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N,N'-Diarylformamidine Dithiocarbamate Ag(I) Cluster and Coordination Polymer

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Abstract: An Ag(I)formamidine cluster Ag_6**L1**$_6$ (**1**) and an Ag(I)formamidine coordination polymer Ag_7(**L2**)$_2$ **2** (**L1** = N,N'-bis(2,6-disopropylphenyl) formamidine dithiocarbamate and **L2** = N,N'-mesityl formamidine dithiocarbamate) have been synthesized from the reactions of **L1** and **L2** with $AgNO_3$ respectively. The complexes were characterized using spectroscopic and analytical methods, including single-crystal X-ray diffraction. In the structure of **1**, a six vertex distorted square bipyramidal octahedron is formed from an Ag_6 core. The N,N'-bis(2,6-disopropylphenyl) formamidine dithiocarbamate ligands stabilize this core through two main –CS_2 bridging modes giving a propeller like structure. In the structure of **2**, each of the two Ag(I) centers are bridged by two N,N'-mesityl formamidine dithiocarbamate ligands forming 8-member $Ag_2(CS_2)_2$ metallacycles with an inversion center in the middle of the Ag—Ag argentophilic bond. The metallacycles are connected through Ag—S bonds forming ribbons in the crystallographic *a*-axis. The Ag(I) centers are coordinated to two N,N'-mesitylformamidine dithiocarbamates through the dithiocarbamate S atoms. The thermal decomposition of complexes **1** and **2** had similar thermograms with one major weight loss activity and the formation of elemental silver particles thereafter.

Keywords: N,N'-diarylformamidine; dithiocarbamates; silver complexes; argentophilic

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1. Introduction

Silver(I) complexes have been applied in various fields, therefore, attracting great attention due to their structural features and functional considerations [1–3]. They have been tested as fluorescent materials [4], semiconductors [5,6], source of nanomaterials [7] and biological imaging agents [8] due to their interesting and fascinating physicochemical properties. Ag(I) complexes have also shown potential medical applications, most especially as antibacterial [9,10], antifungal [11], anticancer [12], and antimalarial agents [13]. Argentophilic bonding interactions which exist between seemingly closed-shell silver(I) atoms center have been reported to be responsible for their significant physical properties as well as their structural details [2]. Structurally, they possess coordination geometries ranging from two-coordinate (linear) to eight-coordinate (tetragonal prism) [14]. Factors, such as reaction conditions, as well as alkyl substitution effects might be responsible for the formation of a variety of complexes with unprecedented structures [15,16]. In the past decades, monomeric, dimeric, hexameric and polymeric structures have been reported [17].

Dithiocarbamates ($R_2CNS_2^-$) belong to a class of mono anionic 1,1-dithiolate ligands, and they are often prepared by nucleophilic addition reaction of primary or secondary amines and carbon disulfide in the presence of a base as a proton acceptor [18]. Dithiocarbamates have been reported to react with silver(I) ions to form Ag(I) complexes of various geometries [19,20] and also serve as efficient stabilizers for silver nanoparticles [21]. Silver(I) dithiocarbamates, $[Ag(S_2CNR_2)]_n$ have been known as far back as the 1950s, but little work had been done on them probably due to their low solubility [17]. They have been widely used as a precursor to acanthite (α-Ag_2S), a potential material for microelectronics [22,23]. Early crystallographic studies revealed the hexameric nature of Ag-S_2CNR_2 (R = Et, Pr, and n-Bu) in the solid states. They have a polymeric chain structure, in which the silver atom is bonded in a distorted manner by three dithiocarbamate ligand, two acting as μ_2-bridges and one acting as a chelate [15,24].

Yin et al. reported the crystal structure of poly [(μ_3-*N*,*N*-dibenzyldithiocarbamato-κ^4S,S′:S:S′) silver(I)] [17]. Each Ag(I) cation in this complex was bonded to two pairs of sulfur atoms from three *N*,*N*′-dibenzyldithiocarbamate ligands, conforming to distorted tetrahedral geometry. The crystal structure of hexakis (μ_3-*N*,*N*-diisopropyldithiocarbamato) hexasilver(I) had also been reported by Yin and co-workers [25]. The metal center of the complex was centrosymmetric, and its hexanuclear structure entails two cyclohexane-like Ag_3S_3 units which are joined together by the S atoms of the thiocarbamate groups with the Ag...Ag distances ranging from 3.0382(5) to 3.0985(5) Å. Herein, we report the synthesis, characterization and thermal analysis of silver(I) dithiocarbamate complexes derived from symmetrical *N*,*N*′-diarylformidine dithiocarbamate ligands.

2. Materials and Instrumentation

All solvents (ACS reagent grades $\geq$ 99.5%) were obtained from Sigma-Aldrich (Johannesburg, South-Africa) and used as purchased without further purification. Reagents: 2,6-diisopropylaniline (97%), 2,4,6-trimethylaniline (98%), triethyl orthoformate (99%), and carbon disulfide were also obtained from Sigma-Aldrich. $AgNO_3$ (98%) and KOH (85%) were obtained from Promark Chemicals, Johannesburg, South Africa.

^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker Avance^{III} 400MHz spectrometer (Karlsruhe, German) at the University of KwaZulu-Natal, Westville Campus. Both ^{1}H NMR and ^{13}C NMR data were measured in parts per million relative to the residual solvent signals (chloroform-*d* for ^{1}H with δ = 7.26 ppm and ^{13}C NMR δ = 77.00 ppm). IR spectra were obtained on a PerkinElmer Universal ATR spectrum 100 FTIR spectrometer (Shelton, CT, USA), UV-Vis absorption spectra were recorded on Shimadzu UV-Vis-NIR spectrophotometer (Kyoto, Japan), and Q series^{TM} Thermal Analyzer DSC/TGA (Q600) (Newcastle, CA, USA), was used to determine the stability of the complexes.

