 3431w, 1600m, 1558w, 1427m, 1388s, 1296s, 1219s, 1188s, 1062vs, 1031s, 866vs, 817s, 779s, 706vs.

[TbCu(tda)(ina)₂(H₂O)]·3H₂O (2). Yield: 51% based on Tb. Anal. calcd for C₁₆H₁₆CuTbN₅O₁₂: C, 27.74; H, 2.335; N, 10.11%. Found: C, 27.69; H, 2.29; N, 10.09%. IR frequencies (KBr, cm^{-1}): 3518w, 3441w, 1599m, 1558w, 1427m, 1389s, 1297s, 1213s, 1180s, 1063vs, 1032s, 868vs, 816s, 777s, 705vs.

[GdCu(tda)(ina)₂(H₂O)]·3H₂O (3). Yield: 47% based on Gd. Anal. calcd for C₁₆H₁₆CuGdN₅O₁₂: C, 27.81; H, 2.33; N, 10.13%. Found: C, 27.79; H, 2.30; N, 10.119%. IR frequencies (KBr, cm^{-1}): 3435w, 1601m, 1557w, 1427m, 1385s, 1297s, 1221s, 1182s, 1065vs, 1026s, 871vs, 814s, 770s, 705vs.

[DyCu(tda)(ina)₂(H₂O)]·3H₂O (4). Yield: 45% based on Dy. Anal. calcd for C₁₆H₁₆CuDyN₅O₁₂: C, 27.60; H, 2.32; N, 10.06%. Found: C, 27.54; H, 2.29; N, 10.03%. IR frequencies (KBr, cm^{-1}): 3441w, 3419w, 1601m, 1553w, 1429m, 1390s, 1298s, 1217s, 1190s, 1066vs, 1037s, 868vs, 818s, 777s, 705vs.

[HoCu(tda)(ina)₂(H₂O)]·3H₂O (5). Yield: 40% based on Ho. Anal. calcd for C₁₆H₁₆CuHoN₅O₁₂: C, 27.50; H, 2.31; N, 10.02%. Found: C, 27.47; H, 2.29; N, 9.99%. IR frequencies (KBr, cm^{-1}): 3433w, 3416w, 1603m, 1560w, 1431m, 1389s, 1298s, 1215s, 1154s, 1063vs, 1032s, 868vs, 814s, 777s, 706vs.

X-ray crystallographic measurements

Diffraction intensities for samples 1–5 were collected with a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Data collection and reduction were performed using the SMART and SAINT software, respectively. Structural solutions of all the compounds and full-matrix least-squares refinements based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages.^{14,15} All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated geometrically. The organic hydrogen atoms were placed in geometrically idealized positions and refined using a riding model. Hydrogen atoms attached to water molecules were located from difference Fourier maps and were also refined using a riding model. The crystallographic data and refinement details of 1–5 are shown in Table 1. Selected bond lengths and angles are listed in Table S1, ESI.† Further crystallographic details for the structures reported here may be obtained free of charge from the Cambridge Crystallographic Data Center, quoting the depository numbers CCDC 888437 (1), 888440 (2), 888438 (3), 888436 (4), 888439 (5).

The crystal quality of compound 4 is not very good, but it is isostructural with other compounds, which has been further approved by powder X-ray diffraction patterns.

Results and discussion

Crystal structure descriptions

Single crystal X-ray diffraction studies revealed that compounds 1–5 are isostructural and crystallize in the same triclinic space group $P\bar{1}$. Thus, we select polymer 5 as the representative example to describe here in detail. Both H₃tda and Hina ligands have contributed to the molecular structure, forming mixed-ligand complexes with a pillared-layer 3D structure, in which the 2D layers are further connected *via* long ina^- pillars.

As shown in Fig. 1, there is one crystallographically independent Ho(III) ion, one Cu(II) ion, one full deprotonated H₃tda ligand, two full deprotonated Hina ligands, one coordinated and three free water molecules in the asymmetric unit.

