

A three-dimensional Ag^I coordination polymer constructed via η^2 Ag–C bonds: Thermal, fluorescence, structural and solution studies

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Abstract

A 3D polymer built with the assistance of η^2 Ag–C bonds, [Ag₂(μ_8 -SB)] (**1**) [H₂SB = 4-[(4-hydroxyphenyl)sulfonyl]-1-benzenol], has been synthesized and characterized and its structure was determined by X-ray crystallography. In addition to the coordination to the O atoms of SB²⁻ the Ag atoms also form strong η^2 Ag–C bonds, resulting in the formation of an AgO₂C₂ environment. The thermal stabilities of **1** and of its thallium(I) analogue, [Tl₄(μ_8 -SB)₂] (**2**), were studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The ligand and compounds **1**–**2** are luminescent in the solution state, with emission maxima at 380, 353 and 468 nm, respectively. The results of studies of the stoichiometry and formation of complexes of **1** and **2** in acetonitrile and DMF solutions were found to be in support of their solid state stoichiometry.

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1. Introduction

The use of bridging ligands for the controlled self-assembly of one-, two- or three-dimensional metallocsupramolecular species has been the subject of enormous study in recent years [1]. These supramolecular architectures are aesthetically appealing and exhibit potential applications as molecular wires [2], electrical conductors [3], molecular magnets [4], in host–guest chemistry [5] and in catalysis [6]. The range and variety of self-assembling inorganic structures that can be constructed relies on the presence of suitable metal–ligand interactions and supramolecular contacts, i.e., hydrogen bonds and other weak interactions [7]. The design of polymeric coinage d¹⁰ metal complexes with fascinating structures has received much attention [8], among these metals, silver has received much attention because silver(I) shows a tendency to form coordination polymers

and unique Ag–C bonds [9]. Previous investigations have addressed that metalheteroatom, metal–carbon and metal–metal interactions are three of the most important interactions in the construction of Ag polymeric networks in the solid state [10–12] and extended systems of silver(I) coordination polymers has concentrated on the use of nitrogen-donor ligands [13] or oxygen-donor ligands [14] or combination with both donor [15]. The use of a combination of oxygen and carbon-donor ligands are rare [9]. In this paper we describe the synthesis and coordination behaviour of SB²⁻ ligand based on O, C-donor atoms, we also compare thermal resistance, emission properties and formation constants of compound **1** with its Tl^I analogue [16].

2. Experimental

2.1. Materials and physical techniques

All chemicals were of reagent grade and were used as commercially obtained without further purification. IR

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spectra were recorded using Perkin-Elmer 597 and Nicolet 510 P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The thermal behavior was measured with a PL-STA 1500 apparatus. The luminescent properties were investigated with a Shimadzu RF-5000 spectrofluorophotometer. ^1H NMR and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz and all chemical shifts are reported in δ units downfield from Me_4Si . All UV–Visible spectra were recorded on a computerized double-beam Shimadzu 2550 spectrophotometer, using two matched 10-mm quartz cells. Crystallographic measurements were made at 100(2) K using a Bruker AXS SMART APEX CCD diffractometer. The intensity data were collected within the range $2.26 \leq \theta \leq 28.25^\circ$ using graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Accurate unit cell parameters and the orientation matrix were obtained from least-squares refinements using the programs SAINT [17] and SAINT [18], and the data were integrated using SAINT [18]. The structure has been solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL [19]. The SO_2 -group and the carbon atom C4 attached to it are disordered around a crystallographic mirror over two positions in a 1:1 ratio. The disorder originates from the location of the $\text{C}=\text{C}$ double bond between C3 and C4. The refined $\text{C}=\text{C}$ and $\text{C}-\text{C}$ distances involving C4 are 1.218(16) and 1.525(16) \AA , which are slightly larger and smaller than would be expected for ideal double and single bonds, which indicates that C3 may also be involved in the disorder but to a much lesser extent. This is also supported by the larger than expected anisotropic displacement parameters of C3. An attempt to refine C3 with split positions, however, gave no satisfactory results, even after application of stringent restraints, and no disorder of for C3 was included in the final structural model. The following restraints were applied for the disordered atoms: SIMU and DELU restraints for C1–C4 and S1, O2 and O3. ISOR restraints for C3, C4 (standard deviation 0.01) and S1, O2 and O3 (standard deviation 0.002). The $\text{S}=\text{O}$ distances were restrained to be the same within a standard deviation of 0.02 \AA . All hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.2 times that of the adjacent carbon atom. The molecular structure plots were prepared using ORTEP [20a] and Mercury [20b]. Crystallographic data and details of the data collection and structure refinements are listed in Table 1. The observed anisotropic thermal parameters, the calculated structure factors, and full lists of bond distances, bond angles and torsion angles are given in supplementary material.

