

An Unprecedented 2D 4f-3d-5d Multimetal-Isonicotinic Acid Complex: Synthesis, Structural Characterization and Magnetic Properties

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A novel heterometallic metal-isonicotinic acid inorganic-organic hybrid complex $[Zn_{0.5}(H_2O)]\{(Hg_2Cl_5)[Er(C_6NO_2H_4)_3(H_2O)_2]\}(HgCl_2)\cdot 0.5CH_3OH\cdot 0.5H_2O$ (**1**) has been successfully synthesized via a hydrothermal reaction and structurally characterized by single-crystal X-ray diffraction. Complex **1** crystallizes in the space group $C2/c$ of the monoclinic system with eight formula units in a cell: $a=34.165(4)$ Å, $b=9.4692(8)$ Å, $c=24.575(3)$ Å, $\beta=115.090(5)^\circ$, $V=7200(1)$ Å³, $C_{18.50}H_{21}Cl_7ErHg_3N_3O_{10}Zn_{0.50}$, $M_r=1495.25$, $D_c=2.759$ g/cm³, $T=293(2)$ K, $\mu(Mo\ K\alpha)=15.954$ mm⁻¹, $F(000)=5400$ and $R_1/wR_2=0.0561/0.0909$ for 3157 observed reflections [$I>2\sigma(I)$] and 6468 unique reflections. Complex **1** is characteristic of a novel 2D $\{(Hg_2Cl_5)[Er(C_6NO_2H_4)_3(H_2O)_2]\}$ layered structure constructed from the $[Er(C_6NO_2H_4)_3(H_2O)_2]$ chains interconnected by the $Hg_2Cl_5^-$ linkers. The 2D $\{(Hg_2Cl_5)[Er(C_6NO_2H_4)_3(H_2O)_2]\}$ layers, mercury chloride and the lattice water molecules are held together via hydrogen bonds to form a three-dimensional framework with the methanol molecules and the hydrated zinc ions located in the cavities. The magnetic properties show that complex **1** exhibits antiferromagnetic-like interactions.

Keywords crystal structure, erbium, isonicotinic acid, lanthanide, magnetic, mercury, zinc

Introduction

Currently, the increasing interest in the field of the crystal engineering of inorganic-organic hybrid materials is justified by the potential applications of these materials as catalysts, zeolite-like materials, biological materials, magnetic functional materials, and so on.¹ There is also an aesthetic perspective: for the vast amount of inorganic-organic hybrid materials, the intriguing varieties of the architectures and topologies that can be obtained by self-assembling metal ions and multifunctional ligands attract chemists. In recent years, although the synthesis of inorganic-organic hybrid materials based on transition metals has become widespread,² there are relatively few reports on lanthanide-based inorganic-organic hybrid materials despite their potential applications to luminescence and other fields.³ To our knowledge, lanthanide-based inorganic-organic hybrid materials with aromatic carboxylic acids exhibit good thermal and luminescent stability for practical application. Moreover, transition metal 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, the well-known

toxicity of cadmium and mercury, semiconductive properties, and the essential role in biological systems of zinc, and so forth. Besides, LN-TM-based (LN=lanthanide, TM=transition metal) inorganic-organic hybrid materials with aromatic carboxylic acids as ligands maybe have novel structural topologies and properties, such as luminescence, semiconductivity, magnetism, electro- and photochemistry, catalysis, thermochromism and so forth. Furthermore, the isonicotinate anion is a quite interesting tecton in constructing extended structures because it is an unsymmetrical divergent ligand with one nitrogen atom at one end and two oxygen atoms from the carboxylato group at the other one. The isonicotinate anion can link two metal centers by coordinating to a metal center with the nitrogen atom and, to the other one, with one or two carboxylato oxygen atoms.⁴ Therefore, our group recently become interested in the crystal engineering of LN-TM-based inorganic-organic hybrid materials with isonicotinic acid as ligands. In this paper, we report the synthesis, crystal structure and magnetic properties of $[Zn_{0.5}(H_2O)]\{(Hg_2Cl_5)[Er(C_6NO_2H_4)_3(H_2O)_2]\}(HgCl_2)\cdot 0.5CH_3OH\cdot 0.5H_2O$ (**1**) with a novel two-dimensional layered structure.

