Synthesis, crystal structure and properties of $[Gd(C_6NO_2H_5)_3(H_2O)_2]_n(1.5nZnCl_4)\cdot nH_2O$ with unprecedented poly-cationic chains

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A new heterometallic 4f-3d inorganic-organic metal-nicotinic acid complex $[Gd(C_6NO_2H_5)_3(H_2O)_2]_n(1.5nZnCl_4)\cdot nH_2O$, (**1**), has been synthesised via hydrothermal reaction and structurally characterised. Complex **1** crystallises in the space group $P2_1/c$ of the monoclinic system with four formula units in a cell: $a = 9.524(2)$, $b = 20.888(4)$, $c = 16.078(3)$ Å $\beta = 104.745(2)°$, $V = 3093.2(9)$ Å^3, $C_{18}H_{21}Cl_6GdN_3O_9Zn_{1.50}$, $M_r = 891.38$ g/mol, $D_c = 1.914$ g/cm^3, $S = 0.997$, $\mu(MoK\alpha) = 3.844$ mm^{-1}, $F(000) = 1732$, $R = 0.0493$ and $wR = 0.1350$. Complex **1** is characteristic of a one-dimensional polycationic chain-like structure. Photoluminescent investigation shows that the title complex displays strong emission in the blue region, which is attributed to the intraligand π–π^* transition of nicotinic ligands. Optical absorption spectra of **1** reveal the presence of a wide optical bandgap of 3.73 eV.

Keywords: crystal structure, gadolinium, lanthanide, nicotinic acid, zinc

In recent years, study of complexes of trivalent lanthanide ions continues to be an active research area, which may be ascribed to the remarkable physical properties of these complexes and their applications as magnetic functional materials, electroluminescent devices, in catalysis, zeolite-like materials, and luminescent probes or labels in biological systems.[1-3] There is also an aesthetic perspective: for the vast amount of inorganic-organic hybrid materials, the intriguing variety of the architectures and topologies that can be obtained by self-assembling metal ions and multifunctional ligands attract chemists. So far, although the synthesis of inorganic–organic hybrid materials based on transition metals has become widespread,[4-9] there are relatively few reports on lanthanide-based inorganic-organic hybrid materials despite their potential applications in luminescence and other fields.[10] To our knowledge, lanthanide-based inorganic-organic hybrid materials with aromatic carboxylic acids exhibit good thermal and luminescent stability for practical application. Metal complexes containing group 12 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, the well-known toxicity of cadmium and mercury, semiconductive properties, the essential role in biological systems of zinc, and so forth. Furthermore, the nicotinic/isonicotinic anion is an interesting tecton in constructing extended structures because it is an unsymmetrical divergent ligand with a nitrogen atom at one side and two oxygen atoms from the carboxylato-group at the other one. The nicotinic/isonicotinic anion 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.[11,12] We propose that LN–IIB-based (LN = lanthanide) inorganic-organic hybrid materials with aromatic carboxylic acids as ligands may have novel structural topologies and properties, such as luminescence, semiconductivity, magnetism, electro- and photochemistry, catalysis, thermochromism and so forth. Therefore, our group recently became interested in the crystal engineering of LN–IIB-based inorganic-organic hybrid materials with nicotinic/isonicotinic acid as ligand.[13] We herein reported the synthesis, crystal structure and properties of $[Gd(C_6NO_2H_5)_3(H_2O)_2]_n(1.5nZnCl_4)\cdot nH_2O$ (**1**).

