Structure and Properties Characteristic of Dimeric Silver(I) Complex: Dinuclear Bis(O,O'-Diphenyldithiophosphato)bis(1,10-phenanthroline) Ag(I)*

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Abstract—The complex *bis*(O,O'-diphenyldithiophosphato)*bis*(1,10-phenanthroline) silver(I), Ag₂[(PhO)₂PS₂]₂(Phen)₂, has been synthesized and structurally characterized. Its crystal structure has been determined by X-ray crystallography. It crystallizes in the monoclinic system, space group $P2_1/c$, with unit cell parameters a = 11.140(2) Å, b = 10.044(2) Å, c = 23.006(6) Å, $\beta = 113.36(3)^\circ$; V = 2363.1(9) Å³, $\rho_{calcd} = 1.600$ g/cm³, and Z = 4 for $R_1 = 0.0961$. The coordination geometry of each Ag atom, by two N atoms from 1,10phenanthroline ligand and by two S atoms from two O,O'-diphenyldithio phosphate anions, is that of a tetrahedron. The two diphenyldithiophosphato ligands each bridge two silver atoms to form an eight-membered Ag₂S₄P₂ ring, while the 1,10-phenanthroline molecule coordinates to a silver atom to complete the local tetrahedral geometry. The Ag···Ag separation is 3.185(2) Å. The data of elemental analysis, IR and UV-vis spectroscopies are in good agreement with the crystal structure. The thermal gravimetry data indicate that there are two decomposition steps with one intense endothermical peak and one weak exothermical peak. The final product of the thermal decomposition is AgS.

Dialkyldithiophosphate complexes of transition metals have received increasing attention in recent years owing to their extensive applications in lubrication engineering and in the plastics industry [1, 2]. In addition to their syntheses and various physicochemical investigations, the crystal structures of many of these compounds and their adducts with nitrogen-containing bases have been reported [3, 4]. Metal chelates in which the metal ion is coordinately unsaturated can act as electron acceptors and yield adducts with the neutral molecules being electron donors [5]. Adducts and their formation reactions have also been found useful in a wide variety of ways. The amines in lubricating oil have a great influence on the properties of metal dialkyldithiophosphate additives [6]. It is interesting to investigate further the interaction between metal dialkyldithiophosphate and amines. In this paper, we report the synthesis and crystal structure of the title compound. The elemental analysis, IR, electronic absorption spectra, and thermal gravimetry (TG) have also been investigated.

EXPERIMENTAL

All chemicals used were of analytical or reagent grade and used directly without further purification. Na[$(RO)_2PS_2$] (R = Ph, PhCH₂, Et, Pr, *et al.*) was prepared according to literature method [7].

Ag[(**RO**)₂**PS**₂] (**J**). Stoichiometric amounts of silver(I) nitrate and sodium O,O'-dialkyldithiophosphate in deionized water were stirred together for 20 min. The brown precipitate was collected by filtering, washed with water, and then dried over P_4O_{10} . The complexes were collected and submitted for elemental analysis. Yield (90–95%).

For $C_{12}H_{10}O_2PS_2Ag$ (R = Ph)				
anal. calcd (%):	C, 37.04;	H, 2.59.		
Found (%):	C, 36.82;	H, 2.67.		

 $Ag_2[(PhO)_2PS_2]_4(Phen)_2$ (II). The silver(I) diphenyldithiophosphate complexes (0.78 g, 2.0 mmol) were dissolved in hot ethanol (50 ml), a slight excess of 1,10phenanthroline (0.38 g, 2.1 mmol) was added, and the resulting solution was refluxed for 4–5 h. The colorless mixture was cooled to room temperature, then filtered off, and the filtrate was left to stand undisturbed. Upon slow evaporation at room temperature, the colorless crystalline solid II appeared several days later and was separated by filtration. The C, H, and N contents were determined by elemental analysis. The yield of $Ag_2[(PhO)_2PS_2]_4(Phen)_2$ was 1.01 g (87%).

For C₄₈H₃₆N₄O₄P₂S₄Ag₂

anal. calcd (%):	C, 50.63;	Н, 3.19;	N, 4.92.
Found (%):	C, 50.15;	Н, 3.06;	N, 4.43.

