Two Nd-Zn and Sm-Zn Isonicotinic/Nicotinic Acid Complexes

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Abstract

The 4f-3d heterometallic complexes $\{[Nd(L)_3(H_2O)_2]_2(ZnCl_4)_3\}_n \cdot 4nH_2O$ (**1**) (L = isonicotinic acid) and $\{[Sm(L')_3(H_2O)_2]_2(ZnCl_4)\}_n \cdot 2nH_2O$ (**2**) (L' = nicotinic acid) have been obtained by hydrothermal reactions and structurally characterized by X-ray single-crystal diffractions. Both complexes feature an infinite 1-D polycationic chain-like structure. Photoluminescent investigations reveal that both complexes display totally different emissions. The emission of complex **1** is attributed to the $\pi \rightarrow \pi^*$ charge-transfer interaction of the isonicotinic acid. Complex **2** exhibits emissions in a wide range, and the emissions are ascribed to the characteristic emissions of $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) of Sm^{3+} ions.

Keywords: Hydrothermal, heterometallic complex, isonicotinic acid, photoluminescence

1. Introduction

Recently, investigations on Ln^{3+} complexes have attracted great interest due to their interesting properties and broad applications in the fields of magnetic functional materials, catalysis and luminescent probes in biological systems, and so forth.[1–5] Besides, group 12 (IIB) element-containing complexes are also attractive for many reasons, such as luminescence and the essential role in biological systems of zinc. Moreover, the isonicotinate/nicotinate anions are useful moieties in forming an extended structure because they are unsymmetrical divergent ligands with a nitrogen atom at one end and two oxygen atoms from the carboxylato group at the other one.[6–7] We deem 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 luminescence, magnetism, electro- and photochemistry, and so on. Therefore, we recently became interested in the crystal engineering of Ln-IIB complexes with isonicotinic/nicotinic acid as ligands. Herein, we report the syntheses, crystal structures, and properties of $\{[Nd(L)_3(H_2O)_2]_2(ZnCl_4)_3\}_n \cdot 4nH_2O$ (**1**)

(L = isonicotinic acid) and $\{[Sm(L')_3(H_2O)_2]_2(ZnCl_4)\}_n \cdot 2nH_2O$ (**2**) (L' = nicotinic acid).

2. Experimental

All reactants of A.R. grade were obtained commercially and used without further purification. The photoluminescence data were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer with slits at 3 nm, increment 1.0 nm and integration time 0.05 second.

2. 1. Synthesis of $\{[Nd(L)_3(H_2O)_2]_2(ZnCl_4)_3\}_n \cdot 4nH_2O$ (1).

This complex was prepared by mixing $NdCl_3 \cdot 6H_2O$ (2 mmol, 718 mg), $ZnCl_2$ (3 mmol, 408 mg), isonicotinic acid (6 mmol, 738 mg) and 10 mL distilled water in a 23 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 10 days. After being slowly cooled to room temperature at 6 °C/h, colorless crystals suitable for X-ray analysis were obtained. The yield was 61% (based on zinc).

2. 2. Synthesis of {[Sm(L')₃(H₂O)₂]₂(ZnCl₄)}ₙ · 2nH₂O (2).

This complex was prepared by the procedure described for 1 using SmCl₃ · 6H₂O (2 mmol, 730 mg) and nicotinic acid (6 mmol, 738 mg) instead of NdCl₃ · 6H₂O and isonicotinic acid. The yield was 65% (based on zinc).

