Syntheses and structures of $[Tb(C_6NO_2H_5)_3(H_2O)_2]_{2n}(3nHgCl_4)\cdot(4nH_2O)$ and $[La(C_6NO_2H_5)_2(C_6NO_2H_4)(H_2O)_2]_n(nZnCl_4)\cdot(2nH_2O)$

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Two new transition metal-lanthanide heterometallic complexes with isonicotinic acid and nicotinic acid as ligands, $[Tb(C_6NO_2H_5)_3(H_2O)_2]_{2n}(3nHgCl_4)\cdot(4nH_2O)$ and $[La(C_6NO_2H_5)_2(C_6NO_2H_4)(H_2O)_2]_n(nZnCl_4)\cdot(2nH_2O)$, have been synthesised via hydrothermal reactions and structurally characterised by single-crystal X-ray diffraction. Both complexes feature an infinite 1-D polycationic chain-like structure.

Keywords: heterometallic, hydrothermal reaction, lanthanide, terbium

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In recent years, lanthanide complexes have attracted more and more interest due to their promising properties and broad applications in many areas such as catalysis, magnetic materials, and luminescent labels in biological systems, *etc*.[1–23] Group 12 (IIB)-containing complexes are also attractive because of their luminescence and their essential role in biological systems of zinc. Moreover, isonicotinate and nicotinate ligands are useful moieties in constructing an extended structure because they are unsymmetrical divergent ligands.[4,5] We believe that LN-IIB (LN = lanthanide) complexes with aromatic carboxylic acids (like isonicotinic acid and nicotinic acid) as ligands might possess novel structural topologies and physical properties, such as magnetism, luminescence, photochemistry, and so on. Therefore, we have become interested in the crystal engineering of LN-IIB complexes with isonicotinic/nicotinic acid as ligands. We report here the syntheses and structures of $[Tb(C_6NO_2H_5)_3(H_2O)_2]_{2n}(3nHgCl_4)\cdot(4nH_2O)$ (**1**) and $[La(C_6NO_2H_5)_2(C_6NO_2H_4)(H_2O)_2]_n(nZnCl_4)\cdot(2nH_2O)$ (**2**).

Experimental

All reactants, of A.R. grade, were obtained commercially and used without further purification.

$[Tb(C_6NO_2H_5)_3(H_2O)_2]_{2n}(3nHgCl_4)\cdot(4nH_2O)$ (**1**): Prepared by mixing $TbCl_3\cdot6H_2O$ (1 mmol, 373 mg), $HgCl_2$ (1.5 mmol, 408 mg), isonicotinic acid (3 mmol, 369 mg) and distilled water (10 mL) in a 23 mL Teflon-lined stainless steel autoclave which was then heated at 200 °C for 10 days. After slowly cooling the system to room temperature at 6 °C/h, colourless crystals suitable for X-ray analysis were obtained. The yield was 69% (based on mercury).

$[La(C_6NO_2H_5)_2(C_6NO_2H_4)(H_2O)_2]_n(nZnCl_4)\cdot(2nH_2O)$ (**2**): Prepared by the procedure described for **1** using $LaCl_3$ (1 mmol, 246 mg), $ZnCl_2$ (1 mmol, 136 mg) and nicotinic acid (3 mmol, 369 mg) instead of $TbCl_3\cdot6H_2O$, $HgCl_2$ and isonicotinic acid. The yield was 75% (based on zinc).

X-ray structure determination

X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-*Kα* radiation (λ = 0.71073 Å) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction.[6] The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software.[7] The difference Fourier maps based on the atomic positions yielded all non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated theoretically, then allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined. A summary of crystallographic data and structure analysis is given in Table 1. Selected bond lengths and bond angles are listed in Table 2. Crystallographic data for the structures

