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Synthesis, crystal structure and catalytic property of a new samarium compound derived from 5-(pyrazin-2-yl)tetrazole-2-acetic acid

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Abstract: [Sm(pztza)₂(H₂O)₆]·pztza·3H₂O has been prepared by the reaction of SmCl₃·6H₂O and 5-(pyrazin-2-yl)tetrazole-2-acetic acid (Hpztza) under the presence of potassium hydroxide. The compound has been structurally characterized by elemental analysis, IR, and single-crystal X-ray diffraction. The X-ray analysis demonstrates this complex display a mononuclear structure. Furthermore, it shows excellent catalytic property for polymerization of vinyl monomers and the polymerization shows controlled characteristics. It can be isolated from the reaction system and reused for at least 10 times.

Keywords: Hpztza, samarium, vinyl monomers, catalytic polymerization

Introduction

Over the past decade, considerable attention given to coordination compounds based on tetrazole-carboxylate stems from not only their diversity in structure, but also their tunable applications in magnetism[1], gas storage[2], luminescence[3] and ferroelectric[4] and so on. On the one hand, tetrazole-carboxylate with both abundant
oxygen atoms of the carboxylate group and nitrogen atoms of the tetrazole ring are more likely to display a variety of coordination modes, forming a great number of intriguing topological structures. On the other hand, however, coordination compounds based on either tetrazole-carboxylate and rare earth elements are potentially excellent candidates for catalysis[5-7], samarium complex in particular, including the polymerizations of ethylene, a-olefine[8-14], styrene [8-13,15] and methyl methacrylate[16-18]. Compared to other families of samarium complexes used as efficient catalyst for vinyl polymerization based on cyclopentadienyl[19], ancillaryl[20], heteroleptic [21] and their derivatives, investigation on samarium-tetrazole-carboxylate are by no means satisfactory and should be further studied. Therefore, tremendous fascination has been exerted on the synthesis and characterization of these complexes, leading us to the exploration of this area.

In our previous work, we have reported a Sm-pytza compound [pytza=5-(3-pyridyl)tetrazole-2-acetato] who shows good catalytic property for polymerization of vinyl monomers. To extend our previous work, in this communication, another tetrazole-carboxylate Hpztza [Hpztza=5-(2-pyrazinyl)tetrazole-2-acetic acid] have been employed to react with SmCl$_3$·6H$_2$O. We anticipate that ptzta will display different coordination modes since it tends to adopt a classic N(pyrazine), N'(tetrazole) chelating mode and the carboxylate group can act as a bridging ligand. Reactions of Hpztza and SmCl$_3$·6H$_2$O with the presence of potassium hydroxide under hydrothermal conditions, produced a new mononuclear complex [Sm(ptzta)$_2$(H$_2$O)$_6$] ptzta·3H$_2$O, which has been applied to the catalysis in vinyl polymerization. It shows excellent catalytic property and can be reused for at least 10 times.

2. Experimental section

2.1 Materials and apparatus

General chemicals were obtained from commercial sources and used without further purification. The elemental analyses for C, H and N were performed with an
EA1110-CHNS elemental analyser. The IR spectra were obtained on a NICOLET380 spectrum using KBr disks in the range 4000–400 cm\(^{-1}\). \(^1\)H NMR spectra were recorded at ambient temperature with a Varian UNITYplus-400 spectrometer. Single crystal X-ray diffraction was carried out by a Rigaku SCXmini-CCD diffractometer. Polymerization was performed on a XPA-1 photochemical reactor, with 300W Hg light source, and the rolling rate was 20rpm, the wavelength of the radiation light was selected as 365nm. Molecular weight and molecular weight distribution of the polymers were measured by PL GPC 50 at 25°C using THF as eluent against polystyrene standards, flow rate: 1mL/min, sample concentration: 1mg/mL.

