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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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To cite this Article Zou, Jian-Ping , Wen, Zhen-Hai , Peng, Qiang , Zeng, Gui-Sheng , Xing, Qiu-Ju and Chen, Mei-Hong(2009) 'A 1-D chain praseodymium complex with chelidamic acid: synthesis, structure, and optical properties', Journal of Coordination Chemistry, 62: 20, 3324 – 3331

To link to this Article: DOI: 10.1080/00958970903062871

URL: <http://dx.doi.org/10.1080/00958970903062871>

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A 1-D chain praseodymium complex with chelidamic acid: synthesis, structure, and optical properties

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(Received 14 February 2009; in final form 3 April 2009)

The title compound $[\text{Pr}(\text{C}_7\text{H}_3\text{NO}_5)(\text{C}_7\text{H}_4\text{NO}_5)(\text{H}_2\text{O})_2]_n \cdot 1.25n\text{H}_2\text{O}$ (**1**) or $[\text{Pr}(\text{HChel})(\text{H}_2\text{Chel})(\text{H}_2\text{O})_2]_n \cdot 1.25n\text{H}_2\text{O}$, where H_3Chel is 4-hydroxypyridine-2,6-dicarboxylic (chelidamic) acid, was synthesized by reaction of chelidamic acid, $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$ and H_2O under hydrothermal conditions, and characterized by X-ray single-crystal diffraction. The crystal structure of **1** reveals that Pr is nine-coordinate with distorted tricapped trigonal prismatic coordination. Coordination polyhedra are interlinked into a 1-D chain, further linked by hydrogen bonds into a 3-D network. Fluorescence spectra exhibit strong green luminescence with maximum emission at 530 nm when excited with $\lambda_{\text{ex}} = 475$ nm, originating from $\pi-\pi^*$ of the ligand.

Keywords: Coordination polymer; Crystal structure; Luminescence; Synthesis

1. Introduction

Lanthanides have potential in luminescence and magnetism and with applications in advanced materials [1–5]. While a variety of structures have been constructed with different chelating-bridging ligands, design and synthesis of a lanthanide complex with good luminescence is a challenging field [6–8]. In order to obtain lanthanide complexes with good optical properties, we selected chelidamic acid (2,6-dicarboxy-4-hydroxypyridine) as chelating-bridging ligand. Herein, we report the synthesis, crystal structure, and optical properties of a 1-D coordination polymer $[\text{Pr}(\text{C}_7\text{H}_3\text{NO}_5)(\text{C}_7\text{H}_4\text{NO}_5)(\text{H}_2\text{O})_2]_n \cdot 1.25n\text{H}_2\text{O}$ (**1**). Although chelidamic acid is widely used in coordination chemistry, biochemistry, organic chemistry, and medicinal chemistry [9–14], lanthanide complexes with chelidamic acid have only been reported for La, Gd, Tb, Nd, Er, Ce, and Dy [15–20]. This report expands the structure types of complexes of chelidamic acid.

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2. Experimental

2.1. Synthesis and characterization

A mixture of $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol), chelidamic acid (0.4 mmol), and water (10 mL) was loaded into a 25-mL Teflon-lined stainless steel autoclave and heated at 433 K for 3 days, and it was cooled to room temperature. White prismatic crystals of **1** that are stable in air were obtained by filtration of the solution. Yield based on chelidamic acid: 46%. Elemental analysis calculated (%) for **1**: C, 29.87; H, 2.40; N, 4.98. Found (%): C, 29.91; H, 2.43; N, 5.01. IR (KBr, cm^{-1}): 3275(m), 2726(w), 2611(w), 2490(w), 1608(vs), 1412(vs), 1336(s), 1250(m), 1120(m), 1024(s), 933(w), 893(m), 808(s), 772(m), 721(s), 586(w), 471(w).

Elemental analyses (C, H, N, and O) were carried out with a Perkin-Elmer 2400 II elemental analyzer. Photoluminescence analysis was performed on an Edinburgh FLS920 fluorescence spectrometer. IR spectrum was recorded on a Magna 750 FT-IR spectrometer as a KBr pellet in the range 4000–400 cm^{-1} .

2.2. Single-crystal X-ray structure determination

Single crystal suitable for X-ray analysis was mounted on a glass fiber. All measurements were performed on a Rigaku Mercury CCD diffractometer using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) from a rotating anode generator at 293(2) K. The intensity data were collected in the range $3.13^\circ < \theta < 25.25^\circ$ with an ω -scan technique and corrected for Lp factors as well as for absorption by the multiscan method. The structure was solved by direct methods and difference Fourier synthesis, refined by full-matrix least-squares, and finally refined anisotropically for all non-hydrogen atoms.