3. General Synthesis Methods

3.1. Preparation of Complexes

The synthesis of *N*,*N*′-bis(2,6-disopropylphenyl) formamidine dithiocarbamate and *N*,*N*′-mesityl formamidine dithiocarbamate salts have been reported in our previous work [26]. The complexes were synthesized by dissolving two equivalents of the potassium dithiocarbamate salts in 15 mL of acetonitrile into which a solution 1 equivalent of $AgNO_3$ in 5 mL of H_2O was added drop-wise with stirring for 30 min at room temperature. The resultant yellow solids were collected by filtration washed three times with diethyl ether, and dried in the oven at 50 °C.

3.1.1. $Ag_6(L1)_6$ **1**

The reaction of **L1** (0.3 g, 0.6 mmol) with $AgNO_3$ (0.05 g, 0.3 mmol) in a mixture of acetonitrile and water gave complex **1** as a yellow powder in 79% yield. m.p. 214–216 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.04(d, 66H, $J_{H,H}$ = 6.68 Hz, CH_3-CH), 1.15(d, 42H, $J_{H,H}$ = 5.92 Hz, CH_3-CH), 1.21(d, 36H, $J_{H,H}$ = 5.92 Hz, CH_3-CH), 2.70(m, 12H, $J_{H,H}$ = 6.0 Hz, CH-CH_3), 2.81(m, 12H, $J_{H,H}$ = 6.56 Hz, CH- CH_3), 7.06(s, 19, Ar-H), 7.16(d, 11H, $J_{H,H}$ = 7.28 Hz, Ar-H), 7.35(t, 6H, $J_{H,H}$ = 7.76 Hz, Ar-H), 9.38(s, 6H, -C(H)=N). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 23.95, 24.09, 25.56, 27.47, 29.16, 123.04, 124.26, 124.54, 129.63, 138.76, 144.87, 151.65 and 214.51. IR υ (cm^{-1}): 2960, 1639, 1474, 1252, 982, 844, 481. UV-Vis ($CHCl_3$, λ_{max}, nm): 238 and 314.

3.1.2. $Ag_2(L2)_2$ **2**

The reaction of **L2** (0.3 g, 0.80 mmol) and $AgNO_3$ (0.07 g, 0.4 mmol) in acetonitrile furnished complex **2** as a yellow powder. Yield 64% Melting point 220–222 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.99(s, 9H, CH_3), 2.11(s, 9H, CH_3), 2.22(m, 18H, $J_{H,H}$ = 5.92 Hz, CH_3), 6.77(s, 3H, Ar-H), 6.87(s, 2H, Ar-H), 6.91(s, 1H, Ar-H), 6.97(s, 2H, Ar-H), 9.43(s, 2H, -CH=N). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 17.84, 18.06, 18.58, 18.67, 20.67, 20.73, 20.76, 21.28, 127.54, 128.41, 128.73, 128.86, 128.99, 129.35, 132.18, 133.89, 134.51, 136.05, 138.16, 138.50, 142.49, 144.79, 147.24, 151.27 and 214.01. IR υ (cm^{-1}): 2916, 1634, 1476, 1246, 982, 845, 482. UV-Vis ($CHCl_3$, λ_{max}, nm): 238 and 312.

All the spectra for complexes **1** and **2** are given in the supplementary materials.

3.2. Single Crystal X-ray Diffraction

The structure refinement parameter, as well as the crystallographic data for complexes **1** and **2,** are given in Table 1. Evaluation of crystals and collection of data was done on a Bruker Smart APEXII diffractometer with Mo Kα radiation (I = 0.71073 Å) equipped with an Oxford Cryostream low-temperature apparatus operating at 101 K for all samples. Reflections were collected at different starting angles, and the APEXII program suite was used to index the reflections [27]. Reduction of data was carried out using the SAINT software [28], and the absorption corrections and scaling were applied using the SADABS multi-scan technique [29]. The two structures were solved by the direct method using the SHELXS program and refined using the SHELXL program [30]. Graphics of the crystal structures were drawn using Mercury software [31]. Non-hydrogen atoms were first refined isotropically and then by anisotropic refinement with the full-matrix least square method based on F^2 using SHELXL. All hydrogen atoms were positioned geometrically, allowed to ride on their parent atoms, and refined isotropically. The crystallographic data and structure refinement parameters for complexes **1** and **2** are given in Table 1.

Table 1. The summary of X-ray crystal data collection and structure refinement parameters for complexes **1** and **2**.

