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Synthesis, structures and conductivity properties of silver 3-sulfobenzoate coordination polymers

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ABSTRACT

Four coordination polymers based on Ag^I/3-sulfobenzoate/N-donor ligands, $[Ag_2Na_2(3\text{-sb})_2(H_2O)_7]_n$ (**1**), $\{[Ag_2(3\text{-sb})(apy)]\cdot(H_2O)\}_n$ (**2**), $\{[Ag_2(4,4'\text{-bipy})_2(H_2O)_3]\cdot[Ag_2(4,4'\text{-bipy})_2(H_2O)_2]\cdot 2(3\text{-sb})\cdot 4(H_2O)\}_n$ (**3**) and $\{[Ag(3\text{-sb})(bpe)(H_2O)][Ag(bpe)(H_2O)]\cdot 3(H_2O)\}_n$ (**4**) where 3-sb is 3-sulfobenzoate, apy is 2-aminopyridine, bipy is 4,4′-bipyridine and bpe is 1,2-bis(4-pyridyl)ethylene, were prepared and characterized, and their fluorescence and electric conductivity properties were studied. Complex **1** is a 3D architecture in which 3-sb ligands exhibit μ_4-κ^1(O1,O2-Ag): κ^1(O3,O5-Na) *trans–trans* coordination mode. The molecular structure of **2** is a 2D layer. Complexes **3** and **4** are cation–anion species and 1D polymers. In these complexes hydrogen bonds provide additional assembly forces, giving 3D hydrogen bonding networks for **1** and **3**, and 2D layers for **2** and **4**. Abundant weak interactions, such as Ag–Ag interactions in **1**–**3**, Ag–π interactions in **1**–**4**, π–π interactions in **1**, **3**–**4**, and C–H···π interactions in **3**–**4**, also can be found. The weak interactions are strongly related to the fluorescence and electric conductivity properties, providing the way for understanding the relationship between structures and properties.

1. Introduction

In recent years, the aim of crystal engineering is to control and tune desired crystal properties through introducing rational molecular building blocks [1]. However, due to our limited understanding of weak interactions in metal complexes, synthesis of complexes with predictable assembly is still a challenge. Therefore, careful selection of suitable organic ligands and metal centers for construction of supra-molecular architectures with abundant weak interactions is an important strategy in crystal engineering.

Ag^I is among the most labile metal ions [2] due to its d^{10} electronic configuration and has a coordination number varying from 2 to 6 and various geometries (linear, trigonal, tetrahedral, trigonal pyramidal, and octahedral) [3–5]. Silver complexes can be used in the field of non-electric gas sensor [6], optical or electrical conductivity [7], host–guest chemistry [8,9], and catalysis [10]. Multifunctional ligands with sulfonate and carboxylate groups, such as 5-sulfoisophthalate [11–20] and 5-sulfosalicylic acids [21–28], have been widely used in the synthesis of specific structures with potential application as functional materials. However, ditopic ligands with just one carboxylate and one sulfonate used in the synthesis of novel complexes are still very limited [29–31]. For example, only 26 metal complexes with 3-sulfobenzoate (3-sb) have been synthesized and most of them were obtained in our laboratory (CSD; Feb 2010 update) [32–52].

In metallo-assembled architectures, the dominant factor that controls the final supra-molecule is usually the metal–ligand interaction [53], therefore any structure with weak interactions [54] must fulfill the requirements of primary synthon obtained from the metal–ligand interactions. Ag(I) center, with close-shell configuration, is lacking of strong coordination preferences, and thus, non-covalent weak interactions involved in the overall observed structure (topology, geometry and packing arrangement) may have a strong effect and determine the organization of the supra-molecular networks [55–57]. In addition, the agility and lability of Ag–N(pyridine) bonds in solution, whose energy has been reported is similar to that of a strong hydrogen bond [2], would lead, through a self-assembly process [58], toward the thermodynamically more stable architecture [53]. Therefore, some N-neutral ligands, 2-aminopyridine (apy), 4,4′-bipyridine (4,4′-bipy), and 1,2-bis(4-pyridyl)ethylene (bpe) were chosen for this study. Although the silver complexes with 2-aminopyridine [59–69], 4,4′-bipy [70–82], and bpe [83] have been extensively investigated, there is no any report associated with the 3-sulfobenzoate. In this paper, we present syntheses, structures (including weak interactions), and properties of four novel Ag^I/3-sb polymeric complexes, namely $[Ag_2Na_2(3\text{-sb})_2(H_2O)_7]_n$ (**1**), $\{[Ag_2(3\text{-sb})(apy)]\cdot(H_2O)\}_n$ (**2**), $\{[Ag_2(4,4'\text{-bipy})_2(H_2O)_3]\cdot[Ag_2(4,4'\text{-bipy})_2(H_2O)_2]\cdot 2(3\text{-sb})\cdot 4(H_2O)\}_n$ (**3**), and $\{[Ag(3\text{-sb})(bpe)(H_2O)][Ag(bpe)(H_2O)]\cdot 3(H_2O)\}_n$ (**4**).

