

一维梯形蓝色荧光磺酸锶配位聚合物

谢永荣* 钟海山 袁小勇 付大伟 杨瑞卿

(赣南师范学院化学与生命科学系, 江西省有机药物化学重点实验室, 赣州 341000)

关键词: 1D 聚合物; 锶; 蓝色荧光; 3-羧基-4-羟基苯磺酸

中图分类号: O614.23*2

文献标识码: A

文章编号: 1001-4861(2006)08-1550-05

A Novel 1D Ladderlike Strontium Coordination Polymer of Sulfonate Ligand with Strong Blue Fluorescent Emission

XIE Yong-Rong* ZHONG Hai-San YUAN Xiao-Yong FU Da-Wei YANG Rui-Qing

(Department of Chemistry and Life Science, Gannan Normal University, Key Laboratory of Organo-pharmaceutic

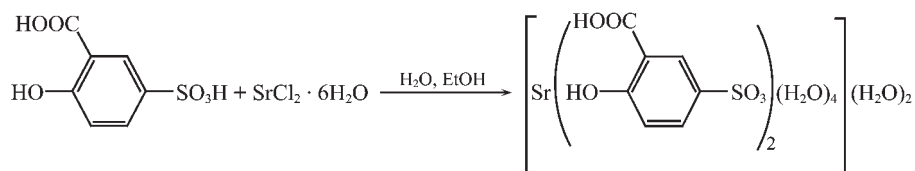
Chemistry of Jiangxi Province, Ganzhou, Jiangxi 341000)

Abstract: The reaction of 3-carboxy-4-hydroxybenzenesulfonic acid with $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ yields one-dimensional double-chain coordination polymer $\{[\text{Sr}(\text{H}_2\text{SSA})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$ (**1**), which displays strong blue fluorescence emission ($\lambda_{\text{max}}=423 \text{ nm}$) in the solid-state at room temperature. Crystal data for **1**: Triclinic, space group $P\bar{1}$, $a=0.68848(2) \text{ nm}$, $b=0.70686(2) \text{ nm}$, $c=2.47422(7) \text{ nm}$. $\alpha=96.458(2)^\circ$, $\beta=90.796(2)^\circ$, $\gamma=108.6280(10)^\circ$, $V=1.13219(6) \text{ nm}^3$, $Z=2$, 16 575 unique data ($\theta_{\text{max}}=25.99^\circ$), $R=0.0211$ (4 411 [$I \geq 2\sigma(I)$] reflections), $wR=0.0525$ (all data), $\rho_{\text{max}}=0.881 \text{ e} \cdot \text{nm}^{-3}$. CCDC: 279677.

Key words: 1D coordination polymer; strontium(II); blue fluorescent emission; 3-carboxy-4-hydroxybenzenesulfonic acid

The sulfonate group, RSO_3^- , with a strong structural analogy to the phosphonate group, RPO_3^{2-} , may bridge multiple metal centers to form highly regular and rigid coordination polymers^[1]. We have performed the reactions of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, H_3SSA) with $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and obtained a novel one-dimensional double-chain

coordination polymer $\{[\text{Sr}(\text{H}_2\text{SSA})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$ (**1**) (Scheme 1). To the best of our knowledge, Sr-complexes used sulfonate ligands as building block are nearly unexplored^[2] although there are some alkaline earth coordination polymers containing sulfonate ligands as building blocks^[3]. Herein we would like to report the synthesis, crystal structure and fluorescent



Scheme 1

收稿日期: 2006-05-23。收修改稿日期: 2006-06-12。

江西省教育厅科技基金项目(No.200407029; No.2006-237)资助。

*通讯联系人。E-mail: yongrongxie@yahoo.com.cn

第一作者: 谢永荣, 男, 42 岁, 博士, 教授; 研究方向: 功能配合物合成、结构和性质。

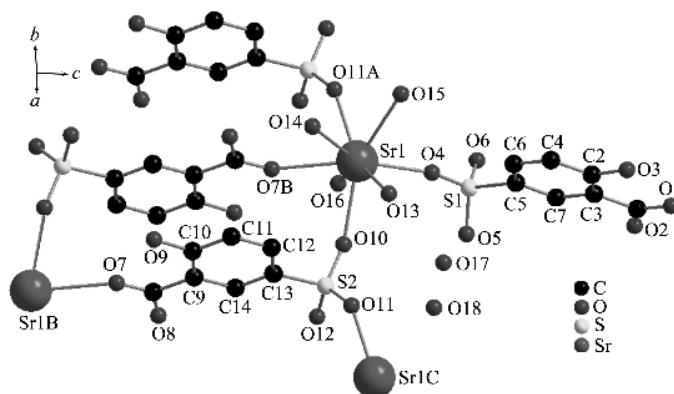
property of **1**.