Table 1 Summary of crystallographic data and structure analyses

Compound	1	2
Empirical formula	$C_{36}H_{46}Cl_{12}Hg_3N_6O_{20}Tb_2$	$C_{18}H_{22}Cl_4LaN_3O_{10}Zn$
Formula weight	2227.80	786.47
X-rays	MoKα	MoKα
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
Unit cell dimensions	a = 24.206(3) Å b = 20.787(2) Å c = 15.332(2) Å β = 127.942(1)°	a = 9.566(4) Å b = 21.526(8) Å c = 15.906(6) Å β = 103.396(6)°
Z	4	4
V	6084(1) Å^3	3186(2) Å^3
D_x	2.432 Mg m^{-3}	1.639 Mg m^{-3}
Absorption coefficient	10.437 mm^{-1}	2.458 mm^{-1}
Crystal size	0.10 × 0.08 × 0.05 mm	0.27 × 0.15 × 0.05 mm
No. of reflections collected/unique	17215/5141 [$R_{(int)}$ = 0.0421]	17829/5277 [$R_{(int)}$ = 0.0683]
Refinement	Full matrix least squares on F^2	Full matrix least squares on F^2
Goodness-of-fit on F^2	0.996	1.004
Parameter/restraints/data	385/16/4252	327/61/2143
Final R indices	R^1 = 0.0382, wR^2 = 0.0946	R^1 = 0.0698, wR^2 = 0.1580
R indices (all data)	R^1 = 0.0448, wR^2 = 0.0967	R^1 = 0.1416, wR^2 = 0.1694
Index ranges	$-28\leq h\leq27$, $-24\leq k\leq24$, $-18\leq l\leq18$	$-11\leq h\leq10$, $-25\leq k\leq25$, $-18\leq l\leq18$
Measurement	Rigaku Mercury CCD diffractometer	Rigaku Mercury CCD diffractometer
Monochromator	Graphite	Graphite
Structure determination	Siemens SHELXTL	Siemens SHELXTL

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Table 2 Selected bond lengths (Å) and bond angles (°)

Complex **1**

Tb(1)–O(1)	2.381(3)	O(5)–Tb(1)–O(4)#1	138.0(1)
Tb(1)–O(2)#1	2.387(3)	O(2)#1–Tb(1)–O(4)#1	76.1(1)
Tb(1)–O(3)	2.417(3)	O(6)#2–Tb(1)–O(4)#1	80.3(1)
Tb(1)–O(4)#1	2.417(3)	O(3)–Tb(1)–O(4)#1	75.3(1)
Tb(1)–O(5)	2.386(3)	O(1)–Tb(1)–O(2W)	140.5(1)
Tb(1)–O(6)#2	2.399(3)	O(5)–Tb(1)–O(2W)	71.3(1)
Tb(1)–O(1W)	2.527(3)	O(2)#1–Tb(1)–O(2W)	140.5(1)
Tb(1)–O(2W)	2.495(3)	O(6)#2–Tb(1)–O(2W)	73.5(1)
Hg(1)–Cl(1)	2.477(3)	O(3)–Tb(1)–O(2W)	76.7(1)
Hg(1)–Cl(2)	2.428(3)	O(4)#1–Tb(1)–O(2W)	69.1(2)
Hg(1)–Cl(3)	2.406(3)	O(1)–Tb(1)–O(1W)	69.70(9)
Hg(1)–Cl(3)#3	2.744(3)	O(5)–Tb(1)–O(1W)	77.1(1)
Hg(2)–Cl(4)	2.564(1)	O(2)#1–Tb(1)–O(1W)	72.7(1)
Hg(2)–Cl(5)	2.472(1)	O(6)#2–Tb(1)–O(1W)	71.1(1)
Hg(2)–Cl(6)	2.448(1)	O(3)–Tb(1)–O(1W)	140.8(1)
Hg(2)–Cl(7)	2.462(2)	O(4)#1–Tb(1)–O(1W)	139.8(1)
		O(2W)–Tb(1)–O(1W)	124.80(9)
O(1)–Tb(1)–O(5)	78.3(1)	Cl(3)–Hg(1)–Cl(1)	122.05(8)
O(1)–Tb(1)–O(2)#1	76.6(1)	Cl(2)–Hg(1)–Cl(1)	92.13(7)
O(5)–Tb(1)–O(2)#1	145.8(1)	Cl(3)–Hg(1)–Cl(3)#3	110.6(1)
O(1)–Tb(1)–O(6)#2	139.3(1)	Cl(2)–Hg(1)–Cl(3)#3	108.17(9)
O(5)–Tb(1)–O(6)#2	103.0(1)	Cl(1)–Hg(1)–Cl(3)#3	109.73(7)
O(2)#1–Tb(1)–O(6)#2	82.0(1)	Cl(6)–Hg(2)–Cl(7)	116.97(5)
O(1)–Tb(1)–O(3)	74.2(1)	Cl(6)–Hg(2)–Cl(5)	113.85(5)
O(5)–Tb(1)–O(3)	81.3(1)	Cl(7)–Hg(2)–Cl(5)	109.75(5)
O(2)#1–Tb(1)–O(3)	113.2(1)	Cl(6)–Hg(2)–Cl(4)	104.35(5)
O(6)#2–Tb(1)–O(3)	146.5(1)	Cl(7)–Hg(2)–Cl(4)	104.90(4)
O(1)–Tb(1)–O(4)#1	126.0(1)	Cl(5)–Hg(2)–Cl(4)	105.83(4)