The Ho(III) atom is nine-coordinated with a tricapped trigonal prism geometry by four oxygen atoms from two different H₃tda ligands, four oxygen atoms from two different Hina ligands, together with one oxygen from a coordinated water molecule, respectively, where O₂, O₃, O₄, O₅, O₆ and O₈ occupy the distorted trigonal prism positions while O₇, O₃# (1 – x , – y , 2 – z) and O1W occupy the three cap positions. The Ho–O bond distances range from 2.284(4) to 2.544(4) \AA and the O–Ho–O bond angles vary from 51.54(12) to 155.82(11) $^{\circ}$. As far as the Cu(II) ion in the coordination framework is concerned, the coordination number is six and its coordination geometry is elongated octahedron, being coordinated by two nitrogen atoms and two oxygen atoms from different tda^{3-} ligands, and the other two nitrogen atoms from two ina^- ligands. The Cu–O and Cu–N bond lengths fall into the range of 2.420(4)–2.437(4) \AA and from 1.971(4) \AA to 2.061(4) \AA , respectively, which are similar to those found in the related Cu(II) complexes.¹⁶ For 1–5, all the lanthanide ions are nine-coordinated, and the average Ln–O distances are 2.483(4), 2.471(5), 2.464(7), 2.448(3) and 2.445(4) \AA , respectively. The average Ln–O distances decrease

Table 1 Crystal data and structure refinements for compounds 1–5

Compound	1	2	3	4	5
Empirical formula ^a	C ₁₆ H ₁₆ CuEuN ₅ O ₁₂	C ₁₆ H ₁₆ CuTbN ₅ O ₁₂	C ₁₆ H ₁₆ CuGdN ₅ O ₁₂	C ₁₆ H ₁₆ CuDyN ₅ O ₁₂	C ₁₆ H ₁₆ CuHoN ₅ O ₁₂
Formula weight	685.86	692.82	691.14	696.39	698.82
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1
<i>a</i> /Å	10.7491(16)	10.6720(16)	10.725(4)	10.6761(16)	10.6390(16)
<i>b</i> /Å	10.7585(16)	10.7194(16)	10.747(4)	10.7356(16)	10.6982(16)
<i>c</i> /Å	11.8901(18)	11.9351(18)	11.917(4)	11.9637(18)	11.9375(18)
α /°	70.146(2)	70.341(2)	70.146(4)	69.991(2)	70.078(2)
β /°	78.016(2)	77.928(2)	77.912(5)	77.562(2)	77.610(2)
γ /°	61.030(1)	60.854(10)	60.967(4)	60.8412(10)	60.7997(10)
<i>V</i> /Å ³	1129.9(3)	1121.3(3)	1127.9(7)	1123.2(3)	1113.1(3)
<i>Z</i>	2	2	2	2	2
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)	293(2)
λ /Å	0.71073	0.71073	0.71073	0.71073	0.71073
<i>D_c</i> /g cm ^{−3}	2.016	2.052	2.035	2.059	2.085
μ (Mo K α)/mm ^{−1}	3.764	4.149	3.930	4.320	4.557
Obs refl [<i>I</i> > 2 σ (<i>I</i>)]	3594	3479	3915	3105	3480
<i>wR</i> ₂ ^{bc}	0.0751	0.0958	0.1380	0.2726	0.1083
<i>R</i> ₁ ^{cd}	0.0284	0.0395	0.0577	0.1300	0.0434
GOOF on <i>F</i> ²	1.090	1.064	1.017	1.261	1.031
$\Delta\rho_{\max,\min}/e\text{ Å}^{-3}$	1.862, −0.688	1.784, −0.990	1.021, −1.002	6.082, −6.843	2.022, −1.968

^a Including solvate molecules Mo K α radiation, graphite monochromator. ^b $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)|^2 / \sum w|F_o|^2]^{1/2}$. ^c For observed data. ^d $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

with an increase in atomic number due to the lanthanide contraction effect.¹⁷

In complex **5**, the H₃tda ligand only adopts one μ_4 - η^2 - η^2 - η^1 - η^1 - η^1 coordination mode, as depicted in Scheme 1a. Two carboxylic oxygen atoms coordinate to two Ho(III) centers and one Cu center with the tetradentate chelating–bridging mode, another two carboxylic oxygen atoms coordinates to the Ho center and Cu center separately with the monodentate mode, while two nitrogen atoms coordinate to different Cu centers *via* a bridging coordinated fashion.