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Experimental

Materials and methods

All reactants of A.R. grade were obtained commercially and used without further purification. Infrared spectra were obtained with a PE Spectrum-One FT-IR spectrometer using KBr discs. Variable-temperature magnetic susceptibility measurement of the title complex on polycrystalline samples was performed on a PPMS 9T Quantum Design SQUID magnetometer. All data were corrected for diamagnetism estimated from Pascal's constants.

Synthesis of the title complex

The title complex was prepared by mixing $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.383 g), HgCl_2 (1 mmol, 0.272 g), ZnCl_2 (1 mmol, 0.136 g), isonicotinic acid (1 mmol, 0.123 g), 2 mL of methanol and 10 mL of distilled water in a 25 mL Teflon-lined stainless steel autoclave and heating the mixture at 200 °C for 10 d. After cooling slowly the mixture to room temperature at 6 °C/h, colorless crystals suitable for X-ray analysis were obtained. The yield was 82% (based on erbium). IR (KBr) ν : 3534 (s), 3435 (vs), 3215 (w), 3152 (m), 3081 (s), 1694 (w), 1588 (vs), 1411 (vs), 1226 (m), 851 (m), 759 (s) and 681 (s) cm^{-1} .

Single crystal X-ray diffraction

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 an ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections.⁵ The structure was solved by the direct method using the Siemens SHELXTLTM Version 5 package of crystallographic software.⁶ 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 summarized in Table 1. Selected bonded lengths and angles are listed in Table 2.

Results and discussion

X-ray diffraction analysis reveals that the structure of the title complex consists of anionic $\{(\text{Hg}_2\text{Cl}_5)-[\text{Er}(\text{C}_6\text{NO}_2\text{H}_4)_3(\text{H}_2\text{O})_2]\}$ 2D layers, mercury chloride, lattice water molecules, methanol molecules and hydrated zinc cations, as shown in Figure 1. All the crystallographically independent atoms are in general positions except for Er(1), Er(2) and Zn(1) atoms. There

Table 1 Crystal data and structure refinement details for the title complex

Formula	$\text{C}_{18.50}\text{H}_{21}\text{Cl}_7\text{ErHg}_3\text{N}_3\text{O}_{10}\text{Zn}_{0.50}$
M_r	1495.25
Color	colorless
Crystal size/ mm^3	$0.33 \times 0.20 \times 0.12$
Crystal system	Monoclinic
Space group	$C2/c$
$a/\text{Å}$	34.165(4)
$b/\text{Å}$	9.4692(8)
$c/\text{Å}$	24.575(3)
$\beta/(\text{°})$	115.090(5)
$V/\text{Å}^3$	7200(1)
Z	8
$2\theta_{\text{max}}/(\text{°})$	50.70
Reflections collected	22737
Independent, observed reflections (R_{int})	6468, 3157 (0.0723)
$d_{\text{calcd.}}/(\text{g}\cdot\text{cm}^{-3})$	2.759
μ/mm^{-1}	15.954
T/K	293(2)
$F(000)$	5400
R_1, wR_2	0.0561, 0.0909
S	0.985
Largest and mean Δ/σ	0.002, 0
$\Delta\rho(\text{max/min})/(\text{e}\cdot\text{Å}^{-3})$	4.456/−3.663

