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# Sulfur bridging by acetophenone thiosemicarbazone in $[Ag(\mu-dppm)_2(\mu-SR)Ag(ONO_2)](NO_3)$ dimer with a new $\{Ag_2(\mu-P,P)_2(\mu-SR)\}$ core

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## Abstract

Acetophenone thiosemicarbazone (Haptsc) with silver(I) nitrate and  $Ph_2P-CH_2-PPh_2$  (dppm) has formed a first example of triply hetero-bridged [Ag( $\mu$ -P,P-dppm)\_2( $\mu$ -S-Haptsc)Ag(ONO<sub>2</sub>)]NO<sub>3</sub> dimer with a short Ag · · · Ag contact of 2.9939(7) Å. © 2007 Elsevier B.V. All rights reserved.

Keywords: Acetophenone thiosemicarbazone; Silver(I); Bis(diphenylphosphino)methane; Triply bridging; Asymmetrically coordinated

In literature, diphosphine complexes of silver(I) usually adopt modes A–C having two or more than two P, Pbridges (Chart 1) [1–7]. For example, mode A is shown by bis(diphenylphosphino)methane in  $[(NO_3)Ag(\mu-P,P-dppm)_2Ag(NO_3)]$  [1]. Similarly, mode B is shown by bis(diphenylphosphino)pentane in  $[Ag(\mu-P,P-dppp)_2(\mu-Cl)_2Ag]$  [2]. Bis(diphenylphosphino)ferrocene shows coordination mode C in  $[(HCOO)Ag(\mu-P,P-dppf)_3Ag(HCOO)]$ complex [3].

There are a few reports on silver(I)-thiosemicarbazone chemistry, namely, the formation of a hexameric complex  $[Ag_6(HL)_6]$  (HL = anion of salicylaldehyde thiosemicarbazone) with N<sup>2</sup>–S-bridging cum-S-bridging coordination mode, and a few other complexes characterized by analytical data and spectroscopically [8]. As a part of our interest in metal-thiosemicarbazone chemistry [9], it was desired to explore  $Ag_2(\mu$ -P,P)<sub>m</sub> cores (m = 1–3), bonded to thiosemicarbazones.

In a typical reaction, acetophenone thiosemicarbazone was reacted with silver(I) nitrate and dppm, leading to the formation of the dimer,  $[Ag(\mu-P,P-dppm)_2(\mu-S-Hap-$ 

tsc)-Ag(ONO<sub>2</sub>)]NO<sub>3</sub> **1**. It has sulfur bridging across the  $Ag_2(\mu$ -P,P-dppm)<sub>2</sub> core, and it represents a new coordination mode D in metal-thiosemicarbazone chemistry, which is reported in this communication (Scheme 1).

Reaction of AgNO<sub>3</sub> (0.025 g, 0.14 mmol) with one mole of dppm (0.056 g, 0.14 mmol) in CH<sub>3</sub>CN (10 mL) at 40 °C, followed by the addition of one mole of Haptsc ligand (0.028 g, 0.14 mmol) in methanol (5 mL) under magnetic stirring for 2 h, has formed compound,  $[Ag(u-P,P-dppm)_2]$  $(\mu$ -S-Haptsc)Ag(ONO<sub>2</sub>)]NO<sub>3</sub> 1. Its IR spectrum shows the presence of v(N-H) bands at 3342 cm<sup>-1</sup> (due to  $-N^{1}H_{2}$  group), and 3165 cm<sup>-1</sup> (due to  $-N^{2}H$  group), supporting the interaction of thiosemicarbazone ligand with silver(I) as a neutral ligand. A thioamide band, v(C=S) at  $833 \text{ cm}^{-1}$  shifts to lower energy while v(C–N) bands at 999, 1024 cm<sup>-1</sup> show a shift to higher energy with respect to the free Haptsc ligand {v(C=S), 844 cm<sup>-1</sup>; v(C-N), 916, 962 cm<sup>-1</sup>}. Medium to broad peaks are observed in  $1480 - 1605 \text{ cm}^{-1}$ the region corresponding to  $\{\delta NH_2 + v(C=N) + v(C=C)\}$  vibrational modes, which are at slightly higher energy regions vis-à-vis the free ligand. Presence of characteristic  $v(P-C_{Ph})$  band at 1095 cm<sup>-1</sup> indicates the presence of coordinated dppm in the complex, and it shifted to slightly higher energy region