2.2. Synthesis of $[\text{Ag}_2(\mu_8\text{-SB})]$ (1)

One millimole (0.250 g) of 4-[(4-hydroxyphenyl)sulfonyl]-1-benzenol (H_2SB) was dissolved in 20 ml acetonitrile

Table 1
Crystal data and structure refinement for $[\text{Ag}_2(\mu_8\text{-SB})]$ (1)

Identification code	1
Empirical formula	$\text{C}_{12}\text{H}_8\text{Ag}_2\text{O}_4\text{S}$
Formula weight	463.98
Temperature	100(2) K
Wavelength	0.71073 \AA
Crystal system	Orthorhombic
Space group	$Fmm2$
Unit cell dimensions	
a (\AA)	17.9958(18)
b (\AA)	7.0921(7)
c (\AA)	9.2580(9)
Volume (\AA^3)	1181.6(2)
Z	4
Density (calculated) (Mg/m^3)	2.608
Absorption coefficient (mm^{-1})	3.495
$F(000)$	888
Crystal size (mm)	$0.36 \times 0.36 \times 0.22$
θ Range for data collection ($^\circ$)	2.26–28.25
Index ranges	$-23 \leq h \leq 23$, $-9 \leq k \leq 9$, $-12 \leq l \leq 12$
Reflections collected	2893
Independent reflections [$R(\text{int})$]	821 [0.0157]
Completeness to θ ($^\circ$)	28.28: 100.0%
Absorption correction	Multi-scan
Maximum and minimum transmission	0.464 and 0.374
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	821/74/64
Goodness-of-fit on F^2	1.207
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0346$, $wR_2 = 0.1005$
R indices (all data)	$R_1 = 0.0349$, $wR_2 = 0.1026$
Largest difference in peak and hole (e \AA^{-3})	4.110 and -0.842

and was heated and stirred with solution of 2 mmol (0.114 g) KOH in 5 ml H_2O for an hour. After deprotonation of the ligand in this process, the solution was cooled to room temperature and then a solution of 2 mmol (0.340 g) AgNO_3 in 5 ml acetonitrile was added to the mixture and was stirred for an hour. After filtering it was allowed to stand in darkness at room temperature to evaporate for several days to obtain suitable crystals. The crystals were washed with acetone and air dried, d.p. $> 370^\circ\text{C}$. Yield: 0.255 g (55%). Anal. Calc. for $\text{C}_{12}\text{H}_8\text{Ag}_2\text{O}_4\text{S}$; C: 31.03, H: 1.72. Found C: 30.01, H: 1.79%. IR (selected bands; in cm^{-1}): 552s, 696w, 723w, 835m, 1094s, 1138s, 1217m, 1317s, 1400s, 1565s, 2930w, 3050w. ^1H NMR (DMSO, δ): 6.30–6.50 (d, 1H), 7.25–7.45 (d, 1H) ppm. ^{13}C -{1H} NMR (DMSO): 120.8, 121.8, 146.2 and 149.5 ppm.

2.3. Synthesis of $[\text{Tl}_4(\mu_8\text{-SB})_2]$ (2)

Compound 2 was prepared as described previously [16] for evaluation of other data such as thermal stability and luminescent properties. d.p. = 249°C . Anal. calc. for $\text{C}_{12}\text{H}_8\text{Ag}_2\text{O}_4\text{S}$: C: 21.90, H: 1.20. Found C: 21.58, H: 1.41%. IR (selected bands): 551s, 835m, 1094vs, 1131vs, 1316s, 1480s, 1565vs, 3045w. ^1H NMR (DMSO, δ): 6.30–6.50 (d, 1H), 7.20–7.45 (d, 1H) ppm. ^{13}C -{1H} NMR (DMSO): 120.5, 121.7, 146.2 and 149.6 ppm.

3. Results and discussion

3.1. Synthesis and spectroscopy

The reaction between 4-[(4-hydroxyphenyl)sulfonyl]-1-benzenol (H_2SB) and $\text{Ag}^1(\text{NO}_3)$ or $\text{Tl}^1(\text{NO}_3)$ provided crystalline materials of the general formula $[\text{Ag}_2(\mu_8\text{-SB})]$ (**1**) and $[\text{Tl}_4(\mu_8\text{-SB})_2]$ (**2**), respectively. IR spectra display characteristic absorption bands for the SB^{2-} ligand. The absorption bands with variable intensity in the frequency range $1400\text{--}1600\text{ cm}^{-1}$ correspond to vibrations of the phenyl rings. The absorption of the $-\text{CH}_{\text{aromatic}}$ moieties is observed as relatively weak bands at 2930 and 3050 cm^{-1} . The signals at 2930 cm^{-1} are due to the Ag-coordinated $-\text{CH}_{\text{aromatic}}$ moieties that are significantly shifted to lower frequency compared to the non-Ag-coordinated H_2SB C–H groups in compound **1** (ca. 3050 cm^{-1}) and compound **2** (ca. 3045 cm^{-1}). The relatively low frequency of the band is indicative of at least partially covalent Ag–C bonding which is unambiguously confirmed by the crystal structure of compound **1** (see below). The ^1H NMR spectrum of the dissolved complex **1** in DMSO displays two distinct pseudo doublets at ca. 6.40 and 7.35 ppm assigned to the aromatic ring protons of the SB^{2-} ligands. The ^{13}C NMR spectrum of the DMSO solution displays four distinct signals at 120.8, 121.8, 146.2 and 149.5 ppm assigned to the aromatic ring carbon atoms of the SB^{2-} ligands. However, the NMR data of the compound **1** is not significantly different from free ligand H_2SB and from compound **2** [16]. This point shows that compound **1** may break up in DMSO solution and the polymeric structure and η^2 Ag–C bonds may not be retained in this solvent. The compound is not soluble in water or any other of the commonly used organic NMR solvents.

