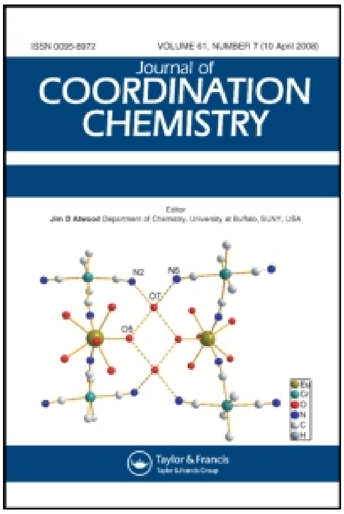

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Qi-Bing Bo[a]; Zhong-Xi Sun[a]
[a] Institute of Chemistry and Chemical Engineering, University of Jinan, 250022 Jinan, Shandong, P.R. China

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Synthesis, characterization and luminescence properties of a coordination polymer based on self-assembly of Pr^{III} with inorganic–organic hybrid bridging ligands

QI-BING BO* and ZHONG-XI SUN

Institute of Chemistry and Chemical Engineering,
University of Jinan, No. 106, Jiwei Road, 250022 Jinan,
Shandong, P.R. China

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A new coordination polymer having the formula $[Pr(\mu_5\text{-}S_2O_3)(\mu_4\text{-tp})_{0.5}(H_2O)]_n$ (**1**) (S_2O_3 = thiosulfate dianion; tp = terephthalate dianions) was obtained by *in situ* reaction of $Pr_2(SO_4)_3 \cdot 6H_2O$ with H_2tp ligands under solvothermal conditions (H_2O/ethanol). The coordination polymer obtained was characterized by elemental analysis, FT-IR, thermogravimetry (TG), fluorescent spectra and single crystal X-ray diffraction analysis. The most intriguing structural feature is that the complex exhibits a 3D open framework resulting from bridge-linking coordination between ligands and praseodymium ions. Additionally, **1** has characteristic emission spectra of Pr^{III} with good fluorescence properties. This is the first coordination polymer based on thiosulfate/terephthalate ligands and a rare earth metal and has an unprecedented pentadentate-bridge-linking coordination mode of the thiosulfate group.

Keywords: Synthesis; Structure; Bridging ligands; Coordination polymer; Luminescence

1. Introduction

Design and construction of coordination polymers have been rapidly expanding because of their structural diversity and potential applications as functional materials [1–4]. The design of metal-organic frameworks containing terephthalate ligands has attracted great interest [5–9]. Thiosulfate ($S_2O_3^{2-}$) in combination with phenanthroline or bipyridyl is a good ligand for assembling transition-metal coordination polymers such as those of nickel [10–13], manganese [14, 15], zinc [16] and cadmium [17, 18]. Copper [19, 20] and cobalt [21] coordination polymers between thiosulfate and other ligands have been reported. However, there is no report of coordination polymers between rare earth metals and thiosulfate. One reason may be that rare earth metal ions are hard acids difficult to form complex with soft S atoms. Sulfur-containing species may undergo disproportionation under suitable redox atmosphere such that coordination polymers may be synthesized in hydrothermal or solvothermal method. Attempts to isolate single crystals from a conventional hydrothermal synthesis using soluble

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*Corresponding author. Email: chm_boqb@ujn.edu.cn

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praseodymium salts or praseodymium oxides with a mixture of $Na_2S_2O_3$ and terephthalic acid were unsuccessful. Metal cations with higher oxidation state can be easily reduced in the presence of aromatic species under solvothermal synthesis conditions [22]. We attempted reaction of praseodymium sulfate with terephthalic acid under *in situ* solvothermal conditions (H_2O/ethanol) and succeeded in synthesizing and fully characterizing $[Pr_2(\mu_5\text{-}S_2O_3)_2(\mu_4\text{-tp})(H_2O)_2]_n$. To the best of our knowledge, this is the first example of a rare earth metal coordination polymer containing thiosulfate and terephthalate ligands. In this article, we report its synthesis, characterization and luminescence properties.