All H atoms of coordinated and discrete water (except for O4W) and the O atoms from the hydroxyl group (O15 and O25) were placed in calculated positions, with O–H distances of 0.85 \AA , and refined in riding mode with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{O})$. Other H atoms were allowed to ride on their respective parent atoms with C–H distances of 0.93 \AA and were included in the refinement with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All calculations were performed with Siemens SHELXTLTM Version 5.0 package of crystallographic software [21]. Further details of the X-ray structural analysis are given in table 1. Selected bond lengths are listed in table 2 and the hydrogen bonds are listed in table 3.

3. Results and discussion

3.1. Crystal structure of **1**

As shown in figure 1, the structure of **1** consists of one Pr(III) ion, two chelidamic acid ligands, two coordinated waters, and two discrete waters. Unlike the La complex with chelidamic acid ligand [19], in which the lanthanum is ten-coordinate, in **1** the praseodymium is nine-coordinate by four oxygens and two nitrogens from two tridentate chelating chelidamic acids, one carboxylic oxygen from an adjacent

Table 1. Crystal data and structure refinement of 1.

Empirical formula	C ₁₄ H _{13.50} N ₂ O _{13.25} Pr
Formula weight	562.68
Crystal system	Triclinic
Space group	<i>P</i> - <i>1</i>
Unit cell dimensions (Å, °)	
<i>a</i>	6.7962(8)
<i>b</i>	11.846(1)
<i>c</i>	11.976(1)
α	94.311(3)
β	101.151(4)
γ	101.558(5)
Volume (Å ³), <i>Z</i>	920.29(17), 2
Crystal size (mm ³)	0.200 × 0.150 × 0.050
Absorption coefficient (mm ⁻¹)	2.725
Calculated density (g cm ⁻³)	2.031
<i>F</i> (000)	553
θ range for data collection (°)	3.13–25.25
Reflections collected	5952
Independent reflection	3295 [<i>R</i> (int) = 0.0223]
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ ^a = 0.0305, <i>wR</i> ₂ ^b = 0.0805
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0332, <i>wR</i> ₂ = 0.0838
Goodness-of-fit on <i>F</i> ²	1.003

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum w(F_o^2) \}^{1/2}.$$

Table 2. Selected bond lengths (Å) of 1.

Pr(1)–O(12) ⁱ	2.457(3)	Pr(1)–O(1W)	2.513(3)
Pr(1)–O(23)	2.480(3)	Pr(1)–O(11)	2.517(3)
Pr(1)–O(21)	2.484(3)	Pr(1)–O(2W)	2.541(3)
Pr(1)–O(13)	2.485(3)	Pr(1)–N(2)	2.557(4)
Pr(1)–N(1)	2.569(3)		
C(16)–O(11)	1.276(5)	C(26)–O(21)	1.230(5)
C(16)–O(12)	1.227(5)	C(26)–O(22)	1.267(5)
C(17)–O(13)	1.239(5)	C(27)–O(23)	1.267(5)
C(17)–O(14)	1.266(5)	C(27)–O(24)	1.237(5)
C(13)–O(15)	1.346(5)	C(23)–O(25)	1.350(5)

Symmetry transformations used to generate equivalent atoms: (i) $x + 1, y, z$.

Table 3. Hydrogen bonds of 1.

D–H...A	d(D–H) (Å)	d(H...A) (Å)	d(D...A) (Å)	\angle (DHA) (°)
O(1W)–H(1WA)...O(3W)	0.82(4)	1.93(4)	2.741(5)	169(7)
O(1W)–H(1WB)...O(2W) ⁱ	0.82(4)	2.25(5)	2.843(5)	129(6)
O(2W)–H(2WA)...O(3W) ⁱⁱ	0.83(4)	1.96(4)	2.770(5)	166(6)
O(2W)–H(2WB)...O(23) ⁱ	0.87(4)	1.92(5)	2.695(4)	148(5)
O(3W)–H(3WA)...O(25) ⁱⁱⁱ	0.88(4)	2.13(4)	2.924(5)	150(6)
O(3W)–H(3WB)...O(14) ^{iv}	0.85(4)	2.17(5)	2.915(5)	146(6)
O(15)–H(15A)...O(24) ^v	0.82	1.79	2.604(5)	176.9
O(25)–H(25A)...O(11) ^{vi}	0.82	1.87	2.684(4)	172.2

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y, -z + 1$; (ii) $x - 1, y, z$; (iii) $x, y - 1, z$; (iv) $-x + 1, -y, -z + 2$; (v) $x, y, z + 1$; and (vi) $-x, -y + 1, -z + 1$.