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with respect to the free ligand  $(1091 \text{ cm}^{-1})$ . The coordinated and ionic nitrate bands in the complex appear at 1605, 1384 and 1304 cm<sup>-1</sup> and could not be assigned separately due to various other bands in this region [10]. In order to resolve the bonding by nitrate and to establish the geometry around silver atoms, single crystal structure determination has been carried out.

The crystal structure of complex 1 shows the presence of two silver(I) atoms bridged by two dppm and one acetophenone thiosemicarbazone ligands, resulting in a triply bridged dinuclear complex [Ag(µ-P,P-dppm)<sub>2</sub>(µ-S-Haptsc)Ag(ONO<sub>2</sub>)]NO<sub>3</sub> 1 (Fig. 1). Compound 1 has one unidentate NO<sub>3</sub><sup>-</sup> coordinating to one Ag(I) center and the second  $NO_3^-$  is outside the coordination sphere. Further, compound 1 has two asymmetrically coordinated silver(I) centers, one is three coordinated and second is four coordinated. It is known that the complex of silver(I) nitrate with dppm is dinuclear  $[(NO_3)Ag(\mu-P,P-dppm)_2Ag(NO_3)]$  [1] and has P, P bridges along with chelating nitrates. The formation of 1 may be treated as sulfur bridging across  $Ag(\mu$ -P,P-dppm)<sub>2</sub>Ag core of  $[(NO_3)Ag(\mu-P,P-dppm)_2Ag(NO_3)]$ with simultaneous movement of one nitrate outside the coordination sphere.



Fig. 1. Structure of complex 1 with atomic numbering scheme. Selected bond lengths (Å) and angles (°): Ag(1)-Ag(2) 2.9939(7), Ag(1)-S(1) 2.6282(18), Ag(1)-P(11) 2.4612(7), Ag(1)-P(41) 2.4500(17), Ag(2)-S(1) 2.5971(18), Ag(2) -P(31) 2.4375(17), Ag(2)-P(21) 2.4575(17), S(1)-C(18) 1.704(7), Ag(2) -O(11) 2.462(5), P(41)-Ag(1)-P(11) 128.47(6), P(41)-Ag(1)-S(1) 107.29(6), P(11)-Ag(1)-S(1) 114.55(6), P(31)-Ag(2)-P(21) 132.56(6), P(31)-Ag(2)-O(11) 109.14(14), P(21)-Ag(2)-O(11) 88.85(12), P(31)-Ag(2)-S(1) 110.78(6), P(21)-Ag(2)-S(1) 109.76(6), O(11)-Ag(2)-S(1) 97.38(14), C(18)-S(1)-Ag(2) 100.2(2), C(18)-S(1)-Ag(1) 105.8(3), Ag(2)-S(1)-Ag(1) 69.91(5).

In complex 1, the bond angles around one of the silver atoms, 107.29(6)–128.47(6)° support a distorted trigonal planar geometry with the P(41)–Ag(1)–S angle being the smallest (107.29(6)°) and the P(41)–Ag(1)–P(11) being the largest angle (128.47(6)°). The second silver atom exhibits a distorted tetrahedral geometry as the bond angles range from  $88.85(12)^\circ$  to  $110.78(6)^\circ$ . The P–Ag–P' bond angles in 1 are nonlinear resulting in the folding of the central Ag<sub>2</sub>P<sub>4</sub> core across Ag···Ag axis. The introduction of sulfur bridging across Ag<sub>2</sub>P<sub>4</sub> core bends P–Ag–P' angles to  $128.47(6)^\circ$  and  $132.56(6)^\circ$ , shorter than  $138.3(1)^\circ$  in the compound [(NO<sub>3</sub>)Ag(µ-P,P-dppm)<sub>2</sub>Ag(NO<sub>3</sub>)] [1].