2. Experimental

2.1. *Materials and methods*

All chemicals were commercially purchased from Acros Ltd. and used without further purification. Elemental analyses (C, H and S) were performed on a Perkin-Elmer 2400 Series II CHNS/O elemental analyzer. Pr was determined by Inductively Coupled Plasma (ICP) analysis performed on a Perkin-Elmer Optima 3300DV spectrometer. FT-IR spectra were recorded in the range 400–4000 cm^{-1} on a Perkin-Elmer FTIR spectrometer using KBr pellets. Thermal analyses were performed on a Perkin-Elmer Diamond TG/DTA instrument in flowing air with a heating rate of $10^\circ C\,min^{-1}$. Fluorescence spectra were measured on an Edinburgh Instruments analyzer model FL920.

2.2. *Crystal growth*

Compound **1** was prepared solvothermally from a mixture of $Pr_2(SO_4)_3 \cdot 6H_2O$, H_2tp, ethanol and H_2O in a molar ratio of 0.5 : 1 : 160 : 900, heated in a teflon-lined stainless steel autoclave at 160°C for 3 days under static conditions with filling volume 75%. After cooling the reaction mixture to room temperature, the viridescent prism-like crystals were separated and washed by distilled water and ethanol many times. Finally, the products were dried in air at room temperature. The average size of the crystals is about $3.0 \times 2.0 \times 1.5\,mm^3$ with yield of 50%.

2.3. *Crystal structure determination and refinement*

A suitable single crystal with dimensions $0.68 \times 0.23 \times 0.09\,mm^3$ was carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. X-ray intensity data were measured at 298(2) K on a Bruker SMART APEX CCD-based diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å). The raw frame data for the compound were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT [23]. Corrections for incident and diffracted beam absorption effects were applied using SADABS [23].

Compound **1** crystallized in the space group $P21/c$, as determined by systematic absences in the intensity data, intensity statistics, and the successful solution and

Table 1. Summary of crystallographic data and structure refinement for **1**.

Empirical formula	$C_4H_4O_6PrS_2$
Formula weight	353.10
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	15.444(3)
b (Å)	6.795(3)
c (Å)	7.144(3)
α (°)	90
β (°)	98.095(3)
γ (°)	90
Volume (Å^3)	742.2(4)
Z	4
ρ_{calcd} (g cm^{-3})	3.160
μ (mm^{-1})	7.118
F (000)	668
Crystal size (mm^3)	$0.68 \times 0.23 \times 0.09$
Reflections collected	3204
Independent reflections	1276 [$R_{int} = 0.1061$]
GOF	1.000
Final R indices	$R_1 = 0.0863$
[$I > 2\sigma(I)$]	$wR_2 = 0.2361$
R indices (all data)	$R_1 = 0.0931$, $wR_2 = 0.2450$

refinement of the structure. The structure was solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full matrix least-squares technique. Crystal data, data collection parameters, and refinement statistics for **1** are listed in table 1. Selected bond distances and bond angles are also given (see supporting information, table S1).

2.4. *Composition analysis*

The elemental analysis (C, H and S) showed that **1** contains 13.58, 1.10 and 18.12 wt% of C, H and S (Calcd 13.61, 1.14 and 18.16 wt%), respectively. Inductively Coupled Plasma (ICP) analysis (Pr) indicates that **1** contains 39.85 wt% of Pr (Calcd 39.90 wt%). The composition analysis is in good agreement with calculated values based on the empirical formula of $C_4H_4O_6PrS_2$ given by single-crystal structure analysis.

