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Synthesis and crystal structure of new lanthanide coordination polymers with Pyridine-2, 6-dicarboxylic acid

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ABSTRACT

Reactions between $Ln(NO_3)_3$ aq (Ln = La (1), Ce (2), Pr (3) and Nd(4)), pyridine-2, 6-dicarboxylic acid (2, 6-pdc), and sodium nitroprusside $Na_2[Fe(CN)_5NO]$ lead to three-dimensional network structures: $\{[Ln_2(2,6\text{-pdc})_2(H_2O)_8][Fe(CN)_5NO]\cdot 4H_2O\}_n$ (Ln = La (1), Ce (2), Pr (3) and Nd(4)). The complexes **1** and **2** crystallize in the monoclinic space group *Cc* while complexes **3** and **4** crystallize in the monoclinic space group *I*2. The Ln(III) ion is nine-coordinate by four oxygen atoms of three 2, 6-pdc ligands, four oxygen of water and one nitrogen atom of 2, 6-pdc. Ln(III) ions are bridged by 2, 6-pdc ligands *via* bridging/chelating-bridging pentadentate coordination to form 3-D framework structures. Hydrogen bonds provide additional stabilization of the crystal structures. The magnetic properties of **2-4** have been investigated.

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1. Introduction

Polynuclear complexes containing both 4f and 3d ions have attracted increasing attention in view of their magnetic properties [1–5]. Recently, several rare-earth and polycyanometalates(III) complexes with differing dimensionality have been reported and subjected to single-crystal X-ray and magnetic susceptibility measurements, such as (i) dinuclear complexes [6–8]; (ii) trinuclear complexes [9]; (iii) tetranuclear complexes [10,11]; (iv) serials one-dimensional complexes [12–16]; (v) two-dimensional complexes [17,18] and (vi) three-dimensional complexes [19,20]. In most cases the magnetic properties of these complexes do not seem exciting, as the coupling between the lanthanide and transition metals is very weak because of the effective shielding of the 4f electrons by the outer-shell electrons. Most complexes have been obtained by using DMF (N, N-dimethylformamide), DMSO (dimethylsulfoxide), 1, 10-phenanthroline, 2, 2′-bipydine, 4, 4-bipyridine-*N*, *N*′-dioxide as a building ligand. Surprisingly, in comparison with these ligands, the potentialities of carboxylate in the construction of coordination networks and crystal engineering have been little exploited. Pyridine-2, 6-dicarboxylic acid (2, 6-$pdcH_2$), a multidentate organic ligand with relatively high coordination numbers and versatile coordination behaviors (Scheme 1) has been selected to construct lanthanide coordination polymers [21–25]. In this paper, we report the synthesis, structural characterization and magnetic properties study of the four lanthanide coordination polymers with 2, 6-pdc:$\{[Ln_2(2,6\text{-pdc})_2(H_2O)_8][Fe(CN)_5NO]\cdot 4H_2O\}_n$, (Ln = La (**1**), Ce (**2**), Pr (**3**) and Nd(4)) ($[Ln2Fe]_n$).

2. Experimental section

2.1. General considerations

All chemicals purchased were of reagent grade and used without further purification. C, H, N elemental analyses were performed on Perkin–Elmer 240c elemental analyzer. Infrared spectra were recorded as KBr pellets on a Nicolet 170SFT/IR spectrometer. The magnetic susceptibility data were recorded over the 2–300 K temperature range using a Quantum Design MPMS-5S SQUID susceptometer. The experimental susceptibilities were corrected for the sample holder and the diamagnetism contributions estimated from Pascal's constants.

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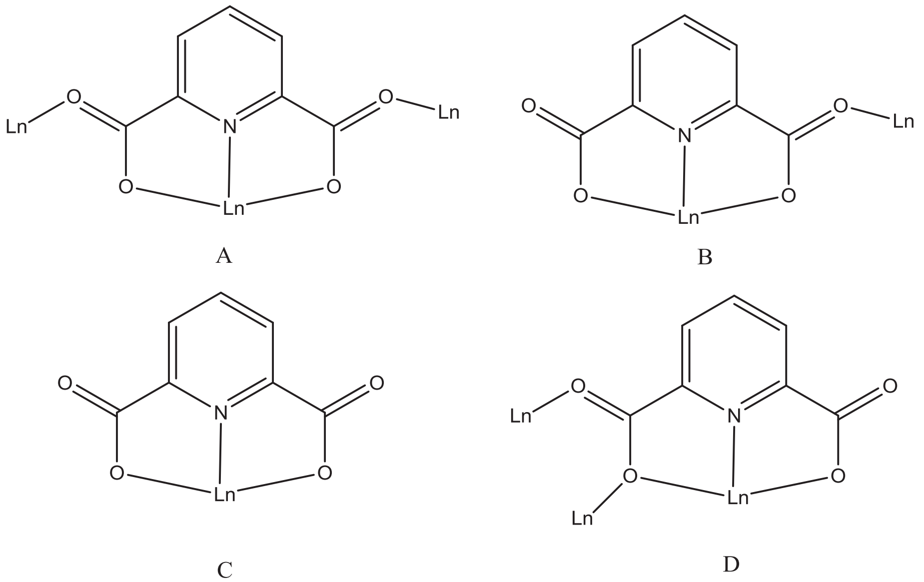

Scheme 1. The coordination mode of 2, 6-pdc ligands in lanthanide compounds.