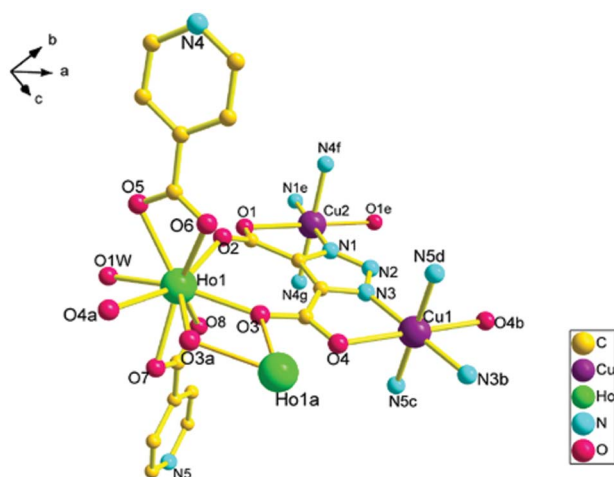
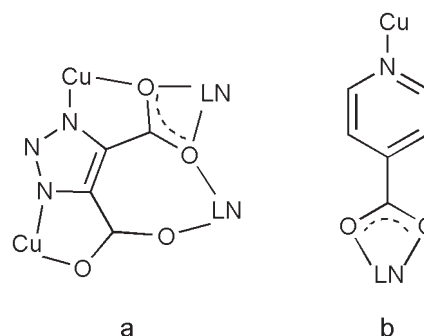


Fig. 1 The asymmetric unit of **5**. The thermal ellipsoids are drawn at 30% probability. All H atoms and non-coordinated water molecules are omitted for clarity. Symmetry code: (a): 1 − *x*, −*y*, 2 − *z*; (b): 2 − *x*, −*y*, 2 − *z*; (c): 2 − *x*, −1 − *y*, 2 − *z*; (d): *x*, 1 + *y*, *z*; (e): 2 − *x*, −*y*, 1 − *z*; (f): 1 − *x*, 1 − *y*, 1 − *z*; (g): 1 + *x*, −1 + *y*, *z*.

In light of these connection modes, two Ho(III) centers, Ho1 and Ho1# (1 − *x*, −*y*, 2 − *z*), are linked by two bridging tetradentate tda^{3−} ligands to construct a dimeric subunit [Ho₂(tda)₂(ina)₄] (Fig. 2) with a Ho⋯Ho distance of 4.153 Å and the Ho1–O3–Ho1A bond angle is 116.34° (Table S1, ESI†). If the coordination interactions between the Cu–Hina are neglected, the neighboring binuclear subunits are connected *via* the Cu(II) ions to form a two-dimensional (2D) heterometallic layer fabric lying in the *ac* plane (Fig. 3a).

Such 2D nets are further connected together by the ina[−] ligands to give rise to a 3D layer-pillared framework as illustrated in Fig. 3b. Hina ligands, however, adopt the same μ_2 - η^1 - η^1 - η^1 bridging mode: the nitrogen atom coordinates to the Cu center and two carboxylic oxygen atoms coordinate to one Ho center with the chelating bridging mode (Scheme 1b). The Cu atom has a nearly linear conformation defined by two N atoms from two bridging Hina ligands. Although Cu(I) salts were used as starting materials, the Cu center in the product is in the +2 oxidation state,



Scheme 1 Coordination modes of the H₃tda and Hina ligands in the complexes.