2.2 Synthesis of 5-(pyrazin-2-yl)tetrazole-2-acetic acid

5-(2-pyrazinyl)tetrazole (Hpztz) was prepared according to the Demko and Sharpless \([2+3]\) cycloaddition reactions method[22]. Chloroacetic acid (4.37 g, 0.05 mol), Hpztz (7.40 g, 0.05 mol), and potassium hydroxide (5.62 g, 0.10 mol) in 100 mL of methyl alcohol was refluxed 24 h at 70 °C. After the mixture was cooled to room temperature, the new precipitate was then filtered, washed with 2 \(\times\) 30 mL methanol, the precipitate was dissolved in distilled water (30 mL) and the pH of the solution was adjusted to 2 with concentrated HCl, white powder 5-(pyrazin-2-yl)tetrazole-2-acetic acid(Hpztza) was obtained, 62.8% yield (based on pz tz), mp: 235~240°C. \(^1\)H NMR (400MHz, in DMSO-\(d_6\)) \(\delta\) (ppm) 13.85 (1H), 8.76-9.40 (3H), 5.78 (2H); Anal. Calcd for C\(_7\)H\(_6\)N\(_6\)O\(_2\): C, 40.78; H, 2.93; N, 40.76%. Found: C, 40.49; H, 2.75; N, 40.61%. IR (KBr, cm\(^{-1}\)): 3426 (s), 1730 (s), 1449 (s), 1420 (s), 1347 (s) 1257 (s), 1209 (m), 1146 (m), 1064 (m), 1018 (m), 905 (m), 868 (s), 830 (m), 666 (m).

2.3 Synthesis of [Sm(pztza)\(_2\)(H\(_2\)O)\(_6\)]·pztza·3H\(_2\)O

Hpztza (0.618 g, 3mmol) was added to distilled water (70 mL) and the pH value of the solution was adjusted to 6 with KOH (0.2mol/L). Then SmCl\(_3\)-6H\(_2\)O (0.364 g, 1 mmol) were added to this solution. The mixture was sealed in a 250 mL Teflonlined stainless steel container, which was heated at 120°C for 48 h and then cooled to room
temperature, crystals of [Sm(pztza)$_2$(H$_2$O)$_6$] pztza·3H$_2$O were obtained. Yield: 556.8 mg (60% based on Sm). Anal. Calcd for C$_{21}$H$_{33}$SmN$_{18}$O$_{15}$: C:27.18; N:27.17; H:3.58 %. Found: C:27.26; N:27.23; H:3.51 %. IR (KBr, cm$^{-1}$): 3436(s), 1630(s), 1600(s), 1387(s), 1303(m), 1205(w), 1151(m), 1071(m), 1024(m), 822(w), 721(w).

2.4 Single crystal X-ray crystallography

Single crystal X-ray crystal data were collected on a Rigaku SCX mini CCD diffractometer equipped with graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.071073 Å). The intensity data were collected by the $\omega$ scan technique and were reduced using the Crystal-Clear program [23], and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined on F$^2$ by full matrix least squares using SHELXTL[24-25]. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they were bonded.

2.5 Typical polymerization process

0.01 g of Sm/pztza complex was mixed with 10 g of acetone in a quartz reaction tube, stirred by magnetic power. The dry nitrogen was input for about 20 minutes to eliminate effect of the possible air, and then 2 g of monomer was added. The polymerization was performed on a XPA-1 photochemical reactor, with 300W Hg light source and the rolling rate was 20rpm, the wavelength of the radiation light was selected as 365nm.

3. Results and discussions

3.1 Crystal structure of [Sm(pztza)$_2$(H$_2$O)$_6$]-pztza·3H$_2$O

The X-ray diffraction reveals that [Sm(pztza)$_2$(H$_2$O)$_6$]-pztza·3H$_2$O crystallizes in monoclinic space group $P2_1/c$. As is shown in Fig.1, each Sm(III) center is
nine-coordinated by three oxygen atoms from two pztza ligands and six oxygen atoms from six water molecules, forming a monocapped square-antiprism coordination geometry. Two pztza ligands act as a bidentate chelating or a monodentate ligand to coordinate to the same Sm(III) center, respectively, whereas the third pztza ligand is not coordinated, only to balance the charge, therefore it displays a mononuclear structure. Compared to the Sm-pytza complex, pztza adopts a relatively simple coordination mode and the structure transforms from a 1D chain to a mononuclear one. However, when the pyridyl ring is replaced by the pyrazinyl ring, more hydrogen bonds exist to stabilize the supramolecular assembly. Adjacent mononuclear units are further held together by various hydrogen bonds to form a 3D supramolecular network (Fig2). Important crystal data and refinement parameters: Formula C_{21}H_{33}SmN_{18}O_{15}, Mr = 928.00, colorless crystal, monoclinic, space group P2_{1}/c, a = 10.562(2) Å, b = 23.525(5) Å, c = 14.459(3) Å, β = 105.93(3)°, V = 3454.7(12) Å³, Z = 4, T = 291(2)K, D_{calc} = 1.784 g.cm⁻³, μ = 1.795 mm⁻¹, R (wR) = 0.0584 (0.1396) and GOF = 0.949 for 5041 reflections with I > 2.00σ(I).

