A novel 2-D 5d-4f-3d trimetal-isonicotinic acid complex: synthesis and characterisation

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A novel trimetallic–isonicotinic acid complex $[Zn_{0.5}(H_2O)]\{(Hg_2Cl_5)[Eu(C_6NO_2H_4)_3(H_2O)_2]\}(HgCl_2)\cdot H_2O$ (**1**) has been synthesised and structurally characterised by single-crystal X-ray diffraction. Complex **1** features a novel 2-D $\{(Hg_2Cl_5)[Eu(C_6NO_2H_4)_3(H_2O)_2]\}$ layer constructed from $[Eu(C_6NO_2H_4)_3(H_2O)_2]$ chains interconnected by $Hg_2Cl_5^-$ linkers. The 2-D $\{(Hg_2Cl_5)[Eu(C_6NO_2H_4)_3(H_2O)_2]\}$ layers are held together *via* hydrogen bonds and π–π interactions to yield a 3-D supramolecular framework with the lattice water molecules, the mercury chloride and the hydrated zinc ions located in the cavities.

Keywords: europium, isonicotinic acid, lanthanide, mercury, zinc

The growing interest in the field of crystal engineering of inorganic–organic hybrid materials is justified by the potential applications of these materials as biological materials, catalysts, *etc*.[1-4] Although the synthesis of inorganic–organic hybrid materials based on the transition metals has become widespread,[5-11] there are relatively few reports on lanthanide-based inorganic–organic hybrid materials despite their potential applications to luminescence and other fields.[12] To our knowledge, lanthanide (LN)-based inorganic–organic hybrid materials with aromatic carboxylic acids have good thermal and luminescent stability for practical application. Moreover, transition metal (TM) complexes containing group 12 (IIB) elements are particularly attractive for many reasons such as the variety of coordination numbers and geometries provided by the d^{10} configuration of the IIB metal ions. Moreover, the isonicotinate anion is an interesting tecton in constructing extended structures because it can link two metal centres by coordinating to a metal centre with the nitrogen atom and, to the other one, with one or two carboxylato-oxygen atoms.[13,14] Therefore, we have become interested in the crystal engineering of LN–TM-based inorganic–organic hybrid materials with isonicotinic acid as ligand. We report here the synthesis and structure of a 2-D 5d–4f–3d complex $[Zn_{0.5}(H_2O)]\{(Hg_2Cl_5)[Eu(C_6NO_2H_4)_3(H_2O)_2]\}(HgCl_2)\cdot H_2O$ (**1**) with a novel two-dimensional layered structure.

Experimental

All reagents of A.R. grade were obtained commercially and used without further purification. The title complex was prepared by mixing $EuCl_3\cdot 6H_2O$ (1 mmol, 0.366 g), $HgCl_2$ (3 mmol, 0.816 g), $ZnCl_2$ (0.5 mmol, 0.068 g), isonicotinic acid (3 mmol, 0.369 g), and distilled water (10 mL) in a 25 mL Teflon-lined stainless steel autoclave and heating the mixture at 200 °C for 10 days. After the mixture cooled slowly to room temperature at 6 °C/h, colourless crystals suitable for X-ray analysis were obtained. The yield was 75% (based on europium).

X-ray structure determination

The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) by using an ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections.[15] The structure was solved by direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software.[16] The difference Fourier maps based on these atomic positions yielded the other non-hydrogen atoms. The hydrogen atom positions were generated theoretically, except for those on the lattice water molecules that were yielded by the difference Fourier maps, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined. The structures were refined using a full-matrix least-squares refinement on F^2. All atoms were refined anisotropically. Crystal data as well as details of data collection and refinement for the title complex are summarised in Table 1. Selected bonded lengths and angles are listed in Table 2. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 745895. 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).