4. Structure description

Single crystal X-ray analysis reveals that compound $[\text{Ag}(\mu_8\text{-SB})_2]$ (**1**) crystallizes in an orthorhombic setting with space group of Fmm2, and the structure of this complex may be considered as a three-dimensional coordination polymer (Figs. 1–3). The SO_2 -group and the carbon atom C4 attached to it are disordered around a crystallographic mirror plane, resulting in a disorder of the location of the $\text{C}=\text{C}$ double bond between C3 and C4 (see Section 2 for details). The phenolic oxygen atoms of the SB^{2-} ligand act as bi-donor bridging atoms where each oxygen atom of the Ph–O groups link to two different silver(I) ions, (Fig. 1). The Ag atoms in this compound are involved in an η^2 interaction with two C_{ph} atoms of neighboring molecules. Thus, the Ag atoms in compound **1** are linked to two carbon atoms of phenyl moieties of SB^{2-} with distances $\text{Ag}-\text{C}2^i$ ($i: x, y + 1/2, z + 1/2$) = $\text{Ag}-\text{C}2^{iv}$ ($iv: -x + 1/2, -y, z + 1/2$) of $2.426(5)\text{ \AA}$, (Fig. 3). Hence, the Ag^1 coordination sphere is augmented to four and rather than exhibiting a AgO_2 coordination sphere, the compound can be considered to have a bihapto ($\text{O}_2\text{C}_2\text{Ag}$) center with coordi-

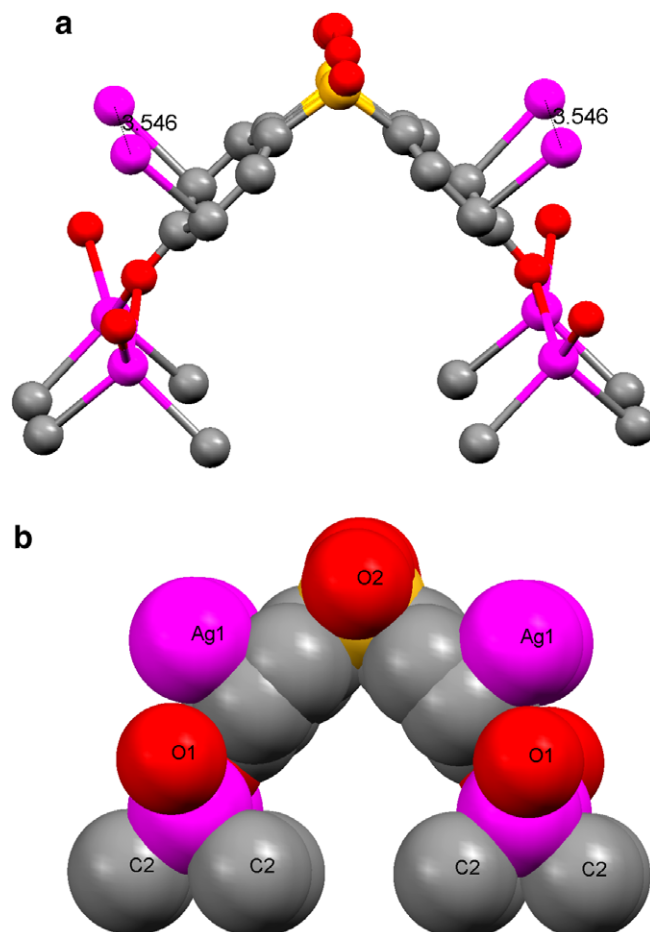


Fig. 1. (a) Molecular structure representations of compound **1** and (b) Space-filling representations of compound **1**, close approaches of Ag to the two of carbon atoms of phenyl rings could be seen. (Ag = violet, O = red, C = gray, S = yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

nation number of four. Ag–C bond lengths in other compounds with similar η^2 Ag–C interactions range from 2.40 to 2.70 Å [21–24], for example in the $[\text{Ag}(\text{benzene})\text{ClO}_4]$ are 2.496 and 2.634 Å [23]. Some other $\text{Ag}(\text{I})$ polycyclic aromatic polymeric complexes containing of $\text{Ag}-\text{C}(\text{sp}^2)$ bond report mean Ag–arene distances of 2.82 to 3.37 Å [25–31]. The dihedral angle formed by Ag–C2–C3 and C3–C2–C1 is $105.9(2)^\circ$ and also the dihedral angle of $\text{C}2^i(i: x, -y + 1, z)-\text{C}1-\text{C}2-\text{C}3$ is $5.3(8)^\circ$, indicating that the silver atoms interact with the π electrons of the aromatic rings. The phenolic rings in the compound **1** are not planar, and the bond distances and angles are not similar to those of compound **2** [16]. In compound **1** the C–C bonds adjacent to the carbon of the Ag–C interaction have been elongated (Table 2). However, the bonds of C4 and C3 and its symmetry related counterpart are pure single and double bonds. It seems that the ring is not aromatic any more and there is a delocalized system involving C1, C2, $\text{C}2^i$, and C3, and a localized double and single bond.

