A Two-dimensional Rare Earth Metal-Organic Polymer $\{[Pr_2(csph)_2(H_2O)_4]\cdot 6H_2O\}_n$ with 3-Carboxylate-4-sulfonato-phenolate (csph) Ligands

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A two-dimensional rare earth metal-organic polymer $\{[Pr_2(csph)_2(H_2O)_4]\cdot 6H_2O\}_n$ (**1**) with 3-carboxylate-4-sulfonato-phenolate (csph) ligands was obtained by hydrothermal synthesis and characterized by elemental analysis and IR spectroscopy, and also by single-crystal X-ray diffraction. The crystal is orthorhombic, space group *Pbcn* with $a = 15.9113(6)$, $b = 9.3563(4)$, $c = 16.0497(6)$ Å, $Z = 4$, and $V = 2240.46(16)$ Å^3. The praseodymium atom is coordinated to eight oxygen atoms from the csph^{3-} ligands and two water molecules to form a distorted dodecahedron. The csph^{3-} ligands involved in forming a two-dimensional framework are all multiply bridging *via* the sulfonate (μ_2, η^2) and the carboxylate groups (μ_3, η^2:η^1). The thermal stability of complex **1** was studied by thermogravimetric analysis (TGA), and the photoluminescence properties of complex **1** were also investigated.

Key words: Praseodymium, Sulfosalicylic Acid, Fluorescence, Thermogravimetry

Introduction

In recent years, the rational design of novel metal-organic frameworks (MOFs) has attracted great interest among chemists [1 – 4]. Considerable efforts have been focused on the synthesis and characterization of novel multidimensional MOFs not only because of their intriguing variety of architectures and topologies but also because of their potential applications in the fields of electronic, magnetic, optical, absorbent, and catalytic materials [5 – 11]. Most of the reported studies so far were dedicated to coordination frameworks with transition metal salts, however, there has been an upsurge in the use of lanthanide salts for constructing coordination frameworks for their high coordination numbers along with their special magnetic and luminescence properties [12 – 15]. Luminescent lanthanide complexes and labels offer numerous advantages over fluorescent organic compounds or other luminescent coordination complexes [16]. Due to the unique nature of lanthanide ions, such as their large radius, high and variable coordination numbers, and the existence of multi-single electrons, the assembly of lanthanide complexes with novel structures and specific properties offers great challenges and opportunities in terms of controlling their shape and dimensionality [17 – 21].

Numerous combinations of rare earth metals and ligands have resulted in the synthesis of many MOFs with different structures and topologies, where the ligand can be judiciously selected to influence the overall chemical and physical properties of the MOF [22 – 24]. Among the ligands used, organic ligands with carboxylate or sulfonate groups are especially interesting because they can adopt a variety of coordination modes resulting in diverse multidimensional architectures [25 – 29]. Since, compared with the carboxylate group, the sulfonate group has one more oxygen atoms, it is evident that the combination of carboxylate and sulfonate groups can lead to new coordination modes with the formation of complexes with interesting structures and unique properties.

In this paper we report the synthesis, structure, thermogravimetric analysis (TGA), and photoluminescence properties of a two-dimensional rare earth metal-organic polymer $\{[Pr_2(csph)_2(H_2O)_4]\cdot 6H_2O\}_n$ (**1**) with 3-carboxylate-4-sulfonato-phenolate (csph) ligands.

Table 1. Crystal data, data collection parameters and details of the structure refinement for complex $\{[Pr_2(csph)_2(H_2O)_4]\cdot 6H_2O\}_n$ (**1**).

Empirical formula	$C_{14}H_{18}O_{18}S_2Pr_2$
Formula weight	820.22
Color, habit	colorless, bar
Crystal size, mm^3	0.06 × 0.04 × 0.03
Crystal system	orthorhombic
Space group	*Pbcn*
a, Å	15.9113(6)
b, Å	9.3563(4)
c, Å	15.0497(6)
Volume, Å^3	2240.46(16)
Z	4
Density (calcd.), g cm^{-3}	2.43
Absorption coefficient, mm^{-1}	4.6
Temperature, K	296(2)
$F(000)$, e	1584
Radiation; λ, Å	MoK_α; 0.71073
Reflections collected	17648
Independent reflections / R_{int}	2519 / 0.0136
Reflections with $I \geq 2\ \sigma(I)$	2366
Parameters refined	181
Final $R1$ / $wR2$ indices (all data)[a]	0.018 / 0.039
Goodness of fit (GoF)[b]	1.06
Final max / min difference peaks, e Å^{-3}	+0.66 / −0.42