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2. Experimental

2.1. General information and material

Chemicals were obtained from commercial sources with reagent grade. Elemental analyses for C, H, and N were carried out on a Perkin–Elmer analyzer model 1110. The infrared spectra were taken on a Nicolet Nexus 470 infrared spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. The fluorescence spectra were measured using SHIMADZU RF-540 spectrometer on powdered sample in the solid state at room temperature.

The measurements for electric conductivity were made by a conventional two-probe technique at room temperature with compacted pellets using Keithley-2182A Nanovoltmeter and Keithley-2400 Sourcemeter. A papery mold with the size of $3 \times 1 \times 1\ mm^3$, was filled with the powder sample of the synthesized complex and pressed with tablet machine in about 500 Kgf/cm^2. The two copper probes were set onto the sample to place the circuit, and the resistance of the compacted pellet for the complex was recorded until its value becomes constant. In order to avoid the reaction of Ag(I) with copper generating metal silver, the ends of the copper probes were covered with a layer of silver metal.

2.2. Synthesis of $[Ag_2Na_2(3\text{-sb})_2(H_2O)_7]_n$ (**1**)

A mixture of $AgNO_3$ (0.085 g, 0.50 mmol), NaOH (0.02 g, 0.50 mmol), and 3-sulfobenzoic acid monosodium salt (0.112 g, 0.50 mmol) was dissolved in distilled water (5 ml) and allowed to evaporate in the dark. After 2 weeks, colorless block-shaped crystals were obtained. Yield 65% (128 mg). The complex easily lost two water molecules and the elemental analysis gave the dehydrated material **1**. *Anal.* Calc. for $Ag_2Na_2C_{14}H_{18}O_{15}S_2$: C, 22.36; H, 2.41. Found: C, 22.42; H, 2.64%. The immediately IR spectrum for **1** (KBr): ν = 3585(s), 3449(s), 3291(w), 3183(w), 1595(m), 1550(s), 1387(s), 1203(s), 1183(s), 1097(m), 1038(s), 998(m), 876 (m), 763(m), 668 (m), 619(s), 575(m), 527(w), 490(w), 417(w) cm^{-1}.

2.3. Synthesis of $\{[Ag_2(3\text{-sb})(apy)]\cdot(H_2O)\}_n$ (**2**)

A mixture of $AgNO_3$ (0.170 g, 1.00 mmol), 2-aminopyridine (0.094 g, 1.00 mmol), and 3-sulfobenzoic acid monosodium salt (0.112 g, 0.50 mmol) was dissolved in distilled water (10 ml), heated to fully dissolve and allowed to evaporate in the dark. After 3 weeks, pale yellow block-shaped crystals were obtained. Yield 89% (235 mg). *Anal.* Calc. for $Ag_2C_{12}H_{12}N_2O_6S$: C, 27.77; H, 2.14; N, 5.40. Found: C, 27.76; H, 2.14; N, 5.33%. IR (KBr): ν = 3419(s), 3327(s), 3063(w), 1604(s), 1564(s), 1487(m), 1442 (m), 1386(s), 1322(w), 1273(w), 1206(s), 1164(w), 1099(m), 1081 (w), 1043(m), 997(w), 871(w), 768(m), 689(w), 668(m), 622(s), 579(w), 523(w), 416(w) cm^{-1}.

2.4. Synthesis of $\{[Ag_2(4,4'\text{-bipy})_2(H_2O)_3]\cdot[Ag_2(4,4'\text{-bipy})_2(H_2O)_2]\cdot 2(3\text{-sb})\cdot 4(H_2O)\}_n$ (**3**)

A mixture of $AgNO_3$ (0.085 g, 0.5 mmol), 3-sulfobenzoic acid monosodium salt (0.112 g, 0.50 mmol), NaOH (0.04 g, 1.0 mmol), 4,4′-bipy (0.078 g, 0.50 mmol), and distilled water (15 ml) was added ammonia to dissolve mostly. After being filtered the solution was allowed to evaporate in the dark. After 2 days, colorless needle-shaped crystals were obtained. Yield 97% (196 mg). *Anal.* Calc. for $Ag_4C_{54}H_{58}N_8O_{19}S_2$: C, 40.07; H, 3.61; N, 6.92. Found: C, 40.12; H, 3.61; N, 6.90%. IR (KBr): ν = 3393(s), 3093(w), 3047(w), 1600(s), 1564(s), 1532(w), 1485(w), 1409(m), 1385(s), 1324(w), 1299(w), 1273(w), 1215(s), 1164(w), 1099(m), 1072(w), 1042(s), 995(m), 871(w), 853(w), 805(s), 767(w), 754(w), 7268(m), 689(w), 667(m), 620(s), 579(w), 494(w), 415(w) cm^{-1}.