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Formula	$C_{24}H_{18}AgN_2O_2PS_2$
М	569.36
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>a</i> , Å	11.140(2)
b, Å	10.044(2)
<i>c</i> , Å	23.006(6)
β, deg	113.36(3)
<i>V</i> , Å ³	2363.1(9)
Ζ	4
$\rho_{calc}, g/cm^3$	1.600
μ , mm ⁻¹	1.121
<i>F</i> (000)	1144
θ ranges, deg	1.93 to 24.98
Interval of reflection indices	$0 \le h \le 13, -11 \le k \le 0, \\ -27 \le l \le 25$
Reflections collected	$4344/4117 \ (R_{\rm int} = 0.0302)$
Data/restraints/parameters	4117/0/290
GOOF	1.346
Final <i>R</i> indices $(I > 2\sigma(I))$	$R_1 = 0.0961, wR_2 = 0.2885^*$
<i>R</i> indices (all data)	$R_1 = 0.1385, wR_2 = 0.3461*$
Largest difference peak and hole/ e Å ⁻³	1.362 and -2.329

 Table 1. Crystal data and summary of collection and refinement for the structure II

Table 2. Selected bond lengths (*d*) and bond angles (ω) in the structure **II**

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Ag(1)–N(1)	2.338(10)	Ag(1)–S(1)	2.482(3)
$Ag(1)-Ag(1A)^*$	3.185(2)	S(2)–P(1)	1.944(5)
O(1A)–C(1)	1.47(2)	Ag(1)–N(2)	2.443(8)
Ag(1)–S(2A)	2.705(3)	S(1)–P(1)	1.963(4)
P(1)–O(1A)	1.587(18)	N(1)–C(13)	1.339(17)
Angle	ω, deg	Angle	ω, deg
N(1)Ag(1)N(2)	68.5(3)	N(2)Ag(1)S(1)	120.2(2)
N(2)Ag(1)S(2A)	88.9(3)	N(1)Ag(1)Ag(1A)	114.2(2)
S(1)Ag(1)Ag(1A)	65.91(9)	O(1A)P(1)O(2)	109.4(9)
N(2)Ag(1)S(1)	120.2(2)	N(1)Ag(1)S(2A)	130.9(3)
S(1)Ag(1)S(2A)	106.2(1)	N(2)Ag(1)Ag(1A)	171.4(2)
O(2)P(1)S(2)	111.3(3)		

 $w = 1/[\sigma^2(F^2) + (0.0512P)^2 + 0.0000P]$, where $P = (F^2 + 2Fc^2)/3$.

Elemental analysis for carbon, hydrogen and nitrogen was performed on a Perkin-Elmer 240 C analysis instrument. IR spectra were recorded in the range of 4000–300 cm⁻¹ on a Perkin-Elmer 467 spectrometer using KBr pellets. Electron absorption spectra in solution were recorded on a Shimadzu UV-240 spectrophotometer. Thermal gravity and differential thermal analysis (DTA) were recorded on an SDT 2980 simultaneously for the samples of ca. 10 mg under a nitrogen atmosphere (150 ml/min) at a heating rate of 20 K/min.

X-ray diffraction analysis. Single crystals of the **II** were grown from the ethanol solution by evaporating the solvent slowly at room temperature. The experimental diffraction arrays were collected on Enraf-Nonius CAD4 automated diffractometer. Reflection data and reflections for the unit cell determination were measured at 20°C using Mo K_{α} radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. The tech-

* Symmetric transformation for atoms with index A: -x, -y, -z + 1.

nique used was ω -scan. Intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction using SADABS [8] program.

The structure of **II** was solved by direct method and refined by least squares on F_{obs}^2 by using the SHELXTL [9] software package. All nonhydrogen atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The molecular graphics were plotted using SHELXTL [9]. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [10]. A summary of the key crystallographic information is given in Table 1.

RESULTS AND DISCUSSIONS

The molecular structure of the \mathbf{II} illustrated in Figs. 1 and 2 shows a perspective view of the crystal packing in the unit cell. Selected bond distances and angles of the \mathbf{II} are listed in Table 2.

The molecular structure of the compound **II** consists of discrete molecules of $Ag_2[(PhO)_2PS_2]_4(Phen)_2$. It is built up of centrosymmeric dimeric entities. The coordination sphere of the silver(I) ion is best described as a distorted tetrahedral geometry. The two diphenyldithiophosphato ligands each bridge two silver atoms to form an eight-membered $Ag_2S_4P_2$ ring, while two 1,10-phenanthroline molecules coordinate to a silver



Fig. 1. The molecular structure of $Ag_2[(PhO)_2PS_2]_4(Phen)_2$ showing the atom labeling scheme. Atoms are represented as thermal ellipsoids at 50% level.

