

Synthesis and Crystal Structure of $[\text{Nd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_n n[\text{ZnCl}_4] \cdot n\text{Cl} \cdot 2.5n\text{H}_2\text{O}$ with Novel Poly-Cationic Chain

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(Received 17 August 2007, Accepted 24 November 2007)

The title complex, $[\text{Nd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_n n[\text{ZnCl}_4] \cdot n\text{Cl} \cdot 2.5n\text{H}_2\text{O}$ (**1**), was obtained by hydrothermal reactions and structurally characterized by X-ray diffraction. The crystal structure analysis reveals that the title complex is characteristic of a novel poly-cationic $[\text{Nd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_n^{3n+}$ one-dimensional chain-like structure.

Keywords: Crystal structure, Neodymium, Hydrothermal reaction, Nicotinic acid, Rare earth

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 to the fields of catalysis, zeolite-like materials, biology, magnetic functional materials, and so on [1-4]. As 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 has attracted chemists. In recent years, although the synthesis of inorganic-organic hybrid materials based on transition metals has become widespread [5-11], there are relatively few reports on lanthanide-based inorganic-organic hybrid materials despite their potential applications in luminescence and other fields [12]. To our knowledge, lanthanide-based inorganic-organic hybrid materials with aromatic carboxylic acids exhibit good thermal and luminescent stability for practical application. Furthermore, LN-TM-based (LN = lanthanide, TM = transition metal)

inorganic-organic hybrid materials with aromatic carboxylic acids as ligands may have novel structural topologies and properties. Therefore, our group has recently become interested in the crystal engineering of LN-TM-based inorganic-organic hybrid materials with nicotinic acid as ligand. In this paper, we reported the synthesis and crystal structure of $[\text{Nd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_n n[\text{ZnCl}_4] \cdot n\text{Cl} \cdot 2.5n\text{H}_2\text{O}$ (**1**), which possesses a novel poly-cationic one-dimensional chain-like structure.

EXPERIMENTAL

Chemicals and Instrumentation

All reactants of A.R. grade were obtained commercially and used without further purification.

X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using a ω scan technique. The CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software. The difference Fourier

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maps based on the atomic positions yield all non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2 . All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms 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.

Synthesis

The title $[\text{Nd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_n n[\text{ZnCl}_4] \cdot n\text{Cl} \cdot 2.5n\text{H}_2\text{O}$ complex was prepared by mixing $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 359 mg), ZnCl_2 (1 mmol, 136 mg), nicotinic acid (1 mmol, 123 mg)

and 10 ml distilled water in a 25 ml Teflon-lined stainless steel autoclave and heated at 150 °C for 7 days. After being slowly cooled to room temperature at 6 °C h⁻¹, colorless crystals were obtained. The yield was 78% (based on neodymium). Although we tried our best, no high quality single crystals suitable for X-ray analysis can be obtained.

RESULTS AND DISCUSSION

An ORTEP drawing of **1** is shown in Fig. 1. The structure of **1** consists of $[\text{Nd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]^{3+}$ poly-cationic chains, ZnCl_4^{2-} and Cl^- anions, and isolated water molecules. All the crystallographic independent atoms are in the general positions. The Zn atom is tetrahedrally bounded by four chlorine atoms to form a ZnCl_4^{2-} anion with the bond lengths

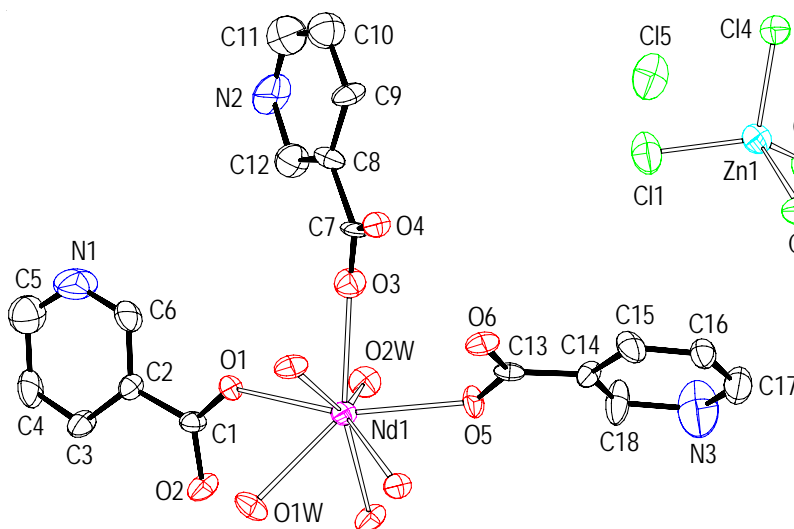
Table 1. Crystal Data of $[\text{Nd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_n n[\text{ZnCl}_4] \cdot n\text{Cl} \cdot 2.5n\text{H}_2\text{O}$