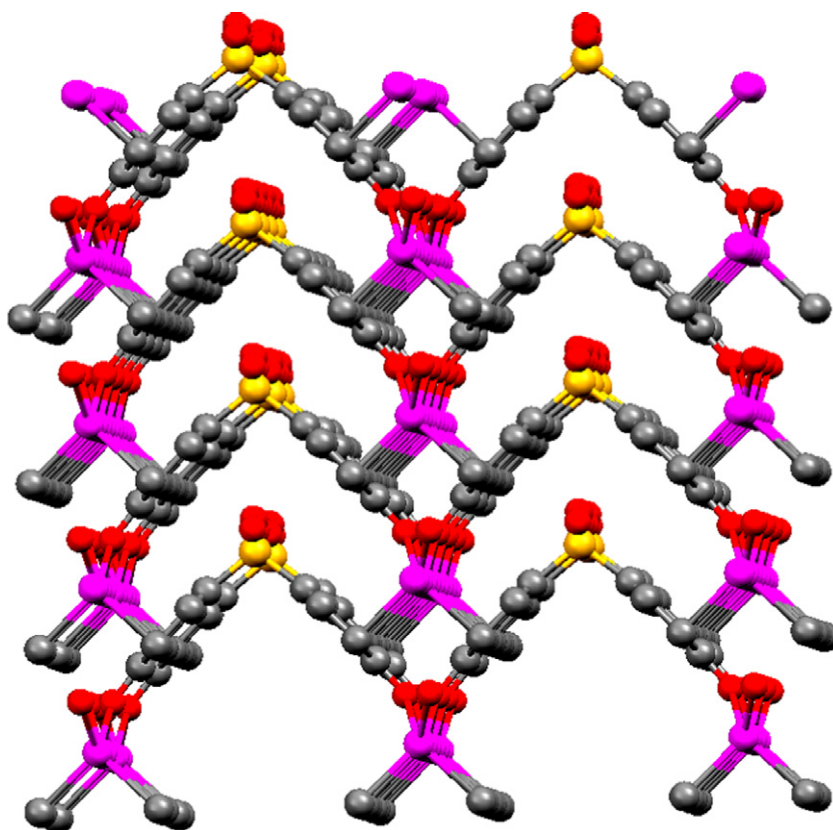


Fig. 2. A fragment of the three-dimensional network in compound 1, showing the Ag–C and Ag–O interactions. H atoms are omitted for clarity.

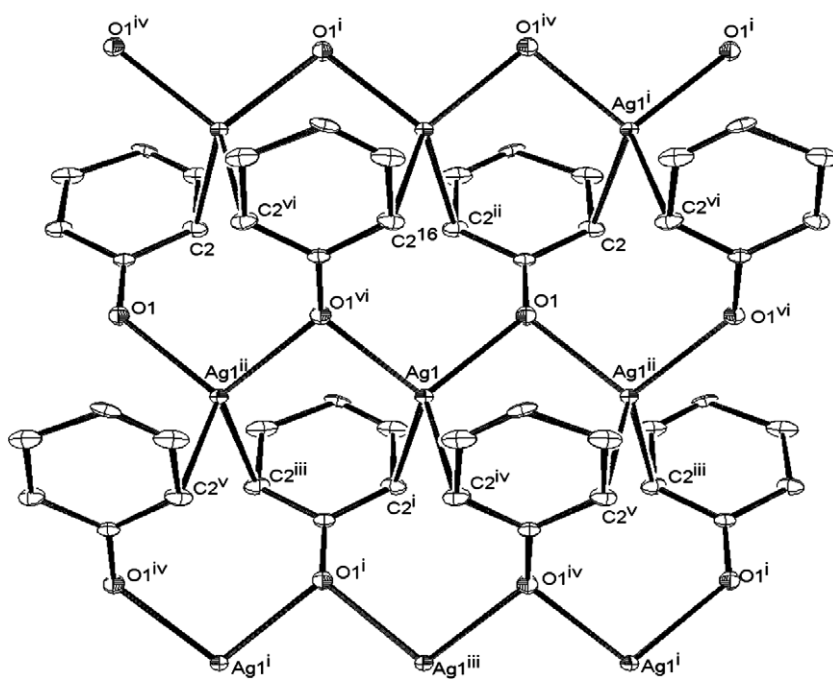


Fig. 3. ORTEP diagram and view of the Ag environment in compound 1; some of the six membered rings, every second disordered carbon atom C4, the SO₄ groups and all hydrogen atoms have been omitted for clarity. i: $x, y + 1/2, z + 1/2$; ii: $x, -y, z$; iii: $x, -y + 1/2, z + 1/2$; iv: $-x + 1/2, -y, z + 1/2$; v: $-x + 1/2, y, z + 1/2$; vi: $-x + 1/2, -y + 1/2, z$.