2.2. Synthesis

The four $[Ln2Fe]_n$ coordination polymers were obtained by adding a solution of $Ln(NO_3)_3.nH_2O$ ($n = 5, 6$) (0.5 mmol) in water (5 mL) to an equimolar solution of $Na_2[Fe(CN)_5NO]$ in water (5 mL). To this mixture a methanolic solution (5 mL) of 2, 6-pdcH_2 (1.1 mmol) was added. The solution was left undisturbed, and well-formed nacarat crystals were obtained after several days in 35–58% yield based on $Ln(NO_3)_3$. Anal. Calcd for **1**, $C_{19}H_{30}FeLa_2N_8O_{21}$: C, 21.9; H, 2.9; N, 10.8. Found: C, 21.7; N, 10.5; H, 3.0; IR (cm^{-1}, KBr): $\nu_{C\equiv N}$2141(s), 1914(vs), $\nu_{C=O}$1612 (s), 1601 (s), 1581 (s). Anal. Calcd for **2**, $C_{19}H_{30}Ce_2FeN_8O_{21}$: C, 21.9; H, 2.9; N, 10.7. Found: C, 21.6; N, 10.8; H, 3.1; IR (cm^{-1}, KBr): $\nu_{C\equiv N}$ 2141(s), 1914(vs), $\nu_{C=O}$ 1619(s), 1602 (s), 1580 (s). Calcd for **3**, $C_{19}H_{30}FeN_8O_{21}Pr_2$: C, 21.8; H, 2.9; N, 10.7. Found: C, 21.9; N, 10.9; H, 3.0; IR (cm^{-1}, KBr): $\nu_{C\equiv N}$ 2141(s), 1913(vs), $\nu_{C=O}$ 1615(s), 1602 (s), 1582 (s). Calcd for **4**, $C_{19}H_{30}FeN_8Nd_2O_{21}$: C, 21.7; H, 2.9; N, 10.6. Found: C, 21.8; N, 10.7; H, 3.0; IR (cm^{-1}, KBr): $\nu_{C\equiv N}$ 2141(s), 1913(vs), $\nu_{C=O}$ 1618(s), 1600 (s), 1579 (s).

2.3. Crystallographic studies

Single-crystal X-ray data for four $[Ln2Fe]_n$ Coordination polymers were collected on a Bruker Apex SMART CCD system equipped with Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. The four structures were solved by direct methods and

Table 1
Crystal data and structure refinement of **1-4** compounds.

Compounds	1	2	3	4
Empirical formula	$C_{19}H_{30}FeLa_2N_8O_{21}$	$C_{19}H_{30}Ce_2FeN_8O_{21}$	$C_{19}H_{30}FeN_8O_{21}Pr_2$	$C_{19}H_{30}FeN_8Nd_2O_{21}$
Formula weight	1040.18	1042.6	1044.18	1050.84
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	*Cc*	*Cc*	*I2*	*I2*
a/Å	17.755(2)	17.629(2)	13.976(3)	13.936(1)
α	90	90	90	90
b/Å	19.838(3)	19.797(3)	13.976(3)	13.936(3)
β	131.834(1)	131.700(1)	90.00(3)	90
c/Å	13.311(2)	13.257(2)	17.531(4)	17.469(2)
γ	90	90	90	90
Volume/$Å^3$	3493.3(8)	3454.3(8)	3424.3(12)	3392.7(5)
Z	4	4	4	4
Calculated density/Mg/m^3	1.978	2.005	2.025	2.057
Absorption coefficient/mm^{-1}	2.905	3.099	3.314	3.533
F(000)	2032	2040	2048	2056
Reflections collected/unique	14587/7583	12977/6304	7839/5626	14147/7764
R(int)	0.0169	0.0157	0.0276	0.0248
Goodness-of-fit on F^2	1.025	1.054	1.031	1.017
Final Rindices[$I > 2\sigma(I)$]	$R1 = 0.0227$, $wR2 = 0.0563$	$R1 = 0.0185$,$wR2 = 0.0449$	$R1 = 0.0285$,$wR2 = 0.0694$	$R1 = 0.0225$,$wR2 = 0.0434$
Rindices(all data)	$R1 = 0.0244$,$wR2 = 0.0575$	$R1 = 0.0201$,$wR2 = 0.0458$	$R1 = 0.0324$,$wR2 = 0.0713$	$R1 = 0.0262$,$wR2 = 0.0445$

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