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Results and discussion

X-ray diffraction analysis shows that the structure of the title complex is comprised of anionic $\{(Hg_2Cl_5)[Eu(C_6NO_2H_4)_3(H_2O)_2]\}$ 2-D layers, mercury chloride, lattice water molecules and hydrated zinc cations (Fig. 1). All the crystallographically independent atoms are in general positions except for Eu(1), Eu(2) and Zn(1) atoms. There are three crystallographically unique isonicotinate anions, two of which are tridentate and the third one is bidentate. The three mercury atoms have three different coordination environments, *i.e*., two-, four- and five-coordination geometries. The Hg(1) atom is two-fold-coordinated with two chlorine atoms in an approximately linear arrangement [Cl(1)–Hg(1)–Cl(2) = 175.86(5)°], which is comparable with that of isolated $HgCl_2$ moieties in the literature.[17] The bond lengths of Hg(1)–Cl(1) and Hg(1)–Cl(2) are 2.286(2) and 2.281(2) Å, which are comparable with their counterparts in the literature.[17-19] The Hg(2) atom is coordinated by three chlorine atoms and two nitrogen atoms from two isonicotinate anions, yielding a distorted square pyramid with the bottom plane and the apex defined by

Table 1 Summary of crystallographic data and structure analysis for **1**

Formula	$C_{18}H_{20}Cl_7EuHg_3N_3O_{10}Zn_{0.50}$
M_r	1472.94
Colour	Colourless
Crystal size/mm³	0.10 0.06 0.05
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	34.165(4)
b (Å)	9.4692(8)
c (Å)	24.575(3)
β (°)	115.090(5)
V (Å³)	7200(1)
Z	8
$2\theta_{max}$/°	50.70
Reflections collected	21382
Independent, observed reflections (R_{int})	6447, 3024 (0.0440)
$d_{calcd.}$ (g cm^{-3})	2.718
μ/mm^{-1}	15.364
T/K	293(2)
F(000)	5328
R1, *w*R2	0.0817, 0.2158
S	0.777
Largest and mean Δ/σ	0.002, 0
Δρ(max, min) (e/Å³)	4.701, –5.696

