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Binuclear Cyclic Silver(I) Complex with the Anion of 4-[(2-Diphenylphosphanylphenyl)methyleneamino]benzoic Acid: Synthesis, Structure, and Optical Properties

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Abstract—4-[(2-Diphenylphosphanylphenyl)methyleneamino]benzoic acid (HL) is obtained by the condensation of *o*-diphenylphosphinobenzaldehyde and *p*-aminobenzoic acid. The reaction of $AgNO_3$ and HL affords complex $[Ag_2L_2] \cdot H_2O$ (**I**). The structure of complex **I** is determined by X-ray structure analysis (CIF file CCDC 1575064), and its reflectance and luminescence spectra are studied. Binuclear complex **I** is a cyclic molecule in which each of two silver(I) atoms coordinates one phosphorus atom and one oxygen atom of two bridging anions L. Compound **I** is characterized by emission in a range of 430–740 nm at λ_{exc} = 340 and 395 nm.

Keywords: Schiff bases, silver complex, structure, luminescence properties

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INTRODUCTION

Coordination compounds of metals with carboxylic acids represent a large class of organometallic compounds that find wide use in catalysis, production of photoactive materials and magnetically active molecules, and medicine [1–6]. Many metal carboxylates are used as precursors for the preparation of nanocomposite and hybrid materials [7, 8]. The presence of additional reactive functional groups in the carboxylic acid molecule makes it possible to form several bonds with complexing metals. This allows one to synthesize both mononuclear and polynuclear molecules and provides the preparation of unusual structures with unique physicochemical characteristics that can find application in the design of new materials based on them. When rigid bridging ligands are used in self-assembling processes, the structures of the formed compounds can be predicted. The presence of flexible fragments in the bridging organic ligands creates conditions for the formation of an unusual supramolecular architecture. The self-assembling process depends on a number of factors, including the solvent nature, molar ratio of reactants, coordination number of the metal ion, geometry of binding ligands, and others.

The silver(I) ion is especially interesting in self-assembling processes of complicated compounds, because this ion is a labile metallic center manifesting various coordination numbers. The silver(I) ion is characterized by the addition of diverse O-, N-, and P-containing ligands. In dimeric carboxylates $Ag_2(RCO_2)_2$ used as secondary building blocks for the preparation of coordination polymers, the silver ions are bound to each other by carboxylate bridges. The synthesis of the silver compound with the anion of 3-(5-furyl-1,3,4-oxodiazol-2-yl)acrylic acid was described [9]. This compound contains the diazolyl fragment with two nitrogen atoms along with the carboxylate group capable of forming dimeric blocks. In the structure of this compound, the silver atoms are bound by the bidentate-bridging oxygen atoms of the carboxylate group of two acid anions into dimeric blocks. In addition, the coordination sphere of silver also contains the nitrogen atom of the diazolyl fragment of the adjacent anion. In the coordination polymer [Ag(4-PA)] (HPA is 3-(4-pyridyl)acrylic acid), the Ag^+ ion forms covalent bonds with the oxygen atoms of the carboxylate group and with the nitrogen atom of the pyridyl fragment [10].

In this work, we present the results of the synthesis of a new ligand, 4-[(2-diphenylphosphanylphenyl)-methyleneamino]benzoic acid (HL), and the silver(I) complex with this ligand. The structure of the isolated complex was determined, and its IR, reflectance, and luminescence spectra were studied.

EXPERIMENTAL

o-Diphenylphosphinobenzaldehyde (97%), *p*-aminobenzoic acid (98%), acetic acid (99%), dimetylformamide (DMF), acetonitrile, isopropanol, $AgNO_3$ (reagent grade), and a 1 M solution of NBu_4OH in methanol (Aldrich) were used for the syntheses of new compounds.

Synthesis of HL. A solution of *p*-aminobenzoic acid (0.25 g, 1.8 mmol) in isopropanol (3 mL) was added to a hot solution of *o*-diphenylphosphinobenzaldehyde (0.5 g, 1.7 mmol) in isopropanol (7 mL). Acetic acid (2 droplets) was added to the obtained solution, and the reaction mixture was refluxed for 4 h. Then the solution was evaporated to 5 mL and left to stay over day. The precipitate formed was filtered off, washed with isopropanol, and recrystallized from an isopropanol–DMF (3 : 1) mixture. The yield of a light yellow amorphous powder was 0.45 g (64%), mp = 224°C.

For $C_{26}H_{20}NO_2P$

Anal. calcd., %	C, 76.27	H, 4.92	N, 3.42	P, 7.57
Found, %	C, 76.72	H, 4.88	N, 3.30	P, 7.81

IR (Nujol, ν, cm^{-1}): 3327 (OH), 1688 (C=O), 1599 (C=N), 1423, 1316, 1295, 1266, 1166, 1120, 941, 885, 774, 742, 697, 544, 509.