Two Ag and one S atoms form an isosceles triangle {S-Ag-Ag, 54.56(4)°, 55.53(4)°, S-Ag-S, 69.91(5)°}, bringing the Ag···Ag contact to 2.9939(7) Å, less than twice the sum of radius of silver(I), (3.4 Å) [11]. This distance is shorter than 3.085(1) Å in [(NO<sub>3</sub>)Ag( $\mu$ -P,P)<sub>2</sub>Ag(NO<sub>3</sub>)] [1]. The S-Ag-S bond angle of 69.91(5)° is slightly shorter than 72–74° in sulfur bridged complex [Ag(CN)<sub>2</sub>(etu)<sub>2</sub>]<sub>n</sub> (et = 2-imidazolidinethione) [11].

Two molecules of dppm bridge the Ag atoms with Ag–P bond distances in the range, 2.437–2.461 Å. The Ag–P bond distances are slightly longer than ca. 2.417–2.436 Å

in [(NO<sub>3</sub>)Ag( $\mu$ -P,P-dppm)<sub>2</sub>Ag(NO<sub>3</sub>)][1]. Neutral acetophenone thiosemicarbazone ligand bridges across Ag( $\mu$ -P,P)<sub>2</sub>Ag core via its sulfur atom, with Ag–S bond distance of 2.6282(18), 2.5971(18) Å. These Ag–S bond distances are longer than 2.573(1) Å in [Ag(pymtH)(PPh<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> (pymtH = pyrimidine-2-thione) [12]. The nitrate is coordinated to silver atom in **1** via one of its oxygen atoms with a bond distance of 2.462(5) Å, comparable with Ag–O distance of 2.689(6) Å in [(NO<sub>3</sub>)Ag( $\mu$ -P,P-dppm)<sub>2</sub>Ag(NO<sub>3</sub>)] [1]. It may be noted that bridging of Ag( $\mu$ -P,P-dppm)<sub>2</sub>Ag core by sulfur atom of Haptsc has brought Ag–Ag contact close to 2.9939(7) Å, less than twice the sum of radius of silver(I), (3.4 Å) [13].

The imino hydrogen  $(-N^2H)$  is engaged in strong intramolecular hydrogen bonding with the coordinated oxygen atom  $(-N^2H\cdots ONO_2, 2.51 \text{ Å})$  as well as with the non-coordinated oxygen atom  $(-N^2H\cdots ONO_2, 2.14 \text{ Å})$  of the bonded nitrate group (Fig. 2). On the other hand, one hydrogen atom of amino group  $(-N^1H_2)$  is engaged in strong intramolecular hydrogen bonding with the azomethine nitrogen  $(-HN^1H\cdots N^3, 2.23 \text{ Å})$  and inter-molecular H-bonding with two oxygen atoms of the non-coordinated nitrate group  $(-HN^1H\cdots O, 2.48, 2.56 \text{ Å})$  while the second hydrogen atom forms a strong intermolecular hydrogen bonding with one oxygen atom of the second non-coordinated nitrate group  $(-HN^1H\cdots O, 2.29 \text{ Å})$ , forming an eight membered cavity in the center. These interactions result in the formation of a hydrogen-bonded tetramer.