2.5. Synthesis of $\{[Ag(3\text{-sb})(bpe)(H_2O)]\cdot[Ag(bpe)(H_2O)]\cdot 3(H_2O)\}_n$ (**4**)

A mixture of $AgNO_3$ (0.085 g, 0.50 mmol), NaOH (0.04 g, 1.0 mmol), 3-sulfobenzoic acid monosodium salt (0.112 g, 0.50 mmol), and 1,2-bis(4-pyridyl)ethylene (0.091 g, 0.50 mmol), was dissolved in a mixture of water (10 ml), methanol (5 ml), and DMF (5 ml). The solution was added ammonia to dissolve completely and after being filtered was allowed to evaporate in the dark. After 8 days, colorless crystals were obtained. Yield 89% (194 mg). *Anal.* Calc. for $Ag_2C_{31}H_{34}N_4O_{10}S$: C, 42.78; H, 3.94; N, 6.44. Found: C, 42.76; H, 3.98; N, 6.50%. IR (KBr): ν = 3431(s), 3039(w), 1601(s), 1557 (m), 1499(w), 1425(m), 1382(s), 1301(w), 1206(s), 1191(s), 1164(w), 1095(m), 1072(w), 1035(s), 1010(m), 998(m), 973(m), 868(w), 827(s), 774(m), 695(w), 619(m), 571(w), 548(s), 413(w) cm^{-1}.

2.6. X-ray structure determination

Crystals of **1**–**4** with suitable sizes were selected for data collection by a Bruker Smart CCD area detector with graphite- monochromatized Mo Kα radiation (λ = 0.71073 Å). The crystal of complex **1** was covered by oil due to it easily lost two water molecules. The data were integrated by use of the SAINT program [84], and this program also did the intensities corrected for Lorentz and polarization effects. The absorptions were done by the SADABS program [85]. The structures were solved by the heavy-atom method and successive Fourier syntheses. Once the heavy-atom peak had been located in the Patterson map, a Fourier synthesis was performed to locate the other non-H atoms. Full-matrix least-squares refinements on F^2 were carried out using the SHELXL-97 package [86]. All non-H atoms were anisotropically refined. H atoms on C atoms were placed in idealized positions and refined as riding atoms, with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. All H atoms bonded to O atoms were located in difference Fourier maps and refined with distance restraints of O–H = 0.85(1) Å and a fixed isotropic displacement parameter of $U_{iso}(H) = 0.08$ Å^2. The drawings of the molecules were realized with the help of ORTEP-3 for Windows and Diamond 2.1e (Diamond-Visual Crystal Structure Information System, Crystal Impact, Postfach 1251, D-53002 Bonn). All of the programs used are included in the WinGX Suite with version 1.70 [87]. Information concerning the crystallographic data collection and structure refinements is summarized in Table 1. The selected bond distances and angles for all these complexes are provided in Table S1.

3. Results and discussion

3.1. Structure **1**

Complex **1** is a 3D structure that consists of $[Ag_2(3\text{-sb})_2]$ units connecting 2D $[Na_2(H_2O)_7]_n$ species. The asymmetric unit contains a 3-sb ligand, one silver ion, two half sodium ions, and three and a half coordinating water molecules (Fig. 1a). Two dimeric units of $[Ag_2(3\text{-sb})_2]$ and $[Na_2O_4(H_2O)_7]$ can be considered as the fundamental building blocks in **1**. In the $[Ag_2(3\text{-sb})_2]$ unit, two silver(I) atoms are located in an approximately square planar environment binding to two oxygen atoms from the carboxylate group of the 3-sb and one water molecule, and one Ag–Ag [88–92,95], in which phenyl groups form Ag···π weak interactions with the Ag–phenyl centroid distance of 3.191(2) Å which is in range of Ag–η^6 arene π interactions [93] (Fig. 1b). In the dimeric unit of $[Na_2O_4(H_2O)_7]$, either the seven-oxygen-coordinated Na1 atom or six-oxygen-coordinated Na2 atom is in distorted octahedral geometry. The Na1 adopts four sulfonate oxygen atoms from two different sulfo-