Synthesis of $[Ag_2L_2] \cdot H_2O$ (I). A solution (0.5 mL) of NBu_4OH (0.4 mmol) in methanol was added with stirring to a suspension of HL (0.24 g, 0.6 mmol), and the obtained mixture was heated for 15 min at 30–40°C to the dissolution of the most part of the acid. The mixture was cooled to room temperature, and the liquid phase was decanted by adding it to a solution of $AgNO_3$ (0.10 g, 0.6 mmol) in acetonitrile (5 mL). The resulting solution was kept in a closed vessel for 0.5 h and filtered off from the polycrystalline film formed on the bottom of the vessel. In a day, golden-yellow prismatic crystals isolated from the filtrate placed in the dark under the conditions of slow evaporation of the solvents. The crystals were separated from the solution and dried in air. The yield of complex **I** was 0.090 g (30%).

IR (ν, cm^{-1}): 3654 w, 3421 br.w, 3049 w, 1628 w, 1591 s, 1548 s, 1495 m, 1437 m, 1407 w, 1378 s, 1357 s, 1184 m, 1160 m, 1127 w, 1098 s, 1072 w, 1014 w, 1000 w, 978 w, 958 w, 895 m, 853 m, 810 w, 782 s, 769 m, 747 s, 695 s, 681 s, 664 m, 517 s, 503 s, 494 s.

X-ray structure analysis of a single crystal of complex **I** was conducted on a Bruker SMART APEX II diffractometer equipped with a CCD detector (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) [11]. A semiempirical absorption correction was applied [12]. The structure was solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of the organic ligands were generated geometrically and refined by the riding model. The calculations were performed using the SHELX-2014 program package [13]. The crystallographic parameters and refinement details for the $[Ag_2L_2] \cdot H_2O$ structure are as follows: $C_{52}H_{40}N_2O_5P_2Ag_2$, $FW = 1050.54$, size of yellow crystals 0.10 × 0.10 × 0.04 mm, $T = 150(2)$ K, triclinic crystal system, space group $P\bar{1}$, $a = 8.8204(9)$, $b = 10.4984(11)$, $c = 12.8358(14)$ Å, $\alpha = 99.775(2)°$, $\beta = 104.851(2)°$, $\gamma = 94.379(2)°$, $V = 1123.2(2)$ Å^3, $Z = 1$, $\rho_{calc} = 1.553$ g/cm^3, $\mu = 0.994$ mm^{-1}, $\theta = 1.98°$–$28.55°$, $-11 \le h \le 11$, $-14 \le k \le 14$, $-17 \le l \le 17$; total number of reflections 12000, independent reflections 5661, reflections with $I \ge 2\sigma(I)$ 4363, $R_{int} = 0.023$, $T_{min}/T_{max} = 0.907/0.961$, $S = 1.63$, $R_1 = 0.047$, $wR_2 = 0.123$ (for all data), $R_1 = 0.041$, $wR_2 = 0.112$ (for $I \ge 2\sigma(I)$), $\Delta\rho_{min}/\Delta\rho_{max} = -0.460/2.118$ e Å^{-3}.

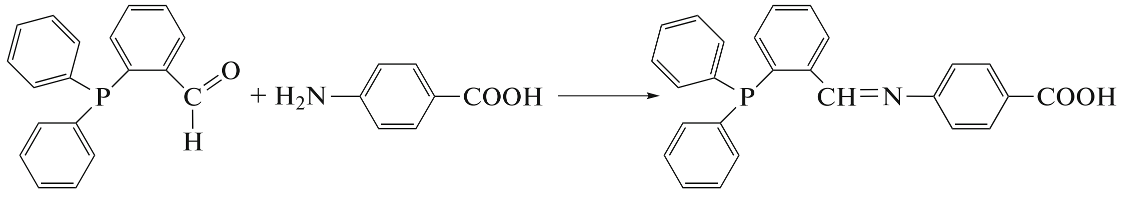
The full array of X-ray diffraction data was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC 1575064; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

X-ray diffraction analysis of a finely crystalline sample of compound **I** was carried out on a Bruker D8 Advance diffractometer (CuK_α, Ni filter, LYNXEYE detector, reflection geometry).

The reflectance spectra of a solid sample were recorded in the UV–near-visible range at room temperature using an Ocean Optics USB 4000 spectrometer equipped with a DH 2000 halogen–deuterium source. The excitation and emission spectra of solid samples were recorded at room temperature in the visible spectral range on a PerkinElmer LS-55 spectrometer. The IR spectra of the compounds were obtained on a PerkinElmer Spectrum 65 FT-IR spectrophotometer using the attenuated total reflectance method in a frequency range of 400–4000 cm^{-1}.

