

Crystal Structure and Nanoparticles of Dinuclear Silver(I) Complex $[\text{Ag}_2(\text{PPh}_3)_2(\mu\text{-S-4nb-tsc})_2(\eta^1\text{-S-4nb-tsc})_2](\text{NO}_3)_2$

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Abstract

Nanoparticles of a new dinuclear silver(I) complex $[\text{Ag}_2(\text{PPh}_3)_2(\mu\text{-S-4nb-tsc})_2(\eta^1\text{-S-4nb-tsc})_2](\text{NO}_3)_2$, where 4nb-tsc = 4-nitrobenzylidene-thiosemicarbazone and PPh_3 = triphenylphosphine, were prepared in an ultrasonic bath and characterized by FT-IR and SEM. The crystal structure of a suitable single crystal prepared by slow evaporation was determined by single crystal X-ray diffraction. The compound crystallized in the triclinic system with space group $P\bar{1}$ and $Z = 2$. X-ray results showed that the neutral thiosemicarbazone ligand 4nb-tsc was coordinated to silver(I) ion in two different bonding modes, $\mu\text{-S}$, and $\eta^1\text{-S}$. The shortest distance between the sulfur-bridged Ag cations was 3.576(5) Å. One P atom and three S atoms from three 4nb-tsc ligands coordinated to the silver(I) ion in a distorted tetrahedral geometry. In the crystal packing of the title compound, several hydrogen bonds were connecting the molecules of the complex.

Keywords: Nanoparticles; Dinuclear silver(I); Thiosemicarbazone; Sulfur-bridged; Tetrahedral geometry.

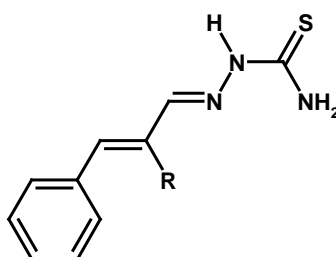
Introduction

Thiosemicarbazones are derivatives of imines formed by a condensation reaction between a ketone or aldehyde and semicarbazide [1]. They show a wide range of biological activities because of their ability to form coordination compounds with metal cations through their sulfur and azomethine nitrogen atoms [2]. Therefore, coordination chemistry of thiosemicarbazones has attracted considerable attention not only for a variety of structures displayed [3,4] but also for their properties [5-9]. The solubility of silver(I) complexes with thiosemicarbazones is low because of the formation of dimeric and polymeric species, causing that the structural chemistry of them remains less

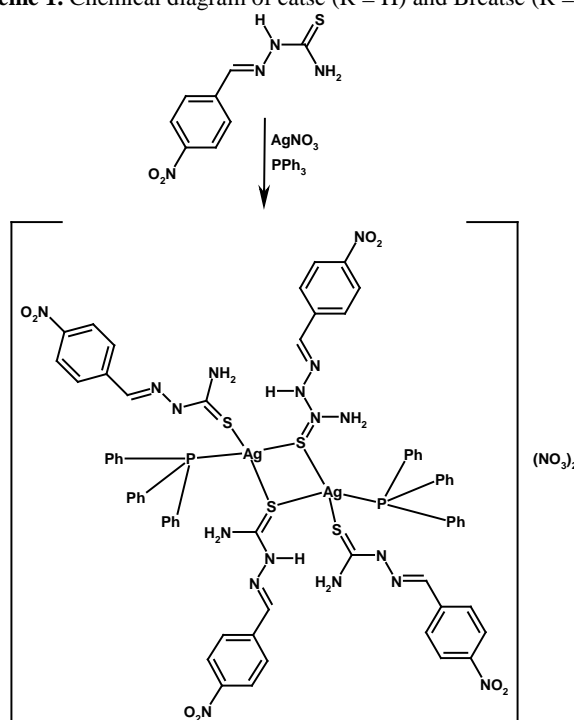
explored [10-13]. Recently, silver(I) complexes of thiosemicarbazone ligands have become the subject of intensive study by several groups due to their several bonding coordination modes [11-15]. For this reason, Lobana et al. reported a systematic investigation of silver(I) complexes with a series of substituted thiosemicarbazones [11-13].