3. Results and discussion

3.1. *Crystal structures*

The crystal structure of **1** is revealed to be polymeric by an X-ray diffraction. A perspective drawing with the atom numbering scheme is shown in figure 1. One crystallographically independent thiosulfate group coordinated to five Pr atoms was found in the molecular motif with two oxygen atoms (O1 and O4), monodentate coordination to one Pr1 atom (S1–O1 1.465(16) Å and S1–O4 1.47(2) Å); one oxygen

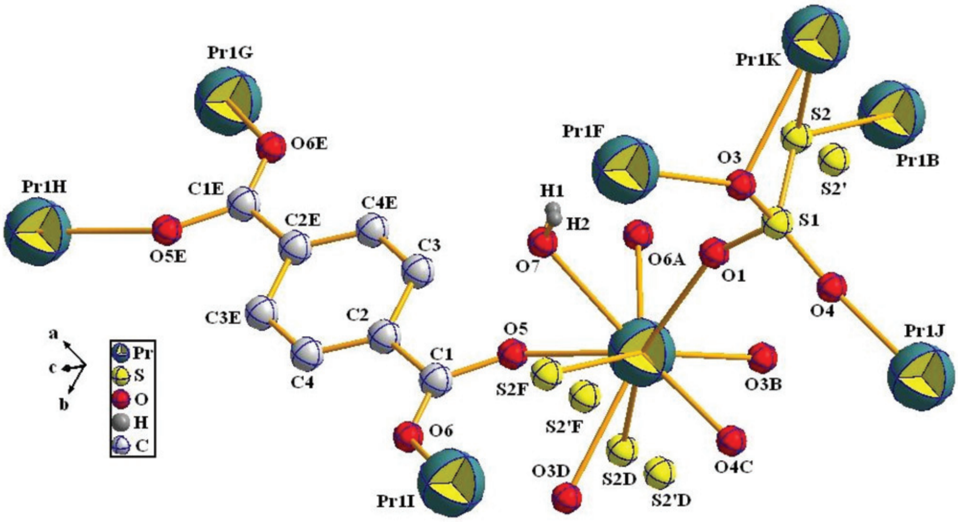

Figure 1. A perspective drawing of **1** with the atom numbering scheme (hydrogen atoms bound to carbon atoms are omitted for clarity). Symmetry codes: *A* (x, $2.5-y$, $-0.5+z$); *B* (x, $1.5-y$, $-0.5+z$); *C* ($1-x$, $0.5+y$, $0.5-z$); *D* (x, $1+y$, z); *E* ($2-x$, $3-y$, $1-z$); *F* (x, $1.5-y$, $0.5+z$);*G* ($2-x$, $0.5+y$, $0.5-z$); *H* ($2-x$, $3-y$, $1-z$); *I* (x, $2.5-y$, $0.5+z$); *J* ($1-x$, $-0.5+y$, $0.5-z$); K (x, $-1+y$, z). Color code: Pr, green; S, yellow; O, red; C, off white; H, grey.

(O3) and one sulfur (S2) coordinate to two Pr^{III} ions adopting bidentate-bridge-linking coordination modes (Pr1F–O3–Pr1K 107.3(5)° and Pr1K–S2–Pr1B 113.1(4)°) with bond distances 1.496(17) and 1.638(11) Å for S1–O3 and S1–S2, respectively. The O–S1–O angles in thiosulfate are 110.4(9)°, 94.0(10)°, 129.9(10)° and 110.9(10)° for O1–S1–O3, O3–S1–S2, S2–S1–O4 and O4–S1–O1, respectively, deviating from an ideal tetrahedron. $S_2O_3^{2-}$ as a μ_5-bridge linking five Pr atoms was observed for the first time. Each *para*-carboxyl group in tp^{2-} is deprotonated and coordinated to two Pr ions adopting bidentate-bridge-linking coordination; the whole tp^{2-} coordinates to four Pr atoms. One carboxylic O–Pr bond distance (O6A–Pr1 2.47(2) Å) is longer than the other one (O5–Pr1 2.41(2) Å) as the result of intermolecular hydrogen bonding of coordinated water/carboxylate oxygens O(7)···O(6), see supporting information, table S2. There is only one crystallographically independent Pr^{III} exhibiting a nine-coordinate environment. Two *O*-μ_4-tp, four *O*-μ_5-S_2O_3 and two *S*-μ_5-S_2O_3 ligands coordinated to the same Pr^{III} ion occupying two (O5–Pr1 2.41(2) Å and O6A–Pr1 2.47(2) Å), four (O1–Pr1 2.415(16) Å, O3B–Pr1 2.483(17) Å, O3D–Pr1 2.744(18) Å and O4C–Pr1 2.36(2) Å) and two (S2D–Pr1 2.440(10) Å and S2F–Pr1 2.607(13) Å) coordination sites, respectively. One oxygen from water completes the coordination geometry of Pr^{III} with O7–Pr1 bond distance of 2.60(2) Å. The S2 of the μ_5-S_2O_3 ligand is disordered over two positions with the atom occupancy of 0.667(14) and 0.333(14) for S2 and S2′ (S2′D-Pr1 2.68(2) Å and S2′F-Pr1 2.404(19) Å), respectively.