RESULTS AND DISCUSSION

Ligand HL was obtained by the condensation of *o*-diphenylphosphinobenzaldehyde and *p*-aminobenzoic acid.



(HL)

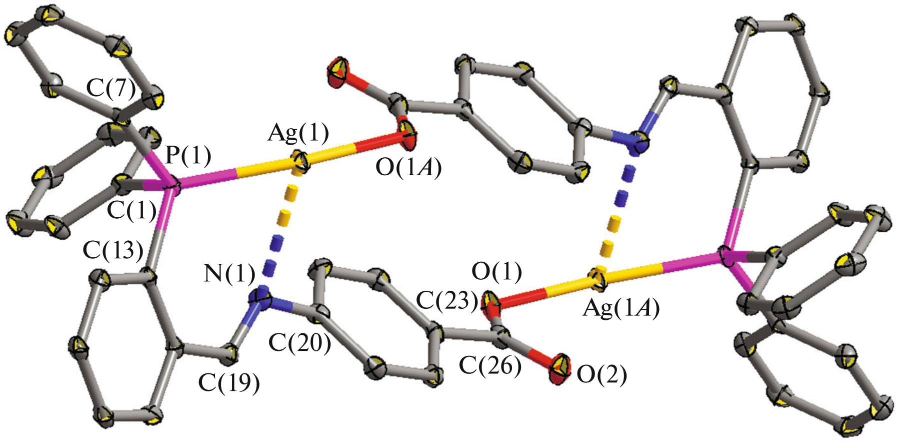


Fig. 1. Molecular structure of complex **I** (hydrogen atoms and the solvate water molecule are omitted, 30% probability thermal ellipsoids).

Since HL contains functional groups of three types (phosphine, imine, and COO^-), the ligand is attractive for the synthesis of complexes, including those with silver(I) ions, capable of forming coordination bonds with each group.

Complex **I** was synthesized by the reaction of HL neutralized with a solution of NBu_4OH in methanol followed by the addition of a solution of $AgNO_3$ in acetonitrile with the HL to Ag ratio equal to 1 : 1. Complex **I** crystallizes as a solvate with a water molecule. The inversion center is arranged between the silver atoms Ag(1) and Ag(1*A*) (Ag···Ag 8.920 Å, Fig. 1). Each metal atom coordinates one phosphorus atom and one oxygen atom (Ag(1)–P(1) 2.3456(8), Ag(1)–O(1) 2.149(2) Å, angle O(1)Ag(1)P(1*A*) 164.45(7)°) of two bridging anions L. The formation of a contact with the imine nitrogen atom (C–N 1.264(4), 1.421(4), Ag(1)···N(1) 2.754 Å) is observed with the formation of the six-membered ring $AgPC_3N$. This Ag···N distance indicates a rather weak contact. The carboxylate group is coordinated to the silver atom via the monodentate mode and, according to the structural data (C–O 1.247(4), 1.271(4) Å), corresponds to the deprotonated form of carboxylic acid. For example, in compound $[Ag(Gly)]_2 \cdot H_2O$ (Gly is glycine), the C–O distances in the monodentate form are 1.222 and 1.275 Å [14]. The molecules of complex **I** in crystal are isolated, and no intermolecular argentophilic interactions were revealed. The nearest silver atom of the adjacent molecule is localized at a distance of 5.674 Å, which is significantly more than typical values of Ag–Ag interactions (3.0–3.2 Å) [15].

The structural wholeness and phase purity of the finely crystalline sample of compound **I** obtained as the major reaction product were confirmed by X-ray powder diffraction analysis (Fig. 2). Slight divergences between the experimental and calculated diffractograms for the crystalline sample of compound **I** can be a consequence of the partial dehydration of the sample during its preparation to measurements.

The reflectance spectrum for the solid sample of compound **I** is characterized by a broad band in a range of 250–480 nm with a maximum at 396 nm (Fig. 3).

A comparison of the IR spectra of HL and **I** shows that the ν(C=O) stretching vibration band of the COO^- group observed in the spectrum of the free ligand at 1688 cm^{-1} disappears in the spectrum of compound **I**. Two intense bands at 1591 and 1357 cm^{-1} corresponding to antisymmetric and symmetric vibrations of the indicated group appear instead of the band discussed. The difference in the values of ν_{as} and ν_s (234 cm^{-1}) substantially exceeds similar values for the metal carboxylate complexes with the bridging and chelate-bound COO^- groups and indicates the monodentate character of the coordination mode of the latter in compound **I** [16]. The ν(C=N) stretching vibration band at 1599 cm^{-1} in the spectrum of HL shifts in the spectrum of **I** to 1548 cm^{-1}, which is due, most likely, to the participation of the N atom of the ligand in the coordination bond with Ag(I). The ν(O–H) stretching vibrations of the water molecule appear in the spectrum of complex **I** as a broad band at 3421 cm^{-1}, which possibly indicates that the structure contains hydrogen bonds.