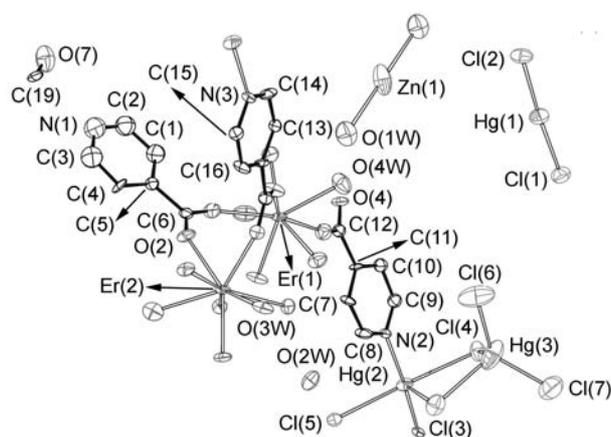


Figure 1 ORTEP-plot of **1** with 40% thermal ellipsoids where hydrogen atoms are omitted for clarity.

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 [$\text{Cl}(1)\text{-Hg}(1)\text{-Cl}(2)=175.96(4)^\circ$], which is comparable with that of isolated HgCl_2 moieties in the literature.⁷ The bond lengths of $\text{Hg}(1)\text{-Cl}(1)$ and $\text{Hg}(1)\text{-Cl}(2)$ are 2.287(1) and

Table 2 Selected bond lengths (Å) and bond angles (°) for the title complex^a

Hg(1)—Cl(1)	2.287(1)	Cl(6)—Hg(3)—Cl(3)	107.19(5)
Hg(1)—Cl(2)	2.306(1)	Cl(4)—Hg(3)—Cl(3)	94.46(3)
Hg(2)—N(2)	2.139(3)	O(3)—Er(1)—O(3)#2	98.0(1)
Hg(2)—N(3)#1	2.158(3)	O(3)—Er(1)—O(5)	140.64(9)×2
Hg(2)—Cl(3)	2.816(1)	O(3)#2—Er(1)—O(5)	81.20(9)×2
Hg(2)—Cl(4)	2.883(1)	O(5)#2—Er(1)—O(5)	123.6(1)
Hg(2)—Cl(5)	2.857(1)	O(3)—Er(1)—O(1)	145.15(8)×2
Hg(3)—Cl(3)	2.683(1)	O(3)#2—Er(1)—O(1)	80.2(1)×2
Hg(3)—Cl(4)	2.553(1)	O(5)#2—Er(1)—O(1)	79.0(1)×2
Hg(3)—Cl(6)	2.375(2)	O(5)—Er(1)—O(1)	73.89(9)×2
Hg(3)—Cl(7)	2.338(2)	O(1)#2—Er(1)—O(1)	120.6(1)
Er(1)—O(1)	2.317(3)×2	O(3)—Er(1)—O(4W)	70.56(9)×2
Er(1)—O(3)	2.235(3)×2	O(3)#2—Er(1)—O(4W)	74.6(1)×2
Er(1)—O(5)	2.295(2)×2	O(5)#2—Er(1)—O(4W)	138.6(1)×2
Er(1)—O(4W)	2.462(3)×2	O(5)—Er(1)—O(4W)	71.37(9)×2
Er(2)—O(2)	2.358(3)×2	O(1)#2—Er(1)—O(4W)	72.00(9)×2
Er(2)—O(4)#3	2.259(3)×2	O(1)—Er(1)—O(4W)	139.5(1)×2
Er(2)—O(6)	2.291(2)×2	O(4W)#2—Er(1)—O(4W)	125.8(1)
Er(2)—O(3W)	2.457(3)×2	O(4)#3—Er(2)—O(4)#4	103.4(1)
Zn(1)—O(1W)	2.284(3)×2	O(4)#3—Er(2)—O(6)#2	144.60(9)×2
Cl(1)—Hg(1)—Cl(2)	175.96(4)	O(4)#3—Er(2)—O(6)	80.12(8)×2
N(2)—Hg(2)—N(3)#1	170.57(9)	O(6)#2—Er(2)—O(6)	117.4(1)
N(2)—Hg(2)—Cl(3)	86.53(7)	O(4)#3—Er(2)—O(2)#2	143.04(8)×2
N(3)#1—Hg(2)—Cl(3)	102.84(7)	O(4)#3—Er(2)—O(2)	77.54(9)×2
N(2)—Hg(2)—Cl(5)	88.65(7)	O(6)#2—Er(2)—O(2)	79.29(9)×2
N(3)#1—Hg(2)—Cl(5)	90.42(7)	O(6)—Er(2)—O(2)	72.35(8)×2
Cl(3)—Hg(2)—Cl(5)	88.77(3)	O(2)#2—Er(2)—O(2)	123.8(1)
N(2)—Hg(2)—Cl(4)	90.46(7)	O(4)#3—Er(2)—O(3W)	73.4(1)×2
N(3)#1—Hg(2)—Cl(4)	91.49(7)	O(6)—Er(2)—O(3W)	75.20(8)×2
Cl(3)—Hg(2)—Cl(4)	84.85(3)	O(2)#2—Er(2)—O(3W)	71.88(9)×2
Cl(5)—Hg(2)—Cl(4)	173.60(3)	O(2)—Er(2)—O(3W)	139.37(8)×2
Cl(7)—Hg(3)—Cl(6)	128.10(5)	O(4)#3—Er(2)—O(3W)#2	72.35(8)×2
Cl(7)—Hg(3)—Cl(4)	102.20(5)	O(6)—Er(2)—O(3W)#2	138.6(1)×2
Cl(6)—Hg(3)—Cl(4)	111.43(5)	O(3W)—Er(2)—O(3W)#2	123.2(1)
Cl(7)—Hg(3)—Cl(3)	108.32(5)	O(1W)—Zn(1)—O(1W)#5	180.000(1)