Each $S_2O_3^{2-}$ ligand is μ_5-bridge linking five Pr centers, and each Pr center attaches to six $S_2O_3^{2-}$ ligands to form a interpenetrated 2-D layer structure with the nearest Pr–Pr distance of 7.144(3) Å (figure 2). The 2-D layers are further connected by *O*-μ_4-tp ligands. As a result, a 3-D supramolecular open framework structure with many

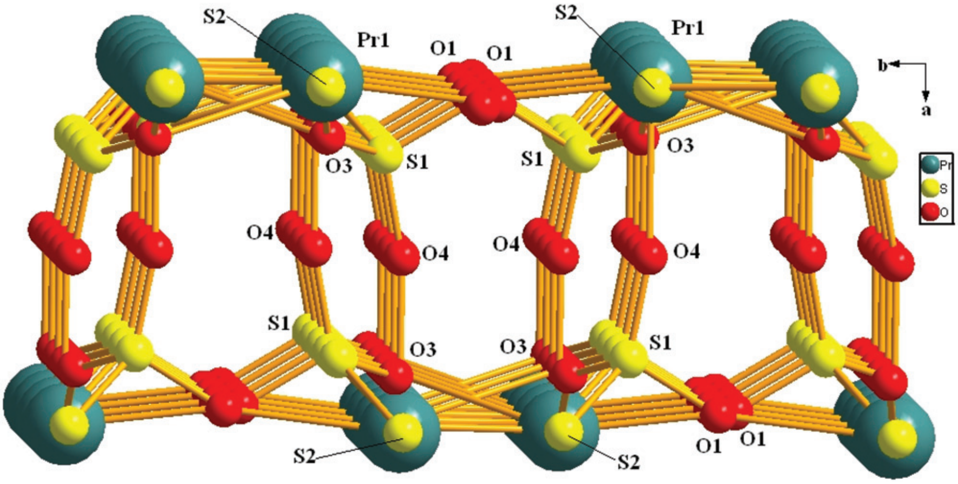

Figure 2. An interpenetrated 2-D layer structure constructed by $S_2O_3^{2-}$ ligand.