	1	2
Empirical formula	$C_{156}H_{210}Ag_6N_{12}S_{12}$	$C_{40}H_{46}Ag_2N_4S_4$
Formula weight	3285.29	926.79
Crystal system	Trigonal	Triclinic
Space group	R-3: H	P-1
a/Å	30.0941(6)	8.1650(5)
b/Å	30.0941(6)	15.5778(9)
c/Å	50.6555(11)	16.2365(10)
α/°	90	77.7000(10)
β/°	90	87.3590(2)
γ/°	120	83.1580(3)
Space group no.	148	2
Volume/Å^3	39,730(2)	2002.9(2)
Z	9	2
ρ_{calc}g/cm^3	1.236	1.537
μ/mm^{-1}	0.841	1.220
F(000)	15,336	944
Crystal size/mm^3	0.320 × 0.210 × 0.140	0.32 × 0.19 × 0.11
2θ range for data collection/°	1.614 × 26.389	1.655 to 26.999
Index ranges	$-31 \leq h \leq 37$	$-9 \leq h \leq 10$
	$-37 \leq h \leq 24$	$-19 \leq k \leq 18$
	$-62 \leq l \leq 61$	$-20 \leq l \leq 12$
Reflections collected	91,820	6320
Independent reflections	17,643	8656
Data/restraints/parameters	17,643/0/862	8657/7/1474
Goodness-of-fit on F^2	0.935	0.983
Final R indexes [I > = 2σ(I)]	R_1 = 0.0409 wR_2 = 0.0868	R_1 = 0.0610 wR_2 = 0.110
Final R indexes [all data]	R_1 = 0.0869, wR_2 = 0.1009	R_1 = 0.0610, wR_2 = 0.1196
Largest diff peak & hole (e Å^{-3})	1.597 and −0.799	1.551 and 0.879

4. Results and Discussion

4.1. Synthesis of N,N′-Diarylformamidines Dithiocarbamate Ag(I) Complexes

Complexes **1** and **2** were synthesized by reacting acetonitrile potassium salt solutions of **L1** and **L2** (Figure 1) with aqueous solutions of $AgNO_3$ in a 2:1 ratio. Both complexes were obtained as thermally stable yellow solids with melting points ranging between 214 and 222 °C, **1** having a lower melting point than **2**. Both complexes are soluble in dichloromethane, chloroform, toluene and benzene.

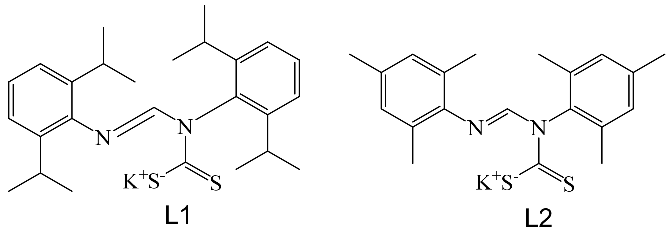


Figure 1. General structures of ligands **L1** and **L2**.

4.2. Spectroscopic Studies

The ^{1}H and ^{13}C NMR spectra for complexes **1** and **2** obtained in chloroform had signature peaks for the methane proton of the **L1** and **L2** as confirmed using their 2D NMR spectra. The azomethine proton of **1** and **2** was observed at 9.38 and 9.43 ppm in the spectra of **L1** and **L2,** respectively, an upfield shift from 10.15 and 9.92 ppm [26]. The signals of aliphatic protons in the spectra of the complexes shifted noticeably downfield. For example, methyl protons in **2** appeared at 1.94, 2.03, and 2.15 ppm but were at 1.99, 2.11, and 2.22 ppm in **L2**. The downfield shift is a result of the drifts of electron density towards the metal ion center [32,33]. There were similar observations in the ^{13}C-NMR spectra of **1** and **2**, and an upfield shift of the carbon atom of -NCS_2 moiety to 214.15 and 214.01 ppm from 220.94 and 218.95 ppm in the spectra of **L1** and **L2**, corroborating coordination of the S atom to Ag.

The FT-IR spectra of complexes **I** and **2** showed a strong absorption band at 1474 and 1476 cm^{-1}, stretching bands for the C—N bond of the thiouride group. These stretching frequencies are intermediate of a typical C—N single bond (1250–1360 cm^{-1}) and a double bond (1640 cm^{-1}), an indication of a partial double bond character of the thiouride bond [34,35]. The two vibrational bands around 1252–1246 cm^{-1} and 982–983 cm^{-1} in the spectra of **1** and **2** are assigned to the asymmetric C—(S)—S and the symmetric C—(S)—S moiety confirming the asymmetric linking of the sulfur atoms to the silver atoms [36]. The vibrational bands for υ(C=Nstr) of the azomethine (C(H)=N) in the formamidine backbone of the complexes were observed around 1634–1639 cm^{-1}.

In the electronic spectra of **1** and **2**, two bands were observed at 238 and 312, and 314 nm and these are attributed to intraligand $\pi \rightarrow \pi^*$ transition associated with N—C=S and $\pi \rightarrow \pi^*$ transition within S—C=S groups of the coordinated dithiocarbamate ligands [37].