Table 2
Selected bond lengths (Å) and angles (°) for compound **1**

Ag(1)–O(1) ⁱ	2.294(4)
Ag(1)–C(2) ⁱⁱ	2.426(5)
C(1)–C(2)	1.436(5)
C(2)–C(3)	1.399(6)
C(3)–C(4)	1.218(16)
O(1) ⁱ –Ag(1)–O(1)	104.6(3)
O(1) ⁱ –Ag(1)–C(2) ⁱⁱ	118.28(16)
O(1)–Ag(1)–C(2) ⁱⁱ	111.05(15)
O(1) ⁱ –Ag(1)–C(2) ⁱⁱⁱ	111.04(15)
C(2) ⁱⁱ –Ag(1)–C(2) ⁱⁱⁱ	94.2(3)

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

The Ag...Ag distances in the compound **1** are 3.546 Å, and considerably longer than in the other polymeric structure[32]. Each SB²⁻ anion in compound **1** acts as a octa-donor bridging ligand, connecting eight Ag^I ions in a μ -8,6 mode (Scheme 1).

The structure of compound [Tl₄(μ ₈-SB)₂] (**2**) has recently been reported [16]. The single-crystal X-ray data of compound **2** showed that the complex is a three-dimensional polymer as a result of bridging SB²⁻ ligands with basic [Tl₄(μ ₈-SB)₂] repeating units. There are four thallium atoms with different coordination spheres in the cubic cage. These thallium atoms have irregular coordination spheres with stereo-chemically active lone pairs and thallium–thallium interactions, i.e. the individual coordination environments are TlO₄, TlO₄Tl₂, TlO₄Tl and TlO₃Tl.

A striking difference between compounds **1** and **2** is that the SB²⁻ anion in compound **1** acts as a eight donating bridging ligand via two O- and four C-atoms, connecting eight Ag^I ions in a μ -8,6 mode (Figs. 1–3 and Scheme 1a), whereas each SB²⁻ anion in compound **2** acts as an eight donating bridging ligand via only four O-atoms of phenolic and sulfonyl groups, connecting eight Tl^I ions in a μ -8,4 mode (Scheme 1b).

We try to synthesis a new mixed-metal compound of silver(I) and thallium(I) ions with the ligand SB²⁻, AgTl(SB), and compare the its structure with compounds **1** and **2**. This idea may help us for attain of similar compound with compound **1** and possibility without disordered. Our attempts to synthesis of this compound were not successful and each time the [Ag_{1.76}Tl_{0.24}(μ ₈-SB)] (**3**) was isolated that when has been refined Ag and Tl together exist on one site as 12% Tl only (so mostly silver). However, the structure of

mixed Ag–Tl, compound **3**, is again the same as compound **1**. The observed anisotropic thermal parameters, the calculated structure factors, and full lists of bond distances, bond angles and torsion angles of compound **3** are given in supplementary material.

5. Thermogravimetric analysis

To examine the thermal stability of the two new compounds, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 700 °C in a static atmosphere of air. Compound **1** is very stable and does not decompose up to 419 °C, at which temperature decomposition starts. In this stage, exothermic removal of SB²⁻ occurs between 419 and 502 °C with a mass loss of 53.0% (calcd 53.5%). Mass loss calculations show that the final decomposition product is metallic silver,

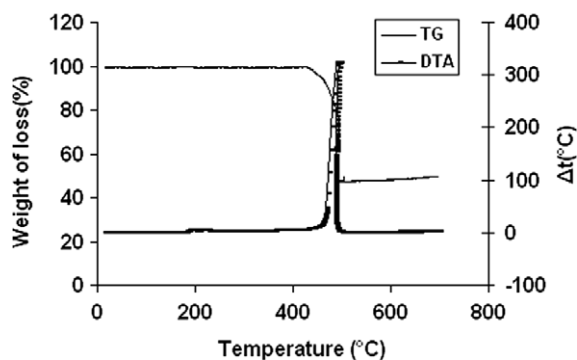


Fig. 4. Thermal behaviour of compound [Ag₂(μ ₈-SB)] (**1**).