2. 3. X-ray structure determination

X-ray single-crystal diffractions data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction.[8] The structures were solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software.[9] The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms and the hydrogen atoms of the lattice water molecules. The structures were refined using a full-matrix least-squares refinement on F². All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms, except for those of the lattice water molecules, were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined. 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.
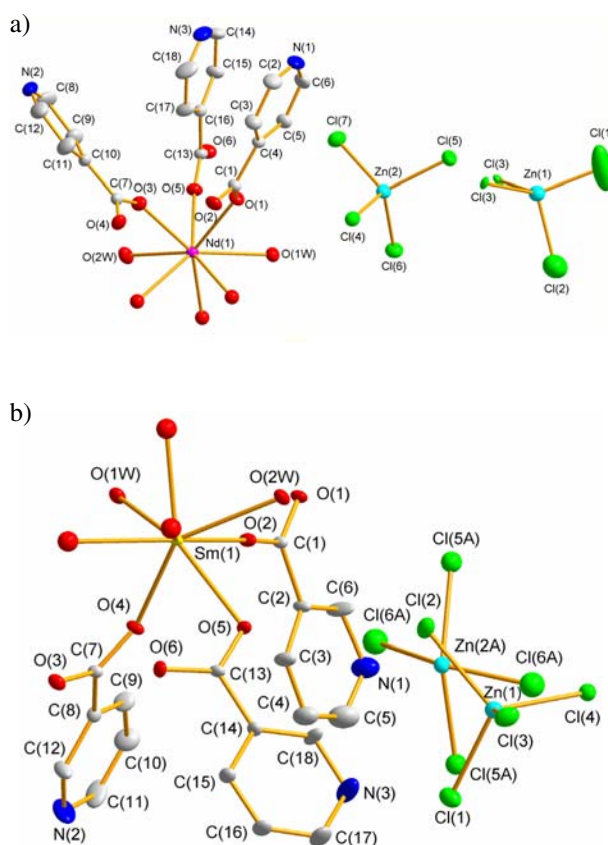
Fig. 1: ORTEP-plots of **1** (a) and **2** (b) with 30% thermal ellipsoids. Lattice water molecules, hydrogen atoms, disordered atoms are omitted for clarity.

Table 1. Summary of Crystallographic Data and Structure Analyses

Compound	1	2
Empirical formula	C₃₆H₄₆Cl₁₂N₆Nd₂O₂₀Zn₃	C₃₆H₄₂Cl₁₂N₆O₁₈Sm₂Zn₃
Color and habit	Colorless block	Colorless prism
Formula weight	1792.78	1768.97
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2₁/*c*
Unit cell dimensions	*a* = 23.791(4) Å	*a* = 9.5430(4) Å
	b = 20.553(3) Å	*b* = 20.900(1) Å
	c = 15.408(2) Å	*c* = 16.1091(7) Å
	β = 126.934(2)	β = 104.842(1)
Z	4	2
V	6022(2) Å³	3105.7(2) Å³
D_x	1.977 Mg/m³	1.892 Mg/m³
Absorption coefficient	3.476 mm⁻¹	3.584 mm⁻¹
Crystal size	0.11 × 0.07 × 0.05 mm³	0.32 × 0.09 × 0.08 mm³
No. of reflections collected/unique	17180/5105 [$R_{(int)}$ = 0.0182]	18441/5391 [$R_{(int)}$ = 0.0363]
Refinement	Full matrix least squares on F^2	Full matrix least squares on F^2
Goodness-of-fit on F^2	1.016	1.020
Parameter/Restraints/Data	391/8/4752	341/19/4152
Final *R* indices	R_1 = 0.0341, wR_2 = 0.0926	R_1 = 0.0544, wR_2 = 0.1554
R indices (all data)	R_1 = 0.0362, wR_2 = 0.0943	R_1 = 0.0693, wR_2 = 0.1687
Index ranges	–28 ≤ h ≤ 28, –24 ≤ k ≤ 24, –18 ≤ l ≤ 18	–11 ≤ h ≤ 11, –24 ≤ k ≤ 24, –19 ≤ l ≤ 19