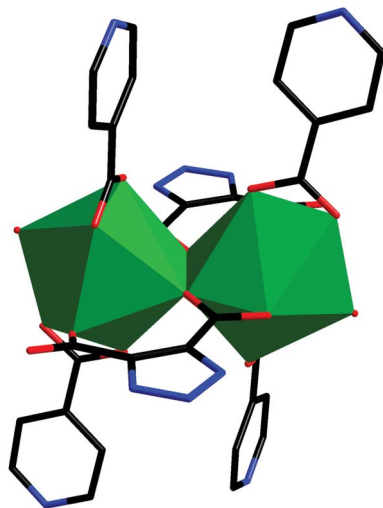


Fig. 2 View of the dimeric subunit $[\text{Ho}_2(\text{tda})_2(\text{ina})_4]$ in complex **5**.

which may be attributed to an oxidation reaction occurring under the hydrothermal conditions caused by the high temperature used. It should be noted that when the CuCN was replaced by CuSO_4 , the title compound could also be attained in this experiment. All carboxyl groups of these ligands are full deprotonated, in agreement with the IR data in which no strong absorption peaks around 1700 cm^{-1} ($-\text{COOH}$) are observed.

The final three-dimensional frameworks are built up from two-dimensional lanthanide-transition heterometallic layers $[\text{Ln}_2\text{Cu}_4\text{tda}_2]_n$ and Hina pillars. One new bridging mode (Scheme 1a) of the H_3tda ligand is observed, which proves that it can be used as an effective bridging ligand in the assembly of MOFs.

In order to better understand the structure of polymers, the topological analysis approach is adopted. As shown in Fig. 4, the H_3tda and Hina ligands can be simplified as connectors, while Ho1, Cu1/Cu2 can be seen as 5-connected and 6-connected nodes, respectively. The bond length for Cu1–Cu2 and the adjacent Ho

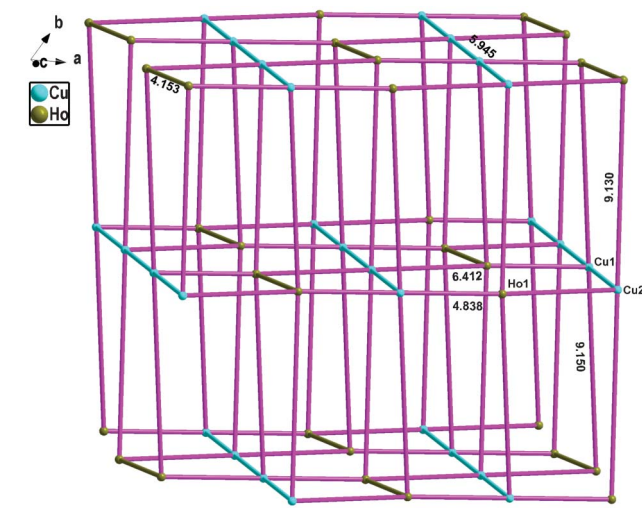


Fig. 4 The 5,6-connected network of compound **5** calculated with TOPOS 4.0.

atoms is 5.945 Å and 4.153 Å , respectively. The bond length for Cu–Ho is in the range of 4.838 Å to 9.150 Å .

Consequently, according to the calculation of TOPOS 4.0,¹⁸ the framework of **5** belongs to tcj/hc type 5,6-connected binodal network with Schläfli symbol of $\{4^8 \cdot 6^2\}c\{4^8 \cdot 6^6 \cdot 8\}$.

Powder X-ray diffraction (PXRD)

The powder X-ray diffraction (PXRD) patterns of complexes **1–5** in the region of $2\theta = 5\text{--}50^\circ$ are shown in Fig. S1, ESI.† For these complexes, the experimental XRD peaks are consistent with the XRD peaks that are simulated from the single-crystal X-ray data, indicating the high purity of the synthesized samples.