Symmetry codes: #1, 1–*x*, *y*, 0.5–*z*; #2, 1.5–*x*, 0.5–*y*, 1–*z*; #3, 2–*x*, *y*, 1.5–*z*.

Complex **2**

La(1)–O(1)#1	2.552(3)	O(5)#2–La(1)–O(1W)	71.40(9)
La(1)–O(2)	2.494(3)	O(1)#1–La(1)–O(1W)	138.38(9)
La(1)–O(3)#1	2.476(3)	O(6)–La(1)–O(2W)	70.56(9)
La(1)–O(4)	2.501(3)	O(3)#1–La(1)–O(2W)	139.56(9)
La(1)–O(5)#2	2.527(3)	O(2)–La(1)–O(2W)	140.87(9)
La(1)–O(6)	2.443(3)	O(4)–La(1)–O(2W)	70.78(9)
La(1)–O(1W)	2.599(3)	O(5)#2–La(1)–O(2W)	72.6(1)
La(1)–O(2W)	2.613(3)	O(1)#1–La(1)–O(2W)	70.6(1)
Zn(1)–Cl(1)	2.275(3)	O(1W)–La(1)–O(2W)	122.73(9)
Zn(1)–Cl(2)	2.181(2)	O(6)–La(1)–O(2)#1	116.59(9)
Zn(1)–Cl(3)	2.233(3)	O(3)#1–La(1)–O(2)#1	65.60(8)
Zn(1)–Cl(4)	2.258(2)	O(2)–La(1)–O(2)#1	76.63(9)
		O(4)–La(1)–O(2)#1	67.97(9)
O(6)–La(1)–O(3)#1	80.29(9)	O(5)#2–La(1)–O(2)#1	140.57(8)
O(6)–La(1)–O(2)	145.28(9)	O(1)#1–La(1)–O(2)#1	45.02(8)
O(3)#1–La(1)–O(2)	76.82(9)	O(1W)–La(1)–O(2)#1	132.71(8)
O(6)–La(1)–O(4)	140.99(9)	O(2W)–La(1)–O(2)#1	103.02(9)
O(3)#1–La(1)–O(4)	129.06(9)	O(6)–La(1)–C(1)#1	96.3(1)
O(2)–La(1)–O(4)	73.19(9)	O(3)#1–La(1)–C(1)#1	69.0(1)
O(6)–La(1)–O(5)#2	99.2(1)	O(2)–La(1)–C(1)#1	99.4(1)
O(3)#1–La(1)–O(5)#2	141.26(9)	O(4)–La(1)–C(1)#1	76.5(1)
O(2)–La(1)–O(5)#2	83.29(9)	O(5)#2–La(1)–C(1)#1	148.04(9)
O(4)–La(1)–O(5)#2	73.89(9)	O(1)#1–La(1)–C(1)#1	22.21(9)
O(6)–La(1)–O(1)#1	76.61(9)	O(1W)–La(1)–C(1)#1	140.3(1)
O(3)#1–La(1)–O(1)#1	75.9(1)	O(2W)–La(1)–C(1)#1	86.7(1)
O(2)–La(1)–O(1)#1	121.52(9)	O(2)#1–La(1)–C(1)#1	22.82(8)
O(4)–La(1)–O(1)#1	85.98(9)	Cl(2)–Zn(1)–Cl(3)	107.63(9)
O(5)#2–La(1)–O(1)#1	142.18(9)	Cl(2)–Zn(1)–Cl(4)	110.03(7)
O(6)–La(1)–O(1W)	73.06(9)	Cl(3)–Zn(1)–Cl(4)	111.00(8)
O(3)#1–La(1)–O(1W)	71.51(9)	Cl(2)–Zn(1)–Cl(1)	118.0(1)
O(2)–La(1)–O(1W)	75.10(8)	Cl(3)–Zn(1)–Cl(1)	104.2(1)
O(4)–La(1)–O(1W)	134.99(9)	Cl(4)–Zn(1)–Cl(1)	105.78(8)

Symmetry codes: #1, 1–*x*, 3–*y*, –*z*; #2, 2–*x*, 3–*y*, –*z*.

reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 744051 and 744050 for **1** and **2**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; E-mail: deposit@ccdc.cam.ac.uk).