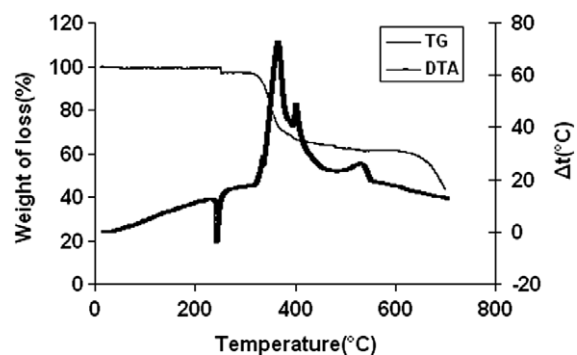
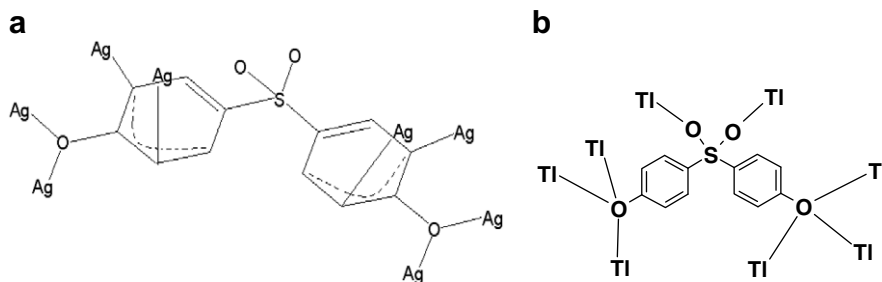


Fig. 5. Thermal behaviour of compound [Tl₄(μ ₈-SB)₂] (**2**).



Scheme 1. The coordination mode of ligand SB²⁻ (a) in the compound **1** and (b) in the compound **2**.

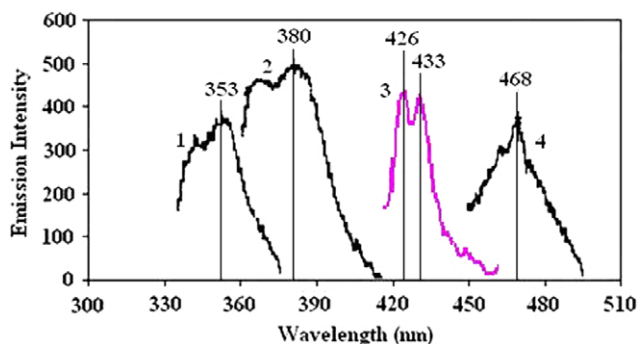


Fig. 6. The fluorescence spectra of ligand H_2SB and compounds **1–2**. Bands **1** for $[Ag_2(\mu_8-SB)]$ (**1**) in DMF solution, **2** for H_2SB ligand in DMF solution, **3** for H_2SB ligand in solid state, **4** for $[Tl_4(\mu_8-SB)_2]_n$ (**2**) in DMF solution, room temperature, $\lambda_{exc} = 300$ nm.

(Fig. 4). Compound **2** is much less stable at starts to decompose at 249 °C. The TG curve exhibits a distinct decomposition stage between 249 and 560 °C with a mass loss of 37.9%, (calcd 36.6% for the formation of thallium(I)oxide). The DTA curve displays a distinct endothermic peak at 240 °C and three exothermic peaks at 362, 398 and 532 °C, (Fig. 5).

6. Luminescent properties

The fluorescence spectra of compounds **1** and **2** have been studied in DMF solution. The compounds show broad emission bands with the maximum intensities at 353 and 468 nm upon excitation at 300 nm, respectively (Fig. 6). Compound **1** shows a blue shift (27 nm) and compound **2** shows a red shift (88 nm) compared with the free ligand H_2SB upon the same excitation at 300 nm. The emission intensity of compounds **1** and **2** are fairly weak when compared to that of the uncoordinated ligand, which can be attributed to the heavy atom effect [33–37], due to the coordination of the ligand to the Ag(I) and Tl(I) centers, respectively. The fluorescent emission of compound **1** can be tentatively assigned to the intraligand fluorescence emission as similar emissions with two shoulders at 380 nm can also be observed for the free ligand H_2SB upon the same excitation at 300 nm (Fig. 6). The strong interactions of Ag^I with the ligand SB^{2-} probably also cause this difference in the luminescent properties of the two compounds. The solid state fluorescence spectra of H_2SB ligand, compound **1** and **2** were studied too. The H_2SB ligand show a broad emission band with the maximum intensities at 426 and 433 nm upon excitation at 300 nm (Fig. 6), but no emission band was observed for compounds **1** and **2**.

7. Solution studies

In a typical procedure, 2.0 ml of deprotonated ligand solution (2.5×10^{-5} M) in CH_3CN was placed in the spectrophotometer cell and the absorbance of the solution was measured. Then a known amount of the concentrated solu-

tion of silver(I) nitrate or thallium(I) nitrate in CH_3CN (1.3×10^{-3} M) was added in a stepwise manner using a 5- μ l Hamilton syringe. The absorbance spectrum of the solution was recorded after each addition. The silver(I) ion or thallium(I) ion solution was continually added until the desired metal to ligand mole ratio was achieved. The electronic absorption spectra of the ligand SB^{2-} in the presence of increasing concentration of silver(I) ion or thallium(I) ions in CH_3CN at room temperature are shown in Figs. 7 and 8 respectively. The strong absorptions of ligand at 284.4 nm decreases and at 253.8 nm increases with increasing concentration of the metal ion, which reveals an isobestic point in the absorbance spectrum at 271.2 nm. The resulting absorbance (at 284.4 and 353.8 nm respectively) against $[Ag^+]/[SB^{2-}]$ and $[Tl^+]/[SB^{2-}]$ mole ratio plots, shown in the inset of Figs. 7 and 8, respectively, reveals distinct inflection points at a metal-to-ligand molar ratio of about 1 and 2 emphasizing the formation of a 1:1 and 2:1 complex in CH_3CN solution.