The studies of the luminescence properties show that, on the one hand, acid HL does not luminesce. On the other hand, the excitation (at 540 nm) spectrum of complex **I** exhibits bands at 340, 387, 432, and 475 nm (Fig. 4), which are observed in the reflectance spectrum as a broad band. The emission spectra (at the excitation wavelengths 340 and 395 nm) exhibit a

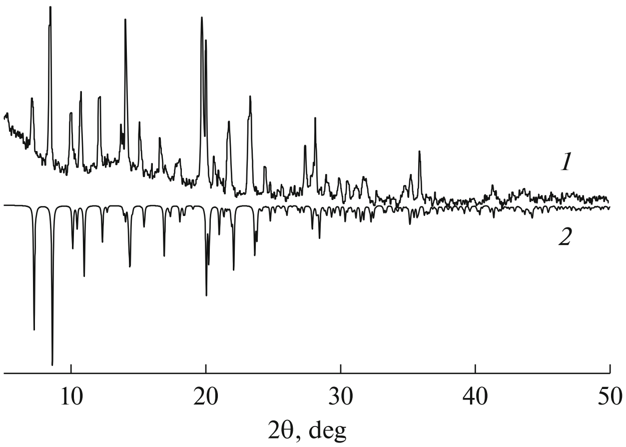


Fig. 2. (*1*) Powder diffractogram of a sample of complex **I** and (*2*) the theoretical diffractogram calculated by the X-ray structure analysis data.

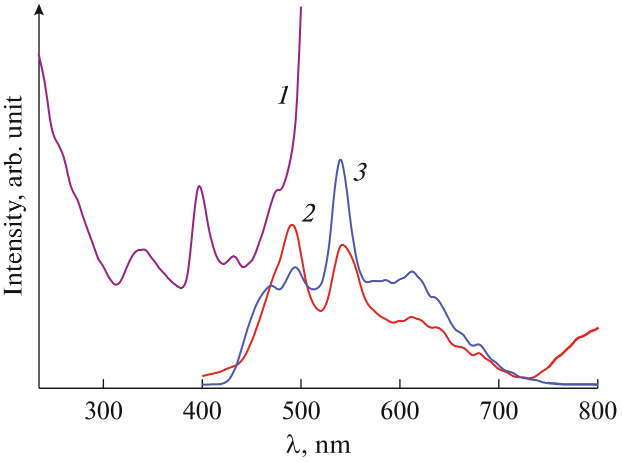


Fig. 4. (*1*) Excitation (λ_{em} = 540 nm) and (*2*, *3*) emission spectra (λ_{exc} = (*2*) 340 and (*3*) 395 nm) for a solid sample of complex **I** at room temperature.

set of bands in a range of 430–740 nm (Fig. 4). The main bands at 491, 542, and 612 nm and a similar set of bands at 470, 494, 540, and 612 nm are observed for λ_{exc} = 340 nm. The appearance of luminescence in the spectrum of compound $[Ag_2L_2] \cdot H_2O$ is related to the coordination of L to the metal ion, which results in a more rigid structure, a lower mobility of L, and, correspondingly, a decrease in the nonradiative energy loss.

Thus, the new Schiff base, 4-[(2-diphenylphosphanylphenyl)methyleneamino]benzoic acid, was obtained. The reaction of ligand HL and silver nitrate gave crystals of the cyclic binuclear complex in which two anions of the acid bind two silver cations through the oxygen atom of the carboxylate group and the phosphorus atom and the contact with the nitrogen atom of the imine group takes place. Ligand HL has no luminescence, but the transition to the anionic form and coordination of silver ions result in the emission of the complex in a range of 430–740 nm.

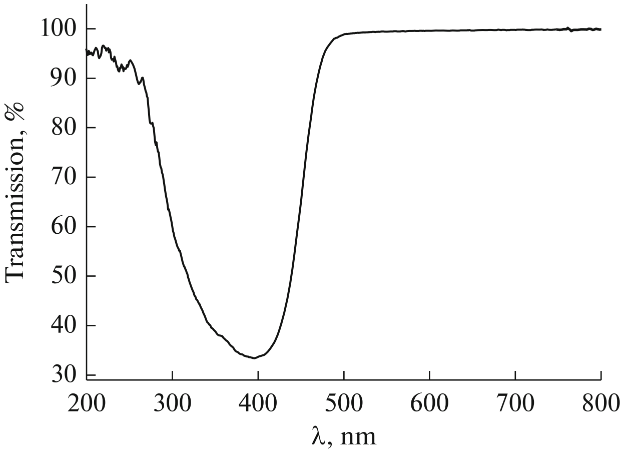


Fig. 3. Reflectance spectrum for a solid sample of complex **I** at room temperature.

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