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

Hg(1)–Cl(1)	2.286(2)	O(1)–Eu(1)–O(1)#2	124.3(2)
Hg(1)–Cl(2)	2.281(2)	O(3)#2–Eu(1)–O(1W)#2	70.1(1)
Hg(2)–N(2)	2.113(4)	O(3)–Eu(1)–O(1W)#2	75.4(1)
Hg(2)–N(3)#1	2.140(4)	O(5)–Eu(1)–O(1W)#2	138.6(1)
Hg(2)–Cl(3)	2.806(1)	O(5)#2–Eu(1)–O(1W)#2	71.1(1)
Hg(2)–Cl(4)	2.874(1)	O(1)–Eu(1)–O(1W)#2	70.2(1)
Hg(2)–Cl(5)	2.856(1)	O(1)#2–Eu(1)–O(1W)#2	139.3(1)
Hg(3)–Cl(3)	2.506(2)	O(3)#2–Eu(1)–O(1W)	75.4(1)
Hg(3)–Cl(4)	2.581(1)	O(3)–Eu(1)–O(1W)	70.1(1)
Hg(3)–Cl(6)	2.482(2)	O(5)–Eu(1)–O(1W)	71.1(1)
Hg(3)–Cl(7)	2.370(3)	O(5)#2–Eu(1)–O(1W)	138.6(1)
Eu(1)–O(3)#2	2.270(4)	O(1)–Eu(1)–O(1W)	139.3(1)
Eu(1)–O(3)	2.271(4)	O(1)#2–Eu(1)–O(1W)	70.2(1)
Eu(1)–O(5)	2.313(3)	O(1W)#2–Eu(1)–O(1W)	126.6(2)
Eu(1)–O(5)#2	2.313(3)	O(3)#2–Eu(1)–Eu(2)	131.2(1)
Eu(1)–O(1)	2.346(4)	O(3)–Eu(1)–Eu(2)	131.2(1)
Eu(1)–O(1)#2	2.346(4)	O(5)–Eu(1)–Eu(2)	61.71(8)
Eu(1)–O(1W)#2	2.467(3)	O(5)#2–Eu(1)–Eu(2)	61.71(8)
Eu(1)–O(1W)	2.467(3)	O(1)–Eu(1)–Eu(2)	62.16(9)
Eu(2)–O(4)#3	2.275(4)	O(1)#2–Eu(1)–Eu(2)	62.16(9)
Eu(2)–O(4)#4	2.275(4)	O(1W)#2–Eu(1)–Eu(2)	116.70(9)
Eu(2)–O(6)#2	2.298(3)	O(1W)–Eu(1)–Eu(2)	116.70(9)
Eu(2)–O(6)	2.298(3)	O(4)#3–Eu(2)–O(4)#4	105.0(2)
Eu(2)–O(2)	2.352(4)	O(4)#3–Eu(2)–O(6)#2	143.7(1)
Eu(2)–O(2)#2	2.352(4)	O(4)#4–Eu(2)–O(6)#2	79.6(1)
Eu(2)–O(2W)	2.431(3)	O(4)#3–Eu(2)–O(6)	79.6(1)
Eu(2)–O(2W)#2	2.431(3)	O(4)#4–Eu(2)–O(6)	143.7(1)
Zn(1)–O(4W)#5	2.280(4)	O(6)#2–Eu(2)–O(6)	118.2(2)
Zn(1)–O(4W)	2.280(4)	O(4)#3–Eu(2)–O(2)	77.5(1)
		O(4)#4–Eu(2)–O(2)	142.7(1)
Cl(2)–Hg(1)–Cl(1)	175.86(5)	O(6)#2–Eu(2)–O(2)	78.2(1)
N(2)–Hg(2)–N(3)#1	168.8(1)	O(6)–Eu(2)–O(2)	73.6(1)
N(2)–Hg(2)–Cl(3)	87.7(1)	O(4)#3–Eu(2)–O(2)#2	142.7(1)
N(3)#1–Hg(2)–Cl(3)	103.3(1)	O(4)#4–Eu(2)–O(2)#2	77.5(1)
N(2)–Hg(2)–Cl(5)	87.8(1)	O(6)#2–Eu(2)–O(2)#2	73.6(1)
N(3)#1–Hg(2)–Cl(5)	90.5(1)	O(6)–Eu(2)–O(2)#2	78.2(1)
Cl(3)–Hg(2)–Cl(5)	88.37(4)	O(2)–Eu(2)–O(2)#2	123.3(2)
N(2)–Hg(2)–Cl(4)	91.8(1)	O(4)#3–Eu(2)–O(2W)	74.0(1)
N(3)#1–Hg(2)–Cl(4)	91.2(1)	O(4)#4–Eu(2)–O(2W)	73.5(1)
Cl(3)–Hg(2)–Cl(4)	84.77(4)	O(6)#2–Eu(2)–O(2W)	139.3(1)
Cl(5)–Hg(2)–Cl(4)	173.13(4)	O(6)–Eu(2)–O(2W)	73.4(1)
Cl(7)–Hg(3)–Cl(6)	122.30(7)	O(2)–Eu(2)–O(2W)	139.4(1)
Cl(7)–Hg(3)–Cl(3)	117.05(7)	O(2)#2–Eu(2)–O(2W)	71.2(1)
Cl(6)–Hg(3)–Cl(3)	109.95(6)	O(4)#3–Eu(2)–O(2W)#2	73.5(1)
Cl(7)–Hg(3)–Cl(4)	97.93(7)	O(4)#4–Eu(2)–O(2W)#2	74.0(1)
Cl(6)–Hg(3)–Cl(4)	107.26(6)	O(6)#2–Eu(2)–O(2W)#2	73.4(1)
Cl(3)–Hg(3)–Cl(4)	97.65(4)	O(6)–Eu(2)–O(2W)#2	139.3(1)
O(3)#2–Eu(1)–O(3)	97.6(2)	O(2)–Eu(2)–O(2W)#2	71.2(1)
O(3)#2–Eu(1)–O(5)	81.9(1)	O(2)#2–Eu(2)–O(2W)#2	139.4(1)
O(3)–Eu(1)–O(5)	139.9(1)	O(2W)–Eu(2)–O(2W)#2	125.2(2)
O(3)#2–Eu(1)–O(5)#2	139.9(1)	O(4)#3–Eu(2)–Eu(1)	127.52(9)
O(3)–Eu(1)–O(5)#2	81.9(1)	O(4)#4–Eu(2)–Eu(1)	127.52(9)
O(5)–Eu(1)–O(5)#2	123.4(2)	O(6)#2–Eu(2)–Eu(1)	59.09(8)
O(3)#2–Eu(1)–O(1)	78.4(1)	O(6)–Eu(2)–Eu(1)	59.09(8)
O(3)–Eu(1)–O(1)	144.7(1)	O(2)–Eu(2)–Eu(1)	61.64(8)
O(5)–Eu(1)–O(1)	74.8(1)	O(2)#2–Eu(2)–Eu(1)	61.64(8)
O(5)#2–Eu(1)–O(1)	79.6(1)	O(2W)–Eu(2)–Eu(1)	117.39(8)
O(3)#2–Eu(1)–O(1)#2	144.7(1)	O(2W)#2–Eu(2)–Eu(1)	117.39(8)
O(3)–Eu(1)–O(1)#2	78.4(1)	O(4W)#5–Zn(1)–O(4W)	180.000(1)
O(5)–Eu(1)–O(1)#2	79.6(1)	Hg(3)–Cl(3)–Hg(2)	88.37(5)
O(5)#2–Eu(1)–O(1)#2	74.8(1)	Hg(3)–Cl(4)–Hg(2)	85.48(4)