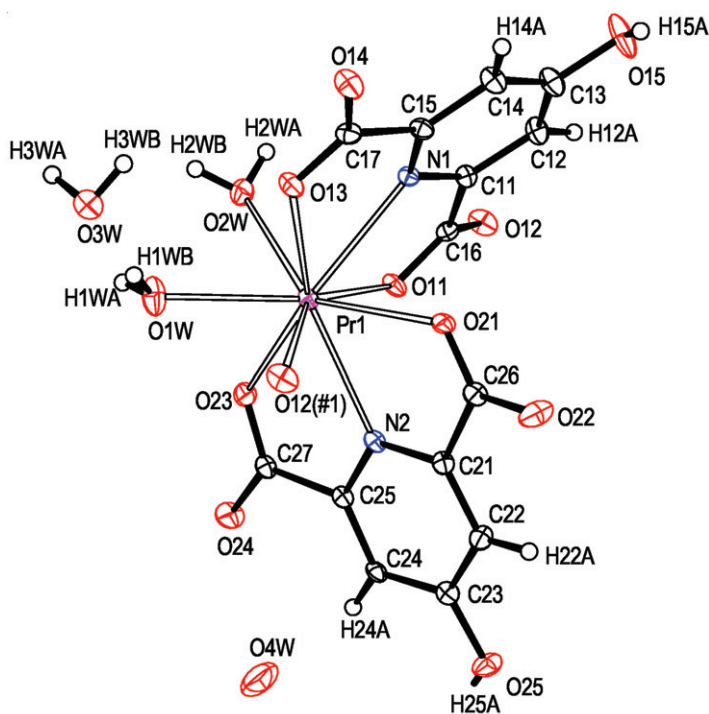


Figure 1. The molecular structure of **1**, showing 30% displacement ellipsoids for non-H atoms.

chelidamic acid, and two coordinated waters. Because of geometric requirements of the tridentate chelating chelidamic acid, the coordination geometry of Pr deviates considerably from the “idealized” tricapped trigonal prismatic geometry [22] that gives the lowest energy configuration for nine atoms surrounding a metal. The bond distances between the Pr and O atoms [Pr(1)–O(11) = 2.517(3) Å, Pr(1)–O(12) = 2.457(3) Å, Pr(1)–O(13) = 2.485(3) Å, Pr(1)–O(21) = 2.484(3) Å, Pr(1)–O(23) = 2.480(3) Å, Pr(1)–O(1W) = 2.513(3) Å, Pr(1)–O(2W) = 2.541(3) Å] follow in the range of those reported for praseodymium complexes in the literature [23, 24]. Pr–N bond distances [Pr(1)–N(1) = 2.557(4) Å, Pr(1)–N(2) = 2.569(3) Å] are shorter than values reported in the praseodymium complexes [25–27].

Unlike the Gd, Tb, and La complexes that have discrete structures, in **1**, the Pr is tridentate-chelated by two crystallographically unique chelidamic acids with one chelidamic acid further bridging adjacent Pr atoms through O12 into an infinite –M–O–M– chain along the *a* direction (M = Pr(III); O = carboxylate group) with the intra-chain PrPr distance = 6.796(2) Å, as shown in figure 2(a). The neighboring chains are connected into layers in the *ab* plane through the hydrogen bonds between O25 and O11, and O2W and O23 (figure 2b and table 3). These layers are inter-linked through a very complex hydrogen bonding network involving water and oxygens from chelidamic acid ligands to form a 3-D network (figure 3 and table 3).

There are two crystallographically independent chelidamic acids with different coordination modes in the structural unit. As shown in figure 1, one is tridentate with two oxygens and one nitrogen coordinated with Pr while the other is also tridentate