Experimental

Materials and instrumentation. All reactants of A.R. grade were obtained commercially and used without further purification. IR spectra were obtained with a PE Spectrum-One FT-IR spectrometer using KBr discs. The fluorescent data were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer. The UV/vis spectra were recorded at room temperature on a computer-controlled PE Lambda 35 UV/vis spectrometer equipped with an integrating sphere in the wavelength range 190 – 2500 nm. $BaSO_4$ plate was used as a reference (100% reflectance), on which the finely ground powder of the samples was coated. The absorption spectra were calculated from reflection spectra by the Kubelka-Munk function: $\alpha/S = (1-R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm, and R is the reflectance. The energy band gaps were determined by extrapolation from the linear portion of the absorption edge in a (α/S) versus energy plot from the UV-vis diffuse spectra.[14,15]

Synthesis of $[Gd(C_6NO_2H_5)_3(H_2O)_2]_n(1.5nZnCl_4)\cdot nH_2O$ **(1):** The title complex was prepared by mixing $GdCl_3\cdot 6H_2O$ (1 mmol, 0.372 g), $ZnCl_2$ (1 mmol, 0.136 g), nicotinic acid (1 mmol, 0.123 g) and 10 ml distilled water in a 25 ml Teflon-lined stainless steel autoclave and heating at 150°C for 7 days. After slowly cooling the resulting solution to room temperature at 6°C/h, colourless crystals suitable for X-ray analysis were obtained. The yield was 88% (based on zinc). IR peaks (KBr, cm^{-1}): 3470(vs), 3180(w), 3081(m), 3004(w), 2939(w), 2876(m), 1694(m), 1616(vs), 1588(vs), 1573(vs), 1418(vs), 1354(m), 1199(w), 1107(w), 1057(w), 838(m), 753(s), 688(m), 623(m), 547(m) and 419(m).

*X-ray structure determination***:** The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo–$K\alpha$ radiation ($\lambda = 0.71073$ Å) by using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections.[16] The structure was solved by the direct method using the Siemens SHELXTL^{TM} Version 5 package of crystallographic software.[17] The difference Fourier maps based on these atomic positions yield 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, and allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The structures were refined using a full-matrix least-squares refinement on F^2. All atoms were refined anisotropically. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond 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 679177. 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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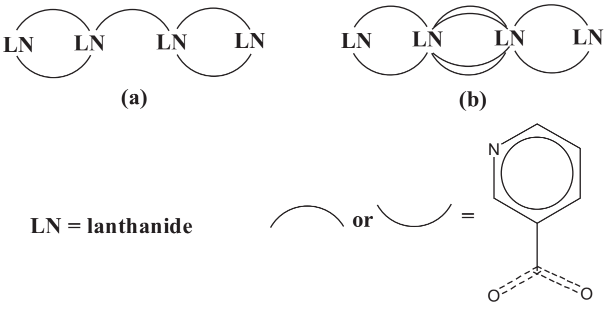
Table 1 Summary of crystallographic data and structure analysis for **1**

Formula	$C_{18}H_{21}Cl_6GdN_3O_9Zn_{1.50}$
FW	891.38
colour	Colourless
Crystal sise/mm^3	0.34 0.12 0.06
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.524(2)
b (Å)	20.888(4)
c (Å)	16.078(3)
β (°)	104.745(2)
V (Å^3)	3093.2(9)
Z	4
$2\theta_{max}$ (°)	50
Reflections collected	18325
Independent, observed reflections (R_{int})	5295, 3784 (0.0324)
$d_{calcd.}$ (g/cm^3)	1.914
μ(mm^{-1})	3.844
T (K)	293(2)
F(000)	1732
$R1$, $wR2$	0.0493, 0.1350
S	0.997
Largest and Mean Δ/σ	0.001, 0
Δρ (max/min) (e/Å^3)	1.786/-1.689