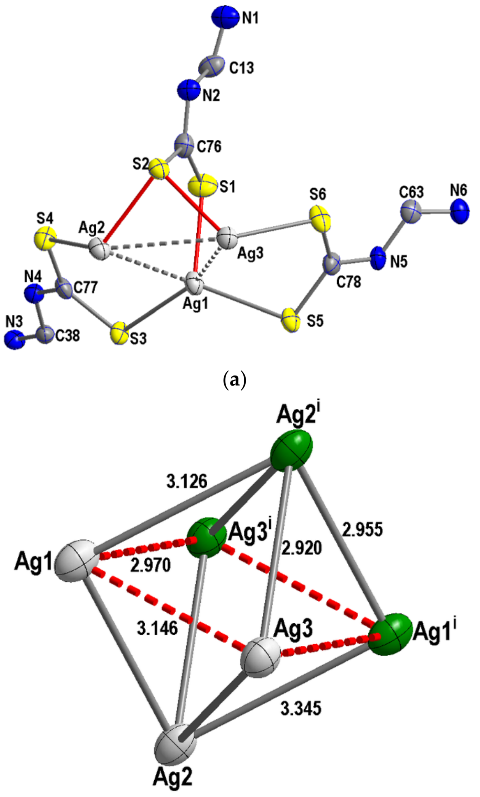
4.3. X-ray Structural Analysis

Suitable crystals for single-crystal X-ray diffraction analysis were obtained by slow diffusion of hexane into a chloroform solution of complexes **1** and **2**, each. While complex **1** is an Ag(I) diarylformamidines dithiocarbamate cluster, **2** is an Ag(I) diarylformamidines dithiocarbamate coordination polymer. Complex **1** is a polymorph of the previously reported structure of $Ag_6[CS_2(2,6\text{-}{}^{i}Pr_2C_6H_3NC(H)=NC_6H_3\text{-}{}^{i}Pr_2)]_6$ which crystallized in the *Ia*3 cubic space group (Table 2). The previously reported structure was synthesized by the insertion of CS_2 into a dinuclear Ag(I) complex of $Ag_2[2,6\text{-}{}^{i}Pr_2C_6H_3N)_2C\text{-}(H)]_2$ using toluene as a solvent for the reaction [38].

Table 2. Comparison of some selected X-ray crystal data collection and structure refinement parameters for complex **1** and its polymorph.

	1	**Polymorph**
Empirical formula	$C_{156}H_{210}Ag_6N_{12}S_{12}$	$C_{174}H_{262}Ag_6N_{12}S_{12}$
Formula weight	3285.29	3553.88
Crystal system	Trigonal	Cubic
Space group	$R\bar{3}$	$Ia\bar{3}$
a/Å	30.0941(6)	32.283(4)
b/Å	30.0941(6)	32.283(4)
c/Å	50.6555(11)	32.283(4)
α/°	90	90
β/°	90	90
γ/°	120	90
Volume/Å^3	39,730(2)	33,644.8(2)
Z	9	8
ρ_{calc}g/cm^3	1.236	1.403
Largest diff. peak & hole (e Å^{-3})	1.597 and −0.799	1.551 and 0.879

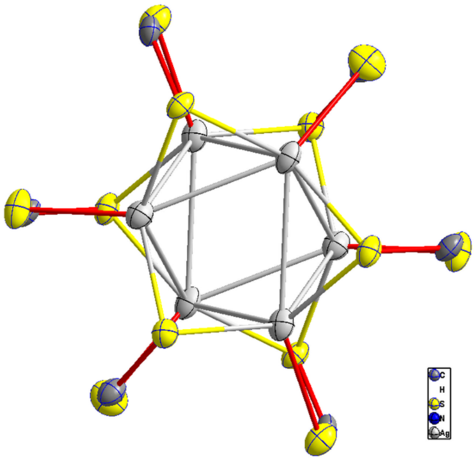
Complex **1** is assembled through six Ag(I) centers and six diarylformamidines dithiocarbamate ligands (1:1 ratio). The asymmetric unit contains one-half of the cluster and is made up of three Ag(I) centers, coordinated through bridging by three diarylformamidines dithiocarbamate molecules (Figure 2a). The other half is generated through an inversion center. In the crystal, a six-vertex distorted square bipyramid octahedron is formed in which Ag3 forms the apexes of the pyramid while $Ag1_2Ag2_2$ (red dashed lines in Figure 2b) for the base of the bipyramid (Figure 2b). The square bipyramid is stabilized by six **L1** ligands which have the coordination modes μ^1- μ^1- for four of the ligands while for the other two have a μ^1- μ^2- coordination mode. With the CS_2 moieties added on, a propeller like core is formed (Figure 2c).



(**a**)

(**b**)

Figure 2. *Cont.*



(**c**)

Figure 2. (**a**) Asymmetric unit of complex **1**. Hydrogen atoms and 2,6-diisopropyl units of the ligands are omitted for the sake of clarity (**b**) Octahedral arrangement of Ag atoms in **1** (**c**) Propeller like core of CS_2 moieties in **1**. Thermal displacement ellipsoids are drawn for all atoms at the 50% probability level.

Comparison of **1** to $Ag_6[CS_2(2,6\text{-}{}^iPr_2C_6H_3NC(H){=}NC_6H_3\text{-}{}^iPr_2)]_6$