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

Complex 1			
Bond Lengths (Å)		O(1)-Nd(1)-O(3)	74.71(8)
Nd(1)-O(1)	2.420(2)	O(6)#2-Nd(1)-O(3)	145.99(9)
Nd(1)-O(2)#1	2.395(2)	O(4)#1-Nd(1)-O(3)	74.15(9)
Nd(1)-O(3)	2.456(2)	O(2)#1-Nd(1)-O(2W)	140.2(1)
Nd(1)-O(4)#1	2.436(2)	O(5)-Nd(1)-O(2W)	71.42(9)
Nd(1)-O(5)	2.414(3)	O(1)-Nd(1)-O(2W)	139.9(1)
Nd(1)-O(6)#2	2.434(3)	O(6)#2-Nd(1)-O(2W)	74.09(9)
Nd(1)-O(1W)	2.554(2)	O(4)#1-Nd(1)-O(2W)	70.12(8)
Nd(1)-O(2W)	2.493(2)	O(3)-Nd(1)-O(2W)	76.64(8)
Zn(1)-Cl(1)	2.120(5)	O(2)#1-Nd(1)-O(1W)	73.08(8)
Zn(1)-Cl(2)	2.262(2)	O(5)-Nd(1)-O(1W)	78.70(8)
Zn(1)-Cl(3)	2.205(2)	O(1)-Nd(1)-O(1W)	69.02(7)
Zn(1)-Cl(3)#3	2.469(2)	O(6)#2-Nd(1)-O(1W)	71.54(8)
Zn(2)-Cl(4)	2.3099(9)	O(4)#1-Nd(1)-O(1W)	139.23(9)
Zn(2)-Cl(5)	2.265(1)	O(3)-Nd(1)-O(1W)	141.56(8)
Zn(2)-Cl(6)	2.269(1)	O(2W)-Nd(1)-O(1W)	125.78(7)
Zn(2)-Cl(7)	2.270(1)	Cl(1)-Zn(1)-Cl(3)	126.72(7)
Bond Angles (°)		Cl(3B)-Zn(1)-Cl(2)	99.5(1)
O(2)#1-Nd(1)-O(5)	146.92(9)	Cl(1)-Zn(1)-Cl(2)	97.06(7)
O(2)#1-Nd(1)-O(1)	77.14(9)	Cl(3)-Zn(1)-Cl(2)	109.22(9)
O(5)-Nd(1)-O(1)	76.91(8)	Cl(1)-Zn(1)-Cl(3)#3	114.60(7)
O(2)#1-Nd(1)-O(6)#2	82.06(9)	Cl(3)-Zn(1)-Cl(3)#3	103.0(1)
O(5)-Nd(1)-O(6)#2	105.16(8)	Cl(2)-Zn(1)-Cl(3)#3	104.14(8)
O(1)-Nd(1)-O(6)#2	139.24(9)	Cl(5)-Zn(2)-Cl(6)	110.09(4)
O(2)#1-Nd(1)-O(4)#1	74.73(9)	Cl(5)-Zn(2)-Cl(7)	109.00(5)
O(5)-Nd(1)-O(4)#1	137.98(8)	Cl(6)-Zn(2)-Cl(7)	113.18(4)
O(1)-Nd(1)-O(4)#1	126.22(7)	Cl(5)-Zn(2)-Cl(4)	109.73(4)
O(6)#2-Nd(1)-O(4)#1	79.87(8)	Cl(6)-Zn(2)-Cl(4)	106.98(4)
O(2)#1-Nd(1)-O(3)	111.09(8)	Cl(7)-Zn(2)-Cl(4)	107.78(4)

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

Complex 2			
Bond Lengths (Å)		O(6)#1-Sm(1)-O(5)	119.85(6)
Sm(1)-O(1)	2.398(2)	O(2)#2-Sm(1)-O(5)	79.47(6)
Sm(1)-O(2)#2	2.359(2)	O(4)#1-Sm(1)-O(5)	74.83(6)
Sm(1)-O(3)	2.395(2)	O(3)-Sm(1)-O(5)	81.61(6)
Sm(1)-O(4)#1	2.394(2)	O(1)-Sm(1)-O(5)	140.98(6)
Sm(1)-O(5)	2.441(2)	O(6)#1-Sm(1)-O(1W)	73.41(6)
Sm(1)-O(6)#1	2.356(2)	O(2)#2-Sm(1)-O(1W)	73.51(6)
Sm(1)-O(1W)	2.507(2)	O(4)#1-Sm(1)-O(1W)	73.68(6)
Sm(1)-O(2W)	2.538(2)	O(3)-Sm(1)-O(1W)	135.79(6)
Zn(1)-Cl(1)	2.266(1)	O(1)-Sm(1)-O(1W)	71.74(6)
Zn(1)-Cl(2)	2.277(1)	O(5)-Sm(1)-O(1W)	141.10(6)
Zn(1)-Cl(3)	2.265(1)	O(6)#1-Sm(1)-O(2W)	141.46(6)
Zn(1)-Cl(4)	2.2657(8)	O(2)#2-Sm(1)-O(2W)	71.23(6)
Bond Angles (°)		O(4)#1-Sm(1)-O(2W)	139.19(6)
O(6)#1-Sm(1)-O(2)#2	143.82(6)	O(3)-Sm(1)-O(2W)	72.11(6)
O(6)#1-Sm(1)-O(4)#1	76.21(6)	O(1)-Sm(1)-O(2W)	71.32(6)
O(2)#2-Sm(1)-O(4)#1	80.83(6)	O(5)-Sm(1)-O(2W)	71.34(6)
O(6)#1-Sm(1)-O(3)	73.49(6)	O(1W)-Sm(1)-O(2W)	123.09(6)
O(2)#2-Sm(1)-O(3)	142.48(6)	Cl(3)-Zn(1)-Cl(1)	112.84(4)
O(4)#1-Sm(1)-O(3)	124.52(6)	Cl(3)-Zn(1)-Cl(4)	110.88(4)
O(6)#1-Sm(1)-O(1)	84.30(6)	Cl(1)-Zn(1)-Cl(4)	107.98(3)
O(2)#2-Sm(1)-O(1)	98.86(7)	Cl(3)-Zn(1)-Cl(2)	105.83(4)
O(4)#1-Sm(1)-O(1)	143.90(6)	Cl(1)-Zn(1)-Cl(2)	108.36(4)
O(3)-Sm(1)-O(1)	76.59(7)	Cl(4)-Zn(1)-Cl(2)	110.94(3)