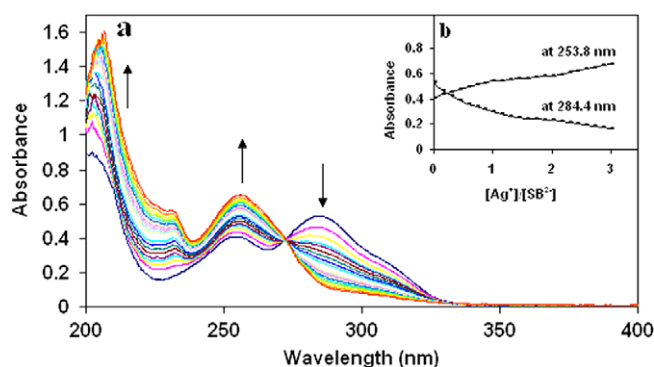


Fig. 7. (a) Electronic absorption spectra of ligand SB^{2-} in CH_3CN (2.5×10^{-5} M) in the presence of increasing concentration of silver(I) ion at room temperature and growth of an absorption maximum at 253.8 nm during the titration, with an isobestic point at 271.2 nm (b) Corresponding mole ratio plot at 253.8 and 284.4 nm.

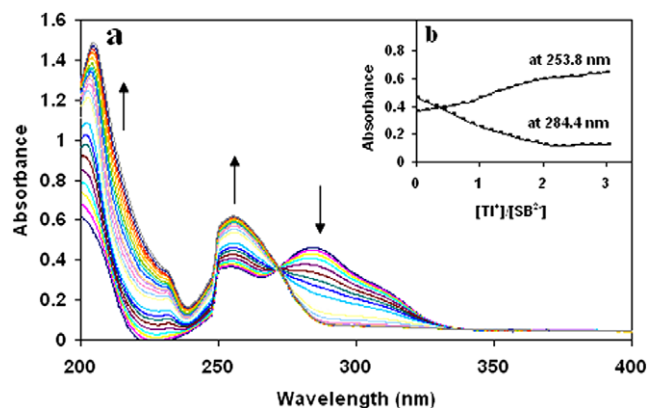


Fig. 8. (a) Electronic absorption spectra of ligand SB^{2-} in CH_3CN (2.5×10^{-5} M) in the presence of increasing concentration of thallium(I) ion at room temperature and growth of an absorption maximum at 253.8 nm during the titration, with an isobestic point at 271.2 nm (b) Corresponding mole ratio plot at 253.8 and 284.4 nm.

We also repeated these studies in 2.0 ml of 5.0×10^{-5} M deprotonated ligand solution in DMF. The electronic absorption spectra of the ligand SB^{2-} in the presence of increasing concentration of silver(I) or thallium(I) ions in DMF at room temperature are shown in Figs. 9 and 10 respectively. The strong absorptions of ligand at 266.0 nm increases with increasing concentration of the metal ion. The stepwise addition of metal ion offered the opportunity for the detection of an isobestic point in the absorbance spectrum at 284.0 nm (Figs. 9 and 10). The resulting absorbance (at 266.0 nm) against $[\text{Ag}^+]/[\text{SB}^{2-}]$ and $[\text{Tl}^+]/[\text{SB}^{2-}]$ mole ratio plots, shown in the inset of Figs. 9 and 10 respectively, again revealed distinct inflection points at a metal-to-ligand molar ratio of about 1 and 2 emphasizing the formation of a 1:1 and 2:1 complex in DMF solution. The isobestic point in Fig. 9 is not as clear as in Fig. 10. Existence of the isobestic point is likely to be due to the accumulation of different concentrations of an intermediate species during formation of compounds **1** and **2** in solution state [38]. For evaluation of the conditional formation constants, the mole ratio data obtained by the physicochemical method employed were fitted to

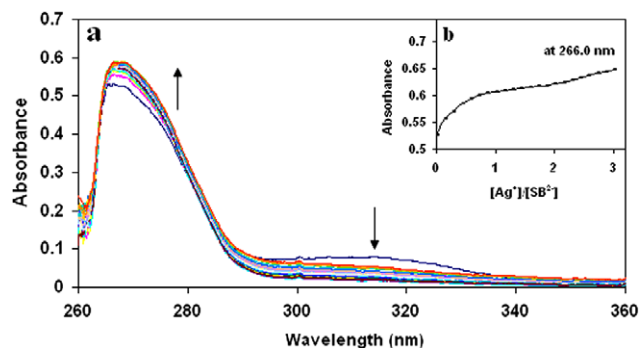


Fig. 9. (a) Electronic absorption spectra of ligand SB^{2-} in DMF (5.0×10^{-5} M) in the presence of increasing concentration of silver(I) ion at room temperature and growth of an absorption maximum at 266.0 nm during the titration, with an isobestic point at 284.0 nm (b) Corresponding mole ratio plot at 266.0 nm.