^a 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 $-x+1/2, -y+3/2, -z+1$.

2.306(1) Å, which are comparable with their counterparts in the reference.^{7,8} 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 N(2), Cl(5), N(3)($x-1/2, y-1/2, z$), 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 2.816(1), 2.883(1) and 2.857(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 2.683(1), 2.553(1), 2.375(2) and 2.338(2) Å, respectively. Obvi-

ously, 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)-centered HgCl₃N₂ square pyramid and the Hg(3)-centered HgCl₄ tetrahedron edge-share the μ_2 -Cl(3) and μ_2 -Cl(4) atoms to form a Hg₂N₂Cl₅ moiety. The Zn²⁺ ion is hydrated by two water molecules with the bond length of Zn(1)—O(1W) being 2.284(3) Å and the O(1W)—Zn(1)—O(1W)($-x+1/2, -y+3/2, -z+1$) being 180°, respectively.⁹ There are two crystallographically independent erbium atoms and the occupancy of them must be set to 0.5 to get a rational struc-

ture model and thermal displacement parameters. Both of the erbium atoms are in eight coordination environments. The Er(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(1), O(5), O(1)($-x, y, -z+1/2$), O(5)($-x, y, -z+1/2$) and O(4W)($-x, y, -z+1/2$), O(3)($-x, y, -z+1/2$), O(4W), O(3) atoms, respectively. Similarly, the Er(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(3W), O(4)($x, y+1, z$), O(3W)($-x, y, -z+1/2$), O(4)($-x, 1+y, -z+1/2$) and O(2), O(6), O(2)($-x, y, -z+1/2$), O(6)($-x, y, -z+1/2$) atoms, respectively. The bond lengths of Er—O_{isonicotinic acid} range from 2.235(3) to 2.358(3) Å with an average value of 2.293(3) Å, which is obviously shorter than that of Er—O_{water} being 2.462(3) and 2.457(3) Å, indicating that the isonicotinic acid ligand has a stronger affinity to Er^{III} ion than that of water. The erbium 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 1D chain running along the axis *b* with the Er...Er distances of *ca.* 5.043 and 4.426 Å, respectively (Figure 2 and Scheme 1d). It is noteworthy that, up to date, the types of the chains formed by LN and isonicotinic acid that have been documented are mainly 1-1-1, 2-1-2 and 2-2-2 types (Schemes 1a, 1b and 1c, respectively). However, the 2-4-2 type is very rare. In **1**, no $\pi\cdots\pi$ stacking interactions are established between the adjacent isonicotinato ligands. The 1D chains are interconnected together by the Hg₂Cl₅ linkers via Hg—N bonds, yielding a 2D layer extending along the *ab* directions (Figure 3). The 2D layers, mercury chloride and the lattice water molecules are held together via hydrogen bonds to form a three-dimensional framework with the methanol molecules and the hydrated zinc ions located in the cavities, as shown in Figure 4.