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

3. Results and Discussion

X-ray single-crystal diffractions analysis shows that the structure of **1** consists of $[Nd(L)_3(H_2O)_2]_n^{3n+}$ 1D polycations, $ZnCl_4^{2-}$ anions and isolated water molecules, as shown in Fig. 1 (a). The neodymium atom is bound by eight oxygen atoms, of which two are from two coordinated 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(4)(1-x, y, 1/2-z), O(3), O(1), O(2)(1-x, y, 1/2-z) and O(1W), O(5), O(2W), O(6)(3/2-x, 1/2-y, 1-z) atoms, respectively. The bond lengths of $Nd-O_L$ range from 2.395(2) to 2.456(2) Å with an average value of 2.426(3) Å, which is obviously shorter than that of $Nd-O_{water}$ being of 2.493(2) and 2.554(2) Å, indicating that isonicotinic acid ligand has a stronger affinity to Nd^{III} ion than that of water. As shown in Fig. 2 (a), the neodymium atoms 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 Nd···Nd distances of ca. 4.615 and 4.953 Å, respectively. The zinc atom is bound by four terminal chlorine atoms to form a $ZnCl_4^{2-}$ tetrahedral anion. The bond lengths of Zn-Cl range from 2.120(5) to 2.469(2) Å with an average value of 2.271(5) Å, which are normal and comparable with the counterparts found in the literatures.[10–13] In complex **1**, there are some π···π 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, i.e. the π···π stacking interaction is not "perfect face alignment" but "slipped stacking". Besides, there are many hydrogen bonding interactions exist in complex **1**. The 1D infinite polycationic chains, $ZnCl_4^{2-}$ anionic moieties and isolated water molecules are interconnected by hydrogen bonding and π···π stacking interactions to yield a 3D supramolecular network (Fig. 3 (a)). Results of the bond valence calculations indicate that the neodymium and zinc atoms are in +3 and +2 oxidation states, respectively (Nd1: 3.277, Zn1: 2.128, Zn2: 1.938).[14]

The structure of **2** is similar to that of **1,** consisting of $[Sm(L')_3(H_2O)_2]_n^{3n+}$ cationic moieties, $ZnCl_4^{2-}$ anions, and isolated water molecules, as shown in Fig. 1 (b). The samarium atom is coordinated by eight oxygen atoms, of which two are from two water molecules and six are from six isonicotinic acid ligands, constructing a distorted square anti-prism. The bond lengths of $Sm-O_{L'}$ range from 2.356(2) to 2.441(2) Å with an average value of 2.391(2) Å, which is obviously shorter than that of $Sm-O_{water}$ being of 2.507(2) and 2.538(2) Å, indicating that nicotinic acid ligand has a stronger affinity to Sm^{III} ion than that of water. The Zn atom is tetrahedrally bound by four chlorine atoms to form a $ZnCl_4^{2-}$ anion. All the three crystallographic independent nicotinic acid ligands act as bidentate ligands to bridge two neighbouring samarium atoms and the nitrogen atoms of the nicotinic acid ligands should be protonated, as the case found in many other references.[15–18] The samarium 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 Sm···Sm distances being of ca. 5.188 and 4.397 Å, respectively (Fig. 2 (b)). Different from **1,** in **2,** no π···π stacking interactions were established between the adjacent nicotinic acid ligands. The 1D cationic chains, $ZnCl_4^{2-}$ moieties and water molecules are linked via hydrogen bonds to give a 3D network (Fig. 3 (b)). It is noteworthy that, to our knowledge, although many TM-nicotinic acid complexes have been documented, Ln-nicotinic acid complexes are relatively rare.