Recently, our group reported some silver(I) complexes with thiosemicarbazones (Scheme 1). From the reaction of catsc, AgNO_3 and PPh_3 , monomeric complex $[\text{Ag}(\text{catsc})(\text{PPh}_3)_2]\text{NO}_3$ [16] was prepared where catsc acts as a chelating NS bidentate ligand. On the other hand, the reaction of Brcatsc, AgNO_3 and PPh_3 provided a dinuclear complex $[\text{Ag}_2(\text{PPh}_3)_2(\mu\text{-S-Brcatsc})_2(\eta^1\text{-S-Brcatsc})_2](\text{NO}_3)_2$ [17] where Brcatsc

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Scheme 1. Chemical diagram of catsc (R = H) and Brcatsc (R = Br).



Scheme 2. Chemical diagram of 4nb-tsc and its silver(I) complex $[Ag_2(PPh_3)_2(\mu\text{-}S\text{-}4nb\text{-}tsc)_2(\eta^1\text{-}S\text{-}4nb\text{-}tsc)_2](NO_3)_2$.

coordinated in two different modes, with sulfur being either terminal or bridging atom. In this work, we changed the thiosemicarbazone ligand and prepared a new dinuclear silver(I) complex $[Ag_2(PPh_3)_2(\mu\text{-}S\text{-}4nb\text{-}tsc)_2(\eta^1\text{-}S\text{-}4nb\text{-}tsc)_2](NO_3)_2$ (Scheme 2). Besides, we also prepared this complex as a nanopowder using an ultrasonic bath assisted synthesis.

Materials and Methods

All materials were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. Fourier transform infrared (FT-IR) spectra were recorded as a KBr disk on an FT-IR Perkin–Elmer spectrophotometer. The scanning electron microscopy (SEM) images were obtained from a Philips XL-30ESEM.

Synthesis of complex $[Ag_2(PPh_3)_2(\mu\text{-}S\text{-}4nb\text{-}tsc)_2(\eta^1\text{-}S\text{-}4nb\text{-}tsc)_2](NO_3)_2$

The methanolic solution of 4nb-tsc (1 mmol) was added to an acetonitrilic solution of 1 mmol $AgNO_3$ and three mmol of PPh_3 and stirred for 20 min until the colorless clear solution was obtained. The solution was left in the refrigerator for several days. The suitable crystals were filtered and washed twice with ethanol and dried at room temperature. *Anal. calcd.* for $C_{34}H_{31}Ag_1N_9O_7P_1S_2$: C, 46.37; H, 3.52; N, 14.32%. *Found:* C, 46.49; H, 3.45; N, 14.37%. FT-IR (KBr, cm^{-1}): 3522, 3420, 3289, 3244 (NH_2 , NH), 3015, 2970 (H aromatic and aliphatic), 1584 (C=N), 1509, 1481, 1446 (C=C), 956 (N-N), 891 (C=S), 476 (Cu-S).

X-ray structure determination

A suitable single crystal of title compound was chosen for the X-ray diffraction study. Crystallographic measurements were performed at 120 K with a four-

Table 1. Crystallographic data and structural refinement details of the title compound

Empirical formula	C ₃₄ H ₃₁ Ag ₁ N ₉ O ₇ P ₁ S ₂ .N _{0.155} C _{0.31}
Formula weight	886.5
Crystal system	Triclinic
space group	P-1
Cell length (Å)	<i>a</i> : 9.5862 (3) <i>b</i> : 14.1170 (5) <i>c</i> : 14.3831 (4)
Cell angles (°)	<i>α</i> : 92.263 (3) <i>β</i> : 95.197 (2) <i>γ</i> : 96.880 (3)
Cell volume (Å ³)	1921.99 (11)
Z	2
T (K)	120(1)
μ (mm ⁻¹)	6.12
R _{int}	0.027
reflections with $I > 3\sigma(I)$	5902
measured reflections	10812
independent reflections	6571
restraints	7
$R[F^2 > 3\sigma(F^2)]$	0.026
$wR(F^2)$	0.033
parameters	517
crystal size (mm)	0.12 × 0.07 × 0.06
T_{\min}	0.647
T_{\max}	0.763
S	1.26
$\Delta\rho_{\max}$ (e Å ⁻³)	0.32
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.22

circle CCD diffractometer Gemini (Oxford Diffraction, Ltd.), equipped with mirror-collimated Cu-K α radiation ($\lambda = 1.54184$ Å). The crystal structure could be easily solved by the charge flipping program SUPERFLIP [18]. The refinement was carried out by the Jana2006 program package [19] employing a full-matrix least-squares technique on F². The molecular structure plots were prepared by Diamond 4.0 [20]. Crystallographic data, details of the data collection, structure solution, and refinements are listed in Table 1.