The IR spectrum of compound **1** shows two very strong peaks at 1 670 and 1 609 cm^{-1} (s) combined with two moderately strong peaks at 1 476 and 1 449 cm^{-1} (m) suggesting that the carboxylic acid group and phenyl ring are present in **1**. Two strong peaks at 1 221 and 1 147 cm^{-1} (s) indicated the presence of the sulfonate group in **1**. In addition, a broad peak at 3 300~3 500 cm^{-1} (s) suggests that there are coordinated or crystalline water molecules in the coordination polymer.

X-ray single-crystal structure determination reveals that **1** has 1D double chains motif with H_2SSA^- acts as tridentate or monodentate ligand to coordinate to Sr centers, In the asymmetric unit there involve one Sr ion coordinated to four different H_2SSA^- ligands (through oxygen atoms of three sulfonate and one carboxylate groups) and two uncoordinated water as shown in Fig.1, and the local coordination geometry around the Sr center in **1** can be best described as a

distorted hexagonal bipyramide. Two oxygen atoms (O4 and O7A) separately from sulfonate group and carboxylate group of different ligands as well as four oxygen atoms from water form the equatorial plane, while two oxygen atoms (O10 and O11B) of sulfonate group occupy two apical positions. In **1**, sulfonate groups are deprotonated, while carboxylate groups and hydroxyl groups are neutral.

There are two crystallographically unique H_2SSA^- ligands in the structure. One ligand binds to three Sr ions as tridentates ligand with the carbonyl oxygen atom of carboxylate group coordinating to one Sr ion, although neutral carboxylate group is a weak coordinating group, and two sulfonate oxygen atoms coordinating to otherwise two Sr ions, respectively to result in the formation of double-chain coordination polymer as shown in Fig.2. Another ligand binds to one Sr ion using one sulfonate oxygen atom as monodentate ligand and arranges in two sides of the chains, while the



Selected bond lengths (nm) and angles ($^\circ$):

Sr(1)-OW1 0.253 04(19); Sr(1)-O(4) 0.253 58(16); Sr(1)-O(11)#1 0.254 46(15); Sr(1)-O(10) 0.256 05(15);

Sr(1)-O(7)#2 0.262 09(15); Sr(1)-OW3 0.265 80(17); Sr(1)-OW2 0.272 54(16); Sr(1)-OW4 0.272 90(17); C(8)-O(7) 0.122 7(3); C(8)-O(8) 0.130 1(3);

OW1-Sr(1)-O(4) 88.65(6); OW1-Sr(1)-O(11)#1 143.75(6); O(4)-Sr(1)-O(11)#1 99.54(6); OW1-Sr(1)-O(10) 72.56(6); O(4)-Sr(1)-O(10) 89.86(6); O(11)A-Sr(1)-O(10) 141.96(5); OW1-Sr(1)-O(7)#2 115.42(6); O(4)-Sr(1)-O(7)#2 145.28(6); O(11)A-Sr(1)-O(7)#2 76.17(5); O(10)-Sr(1)-O(7)#2 75.40(5); OW1-Sr(1)-OW3 76.80(6); O(4)-Sr(1)-OW3 80.59(6); O(11)A-Sr(1)-OW3 69.95(5); O(10)-Sr(1)-OW3 148.07(6); O(7)#2-Sr(1)-OW3 127.31(5); OW1-Sr(1)-OW2 71.67(6); O(4)-Sr(1)-OW2 146.46(6); O(11)#1-Sr(1)-OW2 82.99(5); O(10)-Sr(1)-OW2 108.77(5); O(7)#2-Sr(1)-OW2 68.03(5); OW3-Sr(1)-OW2 68.80(5); OW1-Sr(1)-OW4 141.20(6); O(4)-Sr(1)-OW4 75.12(6); O(11)#2-Sr(1)-OW4 74.60(5); O(10)-Sr(1)-OW4 72.41(5); O(7)#2-Sr(1)-OW4 70.51(5); OW3-Sr(1)-OW4 132.48(5); OW2-Sr(1)-OW4 136.40(5)

Symmetry codes are as follows: #1: $x, y+1, z$; #2: $x+1, y+1, z$; #3: $x, y-1, z$

Hydrogen atoms are omitted for clarity

Fig.1 Asymmetric structure of compound **1**, in which metal center is surrounded by four water and four H_2SSA^- ligands to form a distorted hexagonal bipyramidal geometry