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + 0.0174P^2 + 2.6846P]$, where $P = (F_o^2 + 2F_c^2)/3$; [b] GoF $= [\Sigma w(|F_o| - |F_c|)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

Experimental Section

Materials and measurements

All reagents and solvents were used as supplied without further purification. The infrared spectrum was recorded on a Nicolet FT-IR 360 spectrophotometer using pressed KBr pellets. The photoluminescence spectrum was measured with a Cary Eclipse 300 spectrophotometer. Thermogravimetric analyses (TGA) were performed on a SDT-Q600 thermoanalyzer in nitrogen atmosphere and with a heating rate of 20 °C min^{-1} from 30 to 1200 °C. Elemental analyses were performed on a Perkin-Elmer 240C Elemental Analyzer.

Preparation of $\{[Pr_2(csph)_2(H_2O)_4]\cdot 6H_2O\}_n$ (1)

10 % aqueous NaOH solution was slowly added to a solution of $Pr(NO_3)_3\cdot 6H_2O$ (43.5 mg, 0.10 mmol) and H_3csph (25.4 mg, 0.10 mmol) in 10 mL water until the pH value reached *ca.* 6.0. The mixture was sealed in a 25-mL Teflon-lined stainless steel autoclave. The reactor was heated in an oven to 150 °C for 72 h and then cooled to r. t. at a rate of 5 °C h^{-1}. Colorless, needle-shaped crystals were obtained and air-dried. Yield: 30 mg, 74 % (relative to Pr). – FT-IR (KBr pellet, cm^{-1}): ν = 3363 (bs), 3041 (m), 1607(s), 1551 (m), 1502(s), 1456(m), 1431(s), 1378(m), 1329(m), 1256(m), 1207(m), 1139(s), 1094(m), 1040(m), 906(w), 840(m), 806(w), 748(w). – Anal. for $C_{14}H_6O_{19}S_2Pr_2$: calcd. C 20.4, H 0.73; found C 20.5, H 0.75.

X-Ray crystallographic study

A suitable single crystal of **1** with the size of 0.06 × 0.04 × 0.03 mm^3 was mounted in random orientation on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation using an ω scan mode. The collected frames were processed with the software SAINT [30]. The data were corrected for absorption using the program SADABS [31]. The structure was solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [32]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp^3}–H = 0.96 and C_{sp^2}–H = 0.93 Å) and included in the structure factor calculations with assigned isotropic displacement parameters but were not refined. Crystal data, data collection parameters and details of the structure refinement are given in Table 1.

CCDC 749604 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Hydrothermal reaction of $Pr(NO_3)_3\cdot 6H_2O$ with H_3csph (pH = *ca.* 6.0) in a 1:1 molar ratio at 150 °C produced the new complex $\{[Pr_2(csph)_2(H_2O)_4]\cdot 6H_2O\}_n$ (**1**). The complex is stable in air and insoluble in water and most common organic solvents except DMSO and DMF. The broad band at 3363 cm^{-1} for $\nu(H_2O)$ and a moderate-intense peak at *ca.* 3041 cm^{-1} for ν(O–H) in the IR spectrum indicate the presences of water in the crystalline sample of **1**. The IR absorption bands with variable intensity in the frequency range of 1430 – 1610 cm^{-1} correspond to vibrations of the carboxylate groups of the csph^{3-} ligand. The strong absorption at 1139 cm^{-1} may be attributed to the S=O stretching vibration, and the medium intensity peaks in the range of 840 – 1040 cm^{-1} are due to ν(S–O), which indicates the presence of the sulfonate group [33].

Crystal structural analysis revealed that complex **1** crystallizes in the orthorhombic space group *Pbcn* forming a two-dimensional coordination polymer. The crystal structure of **1** is depicted in Fig. 1, showing the metal atom coordination environment. The praseodymium atom is coordinated to eight oxygen atoms from the csph^{3-} ligands and two water molecules to form a distorted dodecahedron. The Pr–O bond lengths are in the range from 2.3121(18) to