The <sup>1</sup>H NMR spectrum of compound **1** in CDCl<sub>3</sub> (polar solvent) shows the  $-N^{2}H$  signal at  $\delta$  10.53 ppm, which is upfield relative to the free ligand. A single signal at  $\delta$  8.75 ppm, is observed for  $-N^{1}H_{2}$  proton, while second signal is obscured by the multiplet signals due to the phenyl protons

of Haptsc, and dppm ligands ( $\delta$  7.00–7.69 ppm). Methyl protons of Haptsc ligand show a single signal at  $\delta$  2.22 ppm. Methylene protons of dppm ligands appear as a pair of doublets at  $\delta$  3.21, 3.60 ppm. Further, the <sup>31</sup>P NMR spectrum of **1** shows two signals at  $\delta$ , -106.2 ppm, and  $\delta$ , -109.7 ppm with coordination shifts ( $\delta_{complex} - \delta_{ligand}$ ) of 24.01 and 20.5 ppm, respectively, supporting the presence of two non-equivalent phosphorous atoms in the complex.

In conclusion, complex 1 reveals a new coordination core {Ag<sub>2</sub>(µ-P,P)<sub>2</sub>(µ-SR)} in metal-thiosemicarbazone chemistry. In literature, modes close to 1 are shown by heterocyclic thioamides with dppm as a coligand, as in [Rh<sub>2</sub>(CO)<sub>2</sub>(µ-S-L)(µ-P,P-dppm)<sub>2</sub>]Cl · CH<sub>2</sub>CL<sub>2</sub> (L = 1,3-thiazolidine-2-thione), [Cu<sub>2</sub>(µ-S-L)<sub>2</sub>(µ-P,P-dppm)(η<sup>1</sup>-P-dppm)] (L = 6-tertbutyl-dimethylsilylpyridine-2-thione) [14–16].

Compound 1: Mp 190–192 °C, yield: 0.050 g, 52%. C, H, N, analysis for C<sub>59</sub>H<sub>55</sub>Ag<sub>2</sub>N<sub>5</sub>O<sub>6</sub>P<sub>4</sub>S: C, 54.38; H, 4.22; N, 5.38. Found: C, 54.28; H, 4.16; N, 5.13. Main IR peaks (KBr, cm<sup>-1</sup>): v(N–H), 3342 m (–NH<sub>2</sub>) 3165m (–NH);  $\delta$ (NH<sub>2</sub>) + v(C=N) + v(C–C), 1541s, 1483s; v(C=S) + v(C– N), 1024s, 999s, 833s (thioamide moiety); 1095 v(P–C<sub>Ph</sub>). <sup>1</sup>H NMR data ( $\delta$ , ppm; CDCl<sub>3</sub>), 10.53 (s, N<sup>2</sup>H), 8.75 (sb, -N<sup>1</sup>H<sub>2</sub>), 7.00–7.69 (m, Ph + –N<sup>1</sup>H<sub>2</sub>), 3.21, 3.60 (d, –CH<sub>2</sub>), 2.22 (s, CH<sub>3</sub>). <sup>31</sup>P NMR data ( $\delta$ , ppm, CDCl<sub>3</sub>), –106.2, –109.7 ppm,  $\Delta\delta(\delta_{complex} - \delta_{ligand}) = 24.01$ , 20.5 ppm (<sup>31</sup>P NMR spectra were recorded by taking TMP {(MeO)<sub>3</sub>P} as external reference taken at zero position).

Crystallographic data for 1:  $C_{59}H_{55}Ag_2N_5O_6P_4S$ , M = 1301.76, monoclinic, a = 25.057(2) Å, b = 15.3627(14) Å, c = 31.365(3) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 98.4040(10)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 11944.1(18) Å<sup>3</sup>, T = 100(2) K, space group C2/c (No. 15),  $\rho_{calcd} = 1.448$  g cm<sup>-3</sup>, Z = 8,  $\mu$ (Mo-K $\alpha$ ) = 0.850 mm<sup>-1</sup>, 62,522 reflections measured on a Bruker X8 Kappa



Fig. 2. Packing diagram of complex 1.

APEXII diffractometer unique 12,282 ( $R_{int} = 0.0524$ ). The final  $R_1$  0.0672 was for 7030 reflections [ $I > 2\sigma(I)$ ] and  $wR_2$  was 0.1658.

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## Appendix A. Supplementary material

CCDC 653471 contains the supplementary crystallographic data for compound **1**. 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.inoche.2007.08.005.

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