Table 1  Selected bond distances (Å) and angles (°) for the catalyst

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
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<tr>
<td>Sm(1)–O(10)</td>
<td>2.403(3)</td>
<td>Sm(1)–O(3)</td>
<td>2.404(3)</td>
</tr>
<tr>
<td>Sm(1)–O(11)</td>
<td>2.436(3)</td>
<td>Sm(1)–O(8)</td>
<td>2.443(3)</td>
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<td>Sm(1)–O(12)</td>
<td>2.453(3)</td>
<td>Sm(1)–O(9)</td>
<td>2.482(3)</td>
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<td>Sm(1)–O(1)</td>
<td>2.503(5)</td>
<td>Sm(1)–O(7)</td>
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<tr>
<td>Sm(1)–O(2)</td>
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<tr>
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<td>O(10)–Sm(1)–O(11)</td>
<td>68.86(11)</td>
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<td>O(10)–Sm(1)–O(8)</td>
<td>76.12(11)</td>
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<tr>
<td>O(3)–Sm(1)–O(8)</td>
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<td>O(11)–Sm(1)–O(8)</td>
<td>137.22(11)</td>
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<tr>
<td>O(10)–Sm(1)–O(12)</td>
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<td>111.96(12)</td>
<td>O(8)–Sm(1)–O(9)</td>
<td>77.09(10)</td>
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O(12)–Sm (1)–O(9)  70.40(10)    O(10)–Sm(1)–O(1)  35.83(14)
O(3)–Sm (1)–O(1)  75.03(15)    O(11)–Sm (1)–O(1)  71.86(14)
O(8)–Sm (1)–O(1)  124.91(13)   O(12)–Sm (1)–O(1)  86.45(13)
O(9)–Sm (1)–O(1)  145.26(14)   O(10)–Sm (1)–O(7)  70.21(11)
O(3)–Sm (1)–O(7)  140.08(11)   O(11)–Sm (1)–O(7)  71.16(11)
O(8)–Sm (1)–O(7)  74.46(9)     O(12)–Sm (1)–O(7)  134.28(10)
O(9)–Sm (1)–O(7)  135.90(10)   O(1)–Sm (1)–O(7)   78.74(14)
O(10)–Sm (1)–O(2) 135.46(14)   O(3)–Sm (1)–O(2)  112.75(14)
O(11)–Sm (1)–O(2) 114.94(14)   O(8)–Sm (1)–O(2)  74.76(13)
O(12)–Sm (1)–O(2) 67.20(13)    O(9)–Sm (1)–O(2)  132.29(13)
O(1)–Sm (1)–O(2)  50.91(15)    O(7)–Sm (1)–O(2)  69.97(14)

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**Fig. 1-2 Here**

### 3.2 Catalytic property of [Sm(pztza)$_2$(H$_2$O)$_6$]·pztza·3H$_2$O

Polymerization results were presented in Table 2. The vinyl monomers with polar group cannot be initiated by Sm/pztza complex, and could not obtain high $M_n$ (entries 11-14, Table 2), which might be attributed to the strength force between polar group and the center atom of Sm[16-18]. Polymerization of vinyl monomers in this condition proceeds readily under a 359 nm light radiation for 60 minutes at room temperature. This is a fast and smooth reaction, the increase in rate is manifested by a lowering of molecular weight from 8192 to 5003, and broadening of the polydispersity from 1.25 to 3.01, which is ascribed to the chain transfer reaction. Inspired by these observations, we have lowered the radiation power in order to avoid the excessive chain transfer reaction[26-27]. Polymerization proceeds efficiently at reaction 4, reaching 92% conversion after 60 minutes at 300W power.

In Table 2, final molecular weight and conversion data for the polymers synthesized in this work.

<table>
<thead>
<tr>
<th>Reaction $^a$</th>
<th>Time/min</th>
<th>Power/W</th>
<th>Conversion/% $^b$</th>
<th>$M_n$ $^c$</th>
<th>PDI $^c$</th>
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<tr>
<td>O(12)–Sm (1)–O(9)</td>
<td>70.40(10)</td>
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<td>86.45(13)</td>
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<td>O(9)–Sm (1)–O(1)</td>
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<td>O(10)–Sm (1)–O(7)</td>
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<td>O(8)–Sm (1)–O(7)</td>
<td>74.46(9)</td>
<td>O(12)–Sm (1)–O(7)</td>
<td>134.28(10)</td>
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<td>O(9)–Sm (1)–O(7)</td>
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<td>78.74(14)</td>
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<tr>
<td>O(1)–Sm (1)–O(2)</td>
<td>50.91(15)</td>
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<tr>
<td></td>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>300</td>
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</table>