Symmetry transformations used to generate equivalent atoms: #1 x–1/2, y–1/2, z; #2 –x, y, –z + 1/2; #3 –x, y + 1, –z + 1/2; #4 x, y + 1, z; #5 –x + 1/2, –y + 3/2, –z + 1.

N(2), Cl(5), N(3)(–x + 1/2, y–3/2, –z + 0.5), Cl(4) and Cl(3) atoms, respectively. The bond lengths of Hg(2)–Cl(3), Hg(2)–Cl(4) and Hg(2)–Cl(5) are 2.806(1), 2.874(1) and 2.856(1) Å, respectively. The Hg(3) atom is coordinated by four chlorine atoms to yield a distorted tetrahedron with the bond lengths of Hg(3)–Cl(3), Hg(3)–Cl(4), Hg(3)–Cl(6) and Hg(3)–Cl(7) being 2.506(2), 2.581(1), 2.482(2) and 2.370(3) Å, respectively. Obviously, the bond lengths of Hg(2)–Cl are longer than those of Hg(1)–Cl and Hg(3)–Cl. This is probably due to the fact that the formation of the coordinative Hg(2)–N bonds weakens the Hg(2)–Cl bond. The Hg(2)-centred $HgCl_3N_2$ square pyramid and the Hg(3)-centred $HgCl_4$ tetrahedron edge-share the μ_2-Cl(3) and μ_2-Cl(4) atoms to form a $Hg_2N_2Cl_5$ moiety. The Zn^{2+} ion is hydrated by two water molecules with the bond length of Zn(1)-O(4W) being 2.280(4) Å and the O(4W)–Zn(1)–O(4W)(–x + 1/2, –y + 3/2, –z + 1) being 180°, respectively.[20-22] There are two crystallographically independent europium atoms and the occupancies of them are set to 0.5 in order to get a rational structure model and thermal displacement parameters. Both of the two crystallographically independent europium atoms are in eight-coordination environments. The Eu(1) atom is coordinated by eight oxygen atoms, of which two are from two 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(1W), O(3), O(1W)(–x, y, –z + 1/2), O(3)(–x, y, –z + 1/2) and O(1)(–x, y, –z +

