

Hydrothermal synthesis, crystal structures and properties of Tiron-bridged di- and trinuclear strontium complexes containing nitrogen-donor ligands



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ABSTRACT

The hydrothermal reactions of SrCl_2 with 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium ($\text{Na}_2\text{H}_2\text{Tiron}$) and 1,10-phenanthroline ligands yielded two strontium complexes of general formula $[\text{Sr}_2(\text{Tiron})_2(\text{phen})_2(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{phen} \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Sr}_3(\text{Tiron})_2(\text{phen})_3(\text{H}_2\text{O})_5] \cdot \text{Hphen} \cdot 0.5\text{H}_2\text{phen} \cdot 8\text{H}_2\text{O}$ (**2**) (phen = 1,10-phenanthroline). Complexes **1–2** were characterized by X-ray single crystal diffraction, elemental analyses, FT-IR, and thermogravimetric analyses. Complex **1** features a pentadentate Tiron-bridged dinuclear structure, where Sr1 and Sr2 ions exhibit bicapped trigonal prism and monocapped square antiprism geometries, respectively, interconnected through edge-sharing. Complex **2** is a pentadentate and hexadentate Tiron-bridged trinuclear one, where Sr1 and Sr2 ions all exhibit bicapped trigonal prism geometries, interlinked via edge-sharing, and Sr3 ion exhibits a rare triangular prism geometry. The luminescent properties were also studied, and the results exhibit that the luminescence emissions of complexes **1–2** happen the bathochromic shifts, compared with the ligands.

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1. Introduction

In comparison with the carboxylates and phosphonates, sulfonates are weaker ligands and they have been much less used in the design of metal–organic species [1–4]. However, since the first functional pillared metal sulfonate network was synthesized in 2001 by Côté and Shimizu [5], the research on synthesis and properties of metal sulfonate complexes, where sulfonate ligands act as multidentate linkers, has been a fast-growing research field due to the large variety of topologies, dimensionalities, and their potentially useful applications, such as ion-exchange, adsorption, catalytic, fluorescence, and magnetic materials [6–12]. The diverse architectures involving sulfonates have been reported with alkali, alkaline-earth, d-block, and 4f metal cations [13–17]. In addition, the sulfonate groups and hydrogen donors easily connect through hydrogen bonding, which can further cross-link into a higher dimensional and more stabilized structures [18–20].

The sulfonate bridging and chelating ligands are usually used to control the number and spatial arrangement of coordination positions available on the metal ions, hence restricting the growth of structures to generate low-dimensional architectures rather than extended networks [21,22]. However, in the process of

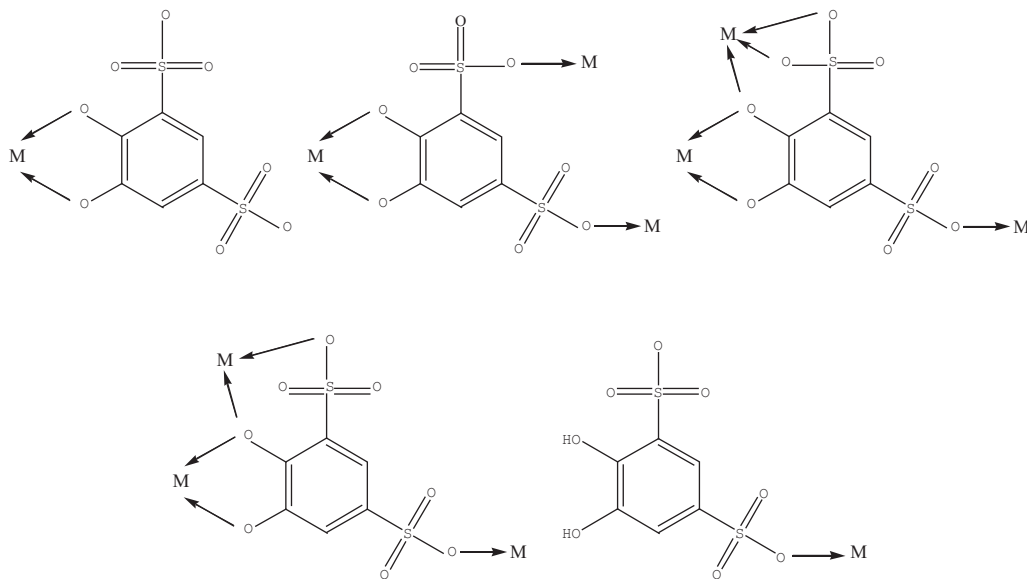
construction of metal-sulfonates, the disulfonated catechol ligands are unusually used as the building blocks [23]. $\text{Na}_2\text{H}_2\text{Tiron}$ can be selected as a bridging and chelating ligand, due to its following characteristics: (a) the ligand containing disulfonate and catechol groups have been less explored; (b) the direct combination of the functional groups with a rigid benzene ring can more easily promote the coordination reaction to form novel structures; (c) the relationship between the phenol group and sulfonate group is the ortho, meta and para positions of a benzene ring, which can exhibit rich coordination modes via their potential oxygen donors. Five types of coordination modes of Tiron have been structurally characterized so far [5,23–26]. The coordination versatility, together with the coordination requirements of specific metal ions, allowed for the construction of different architectures.