<sup>a</sup> All reactions carried were 20% g/g in acetone.  <sup>b</sup> Conversion from integration of gravimetric method.  <sup>c</sup> Determined using PL GPC-50 against polystyrene standards. Vinyl monomer;  
<sup>d</sup> = styrene;  
<sup>e</sup> = butyl carylate;  
<sup>f</sup> = methyl methacrylate;  
<sup>g</sup> = vinyl acetate;  
<sup>h</sup> = acrylic acid;  
<sup>i</sup> = methacrylic acid;  
<sup>j</sup> = acrylamide;  
<sup>k</sup> = 2-Hydroxyethyl methacrylate. [monomer]-[initiator]  
<sup>d</sup> = 2<sup>e</sup> = 3<sup>f</sup> = 4<sup>g</sup> = 5<sup>h</sup> = 6<sup>i</sup> = 7<sup>j</sup> = 100:1;  
<sup>d<sup>e</sup></sup> = 2<sup>e</sup> = 3<sup>f</sup> = 4<sup>g</sup> = 5<sup>h</sup> = 6<sup>i</sup> = 7<sup>j</sup> = 200:1;  
<sup>de</sup> no polymer produced.

Styrene, vinyl acetate, methyl methacrylate, and butyl acrylate were used, as representative of the vinyl monomers, for the photo-polymerization initiated by the Sm/Pztza complex (entries 4, 8, 9 and 10, Table 2). All reactions at 300W with smooth rate and high conversion (larger than 87%) show a low amount of side reactions under these conditions. This corresponds to the relatively narrow PDI values. And the low Mn of the products indicates that the polymerization shows controlled characteristics. When the molar ratio of monomer to Sm/Pztza complex is doubled from 100 to 200, an approximate doubling of the Mn is observed (entries 4 and 7, Table 2), as would be expected for a controlling polymerization. Fig.3 shows the
evolution of the $M_n$ as a function of [M]/[Cat] for reaction 3, 8, 9 and 10, which increases linearly again as would be expected for controlling polymerization. Compound $[\text{Sm(pztza)}_2(\text{H}_2\text{O})_6]\cdot\text{pztza}\cdot3\text{H}_2\text{O}$ is superior to Sm-pytza in the polymerization of butyl acrylate since the $M_n$ value increases sharply. However, $[\text{Sm(pztza)}_2(\text{H}_2\text{O})_6]\cdot\text{pztza}\cdot3\text{H}_2\text{O}$ is inferior to Sm-pytza in the polymerization of methyl methacrylate in that a dramatic decrease in $M_n$ value is observed. When it comes to styrene and vinyl acetate, the catalytic property of $[\text{Sm(pztza)}_2(\text{H}_2\text{O})_6]\cdot\text{pztza}\cdot3\text{H}_2\text{O}$ is similar to that of Sm-pytza.

**Fig. 3** Here

This compound is immiscible with acetone, which leads to the easy isolation of the catalyst from the polymer solution for potential reuse. After 10 cycle reuse in methyl methacrylate polymerization, the catalyst recovery is up to 92%, which indicates that the compound is a recovery catalyst and could be repeated for at least 10 times.

4. Conclusions

To the best of our knowledge, we are the first to report the samarium coordination compound containing pztza. This compound shows specific and excellent catalytic behavior in the polymerization of vinyl monomers. The polymerization reactions are fast and smooth, and shows controlled characteristics. Our research results indicate that Sm-pztza may be potentially used as catalyst for polymerization of vinyl monomers. Other samarium complexes based on tetraole-carboxylate are currently underway.

Acknowledgements

We greatly appreciate the financial support from the 14th Challenge Cup for Domestic College Students, College Students’ Innovation and Entrepreneurship Training Program of Jiangsu Province and the Start Grant from CSLG.

Fig.1 The structure of $\text{Sm(pztza)}_2(\text{H}_2\text{O})_6]\cdot\text{pztza}\cdot3\text{H}_2\text{O}$. Hydrogen atoms are omitted
for clarity.

**Fig.2** The 3D supramolecular network of Sm(pztza)$_2$(H$_2$O)$_6$·pztza·3H$_2$O formed by hydrogen bonds.

**Fig.3** the relationship between Mn of polymers and initial molar ratio [Mo]/[Cat]. ■ styrene, ▲methyl methacrylate, ▼butyl acrylate, ●vinyl acetate.

**References**

264x211mm (96 x 96 DPI)
Graphical Abstract

Sm(III)/pztza complex is an efficient recovery catalyst for polymerization of vinyl monomers

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A new Sm(III)/pztza complex ([Sm(pztza)2(H2O)6] pztza·3H2O) have been synthesized. By using the resulting compound as initiator, we have examined its catalytic actives for polymerization of vinyl monomers and found that the reactions were relatively fast and smooth, and the polymerization showed controlled characteristics.

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