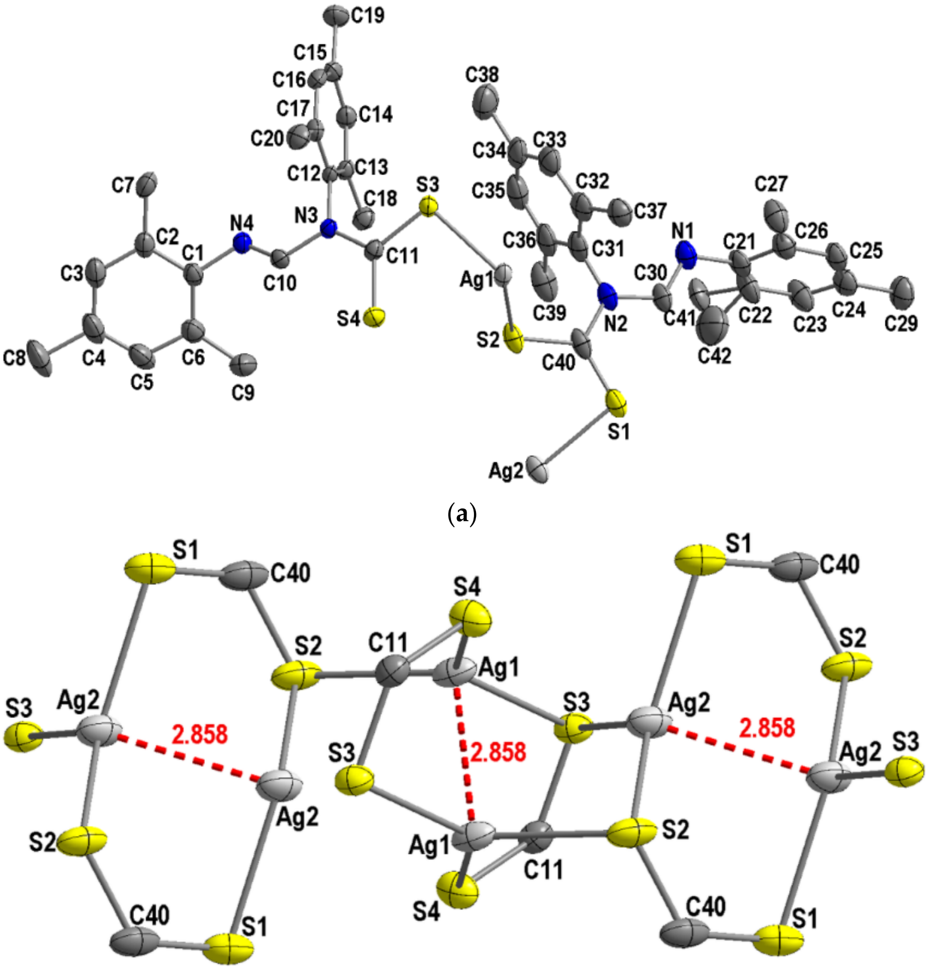
The literature structure is solvated with one molecule of chloroform, while **1** is not. The Ag(I) octahedron core of the literature structure forms a perfect square bipyramid, whereas that of **1** is slightly distorted. The Ag—Ag distances in **1** range between 2.9204(4) and 3.3452(4) Å while the distances are between 3.0001(3) and 3.3178(3) Å for literature structure. In both complexes, the Ag—Ag argentophilic distances are all less than the sum of the van der Waals radii of two Ag atoms, 3.44 Å [23,24].

Each Ag(I) center in **1** is coordinating to three sulfur atoms in a $\kappa^1\kappa^1\kappa^1$-S fashion, a geometry around Ag(I) that can be described as distorted trigonal pyramidal in which the Ag(I) center serves as the apex of the pyramid. The S—Ag—S bond angles range between 107.07(4) and 123.40(3)° in **1** while it ranges between 109.29(3) and 127.14(3) in the literature structure. The Ag—S bond distances are 2.4857(11), 2.5231(10), and 2.5322(9) in comparison to 2.4779(3) and 2.5008(2) for the literature structure.

In the crystal of complex **2**, the asymmetric unit consists of two diarylformamidines dithiocarbamate ligands (**L2**) and two Ag(I) centers (Figure 3a). The Ag(I) centers are bridged by two diarylformamidine dithiocarbamate units in such a way that two Ag1s are paired and likewise two Ag2s. In doing so, each bridged Ag(I) pairs with an 8-member bimetallocycle, and an inversion center is formed. The metallacycles are connected through two centrosymmetrically related Ag—S bonds leading to a ribbon that runs in the *a*-crystallographic axis (Figure 3b).

Just like in **1**, the Ag(I) center is coordinated to three S atoms giving a trigonal pyramidal geometry around the metal center. This differs from the coordination polymer of [Ag(dibenzyldithiocarbamate)]∞ [17] where each Ag(I) cation is bonded to two pairs of sulfur atoms from three dithiocarbamate ligands resulting in a distorted tetrahedral geometry. The S—Ag—S bond angles range from 102.58(3)°—129.07(4)° and these are similar to the ones for coordination polymer of [{Ag(diethyldithiocarbamate)}$_3$]∞ which ranges from 109.49(4)°—128.56(4)° [24].

The Ag—S bond distances are in the range of 2.4757(10)–2.5716(12), i.e., Ag(2)—S(1), Ag(2)—S(2), and Ag(2)—S(3) are 2.5716(12), 2.4757(10), and 2.5660(10) respectively (Table 3) and comparatively, they are similar to those previously reported related complexes [39,40]. The Ag—Ag bond lengths in complex **2** are identical to those observed in **1.** The C—S bond distances in the dithiocarbamate ligand (**L2**) backbone of complex **2**, fall between ideal single and double C—S bonds indicating partial delocalization of π-electron density over the entire S_2CN fragments in the complex [26,41].



(**a**)

(**b**)

Figure 3. (**a**) Asymmetric unit of complex **2** drawn at 50% thermal ellipsoids probability (**b**) Complex **2,** showing the bridging of Ag(I) two diarylformamidine dithiocarbamate units.

Table 3. Selected bond length (Å) and angles (°) for complexes **1** and **2**.