Results and discussion

An ORTEP drawing of **1** is shown in Fig. 1. The structure of **1** consists of $[Gd(C_6NO_2H_5)_3(H_2O)_2]_n^{3n+}$ poly-cationic chains, $ZnCl_4^{2-}$ anions and isolated water molecules. The Zn1 atom is tetrahedrally bounded by four chlorine atoms to form a $ZnCl_4^{2-}$ anion. In the $ZnCl_4^{2-}$ anion, the bond lengths of Zn–Cl range from 2.258(2) to 2.279(2) Å with an average value of 2.268(2) Å, which are normal and comparable with counterparts found in the literature.[18-21] The Zn2 atom is positional disordered and the occupancy of Zn2 must be set to 0.5 to get a rational structure model and thermal displacement parameters. The gadolinium atom is octahedrally coordinated by eight oxygen atoms, of which two are from two water molecules and six are from six nicotinic acid ligands, yielding a distorted square anti-prism with the top and bottom planes defined by O(5), O(3), O(6)(–*x*, 1–*y*, –*z*), O(4)(–*x*, 1–*y*, –*z*) and O(1W), O(2)(–1–*x*, 1–*y*, –*z*), O(2W), O(1) atoms, respectively. The bond lengths of $Gd–O_{nicotinic\ acid}$ range from 2.325(3) to 2.424(3) Å with an average value of 2.365(3) Å, which is obviously shorter than that of $Gd–O_{water}$ being of 2.495(3) and 2.514(3) Å, indicating that nicotinic acid ligand has a stronger affinity to Gd^{III} ion than that of water. All the three crystallographically-independent nicotinic acid ligands act as bidentate ligands to bridge two neighbouring gadolinium atoms and the nitrogen atoms of the nicotinic acid ligands should be protonated, as the case found in many other references.[22-25] The gadolinium atoms are alternately bridged by two or four μ_2-nicotinic acid ligands in a 2–4–2 (the number indicates the number of the bridging nicotinic acid ligands) mode to construct a 1D chain with the Gd…Gd distances being *ca* 5.157 and 4.407 Å, respectively (Fig. 2 and Scheme 1b). The Gd…Gd distances are comparable with those in the analogous structures.[26-29] It is noteworthy that, up to date, the type of chain formed by LN and nicotinic acid that has been documented is only the 2–1–2 type (Scheme 1a).[30] Therefore, the 2–4–2 type is unprecedented in the complexes containing both LN and nicotinic acid. In **1**, no π…π stacking interactions were established between the adjacent nicotinic acid ligands. The 1D poly-cationic $[Gd(C_6NO_2H_5)_3(H_2O)_2]_n^{3n+}$ chains, $ZnCl_4^{2-}$ anions and water molecules are linked by hydrogen bonds to yield a 3D supramolecular network, as shown in Fig. 3.



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

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

Gd1–O1	2.367(3)	O2#2–Gd1–O1	98.7(1)
Gd1–O2#2	2.331(3)	O4#1–Gd1–O1	144.5(1)
Gd1–O3	2.378(3)	O6#1–Gd1–O3	73.6(1)
Gd1–O4#1	2.366(3)	O2#2–Gd1–O3	142.5(1)
Gd1–O5	2.424(3)	O4#1–Gd1–O3	123.5(1)
Gd1–O6#1	2.325(3)	O1–Gd1–O3	77.4(1)
Gd1–O1W	2.495(3)	O6#1–Gd1–O5	119.4(1)
Gd1–O2W	2.514(3)	O2#2–Gd1–O5	79.9(1)
Zn1–Cl1	2.258(2)	O4#1–Gd1–O5	74.5(1)
Zn1–Cl2	2.279(2)	O1–Gd1–O5	140.8(1)
Zn1–Cl3	2.272(2)	O3–Gd1–O5	80.6(1)
Zn1–Cl4	2.264(1)	Cl1–Zn1–Cl4	107.97(6)
		Cl1–Zn1–Cl3	112.86(7)
O6#1–Gd1–O2#2	143.7(1)	Cl4–Zn1–Cl3	110.94(6)
O6#1–Gd1–O4#1	76.1(1)	Cl1–Zn1–Cl2	108.42(7)
O2#2–Gd1–O4#1	81.0(1)	Cl4–Zn1–Cl2	110.95(6)
O6#1–Gd1–O1	84.7(1)	Cl3–Zn1–Cl2	105.69(6)

