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Synthesis, structure and properties of $[Pr(C_6H_5NO_2)_3(H_2O)_2]_{2n}\cdot(nH_5O_2)(nHgCl_5)(2nHgCl_4)\cdot(2nH_2O)$

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ABSTRACT

A new complex $[Pr(C_6H_5NO_2)_3(H_2O)_2]_{2n}\cdot(nH_5O_2)(nHgCl_5)(2nHgCl_4)\cdot(2nH_2O)$ (**1**) has been synthesized via hydrothermal reaction and structurally characterized. Complex **1** is characteristic of a one-dimensional chain-like structure. Photoluminescent investigation displays that the title complex displays interesting emissions in blue, green and orange regions. Optical absorption spectra of **1** reveal the presence of an optical gap of 3.43 eV. The magnetic measurements show that complex **1** exhibits antiferromagnetic interactions.

1. Introduction

The increasing interest in the field of the crystal engineering of complexes is justified by the potential applications of these materials as catalysis, zeolite-like materials, biology, magnetic functional materials, and so on [1]. There is also an aesthetic perspective: for the vast amount of complexes, the intriguing variety of the architectures and topologies that can be obtained by self-assembling metal ions and multifunctional ligands attract chemists. In recent years, although the syntheses of transition metal complexes have become widespread [2], there are relatively few reports on the lanthanide complexes despite their potential applications in luminescence and other fields [3].

To our knowledge, lanthanide complexes with aromatic carboxylic acids exhibit good thermal and luminescent stability for practical application. Furthermore, f–d (f = lanthanide, d = transition metal) complexes with aromatic carboxylic acids as ligands maybe have novel structural topologies and properties. Therefore, our group recently became interested in the crystal engineering of f–d complexes with isonicotinic acid as liagnd. In this paper, we report the hydrothermal synthesis, crystal structure and properties of a new complex: $[Pr(C_6H_5NO_2)_3(H_2O)_2]_{2n}\cdot(nH_5O_2)(nHgCl_5)(2nHgCl_4)\cdot(2nH_2O)$ (**1**).

2. Experimental

2.1. Instrumentation

All reactants, A. R. grade quality, were obtained commercially and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried out with an Elementar Vario EL III microanalyzer. The infrared spectra were recorded on a Thermo Nicolet NEXUS 870 FT–IR spectrophotometer over the frequency range 4000–400 cm^{-1} using the KBr pellet technique. 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 were 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) vs. energy plot from the UV–vis diffuse spectra [4]. 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.

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2.2. Synthesis of the complex

The title complex was prepared by mixing $PrCl_3{\cdot}6H_2O$ (1 mmol, 357 mg), $HgCl_2$ (1.5 mmol, 408 mg), isonicotinic acid (3 mmol, 369 mg) and 10 mL distilled water in a 25 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 10 days. After being slowly cooled to room temperature at 6 °C/h, green crystals suitable for X-ray analysis were obtained. The yield was 71% (based on mercury). Anal. Calcd for $C_{36}H_{47}Cl_{13}Hg_3N_6O_{20}Pr_2$: C, 19.39; H, 2.11; N, 3.77. Found: C, 19.55; H, 2.23; N, 3.56. Fourier transform IR (KBr, cm^{-1}): 3425(vs), 1636(s), 1616(s), 1587(s), 1401(s), 1225(m), 1079(w), 1051(w), 844(m), 761(m), 681(m) and 537(w).

2.3. X-ray crystallographic study

The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by using a 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 SHELXTL™ Version 5 package of crystallographic software [6]. The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. The structures were refined using a full-matrix least-squares refinement on F^2. All atoms were refined anisotropically. Crystallographic data are given in Table 1, and selected bond distances and bond angles are given in Table 2.

Table 1
Crystal data and structure refinement details for **1**.

Formula	$C_{36}H_{47}Cl_{13}Hg_3N_6O_{20}Pr_2$
Mr	2228.24
Color	Green
Crystal size/mm^3	0.23 0.12 0.08
Crystal system	Monoclinic
Space group	C2/c
a (Å)	24.203(3)
b (Å)	20.873(3)
c (Å)	15.403(8)
β (°)	127.712(8)
V (Å^3)	6156(3)
Z	4
$2\theta_{max}$ (°)	50.70
Reflections collected	15,049
Independent, observed reflections (R_{int})	5481, 4139 (0.0580)
$d_{calcd.}$ (g/cm^3)	2.404
μ (mm^{-1})	9.644
T (K)	293(2)
F (0 0 0)	4176
R1, wR2	0.0389, 0.0754
S	0.884
Largest and mean Δ/σ	0.001, 0
$\Delta\rho$ (max/min) (e/Å^3)	1.816/−1.194

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**.