Thermal stabilities

To examine the thermal stabilities of all five compounds, thermogravimetric analyses (TGA) were carried out at a heating rate of 10 °C min^{-1} under a dry air atmosphere at the temperature range from 30 to 800 °C as shown in Fig. S2, ESI.† Owing to all five compounds exhibiting similar thermal stabilities, compound **1** was selected to be discussed in detail. In the temperature range of $46\text{--}90\text{ °C}$, there is only one stage of weight loss of approximately 10.16% , being consistent with three free water molecules and one coordinated water molecule (calcd. 10.49%). It can be seen from the TG curve of **1** that there is a plateau in the temperature range of $90\text{--}300\text{ °C}$, hinting that the skeleton of **1** is thermally stable up to 300 °C . Further heating above 300 °C causes the framework to collapse accompanied by the decomposition of the organic ligands. The remaining weight of 49.96% corresponds to the final products of Eu_2O_3 (calcd. 51.31%).

FTIR spectra

In the IR spectra of complexes **1–5**, the features at $1539\text{--}1637\text{ cm}^{-1}$ and $1383\text{--}1427\text{ cm}^{-1}$ are associated with the asymmetric and symmetric stretching vibrations of carboxylate groups. The strong and broad band in $3130\text{--}3452\text{ cm}^{-1}$ can be ascribed to the O–H stretching vibrations of water molecules in the complexes. Bands

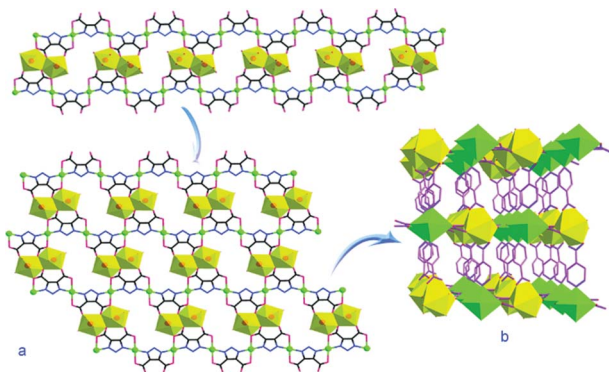


Fig. 3 (a) A polyhedral view of the 2D heterometallic layered network based on $[\text{Ho}_2(\text{tda})_2]$ and Cu(II) in complex **5**. (b) View of the 3D layer-pillared architecture in the ab plane of complex **5**. All H atoms and water molecules are omitted for clarity.

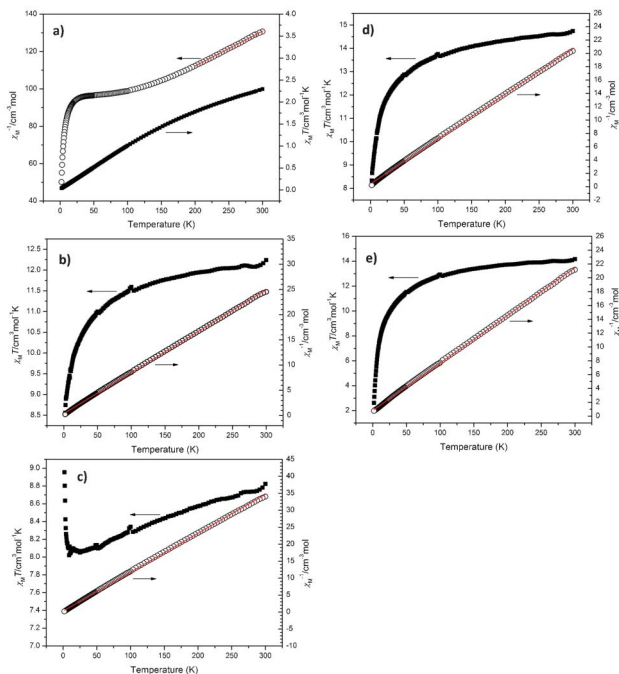


Fig. 5 The $\chi_{\text{M}}T$ vs. T and $1/\chi_{\text{M}}$ vs. T curves for compounds **1–5** (a–e). The solid line represents the Curie–Weiss fitting result.

in the range of 1000–1430 cm^{-1} are attributed to C–N and C–C vibration. The absence of strong absorption bands around 1700 cm^{-1} indicates the ligands are completely deprotonated. The $\delta\text{O–C–O}$ vibration in the plane occurs in the middle intensity peaks within the range of 706–865 cm^{-1} . The IR spectra of **1–5** are in accordance with the results of the X-ray diffraction analysis.