Results and discussion

X-ray diffraction analysis reveals that complex **1** is comprised of $[Tb(C_6NO_2H_5)_3(H_2O)_2]_{2n}^{6n+}$ cationic moieties, $HgCl_4^{2-}$ anions and isolated water molecules, as shown in Fig. 1 (a). The mercury atoms are coordinated by four terminal chlorine atoms to yield $HgCl_4^{2-}$ tetrahedral anions. The bond lengths of Hg–Cl range from 2.406(3) to 2.744(3) Å

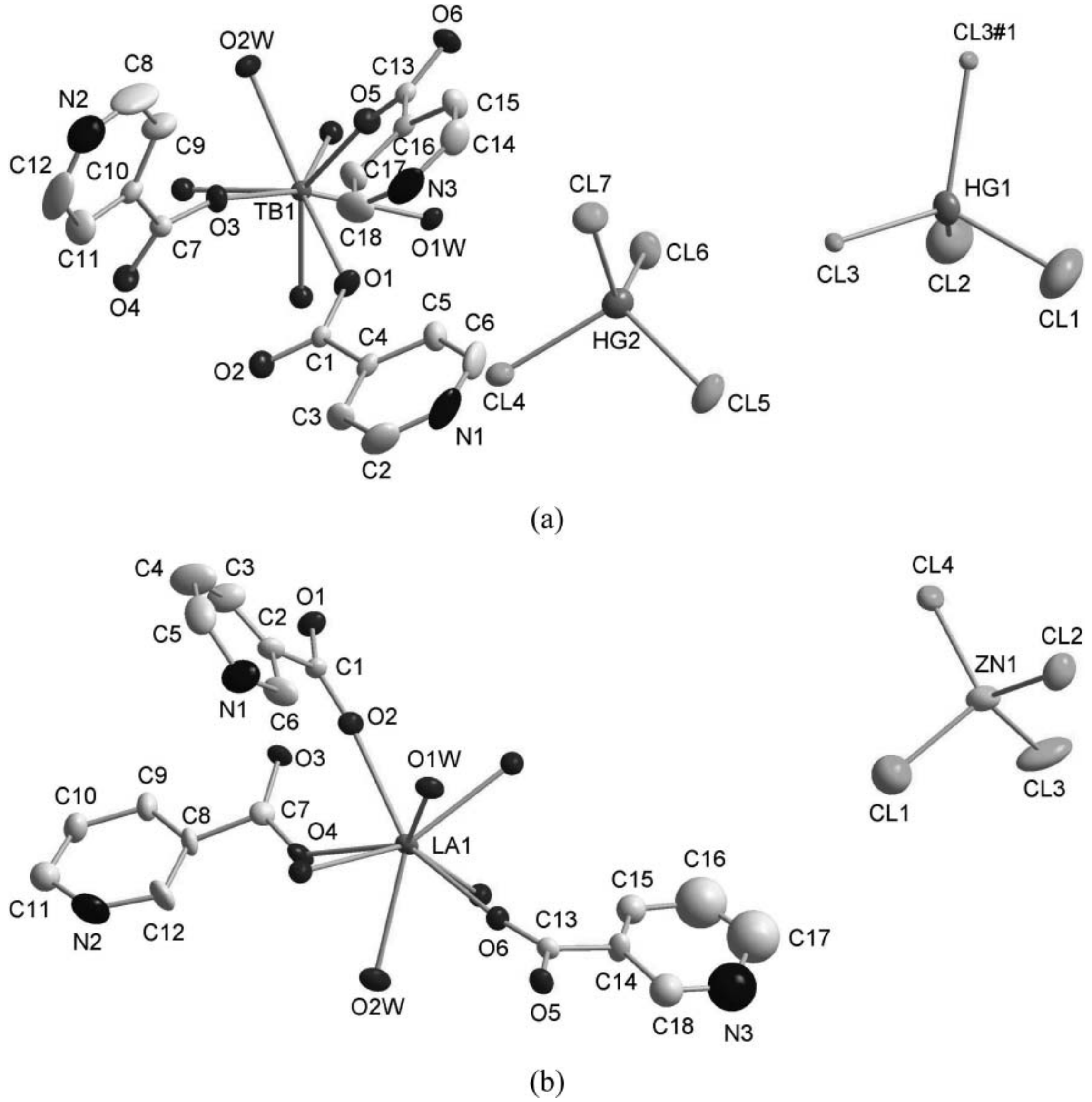

Fig. 1 ORTEP-plots of **1** (a) and **2** (b) with 40% and 10% thermal ellipsoids, respectively. Lattice water molecules, hydrogen atoms, disordered atoms are omitted for clarity. Symmetry code:#1, 2–*x*, *y*, 1.5–*z*.

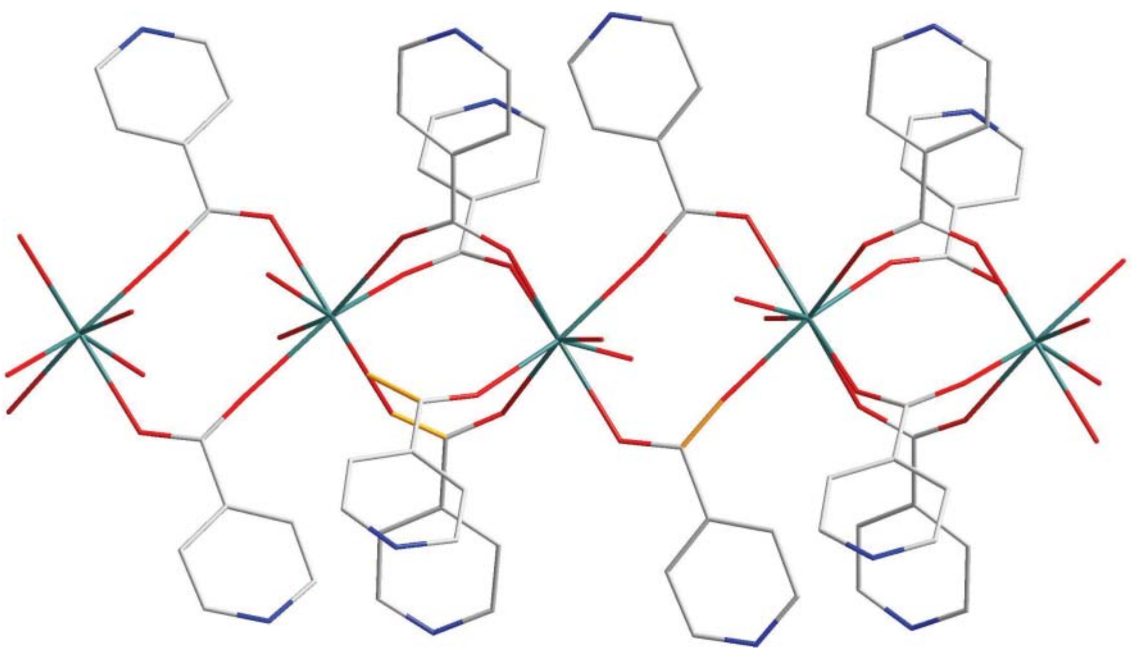

Fig. 2 A 1D polycationic chain of **1** and **2**.