Bond distances (Å)	1	Polymorph	2
Ag—Ag	2.9545(4)	3.0001(1)	2.8829(6)
Ag—Ag	2.9695(4)	3.0001(1)	3.1932(5)
Ag—Ag	3.3452(4)	3.0001(1)	3.0644(5)
Ag—S	2.4857(11)	2.4777(1)	2.5029(9)
Ag—S	2.5322(9)	2.5007 (1)	2.4805(10)
C—S	1.681(4)	1.6962(1)	1.682(5)
C—S	1.739(4)	1.7404(1)	1.723(4)
C—N	1.362(5)	1.3632(1)	1.366(4)
C—N	1.371(4)	1.4639(1)	1.406(5)
Bond angles (°)			
Ag—S—Ag	85.03(3)	82.20	74.38(3)
S—Ag—S	107.07(4)	109.29	111.97(4)
Ag—Ag—S	77.81(2)	80.27	88.90(2)

4.4. Thermal Decomposition Studies

The thermal decomposition of the two silver complexes was examined by thermogravimetric (TG) analysis, and the superimposed TG graphs are represented in Figure 4. It is observed from the TGA curve that the thermal decomposition of the complexes shows one step that is equivalent to about 78% weight loss associated with the decomposition of the dithiocarbamate backbone ligand and the dominant weight loss of complex **1** occur in the temperature region of 250–325 °C while the one for **2** occurs at 250–350 °C. In both complexes, there is almost no weight loss below 100 °C and above 350 °C. The decomposition of **1** and **2** led to the formation of elemental silver residue with about 22% residue, which was about 2% more than the calculated value of 20% for **1** and 1% less than the calculated value of 23% for **2**.

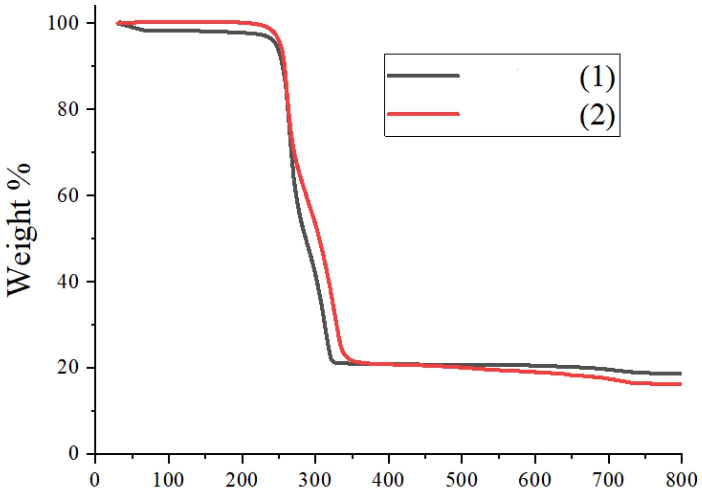


Figure 4. Superimposed thermogravimetric analysis (TGA) profile for complexes **1** and **2**.

5. Conclusions

Conclusively, Ag(I)formamidine cluster and Ag(I)formamidine coordination polymer has been synthesized and characterized by means of thermogravimetric analysis together with FT-IR, UV-vis, ^{1}H, and ^{13}C NMR spectroscopy. X-ray structural analysis showed that the Ag_6 core of structure **1** formed a six vertex distorted square bi-pyramidal octahedron while in structure **2**, each of the two Ag(I) centers are bridged by two *N*,*N*′-mesityl formamidine dithiocarbamate ligands to form an 8-member $Ag_2(CS_2)_2$ metallacycles with an inversion center in the middle of the Ag—Ag argentophilic bond. The thermal analysis of complexes **1** and **2** led to the formation of the elemental silver residue.

Supplementary Materials: The following supporting information is online. Figure S1: 1H-NMR spectrum for **L1**; Figure S2: 1H-NMR spectrum for **L2**; Figure S3: 1H-NMR spectrum for **1**; Figure S4: 1H-NMR spectrum for **2**; Figure S5: 13C-NMR spectrum for **L1**; Figure S6: 13C-NMR spectrum for **L2**; Figure S7: 13C-NMR spectrum for **1**; Figure S8: 13C-NMR spectrum for **2**; Figure S9: FT-IR spectrum for **L1**; Figure S10: FT-IR spectrum for **L2**; Figure S11: UV-Visible spectra of **1** and **2**. CCDC 1976274 and CCDC 1976275 contain the supplementary crystallographic data for complexes **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or via e-mail: deposit@ccdc.cam.ac.uk.

Author Contributions: Conceptualization, S.D.O. and B.O.; methodology, S.D.O.; software, S.D.O. and B.O.; validation, S.D.O. and B.O.; formal analysis, S.D.O. and B.O.; resources, B.O.; data curation, S.D.O. and B.O.; writing—original draft preparation, S.D.O. and B.O.; writing—review and editing, S.D.O. and B.O.; visualization, S.D.O. and B.O.; supervision, B.O.; project administration, B.O.; funding acquisition, S.D.O. and B.O. All authors have read and agreed to the published version of the manuscript.