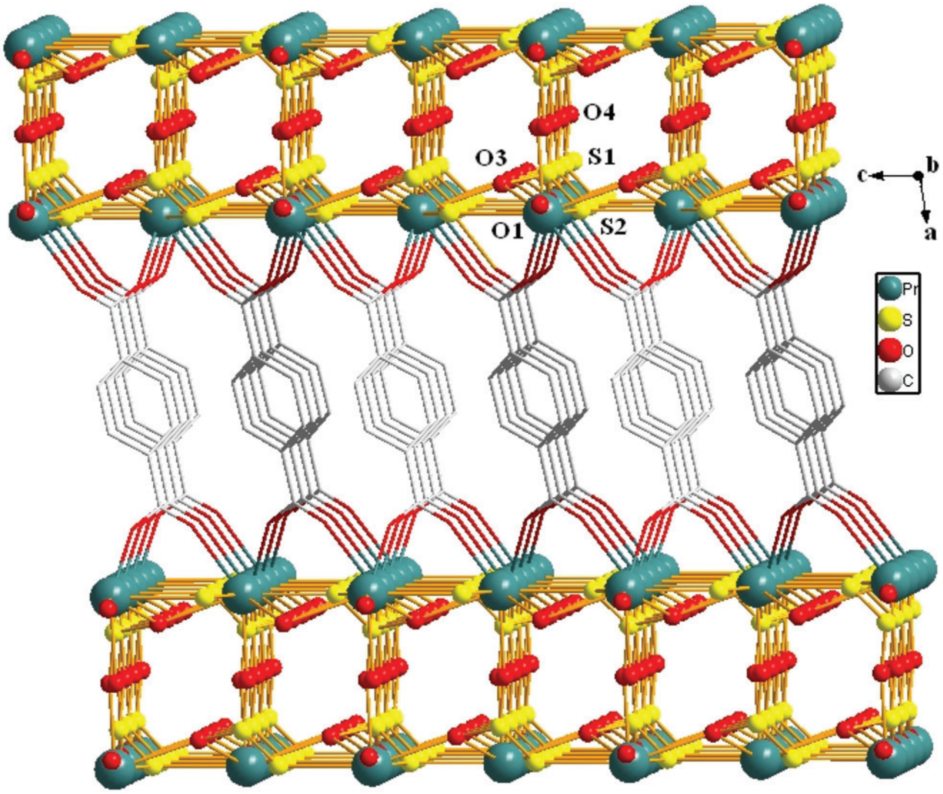

Figure 3. A 3-D open-framework structure for **1** (all hydrogen atoms and water molecules are omitted for clarity).

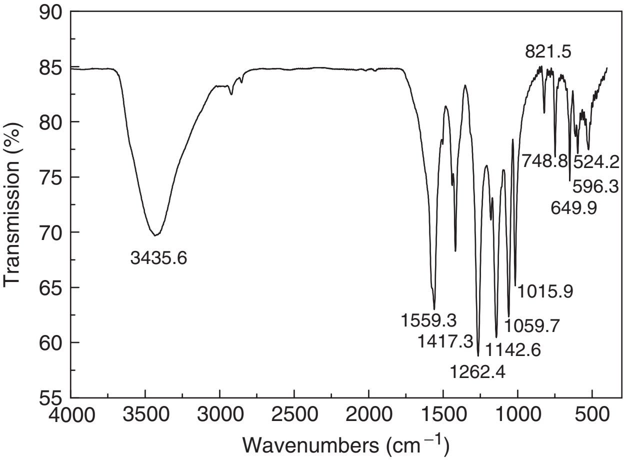

Figure 4. FT-IR spectra for **1**.

irregular channels occupied by coordinated H_2O was formed (figure 3). The open channels in the 3-D network of **1** make it possible to generate porous frameworks by removing the bound water molecules.

3.2. *Infrared spectroscopy*

The presence of coordinated H_2O caused the appearance of strong and broad υ(O–H) stretching bands centered at 3435.6 cm^{-1} in the IR spectrum as shown in figure 4; frequencies at 649.9 and 596.3 cm^{-1} assigned to ρ_r (H_2O) and ρ_w (H_2O) are also observed [24]. The IR spectrum of **1** also shows absorptions centered at 748.8 and 781.2 cm^{-1}, corresponding to O–Pr–O stretching vibration [25]. Other vibrations at 1262.4, 1179.0, 1142.6, 1059.7, 1015.9 and 524.2 cm^{-1} were assigned to the characteristic absorptions of S_2O_3 [26]. The most salient feature in the IR spectra was the existence of two very strong bands centered at 1559.3 and 1417.3 cm^{-1}, attributed to the ν_{as}(COO) and ν_s(COO) stretching vibrations of the tp ligand. Their difference of value ($\Delta = 142$ cm^{-1}) confirmed that the tp ligand coordinated to Pr ions by bidentate-bridge-linking [27], consistent with the results of the single crystal X-ray analysis.