Recently, there is a growing interest in the chemistry of alkaline earth metal ions, due to several possible applications in luminescent and electronic devices. It is also well known that different ligands, different bridging and chelating ways and coordination geometry variations between alkaline-earth metal atoms can largely affect their architectures [24]. Therefore, the selective combination of bridging and chelating ligands and alkaline-earth metal ions with larger radii is an effective strategy for modulating structures and assisting in understanding the ligand–metal-structure correlations. To get a better insight in this problem, by introducing $\text{Na}_2\text{H}_2\text{Tiron}$ and strontium ion, two novel di- and trinuclear

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complexes $[\text{Sr}_2(\text{Tiron})_2(\text{phen})_2(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{phen} \cdot 2\text{H}_2\text{O}$ and $[\text{Sr}_3(\text{Tiron})_2(\text{phen})_3(\text{H}_2\text{O})_5] \cdot \text{Hphen} \cdot 0.5\text{H}_2\text{phen} \cdot 8\text{H}_2\text{O}$ were successfully synthesized, and structurally characterized by single crystal X-ray diffraction, elemental analyses, FT-IR and thermogravimetric analyses. Their luminescent properties were also studied.



Schematic representation of the coordination modes of the $\text{Na}_2\text{H}_2\text{Tiron}$ ligand

2. Experimental section

2.1. Materials and physical measurements

All reagents were purchased from commercial sources and used without further purification. X-ray single crystal diffraction data were collected at 298(2) K from a single crystal mounted atop a glass fiber with a Bruker Apex-II diffractometer using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Elemental analyses were performed on a Perkin-Elmer 240C instrument. FT-IR spectra were recorded from KBr pellets with a Vector22 spectrophotometer in the range of $4000\text{--}400 \text{ cm}^{-1}$. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. Photoluminescence analyses were performed on a Perkin Elmer LS55 fluorescence spectrometer.

2.2. Synthesis of complex 1

A mixture of SrCl_2 (0.159 g), $\text{Na}_2\text{H}_2\text{Tiron}$ (0.314 g) and 1,10-phenanthroline (0.180 g) in the molar ratio of 1:1:1 was dissolved in deionized water. The pH of the resulting solution was carefully raised to 5 with 0.1 M NaOH. The derived reaction mixture was mechanically stirred for 3 h. The clear mixture was then placed in an 18 mL capacity Teflon-lined autoclave and heated statically at $120 \text{ }^\circ\text{C}$ for 2 days. The orange blocked crystals were suction-filtered, rinsed with water and allowed to air-dry. The single crystals were obtained in ca. 70% yields based on strontium ions. Elemental *Anal.* Calc. for $\text{C}_{60}\text{H}_{50}\text{N}_8\text{O}_{21}\text{S}_4\text{Sr}_2$ (**1**): C, 47.33; H, 3.28; N, 7.36. Found: C, 47.53; H, 3.76; N, 7.65%. IR (KBr, cm^{-1}): $\nu(\text{O-H}) = 3421$, $\nu(\text{C=N}) = 1623$, $\nu(\text{C=C}) = 1589$, 1511, 1484, $\nu(\text{C=N}) = 1423$, $\nu(\text{C-O}) = 1284$, $\nu(\text{SO}_3^{2-}) = 1216$, 1176, 1099, 1029, $\delta(\text{C-H}) = 842$, 773, 730, $\nu(\text{C-S}) = 607$ [23,24] (see Fig. S1).

2.3. Synthesis of complex 2

A mixture of SrCl_2 , $\text{Na}_2\text{H}_2\text{Tiron}$ and 1,10-phenanthroline in the molar ratio of 1:2:2 was dissolved in deionized water. The pH of the resulting solution was carefully raised to 5 with 0.1 M NaOH.

The derived reaction mixture was mechanically stirred for 3 h. The clear mixture was then placed in an 18 mL capacity Teflon-lined autoclave and heated statically between $120 \text{ }^\circ\text{C}$ for 2 days. The orange blocked crystals were suction-filtered, rinsed with water and allowed to air-dry. The single crystals were obtained in ca. 75% yields based on strontium ions. Elemental *Anal.* Calc. for $\text{C}_{66}\text{H}_{68}\text{N}_9\text{O}_{29}\text{S}_4\text{Sr}_3$ (**2**): C, 43.02; H, 3.69; N, 6.84. Found: C, 43.35; H, 3.89; N, 6.97%. IR (KBr, cm^{-1}): $\nu(\text{O-H}) = 3436$, $\nu(\text{C=N}) = 1637$, $\nu(\text{C=C}) = 1589$, 1544, 1477, $\nu(\text{C=N}) = 1423$, $\delta(\text{OH}) = 1375$, $\nu(\text{C-O}) = 1288$, $\nu(\text{SO}_3^{2-}) = 1222$, 1159, 1097, 1027, $\delta(\text{C-H}) = 846$, 771, 732, $\nu(\text{C-S}) = 601$ [23,24] (see Fig. S1).

2.4. Single crystal X-ray crystallography

Data collections for the complexes **1–2** were performed on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected by the narrow frame method at the temperature of 298(2) K. The structures were solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [27]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms except those for water molecules were located at geometrically calculated positions and refined with isotropic thermal parameters. Hydrogen atoms for the water molecules were located from difference Fourier maps. The free 2H-protonated 1,10-phenanthroline in complex **2** has been refined as disordered structure, with an occupancy of 0.5 leading to $0.5\text{H}_2\text{phen}$ per formula unit. This is in accordance with the results from TGA and elemental analysis. The sulfonate oxygen atoms (O4, O5, O6, O12, O13 and O14) corresponding to Tiron ligands in complex **2** have been refined as disordered structure. Crystallographic data and structural refinements for the complexes **1–2** are summarized in Table 1, selected bond lengths and bond angles are listed in Table S1. Hydrogen bonding interactions are listed in Table S2.

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