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

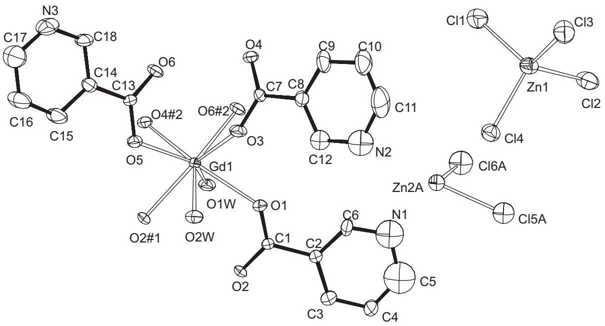


Fig. 1 ORTEP drawing of **1** with 30% thermal ellipsoids. Lattice water molecules, hydrogen atoms and disordered Zn2B, Cl5B, Cl6B atoms are omitted for clarity. The occupancy of the sum of Zn2A and Zn2B is equal to 0.5. [Symmtry codes: #1 –1–*x*, 1–*y*, –*z*; #2 –*x*, 1–*y*, –*z*].

It is noteworthy that, to our knowledge, although many TM-nicotinic acid complexes have been synthesised, LN-nicotinic acid complexes are relatively rare. Especially, only three LN–TM-nicotinic acid complexes are known, one of which is the 1D chain-like structure as the above mentioned 2–1–2 type (Scheme 1a).[30]

Optical absorption spectrum of **1** reveals the presence of an obvious optical bandgap of 3.73 eV (Fig. 4), which suggests that complex **1** is a wide-gap semiconductor. The steep slope of the optical absorption edge for **1** is indicative of the existence of direct transitions.[31] The mainly optical absorption of **1** is likely originated from the charge-transfer excitations mainly from the valence band of the chloride

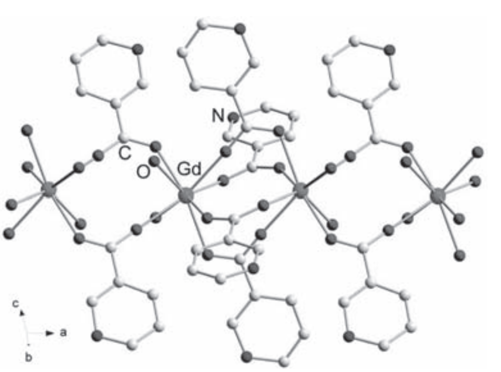


Fig. 2 The 1D poly-cationic chain-like structure of **1**.

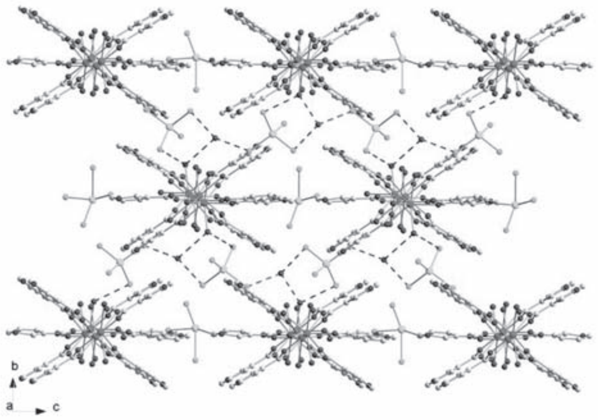


Fig. 3 Packing diagram of **1** with the dashed lines representing hydrogen bonds (Å): O1W...Cl4(–*x*, –1/2+*y*, 1/2–*z*) 3.206(3), O2W...Cl3(–1+*x*, 3/2–*y*, –1/2+*z*) 3.178(3), O2W...O3W 2.749(6), O3W...Cl1(–1+*x*, 3/2–*y*, –1/2+*z*) 3.149(6), and O3W...Cl2(–1+*x*, *y*, –1+*z*) 3.149(5).

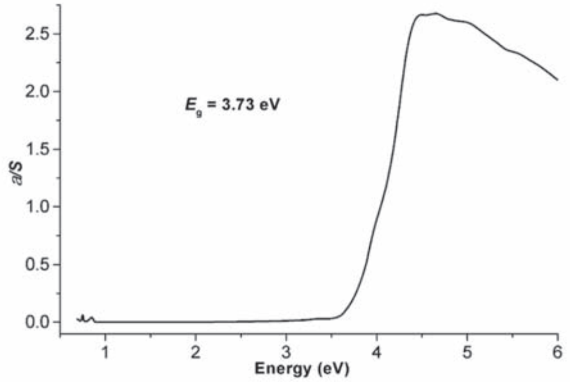


Fig. 4 Solid-state diffuse reflectance spectrum.

ligands to the conduction band of the zinc centre, similar to those reported.[32] Due to the direct wide-gap semiconductive behaviour, complex **1** may be a potential light emitting diode (LED).