The solid-state photoluminescence of **1** was studied under room temperature (Fig. 4). The photoluminescence spectra reveal that the effective energy absorption mainly takes place in the range of 280–330 nm. Complex **1** possesses one main excitation band at 322 nm. We further measured the corresponding emission spectra by using the excitation band of 322 nm, and the emission spectra of **1** show one main and intense emission band with the maximum wavelength of 373 nm. To understand the nature of the photoluminescence of **1**, the photoluminescence of pure isonicotinic acid was also studied under the same condition. For pure isonicotinic acid, the emission spectra
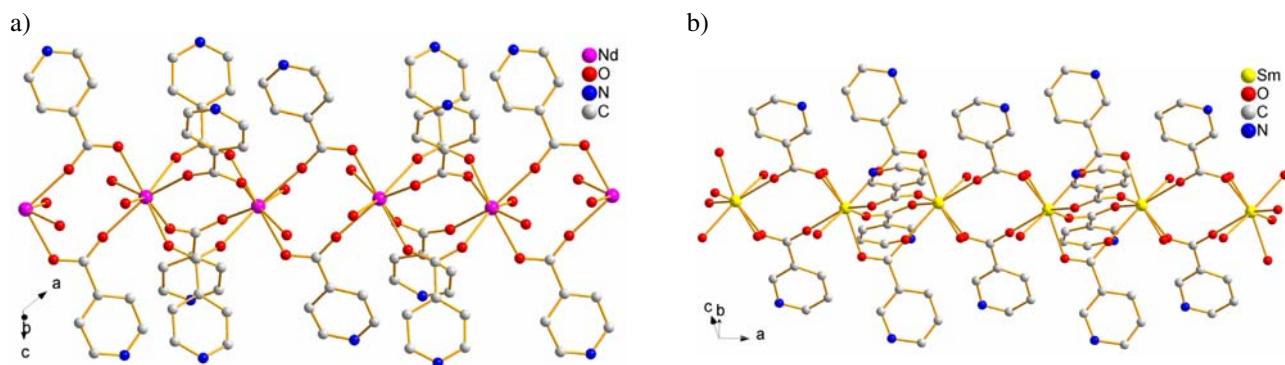

a)

b)

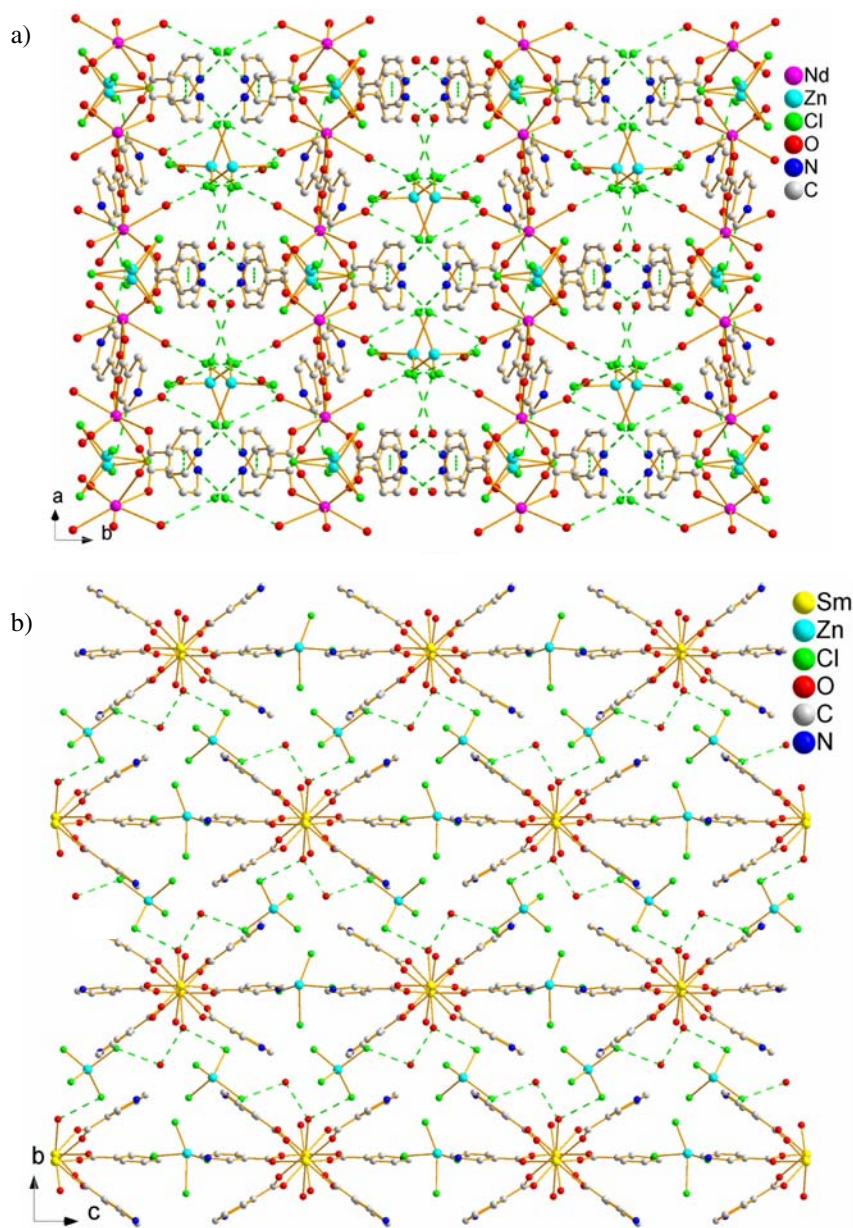**Fig. 2:** The 1D polycationic chains of **1** (a) and **2** (b).