Empirical formula	$\text{C}_{18}\text{H}_{24}\text{Cl}_5\text{N}_3\text{NdO}_{10.5}\text{Zn}$
Formula weight	837.26
X-rays	MoK α
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 9.579(10) \text{ \AA}$ $b = 20.851(7) \text{ \AA}$ $c = 15.565(7) \text{ \AA}$ $\beta = 101.006(4)^\circ$
Z	4
V	$3052(3) \text{ \AA}^3$
D_x	1.822 mg m^{-3}
Absorption coefficient	2.959 mm^{-1}
Crystal size	$0.20 \times 0.10 \times 0.10 \text{ mm}$
No. of reflections collected/unique	19535/5361 [$R_{\text{int}} = 0.1262$]
Refinement	Full matrix least squares on F^2
Goodness-of-fit on F^2	0.945
Final R indices	$R_1 = 0.0868$, $wR_2 = 0.2096$
R indices (all data)	$R_1 = 0.1767$, $wR_2 = 0.2684$
Index ranges	$-7 \leq h \leq 11$, $-24 \leq k \leq 24$, $-18 \leq l \leq 18$
Measurement	Rigaku Mercury CCD diffractometer
Monochromator	Graphite
Structure determination	Siemens SHELXTL
$(\Delta/\sigma)_{\text{max}}$	0.001

Table 2. Selected Bond Lengths and Bond Angles of **1**

Bond lengths (Å)		Bond angles (°)	
Nd(1)-O(1)	2.416(3)	Cl(1)-Zn(1)-Cl(2)	109.17(7)
Nd(1)-O(2)#1	2.377(3)	Cl(1)-Zn(1)-Cl(3)	114.09(8)
Nd(1)-O(3)	2.428(3)	Cl(1)-Zn(1)-Cl(4)	106.56(7)
Nd(1)-O(4)#2	2.421(3)	Cl(2)-Zn(1)-Cl(3)	104.71(6)
Nd(1)-O(5)	2.450(3)	Cl(2)-Zn(1)-Cl(4)	112.54(7)
Nd(1)-O(6)#2	2.377(3)	Cl(3)-Zn(1)-Cl(4)	109.91(7)
Nd(1)-O(1W)	2.536(3)		
Nd(1)-O(2W)	2.509(3)		
Zn(1)-Cl(1)	2.227(2)		
Zn(1)-Cl(2)	2.2523(18)		
Zn(1)-Cl(3)	2.2556(17)		
Zn(1)-Cl(4)	2.265(2)		

Symmetry code: #1 -x+1, -y, -z+1; #2 -x, -y, -z+1.

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

of Zn-Cl ranging from 2.227(2) to 2.265(2) Å with an average value of 2.250(2) Å, which are comparable with those reported in the literature [13-16]. The neodymium 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, -y, 1-z), O(4)(-x,

-y, 1-z) and O(2W), O(1), O(1W), O(2)(1-x, -y, 1-z) atoms, respectively. The bond lengths of Nd-O_{nicotinato} range from 2.377(3) to 2.450(3) Å with an average value of 2.412(3) Å, which is obviously shorter than that of Nd-O_{water} being of 2.509(3) and 2.536(3) Å, indicating that nicotinato ligand has a stronger affinity to Nd(III) ion than that of water. All three crystallographic independent nicotinic acid ligands act as

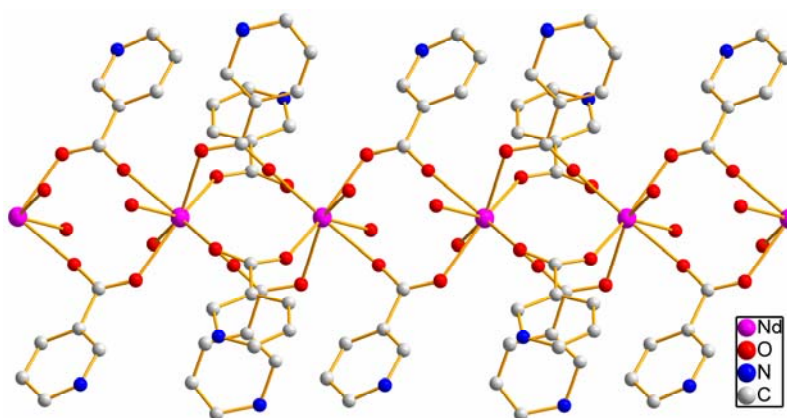
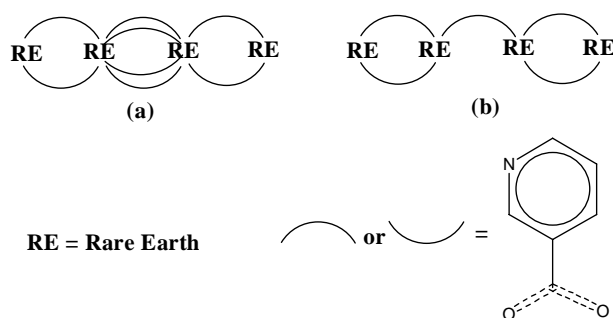


Fig. 2. The 1D poly-cationic chain-like structure of **1**.