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References

1. Young, A.G.; Hanton, L.R. Square planar silver(I) complexes: A rare but increasing observed stereochemistry for silver(I). *Coord. Chem. Rev.* **2008**, *252*, 1346–1386. [CrossRef]
2. Schmidbaur, H.; Schier, A. Argentophilic interactions. *Angew. Chem. Int. Ed.* **2014**, *54*, 746–784. [CrossRef] [PubMed]
3. Adeleke, A.A.; Zamisa, S.J.; Omondi, B. Ag(I) complexes of imine derivatives of unexpected 2-thiophenemethyl homo-coupling and Bis-(E)-N-(furan-2-ylmethyl)-1-(quinolin-2-yl)methanimine. *Molbank* **2021**, *2*, 1235. [CrossRef]
4. Castiñeiras, A.; Pedrido, R. Novel fluorescent cationic silver thiosemicarbazone clusters containing different eight-membered Ag4S4 metallacycles. *Inorg. Chem.* **2009**, *48*, 4847–4855. [CrossRef]
5. Su, W.; Hong, M.; Weng, J.; Cao, R.; Lu, S. A Semiconducting Lamella Polymer [{Ag (C5H4NS)} n] with a Graphite-Like Array of Silver (I) Ions and Its Analogue with a Layered Structure. *Angew. Chem. Int. Ed.* **2000**, *39*, 2911–2914. [CrossRef]
6. Zhong, J.C.; Misaki, Y.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Konaka, H. Silver (I) Coordination Polymer of 2, 5-Bis-(4′, 5′-bis (methylthio)-1′, 3′-dithiol-2′-ylidene)-1, 3, 4, 6-tetrathiapentalene (TTM-TTP) and Its Highly Conductive Iodine Derivative. *Inorg. Chem.* **2001**, *40*, 7096–7098. [CrossRef] [PubMed]
7. Safin, D.A.; Mdluli, P.S.; Revaprasadu, N.; Ahmad, K.; Afzaal, M.; Helliwell, M.; O'Brien, P.; Shakirova, E.R.; Babashkina, M.G.; Klein, A. Nanoparticles and thin films of silver from complexes of derivatives of N-(diisopropylthiophosphoryl) thioureas. *Chem. Mater.* **2009**, *21*, 4233–4240. [CrossRef]
8. Gao, S.; Chen, D.; Li, Q.; Ye, J.; Jiang, H.; Amatore, C.; Wang, X. Near-infrared fluorescence imaging of cancer cells and tumors through specific biosynthesis of silver nanoclusters. *Sci. Rep.* **2015**, *4*, 4384. [CrossRef]
9. Oladipo, S.D.; Tolufashe, G.F.; Mocktar, C.; Omondi, B. Ag(I) symmetrical N,N′-diarylformamidine dithiocarbamate PPh3 complexes: Synthesis, structural characterization, quantum chemical calculations and in vitro biological studies. *Inorganica Chim. Acta* **2021**, *520*, 120316. [CrossRef]
10. Walker, M.; Parsons, D. The biological fate of silver ions following the use of silver-containing wound care products–a review. *Int. Wound J.* **2014**, *11*, 496–504.
11. Mosconi, N.; Giulidori, C.; Velluti, F.; Hure, E.; Postigo, A.; Borthagaray, G.; Back, D.F.; Torre, M.H.; Rizzotto, M.J.C. Antibacterial, Antifungal, Phytotoxic, and Genotoxic Properties of Two Complexes of AgI with Sulfachloropyridazine (SCP): X-ray Diffraction of [Ag (SCP)] n. *ChemMedChem* **2014**, *9*, 1211–1220. [CrossRef]
12. Iqbal, M.A.; Haque, R.A.; Ahamed, M.B.K.; Majid, A.A.; Al-Rawi, S.S. Synthesis and anticancer activity of para-xylyl linked bis-benzimidazolium salts and respective Ag (I) N-heterocyclic carbene complexes. *Med. Chem. Res.* **2013**, *22*, 2455–2466. [CrossRef]
13. Hemmert, C.; Fabié, A.; Fabre, A.; Benoit-Vical, F.; Gornitzka, H. Synthesis, structures, and antimalarial activities of some silver (I), gold (I) and gold (III) complexes involving N-heterocyclic carbene ligands. *Eur. J. Med. Chem.* **2013**, *60*, 64–75. [CrossRef] [PubMed]
14. Steel, P.J.; Fitchett, C.M. Metallosupramolecular silver (I) assemblies based on pyrazine and related ligands. *Coord. Chem. Rev.* **2008**, *252*, 990–1006. [CrossRef]
15. Zhang, W.G.; Zhong, Y.; Tan, M.Y.; Liu, W.S.; Su, C.Y. A Novel Octahedral Hexasilver (I) Cluster: Ag6[SSCN (n-C$_4$H$_9$) $_2$]$_6$. *Chin. J. Chem.* **2010**, *20*, 420–423. [CrossRef]
16. Liu, N.; Fan, J.; Zhang, W.-G.; Yin, X.; Xie, M.-B. Bis (μ-N, N-diethyldithiocarbamato-κ3S, S′: S′) bis [(μ-N, N-diethyldithiocarbamato-κ2S, S′) silver (II)]. *Acta Crystallogr. Sect. E* **2006**, *62*, m2588–m2590. [CrossRef]
17. Yin, X.; Xie, M.-B.; Zhang, W.-G.; Fan, J. Poly [(μ3-N, N-dibenzyldithiocarbamato-κ^{4}S, S′: S: S′) silver (I)]. *Acta Crystallogr. Sect. E* **2007**, *63*, m2273. [CrossRef]
18. Oladipo, S.D.; Omondi, B.; Mocktar, C. Synthesis and structural studies of Ni(II) and Cu(II) N,N′-diarylformamidine dithiocarbamate complexes as antimicrobial and antioxidant agents. *Polyhedron* **2019**, *170*, 712–722. [CrossRef]
19. Kishore, P.V.; Liao, J.-H.; Hou, H.-N.; Lin, Y.-R.; Liu, C.W. Ferrocene-functionalized Cu (I)/Ag (I) dithiocarbamate clusters. *Inorg. Chem.* **2016**, *55*, 3663–3673. [CrossRef]
20. Yamaguchi, H.; Kido, A.; Uechi, T.; Yasukouchi, K. The Crystal and Molecular Structure of Silver (I) N, N-Diethyldithiocarbamate. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1271–1276. [CrossRef]