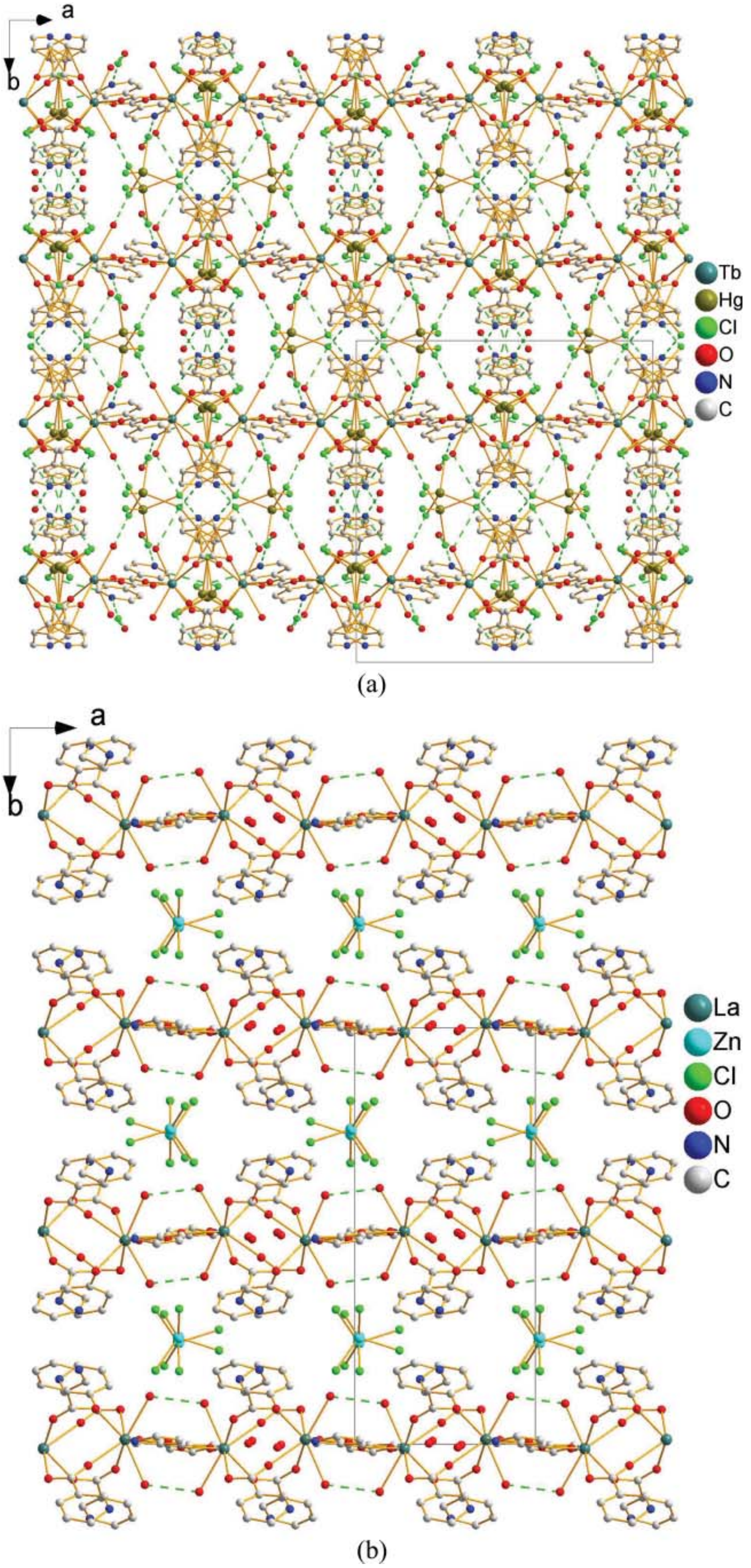

Fig. 3 (a) Packing diagram of **1** with the dashed lines representing hydrogen bonding and π–π staking interactions (Å, °): O1W–H1WA···O3W 2.719(4), 157; O2W–H2WA···Cl7 3.182(3), 169(1); O3W–H3WA···Cl5 3.209(4), 155(1); N1–H1A···Cl4 3.136(5), 155; N2–H2A···O4W 2.830(8), 161; N3–H3A···Cl5 3.289(5), 141; C18–H18A···Cl2 3.377(8), 148; $C_g(1)$–$C_g(1)$ 3.811(3), 0; $C_g(2)$–$C_g(2)$ 3.584(4), 0 [$C_g(1)$ and $C_g(2)$ stands for the centers of gravity of the rings N1(C2–C6) and N2(C8–C12), respectively]. (b) Packing diagram of **2** with the dashed lines representing hydrogen bonding interactions (Å, °): O1W–H1WA···O2W 2.854(4), 163; O2W–H2WA···O1W 2.854(4), 175.