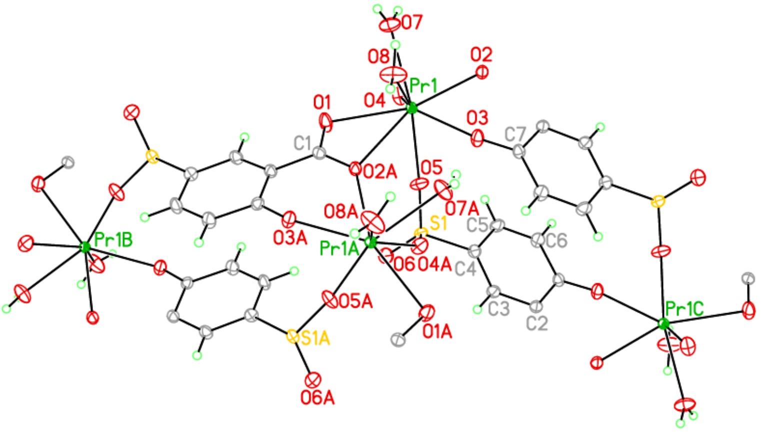

Fig. 1. The structure of $[Pr_2(csph)_2(H_2O)_4]$ showing the metal atom coordination environment (displacement ellipsoids at the 40 % probability level). Selected bond lengths (Å) and angles (deg): Pr–O 2.3127(5) – 2.6903(15), S–O 1.4501(17) – 1.4659(16); O–Pr–O 49.72(5) – 159.51(3), Pr–O–Pr 133.55(6), S–O–Pr 142.7(1) – 145.0(1), O–S–O 110.3(1) – 113.2(1).

2.6888(18) Å, and the O–Pr–O angles are in the range of 49.73(16) – 159.54(3)°. The water molecules are bound terminally to the Pr(III) ion with an average Pr–O bond length of 2.4556(17) Å. The phenolic hydroxyl moiety is also terminally coordinated to the Pr(III) center with the relatively short Pr(1)–O(3) bond length of 2.3127(15) Å as compared to the other Pr–O bonds.

Only two oxygen atoms of each sulfonate group of the $csph^{3-}$ ligand are bound to the Pr(III) ion, adopting a μ_2-bridging coordination mode. The carboxylate group is in a μ_3-η^2:η^1 bridging coordination mode: two oxygen atoms are chelating one Pr(III) ion, and one of the oxygen atoms is bridging two Pr(III) ions. The oxygen atom of the hydroxyl group is bonded to the Pr(III) ion as a monodentate function. Each praseodymium ion is thus coordinated by three oxygen atoms from two bridging carboxylate groups, two oxygen atoms from two bridging sulfonate groups, one oxygen atom from the monodentate phenolic hydroxyl group, and two terminal water molecules.

The carboxylate CO_2^- and hydroxyl OH^- groups and the sulfur atom of the sulfonate group and the phenyl ring in each of the $csph^{3-}$ ligands are nearly coplanar with an average deviation of 0.05 Å. The environment around the sulfur atom of the sulfonate group is a distorted tetrahedron, as indicated by the bond angles at the sulfur atom [105.66(10) – 113.21(10)°] which deviate only slightly from the standard angle of 109.2°. The S=O double bond length [1.4501(17) Å] is shorter than the S–O single bond lengths [*av.* 1.4641(16) Å].

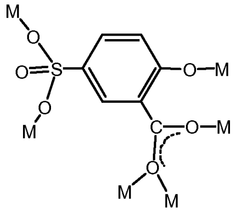

Fig. 2. The coordination mode adopted by the $csph^{3-}$ ligand in complex **1**.

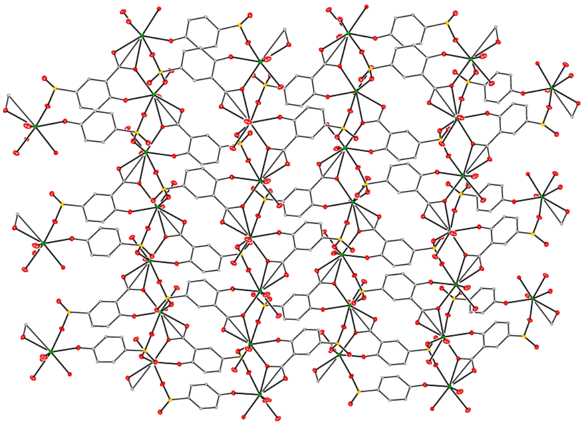

Fig. 3. Packing diagram of $\{[Pr_2(csph)_2(H_2O)_4]\cdot 6H_2O\}_n$ projected onto the *ab* plane. The Pr–O bonds and the csbh bridges establish an infinite two-dimensional framework. The hydrogen atoms have been omitted for clarity.