3.3. *Thermogravimetric analysis*

TG curve indicates that weight loss of **1** can be divided into five steps, as shown in figure 5. A weight loss of 5.2% with maxima at 190°C can be assigned to release of coordinated water, in good agreement with the calculated value (5.1%). With increasing temperature, a medium weight loss occurred at ca 278°C, corresponding to carbonyl oxygen from terephthalate. Evolution of SO_4^{2-} from decomposition of $S_2O_3^{2-}$ occurs at 485°C [28]. The fourth step of weight loss at 652 °C corresponds to removal of the entire organic components. The final stage corresponds to decomposition of the sulfate salt at 833°C into $Pr_2O_2SO_4$ [29]. After heating the viridescent compound **1**, the residue is also

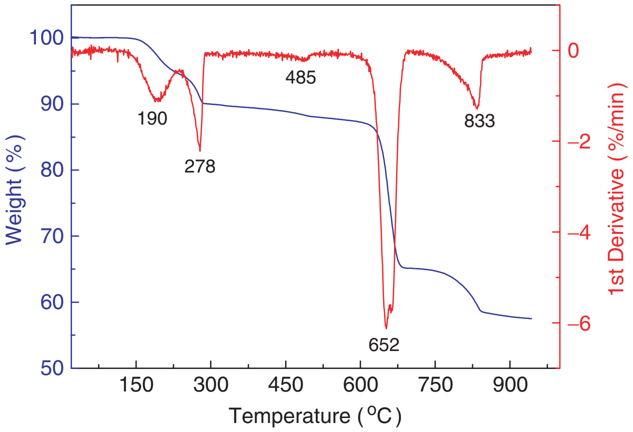

Figure 5. TG-DTG curves for **1**.

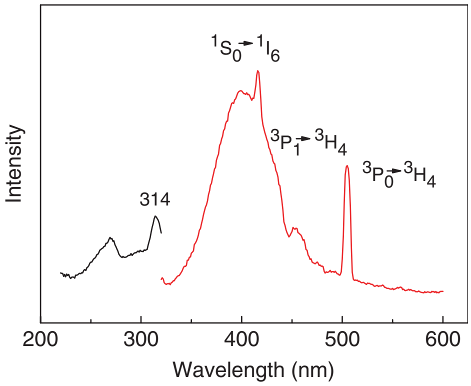

Figure 6. Solid-state excitation and emission spectrum for **1** at room temperature.

viridescent, confirming that the residue is not praseodymium oxide, since it is taupe at room temperature.

3.4. *Luminescence properties*

The solid state luminescence spectra of **1** were investigated because of the excellent luminescent properties of Pr(III). The emission spectrum of **1** at room temperature upon excitation at 314 nm displays intense luminescence and exhibits the characteristic transitions of $^1S_0 \rightarrow {}^1I_6$, $^3P_1 \rightarrow {}^3H_4$ and $^3P_0 \rightarrow {}^3H_4$ of Pr^{III}, as shown in figure 6 [30, 31]. The strongest emission peak in the $^1S_0 \rightarrow {}^1I_6$ transition region is split into two levels at 400 and 416 nm, a result of the coordination environment of the Pr^{III}. The most salient feature in the luminescence spectra was the existence of the emission peak at 505 nm for $^3P_0 \rightarrow {}^3H_4$, which is the second strongest and is very sharp; $^3P_1 \rightarrow {}^3H_4$ transition region has a broad, weak emission centered at 453 nm. The photoluminescent properties also demonstrate that the corresponding emissions of tp were not observed in **1** under the experimental conditions. This suggests energy transfer from the ligand to the Pr^{III} center is highly efficient and **1** may be an excellent candidate for photoactive materials.

4. Conclusion

In summary, we succeeded in using organic/inorganic ligands as bridging units under solvothermal conditions to give structurally characterized coordination polymer $[Pr_2(\mu_5\text{-}S_2O_3)_2(\mu_4\text{-tp})(H_2O)_2]_n$ in an attempt to extend the application of rare earth complexes used as luminescent materials. Compound **1** crystallizes in the 3-D channel framework mainly constituted by two bridge-linking ligands, thiosulfate and terephthalate dianions, and the pentadentate-bridge-linking coordination mode of the former dianion was observed for the first time. Compound **1** presents the characteristic emission spectra of the Pr^{III} ions and has good fluorescence properties.

Supplementary data

Crystallographic information of the $C_4H_4O_6Pr_1S_2$ has been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 643459. Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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