Pr(1)—O(1)	2.463(2)	Hg(2)—Cl(7)	2.243(2)
Pr(1)—O(2)#1	2.451(3)	Hg(2)—Cl(7)#3	2.636(2)
Pr(1)—O(3)	2.428(2)	Cl(1)—Hg(1)—Cl(4)	106.23(3)
Pr(1)—O(4)#2	2.440(2)	Cl(2)—Hg(1)—Cl(1)	113.76(4)
Pr(1)—O(5)	2.423(3)	Cl(2)—Hg(1)—Cl(3)	116.76(4)
Pr(1)—O(6)#1	2.411(3)	Cl(2)—Hg(1)—Cl(4)	104.20(4)
Pr(1)—O(3W)	2.528(3)	Cl(3)—Hg(1)—Cl(1)	109.58(5)
Pr(1)—O(4W)	2.586(3)	Cl(3)—Hg(1)—Cl(4)	105.25(4)
Hg(1)—Cl(1)	2.478(1)	Cl(5)—Hg(2)—Cl(6)	91.77(6)
Hg(1)—Cl(2)	2.454(1)	Cl(5)—Hg(2)—Cl(7)#3	108.68(5)
Hg(1)—Cl(3)	2.468(1)	Cl(6)—Hg(2)—Cl(7)#3	111.44(6)
Hg(1)—Cl(4)	2.559(1)	Cl(7)—Hg(2)—Cl(5)	123.37(5)
Hg(2)—Cl(5)	2.458(3)	Cl(7)—Hg(2)—Cl(6)	108.92(7)
Hg(2)—Cl(6)	2.477(2)	Cl(7)—Hg(2)—Cl(7)#3	111.00(8)

Symmetry codes: #1 $-x, y, -z + 1/2$; #2 $-x + 1/2, -y + 1/2, -z + 1$; #3 $-x + 1, y, -z + 5/2$.

3. Results and discussion

3.1. X-ray crystal structure

The structure of **1** consists of $[Pr(C_6H_5NO_2)_3(H_2O)_2]^{6+}$ cationic chains, $H_5O_2^+$ cations, $HgCl_5^{3-}$ and $HgCl_4^{2-}$ anions, and isolated water molecules. The Hg1 atom is bound by four chlorine atoms to form a $HgCl_4^{2-}$ tetrahedral anion, while the Hg2 atom is coordinated by five chlorine atoms to form a $HgCl_5^{3-}$ anion. In contrast to the numerous complexes containing $HgCl_4^{2-}$ anions, only two complexes containing $HgCl_5^{3-}$ anions were reported thus far [7]. The bond lengths of Hg–Cl range from 2.2433(15) to 2.6360(15) Å with an average value of 2.472(3) Å, which are comparable with the counterparts found in the literature [8]. The Hg2 atom is positional disordered and the occupancy of Hg2 must be set to 0.5 to get rational structure model and thermal displacement parameters. The praseodymium atom is octahedrally 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(3), O(4 W), O(4)(0.5 − x, 0.5 − y, 1 − z), O(3 W) and O(6)(−x, y, 0.5 − z), O(5), O(2)(−x, y, 0.5−z), O(1) atoms, respectively.

The bond lengths of Pr–$O_{isonicotinato}$ range from 2.411(3) to 2.463(2) Å with an average value of 2.436(3) Å, which is obviously shorter than that of Pr–O_{water} being of 2.528(3) and 2.586(3) Å, indicating that isonicotinato ligand has a stronger affinity to Pr^{III} ion than that of water. The praseodymium 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 with the Pr…Pr distances of *ca.* 4.997 and 4.631 Å, respectively (Fig. 1 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 (Scheme 1a–c, respectively). However, the 2-4-2 type is rare. In **1**, some π…π stacking interactions were established between the adjacent isonicotinic acid ligands located in neighboring chains.

The rings of the isonicotinic acid ligands involved in the π…π stacking interactions are arranged in such a way that the six atoms of the ring do not completely eclipse those of the other ring, meaning that the interaction is not "perfect face alignment" but "offset or slipped stacking". For clarity, we define the two pyridyl rings of the isonicotinic acid ligands as R1 and R2, containing N1 and N3 atoms, respectively. The R1 ring in one chain has a π…π contact with a R1′ ring in one adjacent chain; the R2 ring in the same chain connects to a R2′ ring in another adjacent chain via π…π

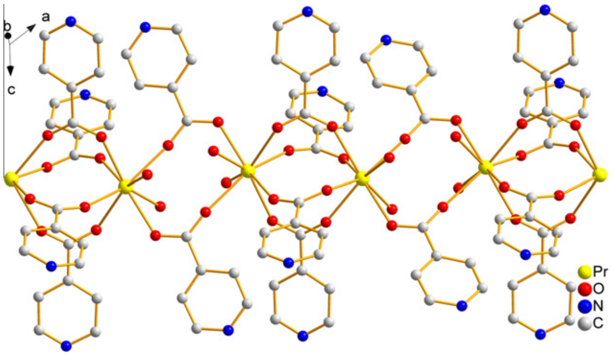

Fig. 1. The 1D cationic chain structure of **1**.