with an average value of 2.500(3) Å, which are normal and comparable with counterparts found in the literature.[8,9] The terbium ion is bound by eight oxygen atoms, among which two are from two coordinate water molecules and six are from six isonicotinic acid ligands, yielding a distorted square anti-prism with the top and bottom planes defined by O(2W), O(3), O(1), O(5) and O(1W), O(6)(1.5–*x*, 0.5–*y*, 1–*z*), O(4)(1–*x*, *y*, 0.5–*z*), O(2)(1–*x*, *y*, 0.5–*z*) atoms, respectively. The bond lengths of $\text{Tb-O}_{\text{isonicotinic acid}}$ range from 2.381(3) to 2.417(3) Å with an average value of 2.398(3) Å, which is obviously shorter than that of $\text{Tb-O}_{\text{water}}$ being of 2.495(3) and 2.527(3) Å, indicating that the isonicotinic acid ligand has a stronger affinity to terbium ions than has water. The terbium ions are alternately linked by two or four μ_2-isonicotinic acid ligands in a 2–4–2 (the number indicates the number of the bridges) mode to construct a 1D infinite polycationic chain with the Tb…Tb distances being of *ca* 4.577 and 5.018 Å, respectively, as shown in Fig. 2. In complex **1**, there are some $\pi\ldots\pi$ stacking interactions between the adjacent isonicotinic acid ligands. The six atoms of the ring of the isonicotinic acid ligand do not completely eclipse those of the other ligand, namely, the $\pi\ldots\pi$ stacking interaction is not "perfect face alignment" but "slipped stacking". Furthermore, there is a lot of hydrogen bonding interactions found in complex **1**. The 1D infinite polycationic chains, $HgCl_4^{2-}$ anionic moieties and isolated water molecules are interconnected by hydrogen bonding and $\pi\ldots\pi$ stacking interactions to construct a 3D supramolecular network [Fig. 3(a)]. Bond valence calculations reveal that the terbium and mercury atoms are in the +3 and +2 oxidation states, respectively (Tb1: 2.913, Hg1: 2.079, Hg2: 2.126).[10]

The structure of **2** is similar to that of **1**, consisting of $[La(C_6NO_2H_5)_2(C_6NO_2H_4)(H_2O)_2]_n^{2n+}$ cationic moieties, $ZnCl_4^{2-}$ anions and isolated water molecules, as shown in Fig. 1(b). Each zinc ion is tetrahedrally coordinated by four chlorine atoms to give a $ZnCl_4^{2-}$ anion with the bond length of Zn-Cl ranging from 2.181(2) to 2.275(3) Å that is normal and comparable with the counterpart found in the literature.[11–121314] The lanthanum atom is coordinated by eight oxygen atoms, of which two are from two water molecules and six are from six nicotinic acid ligands, constructing a distorted square anti-prism. The bond lengths of $\text{La–O}_{\text{nicotinic acid}}$ range from 2.443(3) to 2.552(3) Å with an average value of 2.499(3) Å, which is obviously shorter than that of $\text{La–O}_{\text{water}}$ being of 2.599(3) and 2.613(3) Å, indicating that the nicotinic acid ligand has a stronger affinity to the La^{III} ion than has water. All the three crystallographically-independent nicotinic acid ligands act as bidentate ligands to bridge two neighbouring lanthanum atoms and the nitrogen atoms of two of three nicotinic acid ligands should be protonated, as is the case found in many other references.[15–16171819] The lanthanum atoms are alternately bridged by two or four μ_2-nicotinic acid ligands in a 2–4–2 mode to construct a 1D infinite cationic chain with the La…La distances being of *ca* 4.329 and 5.288 Å, respectively (Fig. 2). Different from **1**, in **2** no $\pi\ldots\pi$ stacking interactions were established between the adjacent nicotinic acid ligands. Moreover, the number of hydrogen bonding interactions of **2** is much less than that of **1**. The $[La(C_6NO_2H_5)_2(C_6NO_2H_4)(H_2O)_2]_n^{2n+}$ cationic moieties, $ZnCl_4^{2-}$ moieties and water molecules are linked via hydrogen bonds to give a 1D structure [Fig. 3(b)].

In summary, we have prepared and characterised two new transition metal-lanthanide heterometallic complexes, $[Tb(C_6NO_2H_5)_3(H_2O)_2]_{2n}(3nHgCl_4)\cdot(4nH_2O)$ and $[La(C_6NO_2H_5)_2(C_6NO_2H_4)(H_2O)_2]_n(nZnCl_4)\cdot(2nH_2O)$, with isonicotinic acid and nicotinic acid as ligands. The crystal structures of the title complexes are characterised by a one-dimensional polycationic infinite chain-like structure.

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