Fig. 3: (a) Packing diagram of **1** with the dashed lines representing hydrogen bonding and π–π staking interactions (Å, °): O1W–H1WA⋯O3W 2.725(4), 153; N1–H1A⋯Cl4 3.214(4), 145; O2W–H2WA⋯Cl7 3.189(3), 143(5); O3W–H3WA⋯Cl6 3.230(4), 136(2); O1W–H1WB⋯Cl4 3.234(2), 156(3); O4W–H4WA⋯Cl6 3.246(3), 178(2); N2–H2A⋯O4W 2.869(6), 152; C18–H18A⋯Cl2 3.287(6), 157; $C_g(1)$–$C_g(1)$ 3.876(2), 0.02; $C_g(2)$–$C_g(2)$ 3.574(3), 0.03 [$C_g(1)$ 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, °): O2W–H2WA⋯O3W 2.749(3), 157; O3W–H3WA ⋯Cl2 3.182(3), 160.6(4); C16–H16A⋯Cl2 3.150(2), 164.

show one intense emission band with the maximum wavelength of 455 nm upon photo-excitation at 397 nm (inset of Fig. 4). The similarity of the photoluminescent spectra of **1** and pure isonicotinic acid indicates that the emission spectra of **1** should be assigned as an intraligand π⋯π* transition of isonicotinic acid ligand. Although the difference of the emission bands between **1** (373 nm) and pure isonicotinic acid (455 nm) is as large as 82 nm, it is still reasonable because much larger shifts in the photoluminescent features have been documented previously.[19–20]

The absence of the characteristic emissions of Nd[3+] and the existence of the ligand-based emissions in the luminescent spectra of **1** implies that isonicotinic acid ligand is not suitable for the sensitization of the Nd[3+] ion.

Taking into account the excellent luminescent property of Sm[3+] ion, the solid-state photoluminescence of **2** was investigated at room temperature (Fig. 5). The solid-state excitation spectra of **2** show that the effective energy absorption mainly takes place in the range of 350–400 nm. The excitation band of **2** under the emission of 593
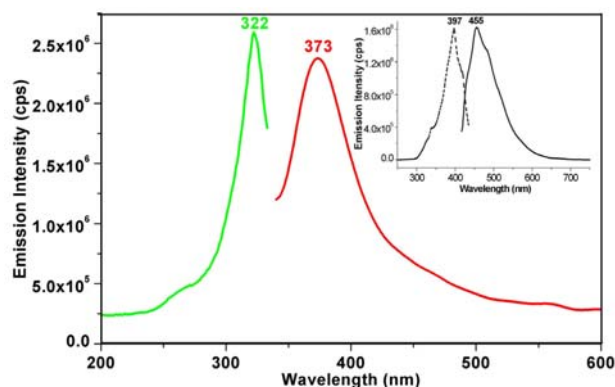
Fig. 4: Solid-state excitation and emission spectra of 1 (inner plot for pure isonicotinic acid). Green line: excitation spectra; red line: emission spectra.