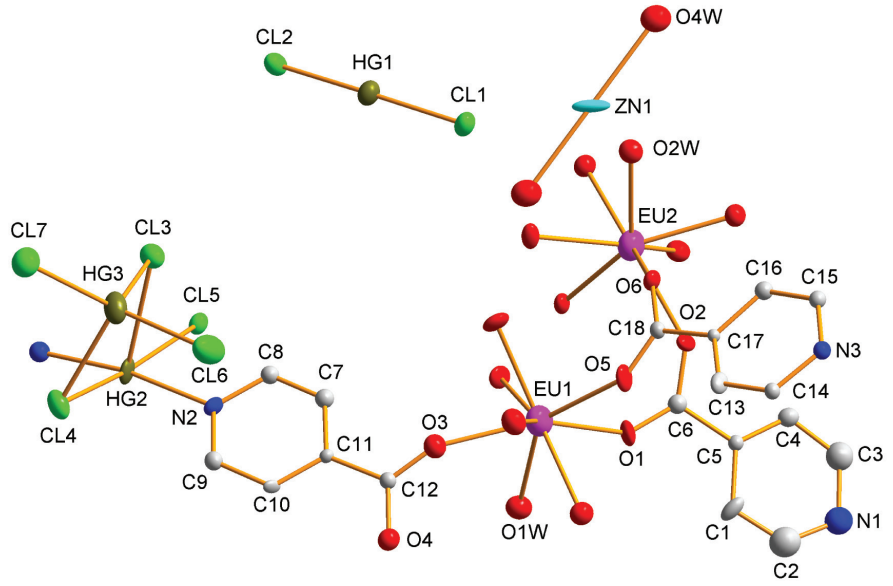


Fig. 1 An ORTEP drawing of **1** with 30% thermal ellipsoids. The lattice water molecules and hydrogen atoms were omitted for clarity.

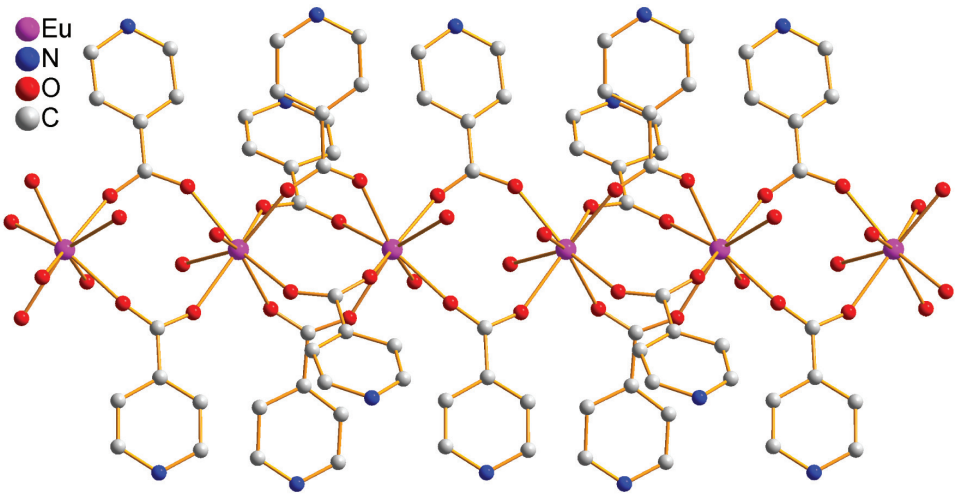
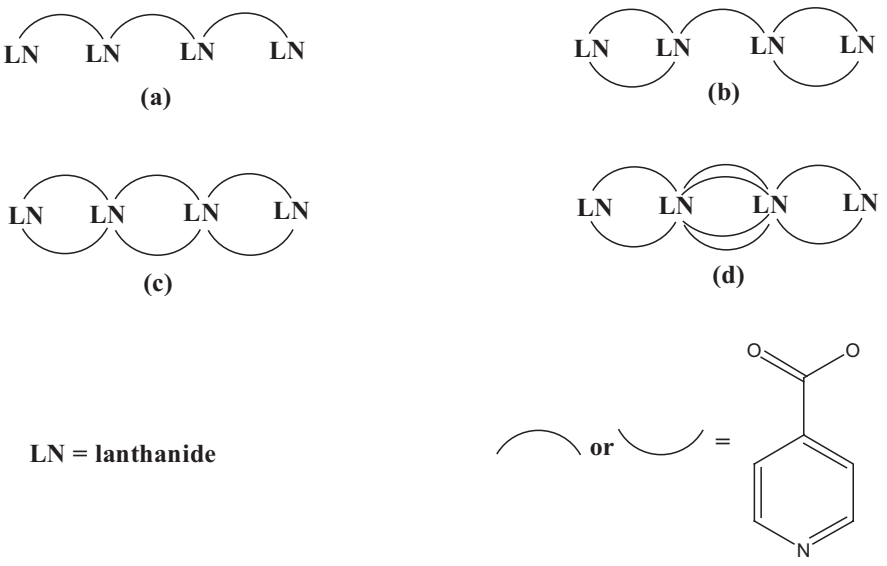


Fig. 2 A 1-D chain of **1** running along the axis *b*.