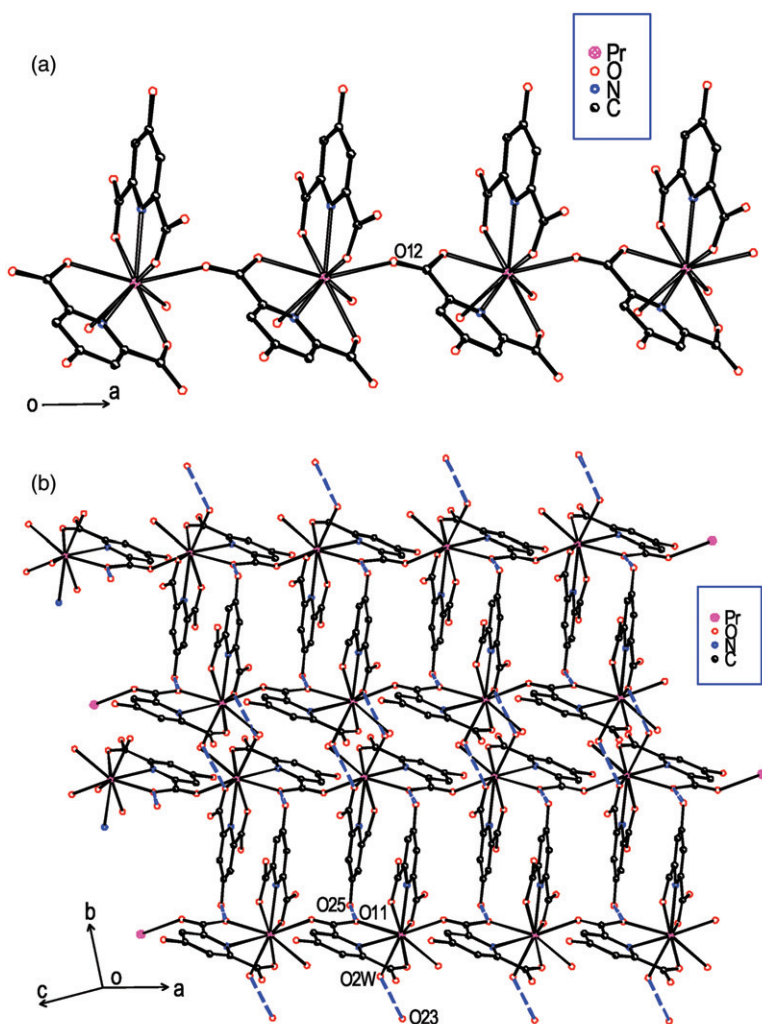


Figure 2. (a) The 1-D chain of **1** extending along the *a*-axis; (b) The 2-D layer of **1** in the *ab* plane. Dashed lines represent the hydrogen bonds. Hydrogen atoms are omitted for clarity.

with two oxygens and one nitrogen coordinated with the Pr atom and another oxygen from carboxylate coordinated with the symmetry generated Pr (figure 2a). The two chelidamic acids are in different ionizations for charge neutralization. One is $(\text{C}_7\text{H}_3\text{NO}_5)^{2-}$ while the other is $(\text{C}_7\text{H}_4\text{NO}_5)^-$, but they are difficult to distinguish as the hydrogens cannot be located from the difference map. Nevertheless, the protonated atom can be confirmed by structural analysis. First, the distances between O22 and O22^{*i*} ($\text{O}(22)\text{--}\text{O}(22)^i = 2.460 \text{ \AA}$; *i*: $-x + 1, -y + 1, -z + 2$) are abnormally short when the structure is packing. In addition, because of the existing hydrogen bonds of $\text{O}(2\text{W})\text{--}\text{H}(2\text{WB})\cdots\text{O}(23)$, $\text{O}(25)\text{--}\text{H}(25\text{A})\cdots\text{O}(11)$, and $\text{O}(3\text{W})\text{--}\text{H}(3\text{WB})\cdots\text{O}(14)$ (table 3), hydrogen should not locate at O11, O14, and O23. O22 should be protonated, and the larger bond distance of $\text{C}(26)\text{--}\text{O}(22)$ ($1.267(5) \text{ \AA}$) supports this deduction.