atom to form a five-membered chelate ring. The Ag-N bond lengths (2.338(10) and 2.443(8) Å) are comparable with those of 2.332(2), 2.342(2) and 2.419(2), Å found in other silver(I) complexes with tetrahedral coordination [11-13]. There are one longer Ag-S bond (2.705(3) Å) and one shorter ones (2.482(3) Å) in the II, which are obvious difference with the Ag–S bonds of other similar tetrahedral structure (2.507–2.644 Å) [5, 14]. It is apparent that the steric and electronic effects of the phenyl group can destabilize the Ag-S bond. It is possible to interpret these results on the basis of a simple electrostatic model. The π conjugated system between O atom and phenyl ring reduces the net positive charge on the O atom and increases the net negative charge on the S atoms. The latter effect results in an increase in the SPS angle $(119.8(2)^{\circ})$ while the former effect lengthens the Ag-S distance and decreases the SAgS angle $(106.16(13)^\circ)$. There are some disorder at O(1), C(2), and C(3) atoms, with the occupation ratios of 60, 50, and 60%, respectively.

The P–S bond lengths and SPS angles in the **II** are normal [15]. The phenanthroline ligand with Ag atoms is coplanar. The average C–C distances in the phenanthroline rings are approximately the expected mean value of 1.40 Å. The Ag…Ag separation in the dimer is 3.185(2) Å, which is in the range 2.93 to 3.52 Å, showing that no significant silver–silver interactions exist in the compound [5].

In the II, there are some $\pi - \pi$ stacking interactions in the lattice [16, 17]. The shortest center-to-center distances between the adjacent moieties are 3.469 Å. It is obvious that they form the slightly stronger $\pi - \pi$ stacking interaction [18]. In the solid state, all above extensive hydrogen bonds stabilize the crystal structure.

The electronic absorption spectrum of the II in EtOH exhibits three intense bands at 200.0, 230.0, and 265.1 nm in the UV range. These bands belong to π - π * or n- π * orbital transitions of the phenanthroline ligands [19]. There are no d-d bands in the UV spectrum. The IR spectrum exhibits characteristic strong bands at 1590 (C=C), 1487, 1423 (C=N), and 845 cm⁻¹ (v(C-H) benzene ring) and 731 cm⁻¹ (v(C-H) pyridine ring) for the coordinated phenanthroline ligands [20]. The significant change in the ligand bands upon complexation is the decrease in v(C-N_{py}). The shift to low frequencies in the spectra of the complexes suggests delocalization of the π -election density around the nitrogen atoms and a lower C=N stretching force due to the coordination through nitrogen atom of the pyridine ring (for the free phenanthroline ligand, v(C=N) at



Fig. 2. A view of the crystal packing down the x axis for $Ag_2[(PhO)_2PS_2]_4(Phen)_2$.

1515 and 1452 cm⁻¹) [21]. The IR spectra of the **II** also exhibit the characteristic absorptions of Ag[(PhO)₂PS₂]: v(P–O_{Ph}) at 1189 s, 908 s, and 883 s, br and v_{as} (PS₂) at 771 s and 731 s, as well as v_s (PS₂) at 578 m and 539 s cm⁻¹, respectively [22]. There are some bands at 2852–3058 cm⁻¹. It may be assigned to the C–H stretching vibrations of the phenyl ring. The strong bands at 1509 s, 1453 s (v_{C-C} phenyl ring) and 684 s cm⁻¹ (v_{C-H} phenyl ring) are also assigned to the phenyl ring.

The TG/DTG curves of the **II** are presented in Fig. 3. Thermogravimetric analysis (TGA) of the II reveals that the decomposition events mainly take place at about 210 and 445°C, respectively. There are one intense heat-absorption peak at 302.6°C and one weak heat-releasing peak at 445°C. It shows no decomposition before 210°C, but at 210°C, decomposition occurs. At 375°C, the weight loss of 64.26 wt % suggests that the residue may be $Ag_2S_4P_2$ (eight-membered $Ag_2S_4P_2$ ring core) (calcd 64.34 wt %). Between 436.7 and 453.4°C, there is about 1.78 wt % weight addition, which is ascribed to the absorption of $Ag_2S_4P_2$. In this process, Ag₂S₄P₂ will adsorb gas and the weight will increase [23]. This phenomenon also appears in the process of thermal decomposition of other dialkyldithiocarbamate metal complexes [24]. With the temperature increasing, the absorption of $Ag_2S_4P_2$ decreases and the weight loses. When the temperature is over 455° C, $Ag_2S_4P_2$ decomposes. The weight loss of 8.49 wt % suggests that the residue may be AgS (found 73.20 wt %; calcd. 75.41 wt %). Meanwhile, no struc-



Fig. 3. TG/DTG curves of the compound II.

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tural transitions were found in the **II**, which implies a high thermal stability.

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