Magnetic properties

The solid state direct current magnetic susceptibilities for compounds **1–5** have been recorded in the range of 2 K–300 K under a field of 1000 Oe as plots of $\chi_{\text{M}}T$ vs. T and $1/\chi_{\text{M}}$ vs. T shown in Fig. 5. For compound **1**, the room temperature $\chi_{\text{M}}T$ value is 2.30 $\text{cm}^3 \text{K mol}^{-1}$ which is inconsistent with the calculated value for a one spin-only Cu(II) (0.375 $\text{cm}^3 \text{K mol}^{-1}$, $S = 1/2$) and one ground-state Eu(III) (0 $\text{cm}^3 \text{K mol}^{-1}$, 7F_0) incorporated into one molecule, which should be ascribed to the thermal population of Eu(III) excited states. The $\chi_{\text{M}}T$ vs. T curve is similar to that reported by Yue-Peng Cai *et al.*¹⁹ When the temperature decreased from 300 K to 2 K, the $\chi_{\text{M}}T$ value steadily decreased from 2.30 $\text{cm}^3 \text{K mol}^{-1}$ to 0.04 $\text{cm}^3 \text{K mol}^{-1}$ (Fig. 4a). The $1/\chi_{\text{M}}$ data above 200 K obey the Curie–Weiss law [$\chi = C/(T - \theta)$] with $C = 5.37 \text{ cm}^3 \text{K mol}^{-1}$, $\theta = -402.5 \text{ K}$. The large negative Weiss constant may reveal the antiferromagnetic couplings within the molecule. Compounds **2**, **4** and **5** have similar magnetic properties (Fig. 4b, d and e), and the Curie–Weiss fitting result based on the $1/\chi_{\text{M}}$ data is $C = 12.22 \text{ cm}^3 \text{K mol}^{-1}$, $\theta = -4.43 \text{ K}$; $C = 14.81 \text{ cm}^3 \text{K mol}^{-1}$, $\theta = -6.13 \text{ K}$; $C = 14.52 \text{ cm}^3 \text{K mol}^{-1}$, $\theta = -11.52 \text{ K}$, respectively. The negative θ value reveals their antiferromagnetic coupling and the thermal depopulation of the Stark sublevels of Tb(III), Dy(III) and Ho(III). However, the magnetic property of compound **3** is different from the above; it has the lowest $\chi_{\text{M}}T$ value around 20 K, which may be due to the

increase of the correlation length with the $S_{\text{Gd}} = 7/2$ spins aligned along the field direction and the $S_{\text{Cu}} = 1/2$ spins aligned along the opposite direction.²⁰

Conclusions

In summary, five novel 3D 3d–4f layer-pillared heterometallic complexes that are built up by dimeric $[\text{Ln}_2(\text{tda})_2]$ cores and inorganic ligands by sharing Cu(II) ions have been successfully synthesized through the self-assembly of H_3tda –Hina mixed ligands and Ln–Cu mixed metal salts under hydrothermal conditions. They are isostructural and exhibit the (5,6)-connected network with $\{4^8 \cdot 6^2\}\{4^8 \cdot 6^6 \cdot 8\}$ topology. They are the first series of 3d–4f heterometallic complexes based on the H_3tda ligands, and these results not only enrich the 3D layer-pillared frameworks, but also provide a broad road for the construction of other neoteric lanthanide–transition metal coordination polymers with engaging structures and beneficial physical–chemical properties.

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