Scheme 1 Important chain-like structural types of isonicotinic acid bridging LN centres: (a), 1–1–1; (b) 2–1–2; (c) 2–2–2 and (d) 2–4–2 types, in which the number indicates the number of the bridges.

1/2), O(5)(–*x*, *y*, –*z* + 1/2), O(1), O(5) atoms, respectively. Similarly, the Eu(2) atom is coordinated by eight oxygen atoms, of which two are from two 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(2), O(6), O(2)(–*x*, *y*, –*z* + 1/2), O(6)(–*x*, 1 + *y*, –*z* + 1/2) and O(2W), O(4)(*x*, *y* + 1, *z*), O(2W)(–*x*, *y*, –*z* + 1/2), O(4)(–*x*, *y* + 1, –*z* + 1/2) atoms, respectively. The bond lengths of Eu–$O_{isonicotinic\ acid}$ range from 2.270(4) to 2.352(4) Å with an average value of 2.309(4) Å, which is obviously shorter than that of Eu–O_{water} being 2.431(3) and 2.467(3) Å, indicating that the isonicotinic acid ligand has a stronger affinity to the Eu^{III} ion than has water. The europium atoms are alternately bridged 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 1-D chain running along the axis *b* with the Eu…Eu distances of *ca* 5.021 and 4.448 Å, respectively (Fig. 2 and Scheme 1d). Note that, up to date, the types of chain formed by LN and isonicotinic acid that have been documented are mainly 1–1–1, 2–1–2 and 2–2–2 types (Scheme 1a, b and c, respectively). However, the 2–4–2 type is rare. The 1-D chains are interconnected together by the $Hg_2Cl_5^-$ linkers *via* Hg–N bonds, yielding a 2-D layer extending along the *ab* directions (Fig. 3). The 2-D layers are held together *via* π–π interactions and hydrogen bonds to form a 3-D supramolecular framework with the lattice water molecules, the mercury chloride and the hydrated zinc ions located in the cavities (Fig. 4).

In conclusion, we have prepared a 5d–4f–3d trimetallic-isonicotinic acid inorganic–organic hybrid complex *via* hydrothermal reactions. The crystal structure of the title complex is characterised by a two-dimensional layered structure constructed from the $[Eu(C_6NO_2H_4)_3(H_2O)_2]$ chains interconnected by the $Hg_2Cl_5^-$ linkers.