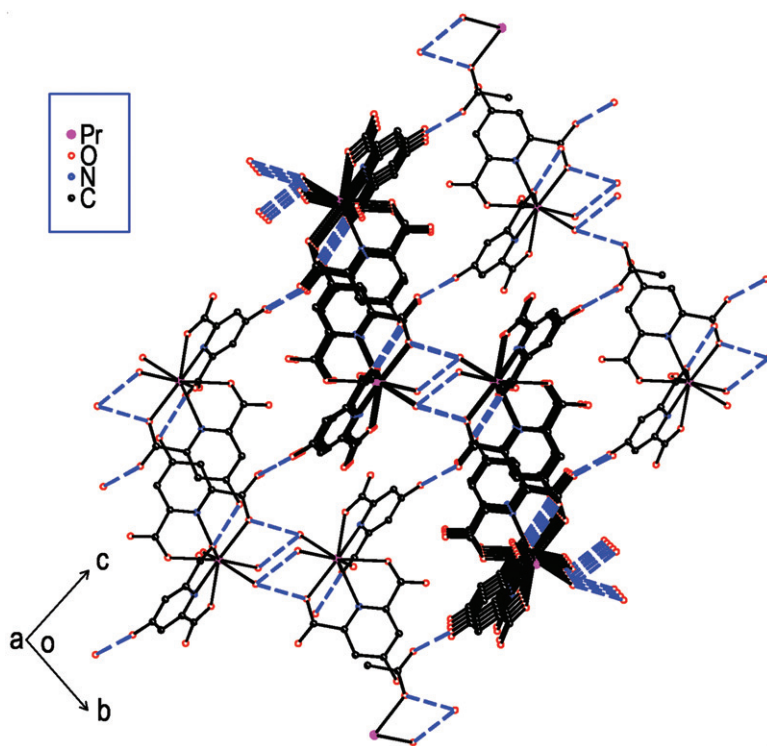


Figure 3. The 3-D network of **1** along the [1 0 0] direction. Dashed lines represent hydrogen bonds. Hydrogen atoms are omitted for clarity.

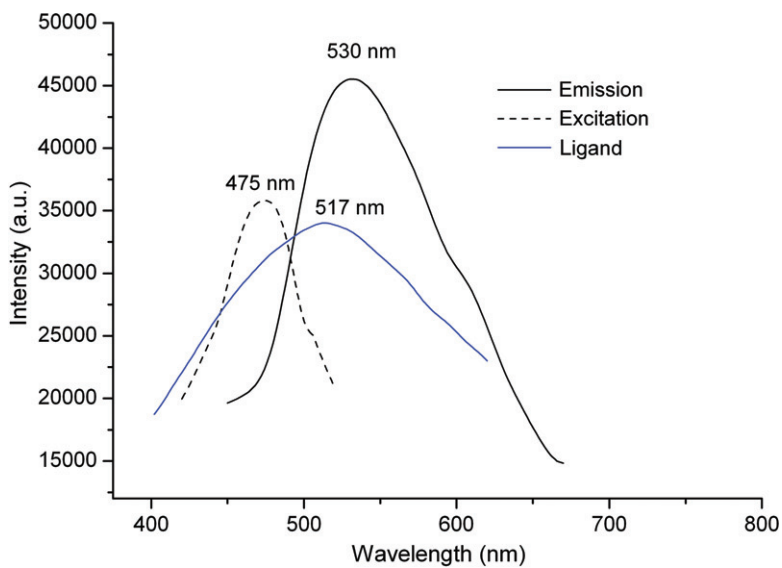


Figure 4. Solid state emission ($\lambda_{em} = 530$ nm) and excitation ($\lambda_{ex} = 475$ nm) spectra of **1** and the emission spectrum ($\lambda_{em} = 517$ nm) of the chelidamic acid with maximum excitation at 360 nm recorded at room temperature.

3.2. Optical property

The emission spectrum of crystalline samples for **1** in the solid state is shown in figure 4. The maximum emission wavelength of **1** is at 530 nm excited with $\lambda_{\text{ex}} = 475$ nm. The emission spectrum of free chelidamic acid features a blue fluorescence with the maximum emission at 517 nm with $\lambda_{\text{ex}} = 360$ nm. Compared to free chelidamic acid, **1** results in much higher emission energy and a little blue shift of emission, indicating that the emission of **1** originates from $\pi\text{-}\pi^*$ transition of the ligand [11, 28–30]. The enhanced luminescence efficiency of the complex is attributed to coordination of chelidamic acid to Pr^{3+} increasing rigidity of the ligand and reducing loss of energy. The shift of emission is complicated. The good luminescence efficiency indicates the complex may be a candidate for luminescent materials.

4. Conclusions

A 1-D coordination polymer, $[\text{Pr}(\text{C}_7\text{H}_3\text{NO}_5)(\text{C}_7\text{H}_4\text{NO}_5)(\text{H}_2\text{O})_2]_n \cdot 1.25n\text{H}_2\text{O}$, has been synthesized and characterized. The fluorescence spectrum of **1** shows a strong green luminescence emission in the solid-state at 530 nm upon photoexcitation at 475 nm. Combined with the fluorescence spectrum of free chelidamic acid, it can be concluded that the emission of **1** originates from $\pi\text{-}\pi^*$ transition of the ligand.

Supplementary material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC-713510. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +441223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We gratefully acknowledge financial support by the NSF of China (20801026), the NSF of Jiangxi Province (2008GQC0036), and the Jiangxi Provincial Department of Education (GJJ09486).

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