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

bidentate ligands to bridge two neighbouring neodymium atoms and the nitrogen atoms of the nicotinic acid ligands should be protonated, as the case found in many other references [17-21]. The neodymium 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 Nd...Nd distances being *ca.* 5.211 and 4.433 Å, respectively (Fig. 2 and Scheme 1a). It is noteworthy that, up to date, the type of the chains formed by RE and nicotinic acid that has been documented is only 2-1-2 type (Scheme 1b) [22]. Therefore, the 2-4-2 type is unprecedented in the complexes containing both RE and nicotinic acid. In **1**, no $\pi \dots \pi$ stacking interactions was established between the adjacent nicotinato ligands. The 1D poly-cationic $[\text{Nd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]^{3+}$ chains, ZnCl_4^{2-} moieties and water molecules are linked by hydrogen bonds to

yield a 3D supramolecular network with the Cl^- anions and the lattice water molecules located in the cavities (Fig. 3). Results of the bond valence calculations indicate that the neodymium and zinc atoms are in +3 and +2 oxidation states, respectively (Nd1: 3.38, Zn1: 2.09) [23,24].

It is noteworthy that, to our knowledge, although many TM-nicotinic acid complexes have been synthesized, LN-nicotinic acid complexes are relatively rare. Especially, LN-TM-nicotinic acid complexes are only three, one of which is the 1D chain-like structure as the above mentioned 2-1-2 type (Scheme 1b) [22].

In conclusion, we have successfully prepared a novel metal-nicotinato complex via hydrothermal reaction. The crystal structure of the title complex is characterized by an unprecedented one-dimensional poly-cationic chain-like structure. It is believed that more and more novel metal-

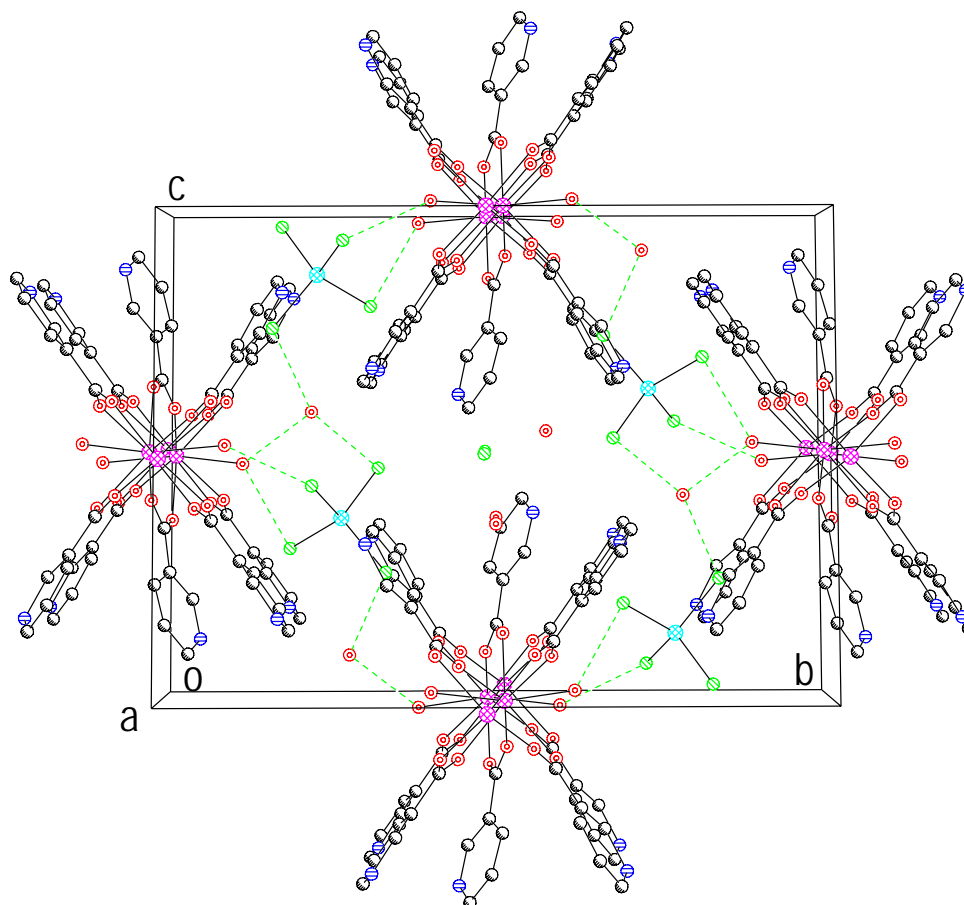


Fig. 3. Crystal packing of **1** with the dashed lines representing hydrogen bonds (Å): O1W...Cl4(x, -1+y, z) 3.155(3), O2W...Cl3(1-x, 1-y, 1-z) 3.159(4), O2W...O5W 2.740(6), O5W...Cl1(1-x, 1-y, 1-z) 3.010(6) and O5W...Cl2(1-x, -0.5+y, 1.5-z) 3.194(5).

nicotinato complexes can be developed.

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 657137. 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).

ACKNOWLEDGMENTS

We are grateful to the doctor scientific research start-up

foundation of Jinggangshan University, China.

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