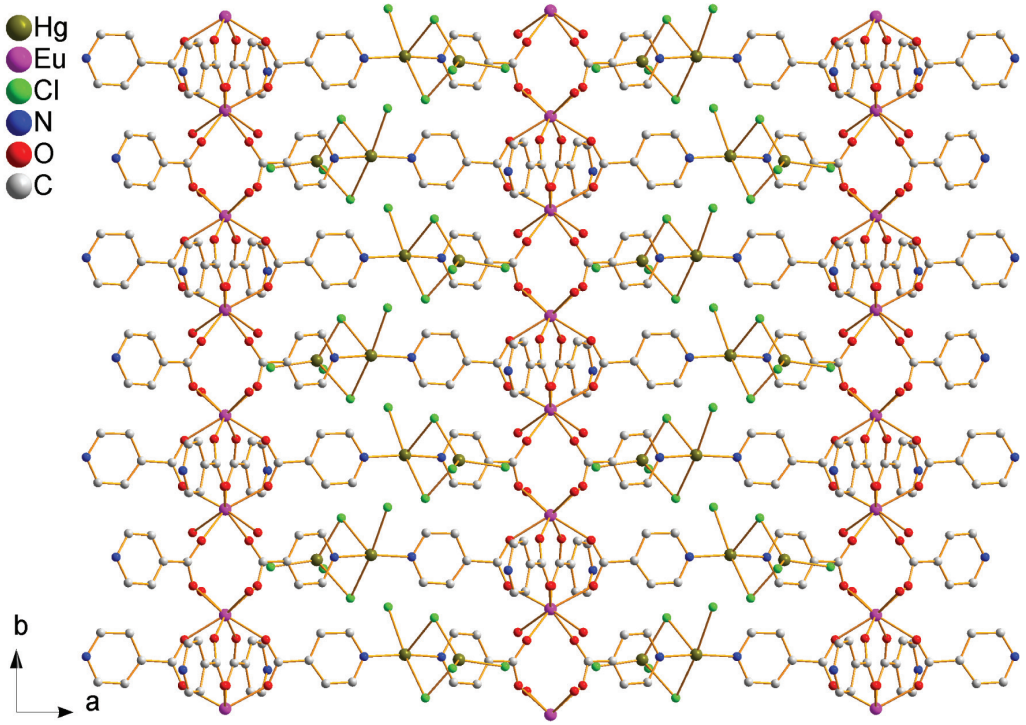


Fig. 3 A 2-D layer constructed from the chains interconnected by the $Hg_2Cl_5^-$ linkers.

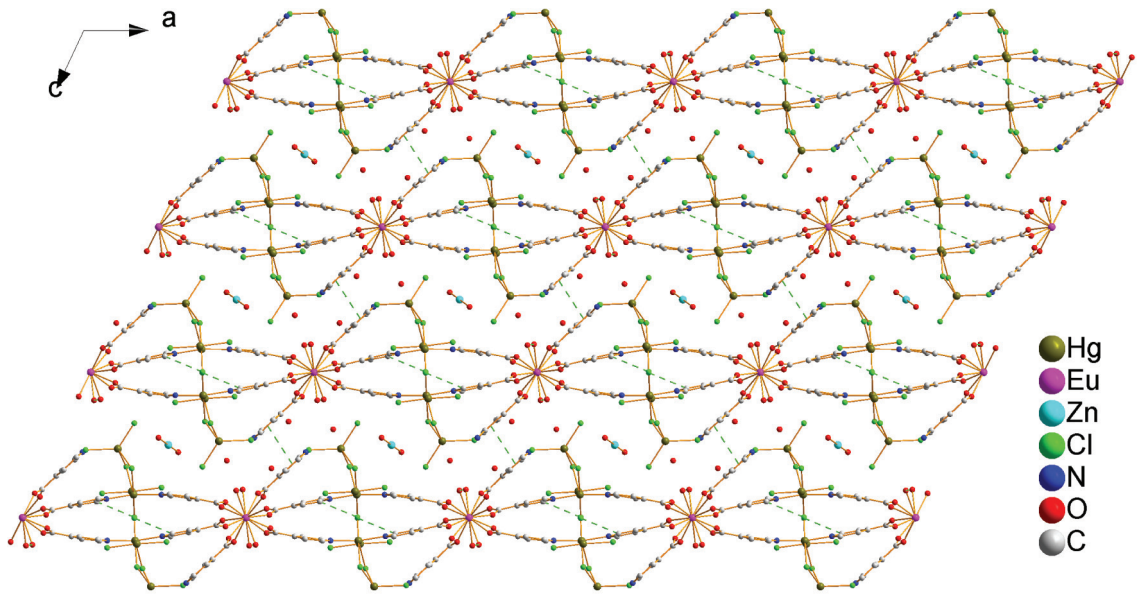


Fig. 4 Packing diagram of **1** with the dashed lines representing hydrogen bonds and π–π interactions (Å): O1W–H(1WA)···O2W 2.839(5), O2W–H(2WA)···O1W 2.839(5), C(8)–H(8A)···Cl5 3.369(5), $C_g(1)$···$C_g(1)$ 3.800(3) [$C_g(1)$ stands for the centre of gravity of the ring N1(C1–C5)].

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