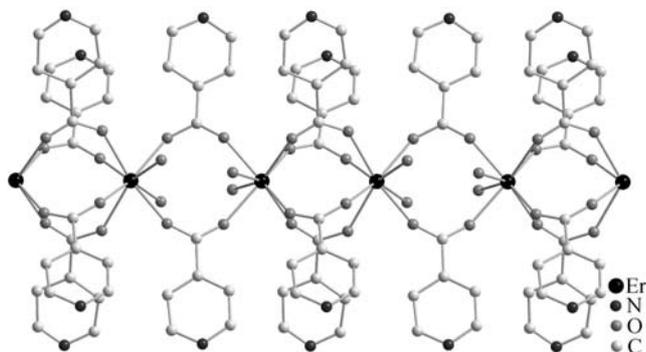


Figure 2 1D chain running along the axis *b*.

The magnetic susceptibility of **1** was investigated from 300 to 5 K at 5000 Oe on the polycrystalline samples (Figure 5). When decreasing the temperature, the $x_M T$ of **1** decreased gradually from 11.38 cm³·K·

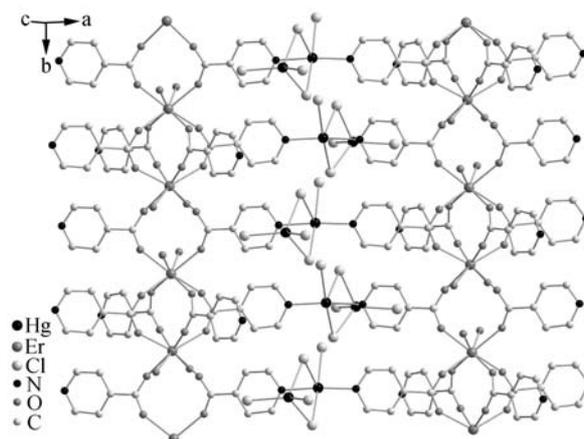


Figure 3 A 2D layer constructed from the chains interconnected by the Hg₂Cl₅ linkers.

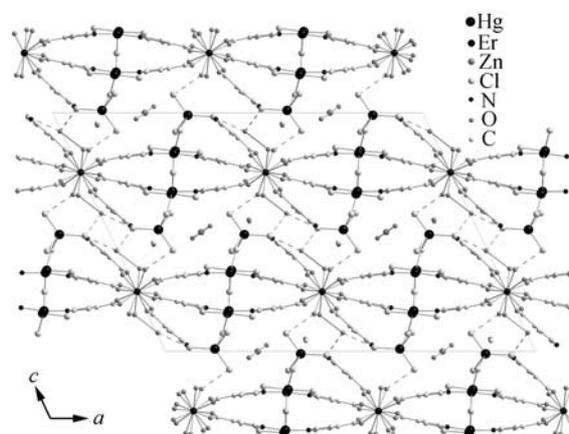
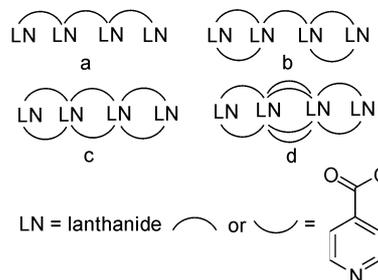


Figure 4 Packing diagram of **1** with the dashed lines representing hydrogen bonds (Å): O(2W)···Cl(6)($x, 1+y, z$) 3.218(6), O(2W)···Cl(6)($-x, 2-y, 1-z$) 3.051(4), O(2W)···O(3W) 2.884(7) and O(4W)···Cl(7)($-x, 1-y, 1-z$) 3.172(3).