Results and Discussion

Reaction of 4nb-tsc with AgNO₃ in the presence of PPh₃ in acetonitrile solution under ultrasonic irradiation formed a new nano-sized silver(I) complex [Ag₂(PPh₃)₂(μ -S-4nb-tsc)₂(η^1 -S-4nb-tsc)₂](NO₃)₂. We used the slow evaporation technique to get suitable single crystals.

The details of the FT-IR spectrum are listed in the experimental section and also is shown in Figure 1. The peak concerning the stretching of the C=S bond appears in 891 cm⁻¹. Also, the complex show the presence of N-H and NH₂ in 3522-3244 cm⁻¹ and C=N 1584 cm⁻¹.

The molecular structure of [Ag₂(PPh₃)₂(μ -S-4nb-tsc)₂(η^1 -S-4nb-tsc)₂](NO₃)₂ is shown in Figure 2. Two halves of the molecules are connected by an inversion

center located between the two Ag₁ ions. The silver(I) ion is coordinated to three S atoms from two bridging and one terminal 4nb-tsc ligand and one terminal P atom from PPh₃, with the coordination geometry of a distorted tetrahedron. The terminal S-bridge ligands 4nb-tsc and PPh₃ molecules occupy trans positions across the central Ag(μ -S-4nb-tsc)₂Ag core with Ag...Ag and S...S distances 3.576(2) and 3.916(3) Å, respectively. The Ag...Ag distance exceeds the sum of Van der Waals radii of Ag⁺ (1.70 Å), therefore no bond between the silver ions. The Ag-S bond distances are between 2.528-2.702 Å, and Ag-P bond distance is 2.432(3) Å. The bond Ag1-S2 = 2.5284(6) Å is shorter than the bridge bond Ag1-S1 = 2.5999(15) Å. The bond angles around the silver(I) ion are in ranges 95 - 124° (S1-Ag1-S2 = 104.609(18), S1-Ag1-P1 = 120.336(19), S2-Ag1-P1 = 124.95(2) and S1-Ag1-S1 = 95.201(3)°). These bond distances and angles are similar to those in already reported dinuclear silver(I) thiosemicarbazone complexes [6,7,9]. The bond angle Ag1-S1-Ag1 = 84.80° and S1-Ag1-S1 = 95.201(3)° depicts the central Ag(μ -S-4nb-tsc)₂Ag core is almost rhombic.

Finally, there are various N-H...O and N-H...N hydrogen bonds in the unit cell of this complex (Table 2). The hydrogen bonds between amino hydrogen atoms of thiosemicarbazone ligands with NO₃ as a counter ion

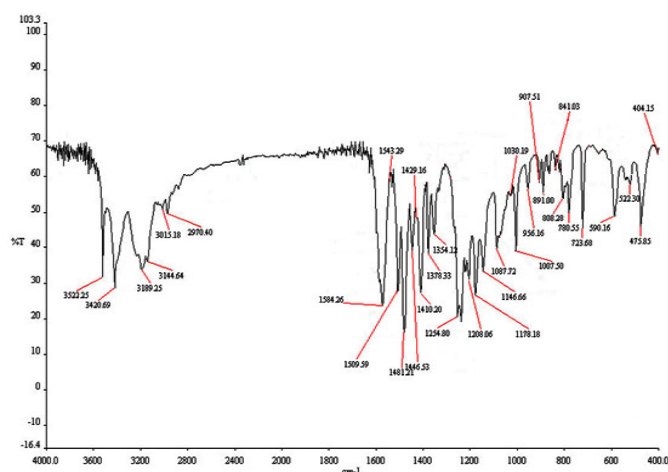


Figure 1. The FT-IR spectrum of $[\text{Ag}_2(\text{PPh}_3)_2(\mu\text{-S-4nb-tsc})_2(\eta^1\text{-S-4nb-tsc})_2](\text{NO}_3)_2$