The solid-state luminescence of **1** was investigated at room temperature (Fig. 5). The solid-state excitation spectra of the title complex show that the effective energy absorption mainly takes place in the ultraviolet region of the range 300–400 nm. The excitation band of complex **1** possesses one main peak at 353 nm. We further measured the corresponding emission spectrum and it shows one main and intense emission band in the blue region with the maximum wavelength of 448 nm upon photo-excitation at 353 nm. To understand the nature of the luminescence of **1**, the luminescent spectra of pure nicotinic acid were also measured under the same conditions. For pure nicotinic acid, the emission spectra show one intense emission band in the blue region, with the maximum wavelength of 409 nm, upon photo-excitation at 351 nm (Fig. 6). The similarity of the luminescent spectra of **1** and pure nicotinic acid suggests that the emission spectra of **1** should be assigned as an intraligand π–π* transition of nicotinic acid ligand. The absence of the characteristic emissions of Gd^{3+} and the existence of the ligand-based emissions in the luminescent spectra of **1** implies that nicotinic acid ligand is not suitable for the sensitisation of the Gd^{3+} ion. In addition, the absence of the characteristic emissions of Gd^{3+} is probably because Gd^{3+} possesses a relatively stable half-full 4f shell.

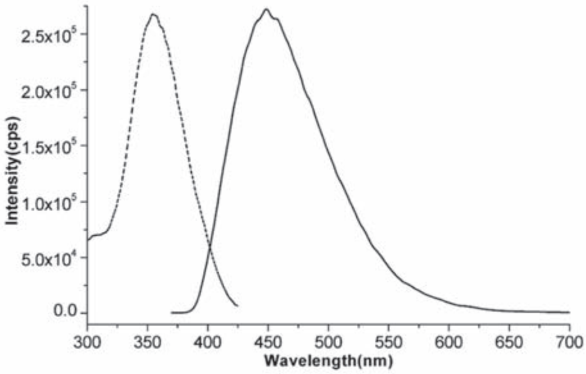


Fig. 5 Solid-state emission and excitation spectra of **1** at room temperature. Solid line: emission spectrum; dashed line: excitation spectrum.

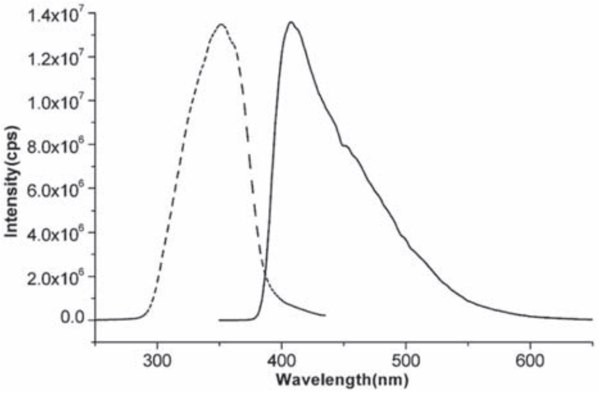


Fig. 6 Solid-state emission and excitation spectra of pure nicotinic acid at room temperature. Solid line: emission spectrum; dashed line: excitation spectrum.

In brief, we have successfully prepared a new heterometallic 4f–3d metal-nicotinic acid inorganic-organic hybrid complex via hydrothermal reaction. The crystal structure of the title complex is characteristic of a novel one-dimensional polycationic chain-like structure. The title complex shows intense emissions in blue region. The emission spectra should be assigned as an intraligand π–π* transition of nicotinic acid ligand. Optical absorption spectra show that the title complex may be a candidate for potential photoelectric material.

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