Each of the $csph^{3-}$ anions in complex **1** acts as a hexa-bridging ligand (see Fig. 2) to connect four Pr(III) ions. Together with the parallel phenyl rings of two pairs of $csph^{3-}$ ligands, a two-dimensional wave-like polymeric array is formed, as shown in Figs. 3 and 4. The Pr–O–Pr angle is 133.55(6)°, and the distance between the nearest two Pr atoms is 4.379(2) Å. Intermolecular hydrogen bonding interactions are observed between the uncoordinated oxygen atoms of the sul-

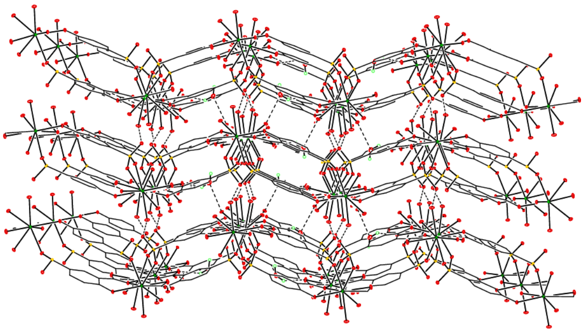

Fig. 4. View of the packing of complex **1** as projected onto the *ac* plane, showing a three-dimensional network built up *via* intermolecular hydrogen-bonding interactions.

fonate groups and the water molecules, as indicated by $(H_2O)O\cdots O(=S)$ and $(H_2OPr)O\cdots O(=S)$ distances of 2.677(3) and 2.725(3) Å, respectively, which result in the formation of a three-dimensional hydrogen-bonded supramolecular network, as shown in Fig. 4.

In order to examine the thermal stability of complex **1**, a thermogravimetric analysis (TGA) was carried out in the range of 30 – 1200 °C under nitrogen atmosphere. The TGA curve shows that the thermolytic pathway for complex degradation involves two successive steps (Fig. 5). One process occurs in the first step (30 – 198 °C), while three distinct peaks can be observed in the latter stage (198 – 662 °C). The experimental weight loss associated with the first step (14.9 %) is consistent with the theoretical value (15.0 %) corresponding to the complete removal of the coordinated and uncoordinated water molecules. The second segment of the complex decomposition pathway corresponds to the loss of the ligand *via* the generation and elimination of carbon dioxide and phenol (expt.: 26.8 %, calcd.: 26.5 %). The identity of these products was also confirmed by GC-MS coupling. The solid residue formed at *ca.* 680 °C is suggested to be a mixture of Pr_2O_3 (22.5 %) and $Pr_2(SO_4)_3$ (77.6 %), with some further evaporation occuring at higher temperature.

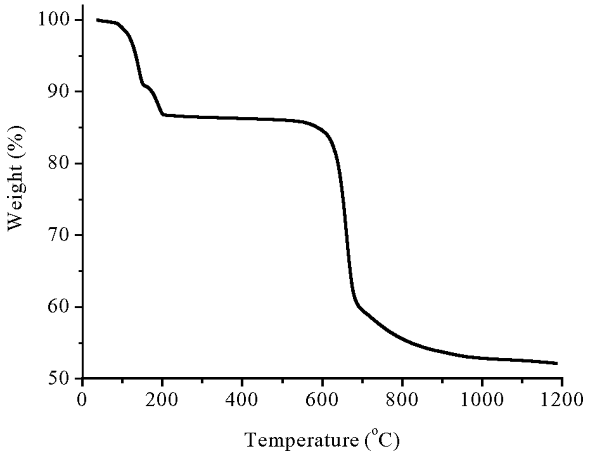

Fig. 5. Thermogravimetric analysis (TGA) of complex **1**.

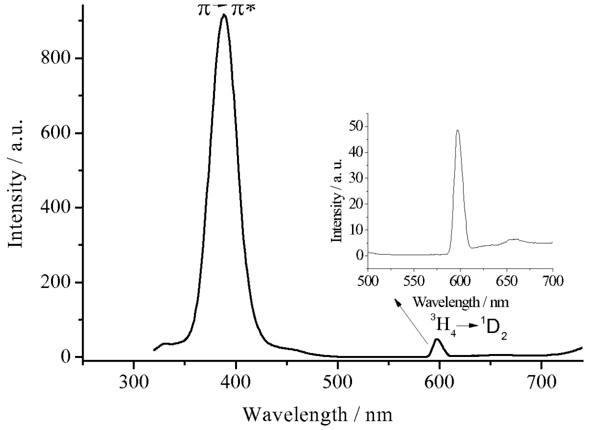

Fig. 6. Emission spectrum of complex **1** in the solid state at room temperature.

Complex **1** exhibits photoluminescence with emission peaks at 398 and 598 nm upon excitation at 300 nm in the solid state at r. t. (Fig. 6). The observed emission at 398 may be attributed to the π-π^* intraligand fluorescence and the peak observed at 598 nm to the excitation $^3H_4$-$^1D_2$ of the Pr(III) ion [34].

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