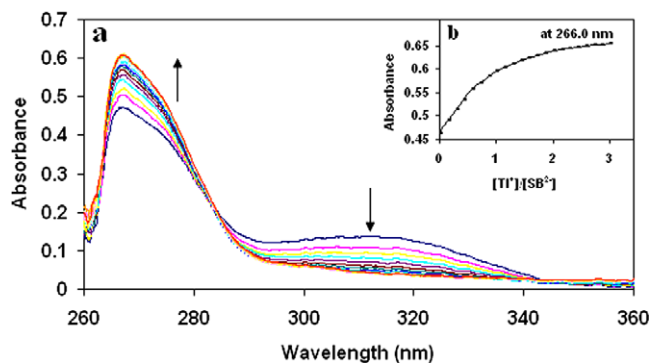


Fig. 10. (a) Electronic absorption spectra of ligand SB^{2-} in DMF (5.0×10^{-5} M) in the presence of increasing concentration of thallium(I) ion at room temperature and growth of an absorption maximum at 266.0 nm during the titration, with an isobestic point at 284.0 nm and (b) Corresponding mole ratio plot at 266.0 nm.

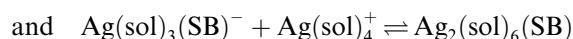
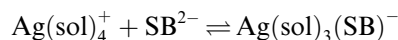
Table 3

The conditional formation constants for compounds **1** and **2** in CH_3CN and DMF solutions

	CH_3CN		DMF	
	253.8 nm	284.4 nm	266.0 nm	
$\log K_1$ for compound 1	3.95 ± 0.02	3.99 ± 0.05	4.00 ± 0.03	
$\log K_2$ For compound 1	2.99 ± 0.03	2.96 ± 0.03	2.99 ± 0.04	
$\log K_1$ For compound 2	3.84 ± 0.04	3.74 ± 0.02	3.79 ± 0.05	
$\log K_2$ For compound 2	2.99 ± 0.03	2.99 ± 0.05	3.00 ± 0.02	

the previously reported equations [39,40], using a non-linear least-squares curve fitting program KINFIT [41]. The conditional formation constants of the two complexes in CH_3CN and DMF solution and in different wavelength are listed in Table 3. The first formation constant for compound **1** is higher than that for compound **2**, probably due to more positive charge density of Ag^+ compared with Tl^+ ion, the second formation constant is the same, with no pronounced difference between the two compounds. The formation constants in two different solvents are also very similar.

Knowing the existence of one or more isobestic points in a system provides information regarding the number of species present [42], and the existence of an intermediate species within the titration of SB^{2-} with metal(I) ions is confirmed by the observation of an isobestic point in Figs. 7–10 [38,42]. From these observations, we assume that formation of compound **1** obeys the following general equations and the intermediate species that exists in solution state is $\text{Ag}(\text{sol})_3(\text{SB})^-$. The solvents, DMF and CH_3CN , probably compete with secondary coordination of the silver(I) ion to the carbon centers, hence $\log K_1$ and $\log K_2$ don't relate directly to structures for **1** and more likely relate to these formation reactions:



We also could consider a similar equation for formation of compound **2** in solution. The related intermediate species for formation of compound **2** in solution state would then be $\text{Tl}(\text{sol})_3(\text{SB})^-$.

8. Conclusions

An organosilver(I) coordination network with an aromatic phenolic ligand H_2SB was synthesized and characterized. The aromatic phenolic ligand in this complex exhibits a less-common η^4 -coordination mode of the phenyl rings, in addition to the normal phenolic coordination modes. The results of studies the stoichiometry and formation of **1** and **2** in DMF and acetonitrile solutions were found to be in support of their solid state stoichiometry and show that the first formation constant of the silver(I) compound is larger than that of its thallium(I) analogue, but the second formation constant is the same for both compounds. Compounds **1-2** and ligand H_2SB have shown luminescent properties in DMF solution. On this perspective, further

systematic study of the Ag(I) coordination chemistry of this type of ligands is ongoing. This work provides a new strategy to the preparation of air-stable multidimensional metallorganic coordination polymers with metal–carbon interaction, which is stable up to 419 °C and exhibits a strong blue photoluminescence behavior at room temperature.

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Appendix A. Supplementary material

CCDC 645562 and 658232 contain the supplementary crystallographic data for compound **1** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorgchem.2008.02.018](https://doi.org/10.1016/j.jorgchem.2008.02.018).

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