21. Tong, M.C.; Chen, W.; Sun, J.; Ghosh, D.; Chen, S. Dithiocarbamate-capped silver nanoparticles. *J. Phys. Chem. B* **2006**, *110*, 19238–19242. [CrossRef] [PubMed]
22. Hussain, S.T.; Bakar, S.A.; Saima, B.; Muhammad, B. Low temperature deposition of silver sulfide thin films by AACVD for gas sensor application. *Appl. Surf. Sci.* **2012**, *258*, 9610–9616. [CrossRef]
23. Ehsan, M.A.; Khaledi, H.; Tahir, A.A.; Ming, H.N.; Wijayantha, K.U.; Mazhar, M. Synthesis and characterization of silver diethyldithiocarbamate cluster for the deposition of acanthite (Ag2S) thin films for photoelectrochemical applications. *Thin Solid Film.* **2013**, *536*, 124–129. [CrossRef]
24. Song, Y.-W.; Yu, Z.; Zhang, Q.-F. γ-Modification of poly [(N, N-diethyldithiocarbamato) silver (I)]. *Acta Crystallogr. Sect. C* **2006**, *62*, m214–m216. [CrossRef] [PubMed]
25. Yin, X.; Xie, M.-B.; Zhang, W.-G.; Fan, J.; Zeller, M. Hexakis (μ3-N, N-diisopropyldithiocarbamato) hexasilver (I)(6 Ag—Ag). *Acta Crystallogr. Sect. E* **2007**, *63*, m2063–m2064. [CrossRef]
26. Oladipo, S.D.; Olotu, F.A.; Soliman, M.; Mocktar, C.; Omondi, B. Formamidibe-based thiuram disulfides: Synthesis, structural characterization, biological studies and preliminary cheminformatics evaluation. *J. Mol. Struct.* **2020**, *1219*, 128553. [CrossRef]
27. Bruker. *APEXII*; Bruker AXS Inc.: Madison, WI, USA, 2009.
28. Bruker. *SAINT*; Bruker AXS Inc.: Madison, WI, USA, 2009.
29. Bruker. *SADABS*; Bruker AXS Inc.: Madison, WI, USA, 2009.
30. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122. [CrossRef]
31. Bruno, C.F.I.J.; Chisholm, J.A.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; Streek, J.V.D.; Wood, P.A. Mercury 2.0-new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* **2008**, *41*, 466–470.
32. Mohammad, A.; Varshney, C.; Nami, S.A. Synthesis, characterization and antifungal activities of 3d-transition metal complexes of 1-acetylpiperazinyldithioc arbamate, M (acpdtc) 2. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **2009**, *73*, 20–24. [CrossRef]
33. Siddiqi, K.; Khan, S.; Nami, S.A.; El-Ajaily, M. Polynuclear transition metal complexes with thiocarbohydrazide and dithiocarbamates. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **2007**, *67*, 995–1002. [CrossRef]
34. Oladipo, S.D.; Omondi, B. Mercury(II) *N,N′*-diarylformamidine dithiocarbamate as single-source precursors for the preparation of oleylamine-capped HgS nanoparticles. *Transit. Met. Chem.* **2020**, *45*, 391–402. [CrossRef]
35. Gölcü, A. Transition metal complexes of propranolol dithiocarbamate: Synthesis, characterization, analytical properties and biological activity. *Transit. Met. Chem.* **2006**, *31*, 405–412. [CrossRef]
36. Korneeva, E.; Ivanov, A.; Gerasimenko, A.; Loseva, O.; Novikova, E.; Ivanov, M. Hexanuclear Silver (I) Hexamethylene Dithiocarbamate Cluster [Ag $_6${S $_2$CN(CH$_2$)$_6$} 6]·2CH 2 Cl 2: Preparation, Molecular Structure (Manifestation of Argentophilic Interaction), and Thermal Behavior. *Russ. J. Gen. Chem.* **2019**, *89*, 1642–1648. [CrossRef]
37. Oladipo, S.D.; Omondi, B.; Mocktar, C. Co (III) N, N′-diarylformamidine dithiocarbamate complexes: Synthesis, characterization, crystal structures and biological studies. *Appl. Organomet. Chem.* **2020**, *34*, e5610. [CrossRef]
38. Lane, A.C.; Vollmer, M.V.; Laber, C.H.; Melgarejo, D.Y.; Chiarella, G.M.; Fackler, J.P.; Yang, X.; Baker, G.A.; Walensky, J.R. Multinuclear Copper(I) and Silver(I) Amidinate Complexes: Synthesis, Luminescence, and CS_2 Insertion Reactivity. *Inorg. Chem.* **2014**, *53*, 11357–11366. [CrossRef]
39. Huang, Z.; Lei, X.; Hong, M.; Liu, H. Synergism in a transition metal cluster compound. Crystal and molecular structure of a polysilver cluster molecule with an unusual bridging sulfur atom, Ag11S (Et2dtc) 9. *Inorg. Chem.* **1992**, *31*, 2990–2991. [CrossRef]
40. Liu, C.; Liao, P.-K.; Fang, C.-S.; Saillard, J.-Y.; Kahlal, S.; Wang, J.-C. An eleven-vertex deltahedron with hexacapped trigonal bipyramidal geometry. *Chem. Commun.* **2011**, *47*, 5831–5833. [CrossRef]
41. Prakasam, B.A.; Lahtinen, M.; Peuronen, A.; Muruganandham, M.; Kolehmainen, E.; Haapaniemi, E.; Sillanpää, M. Spectral and structural studies on Ni(II) dithiocarbamates: Nickel sulfide nanoparticles from a dithiocarbamate precursor. *Inorg. Chim. Acta* **2015**, *425*, 239–246. [CrossRef]