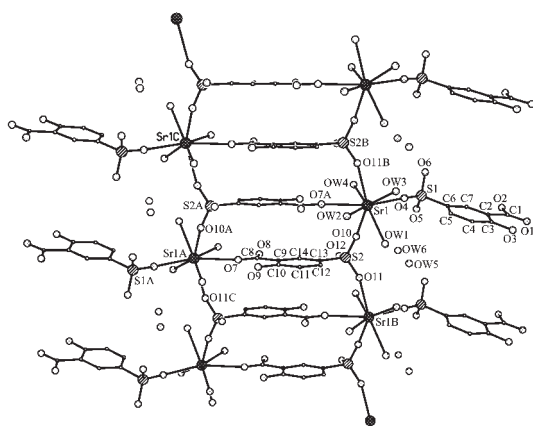


Fig.2 1D double-chain motif with H_2SSA^- acts as tridentate or monodentate ligand to link Sr centers

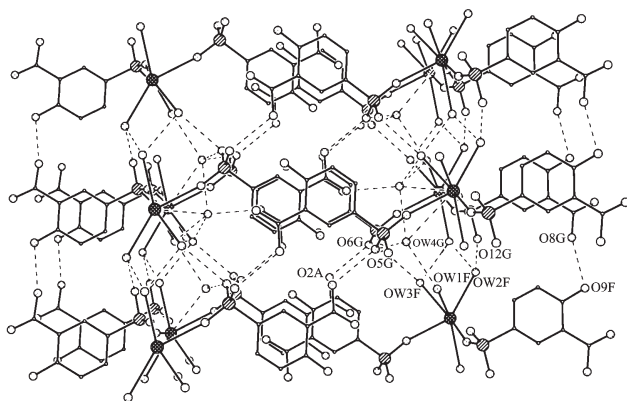
hydroxyl group of **1** is not coordinated to the Sr ion.

Polymer **1** have showed an undulation ladder structure formed by the assembly of strontium ion with tridentate ligand and composed of two different squares in which the edge lengths are 0.892 6 and 0.392 5 nm, and the angles are 74° and 106° for square I (Sr1, S2A, Sr1A and S2), and the edge lengths are 0.892 6 and 0.382 7 nm, and the angles are 112° and 68° for square II (Sr1, S2A, Sr1C and S2B). The dihedral angles between the neighboring parallelograms are 32.6° (Fig.2). Finally, no interpenetration occurs in **1** different from that found in sever-

al ladder structures^[4].

The Sr-O (water) distances ranging from 0.253 04(19) to 0.272 90(17) nm are similar to the reported values. The strontium sulfonate oxygen distances (0.253 58(16) to 0.256 05(15) nm) are near to those found in other strontium sulfonate^[5]. The Sr(1)-O(7)A distances (0.262 09(15) nm), corresponding to the carboxylate, are slightly shorter than those of normal Sr-OCO distances (0.265 5 nm and 0.264 6 nm)^[6].

From its crystal packing view, as shown in Fig.3, the double-chains are held together by a network of hydrogen bonds to result in the formation of 3D network, however, there are five kinds of H-bonds. Those are: (1) one(O2) of two oxygen atoms of carboxylate group from monodentate ligand and one(O6) of three oxygen atoms of sulfonate group from monodentate ligand in the another polymer chain, ($\text{D}\cdots\text{A}$ 0.273 6(3) nm); (2) and one (O8) of two oxygen atoms of carboxylate group as tridentate ligand and one oxygen atom (O9) of hydroxyl group as tridentate ligand of the another polymer chain, ($\text{D}\cdots\text{A}$ 0.283 0(3) nm); (3) coordinated water (OW2 or OW3) and one (O12, or O5) of three oxygen atoms of sulfonate group of the another polymer chain, ($\text{D}\cdots\text{A}$ 0.278 7(2) or 0.289 2(3)nm); (4) coordinated water(OW2 or OW3) and coordinated water (OW4) from the another polymer chain, ($\text{D}\cdots\text{A}$



Typical hydrogen-bond lengths (nm) are shown below:

O2-H2 \cdots O6 0.273 6(3); O3-H3 \cdots O1 0.262 4(3); O8-H8 \cdots O9 0.283 0(3); O8-H8 \cdots OW2 0.266 4(2); O9-H9A \cdots O7 0.257 2(3); OW1-H13A \cdots OW6 0.283 4(3); OW1-H13B \cdots OW5 0.274 3(3); OW2-H14A \cdots O12 0.278 7(2); OW2-H14B \cdots OW4 0.294 8(3); OW3-H15A \cdots O5 0.289 2(3); OW3-H15B \cdots OW5 0.269 8(3); OW4-H16A \cdots O12 0.285 1(2); OW4-H16B \cdots OW3 0.292 3(3); OW5-H17A \cdots O1 0.275 0(2); OW5-H17B \cdots OW6 0.283 6(3); OW6-H18A \cdots O6 0.281 7(3); OW6-H18B \cdots O5 0.276 4(3); C5-H5 \cdots O4 0.293 1(3); C7-H7 \cdots O2 0.330 0; C14-H14C \cdots O12 0.288 6(3)