nm possesses one main band at 393 nm and two smaller bands of 362 nm and 383 nm. For complex **2**, the photoluminescent spectra display several emission bands under the excitation of 393 nm. The bands at 561 nm, 593 nm, 643 nm and 699 nm correspond to the characteristic emissions of $^4G_{5/2} \rightarrow ^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) of Sm^{3+} ions.[21–23] This indicates that effective energy transfer took place and that conjugated systems formed between the ligands and the chelated Sm^{3+} ions in **2**. Among the characteristic emissions of Sm^{3+} ions, the yellow emission intensity of $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition is stronger than other emissions, suggesting that nicotinic acid is more suitable for the sensitization of yellow luminescence of Sm^{3+}. The existence of the characteristic emission bands of Sm^{3+} ions suggests that the intramolecular energy transfer process exist between the triplet state of nicotinic acid ligand to the resonant emissive energy level of Sm^{3+} ion, i.e. "antenna effect".[24–25]
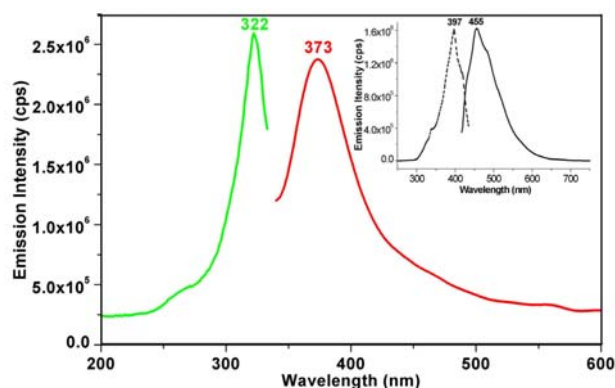

Fig. 5: Solid-state excitation and emission spectra of **2**. Green line: excitation spectra; red line: emission spectra.

Although both complexes have similar structures and ligands, their photoluminescence are very different. The reason is following. Firstly, both complexes have different Ln ions, i.e. Nd^{3+} and Sm^{3+} for **1** and **2**, respectively.

Both ions have totally different photoluminescent activities. As we know, Nd^{3+} is luminescent inactive, while Sm^{3+} is luminescent active. Secondly, when the lowest triplet state energy level of the ligand matches well to the resonance level of the Ln^{3+} ions, a characteristic photoluminescent emission of Ln^{3+} ions can be obtained. That depends on i) the energy differences between the lowest triplet state of the ligand and the resonant energy levels of Ln^{3+}; and ii) the intramolecular energy migration efficiency.[26–30] Therefore, the different photoluminescent behaviors of complexes **1** and **2** are reasonable.

4. Conclusion

We have synthesized and characterized two new 4f-3d heterometallic complexes. The crystal structures of the title complexes feature a one-dimensional polycationic infinite chain-like structure. The title complexes display totally different photoluminescent emissions. The emission of **1** originates from to the $\pi \rightarrow \pi^*$ charge-transfer interaction of the ligand, while that of **2** results from the characteristic emissions of $^4G_{5/2} \rightarrow ^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) of Sm^{3+} ions. Both complexes show strong photoluminescent emission bands, and they are potential luminescent materials.

5. Acknowledgements

6. Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. **7**43487 and 743488 for **1** and **2,** respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www. ccdc.cam.ac.uk).

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Povzetek

Heterometalna kompleksa 4f-3d $\{[Nd(L)_3(H_2O)_2]_2(ZnCl_4)_3\}_n \cdot 4nH_2O$ (**1**) (L = izonikotinska kislina) in $\{[Sm(L')_3(H_2O)_2]_2(ZnCl_4)\}_n \cdot 2nH_2O$ (**2**) (L' = nikotinska kislina) smo pripravili s hidrotermalno reakcijo in strukturno karakterizirali z rentgensko difrakcijo na monokristalih.

Oba kompleksa sta sestavljena iz neskončnih 1-D polikationskih verižnih struktur. Raziskave fotoluminiscence so pokazale, da imata kompleksa drugačna emisijska spektra. Pri kompleksu **1** gre za prehod s prenosom naboja $\pi \rightarrow \pi^*$ izonikotinske kisline, pri kompleksu **2** pa gre za karkateristične emisije $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) Sm^{3+} ionov.