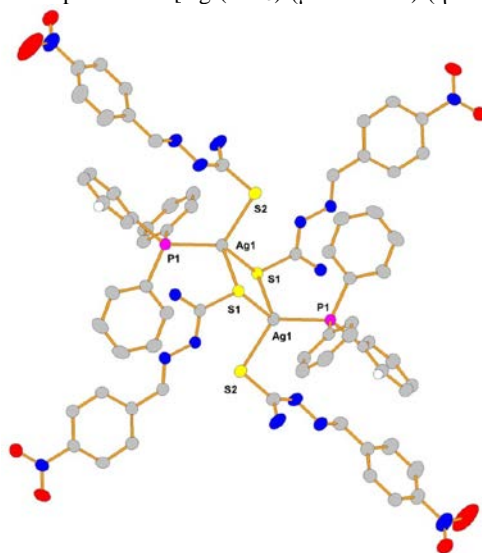


Figure 2. A molecule of $[\text{Ag}_2(\text{PPh}_3)_2(\mu\text{-S-4nb-tsc})_2(\eta^1\text{-S-4nb-tsc})_2](\text{NO}_3)_2$. H atoms, acetonitrile and NO_3^- anions are omitted for clarity.

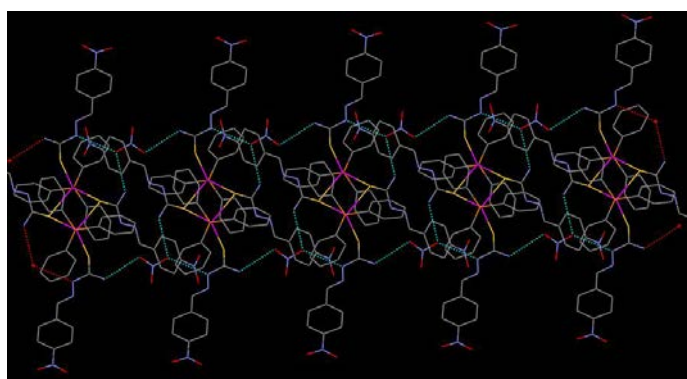


Figure 3. H-bonds between NH_2 and NO_3 groups to form a 1D network.

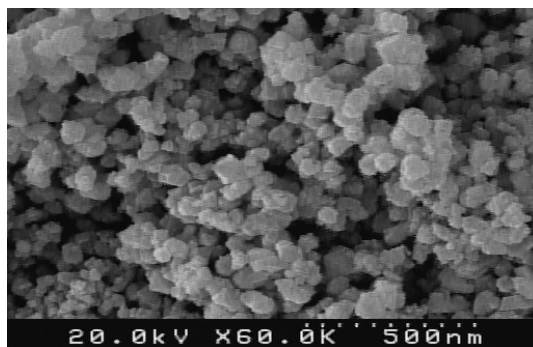
formed a 1D network (Fig. 3).

Nanoparticles of $[\text{Ag}_2(\text{PPh}_3)_2(\mu\text{-S-4nb-tsc})_2(\eta^1\text{-S-4nb-tsc})_2](\text{NO}_3)_2$ were characterized by SEM (Fig. 4). The SEM image showed the particles have practically

uniform shapes and sizes. The average sizes of the particles are < 100 nm.

Table 2. Hydrogen bonds (Å, °) in [Ag₂(PPh₃)₂(μ-S-4nb-tsc)₂(η¹-S-4nb-tsc)₂](NO₃)₂

D-A...H (Å°)	D-H... (Å°)	A...H (Å°)	A...D (Å°)	D-A...H (°)
N5 H1n5 O1	0.854(17)	2.132(17)	2.984(3)	176(2)
N4 H1n4 O2	0.85(2)	2.11(2)	2.952(3)	171(3)
N6 H1n6 O1	0.85(3)	2.24(3)	3.051(3)	159(3)
N4 H2n4 O6	0.85(3)	2.43(3)	3.142(4)	142(3)

**Figure 4.** SEM image of Nano-sized of [Ag₂(PPh₃)₂(μ-S-4nb-tsc)₂(η¹-S-4nb-tsc)₂](NO₃)₂.

Acknowledgments

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Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Center, CCDC No. 1872525. Copies of the data can be obtained free of charge at <http://www.ccdc.cam.ac.uk>.

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