Fig.3 3D network representation of **1** though strong H-bonds

0.294 8(3) or 0.292 3(3) nm); (5) seven hydrogen bonds bind guest water to the framework ($D \cdots A$ 0.269 8(3)~0.28 36(3) nm).

There are no π -stacking interactions between any benzene rings in the structure, the ladder structures of **1** stack in a parallel fashion (Fig.3). To best of our knowledge, compound **1** is the first Sr-complex used H_2SSA^- as building block although a few metal complexes of H_3SSA have been reported^[7].

As shown in Fig.4 compound **1** in the solid state at room temperature has an emission at 423 nm that can be contributed to emission of ligand H_3SSA since a similar emission is observed for free H_3SSA (387 nm). However, it is noteworthy that the emission wavelength in **1** is slightly longer than those of free H_3SSA ligand, probably as a result of that is either MLCT (metal-to-ligand charge transfer) or LMCT (ligand-to-metal charge transfer) in nature, and can probably be assigned to the intraligand fluorescent emission, and can probably be the result of coordination of H_2SSA^- to Sr^{2+} that increases the ligand conformational rigidity, thereby reducing the nonradiative decay of the intraligand excited state. Thus, **1** may be used as an advanced material for blue light emitting diode devices.

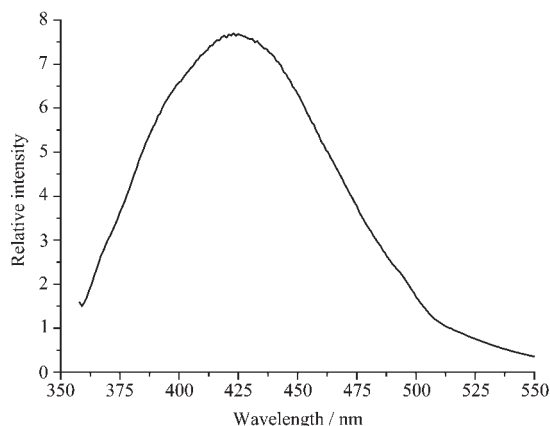


Fig.4 Solid-state fluorescent emission spectrum of powdered **1** at room temperature (λ_{ex} =351 nm)

In summary, we have synthesized a one-dimensional ladderlike strontium sulfonate coordination polymer with strong blue fluorescent emission in which each unit contains two crystallographically unique H_2SSA^- ligands. One ligand binds to three Sr

ions as tridentates ligand to form the one dimension double-chain structure. Another ligand as monodentate ligand arranges in two sides of the double-chain.

Experiment

The mixture of $SrCl_2 \cdot 6H_2O$ (0.799 9 g, 3 mmol) and H_3SSA (0.508 4 g, 2.0 mmol) in 25 mL 30% ethanol solution was stirred for 30 min, the mixture was filtered. Colorless block crystals of $\{[Sr(H_2SSA)_2(H_2O)_4] \cdot 2H_2O\}_n$ (**1**) suitable for X-ray analysis were obtained from the filtrate after standing for several days at room temperature in 80% yield based on H_3SSA . Intensity data were collected at 293(2) K on a Bruker AXS SMART CCD for a colorless block 0.330 mm \times 0.316 mm \times 0.168 mm. $C_{14}H_{22}O_{18}S_2Sr$, $M=630.06$, Triclinic, $P\bar{1}$, $a=0.688\ 48(2)$ nm, $b=0.706\ 86(2)$ nm, $c=2.474\ 22(7)$ nm. $\alpha=96.458(2)^\circ$, $\beta=90.796(2)^\circ$, $\gamma=108.628\ 0(10)^\circ$, $V=1.132\ 19(6)$ nm³, $Z=2$, 16 575 unique data ($\theta_{max}=25.99^\circ$), $R=0.021\ 1$ (4 411 [$I \geq 2\sigma(I)$] reflections), $wR=0.052\ 5$ (all data), $\rho_{max}=0.881\ e \cdot nm^{-3}$, water-H were not located. Programs used: SAINT, SADABS, SHELX-97, ORTEP.

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