Scheme 1 Important chain-like structural types of isonicotinic acid bridging LN centers: (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



mol⁻¹ at 300 K to reach 10.58 cm³·K·mol⁻¹ at about 50 K. On further cooling, $x_M T$ decreased rapidly to about 8.58 cm³·K·mol⁻¹ at 5 K. This behavior is typically observed for paramagnetic systems that exhibit dominating antiferromagnetic interactions. Curve fit for x_M versus *T* plot of **1** with the Curie-Weiss law in the whole range of 5–300 K gave good result with $C=11.12$ cm³·K·mol⁻¹ and $\theta=-1.68$ K for **1**. The small negative Weiss constant suggests weak antiferromagnetic-like interactions

between the Er^{3+} ions. Further analysis of the magnetic data will be carried out later when some suitable model is found to fit the data. The field dependence of the magnetization for **1** measured at 2 K reveals a hysteresis loop with a coercive field of *ca.* 36 Oe and remnant magnetization of *ca.* $6 \times 10^{-3} N\beta$, suggesting the paramagnetic behavior of **1** (Figure 6). The magnetization increased fast with increasing field first, and then slowly. Obviously, the magnetization of **1** still did not reach saturation at 80 kOe with a value of $2.56 N\beta$.

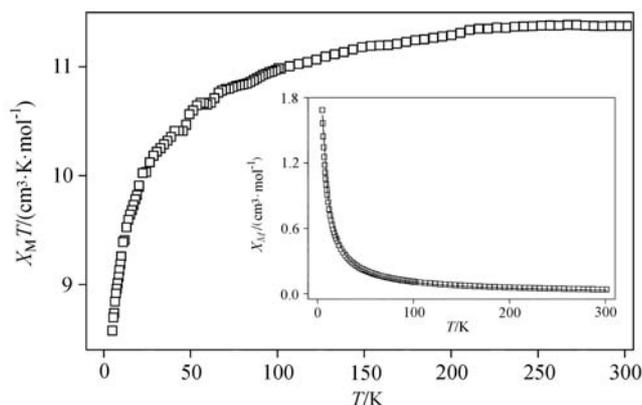


Figure 5 A graph of χ_M and $\chi_M T$ vs. T of **1**. The full line corresponds to the best data fit.

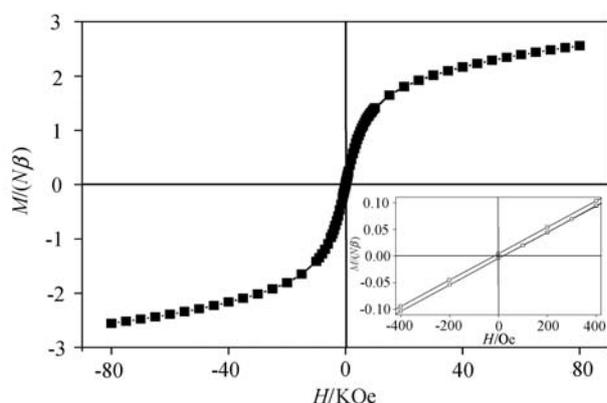


Figure 6 Magnetization vs. H at 2 K for **1**. Inset: Expansion showing the small coercivity.

Conclusion

In conclusion, we successfully prepared a 4f-3d-5d multimetal-isonicotinic acid inorganic-organic hybrid complex via a hydrothermal reaction. The crystal structure of the title complex is characterized by a two-dimensional layered structure. The magnetic properties showed that the title complex exhibited antiferromagnetic-like interactions. It was believed that more and more LN-TM-based inorganic-organic hybrid complexes with good properties could be developed.

Supplementary material

Crystallographic data for the structure reported in

this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 656029. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (0044) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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