

Synthesis, Crystal Structure and Optical Studies of a Tetranuclear Silver(I) Complex with Bis(diphenylphosphino)methane

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Silver(I), whose coordination number ranging from 2 to 4, displays a wide diversity in its structural chemistry. Many silver complexes containing silver halides and neutral ligands formulated as $(\text{AgX})_m\text{L}_n$ are well known, which exist in different molecular ratios, even for the same X and L, and show rather different crystal structures. For example, there are five kinds of structures of $(\text{AgX})_m\text{L}_n$ (X = Br, L = PPh_3).¹ As in the case of the series of $(\text{AgX})_m(\text{dppm})_n$ ² (dppm = bis(diphenylphosphino)methane), they also show very interesting structures. Interest in the coordination chemistry of silver-phosphorus complexes has arisen in part from their important applications as potential antitumor,³ free radical scavengers and catalyzer in industrial processes^{4,5} since the late middle of last century.

By exclusion of all traces of oxygen, a new tetranuclear silver(I) complex containing dppm ligand has been synthesized and isolated, in which the metal atoms are bridged by dppm and I^- anions. The synthesis, X-ray crystal structure and photophysical properties of the complex are reported.

Experimental Section

Materials and physical measurements. Manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. All solvents were distilled and stored under nitrogen atmosphere prior to use. Dppm from Aldrich Corporation was used directly as supplied commercially. The IR spectrum was recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellets in the range 4000–400 cm^{-1} and elemental analysis was carried out on a Vario EL III elemental analyzer. The electronic emission and excitation spectra recorded at room temperature were obtained on an Edinburgh FL/FS 920 TCSPC fluorescence spectrophotometer.

Synthesis of $[\text{Ag}_4(\text{dppm})_2(\mu_3\text{-I})_2(\mu_2\text{-I})_2]$. The colorless solution of dppm (0.151 g, 0.39 mmol) in a mixture of toluene and THF (15 mL, V/V = 21) was added dropwise to a suspension of AgI (0.097 g, 0.40 mmol) in toluene (5 mL). The reaction mixture was heated at 353 K for 24 h, the resulting pale yellow precipitations were isolated and

washed with diethyl ether. Subsequently the pale yellow precipitation was dissolved in DMF, in which yellow crystals were obtained by slow diffusion of diethyl ether. Yield based on AgI: 0.0717 g, 42%. Elemental analysis (%), Found (calcd): C, 35.22 (35.16); H, 2.65 (2.60); IR data (KBr , cm^{-1}), the expected absorption bands due to the dppm ligand: 1484 (w), 1286 (w), 1098 (m), 782 (w), 740 (m), 690 (w).

A colorless prismatic crystal was carefully selected and mounted on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.7107 \text{ \AA}$). The intensity data was reduced using CrystalClear program.⁶ The structure was solved by direct methods using SHELXTLTM package of crystallographic software⁷ and refined by full-matrix least-squares technique on F^2 . All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in the final stage of the refinement on calculated positions bonded to their carrier atoms. Crystallographic data for the title complex are listed in Table 1. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-238434). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road,

Table 1. Crystal and experimental data

Empirical formula	$\text{C}_{50}\text{H}_{44}\text{Ag}_4\text{I}_4\text{P}_4$
F_w	1707.81
Crystal system	orthorhombic
Space group	$Pbca$
a (\AA)	17.2269(15)
b (\AA)	17.4228(14)
c (\AA)	17.8560(13)
$V / \text{\AA}^3$	5359.3(7)
z	4
D_{calcd} (Mgm^{-3})	2.117
μ (mm^{-1})	3.896
$F(000)$	3216
Final R_1 , wR_2 [$I > 2\sigma(I)$]	$R_1^a = 0.0383$, $wR_2^b = 0.1061$
Goodness of fit on F^2	1.090
Largest difference peak and hole ($\text{e}/\text{\AA}^3$)	0.860, -0.724
Largest and Mean Δ/σ	0.005, 0.001

$$^a R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|), \quad ^b wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w|F_o^2|^2)]^{1/2}$$

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Table 2. Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
I(1)-Ag(2A)	2.8923(3)	Ag(1)-Ag(2A)	3.0640(3)
I(1)-Ag(2)	2.9303(3)	Ag(1)-Ag(2)	3.2247(3)
I(1)-Ag(1)	2.9372(3)	Ag(1)-P(1)	2.4060(5)
I(2)-Ag(1A)	2.6839(3)	P(2)-C(1)	1.8306(15)
I(2)-Ag(2)	2.8905(3)	P(1)-C(1)	1.8277(16)
Ag(2)-P(2)	2.4462(5)		
Angles (°)			
Ag(2A)-I(1)-Ag(2)	74.253(8)	I(1A)-Ag(2)-I(1)	105.747(8)
Ag(2A)-I(1)-Ag(1)	63.414(7)	I(2)-Ag(2)-I(1)	99.533(7)
Ag(2)-I(1)-Ag(1)	66.679(6)	P(2)-Ag(2)-Ag(1A)	162.958(13)
Ag(1A)-I(2)-Ag(2)	66.568(6)	I(1A)-Ag(2)-Ag(1A)	59.007(5)
P(1)-Ag(1)-I(2A)	141.229(14)	I(2)-Ag(2)-Ag(1A)	53.486(7)
P(1)-Ag(1)-I(1)	107.361(14)	I(1)-Ag(2)-Ag(1A)	82.916(7)
I(2A)-Ag(1)-I(1)	106.624(7)	P(2)-Ag(2)-Ag(1)	84.367(13)
P(1)-Ag(1)-Ag(2A)	158.455(13)	I(1A)-Ag(2)-Ag(1)	80.734(7)
I(2A)-Ag(1)-Ag(2A)	59.946(5)	I(2)-Ag(2)-Ag(1)	155.519(7)
I(1)-Ag(1)-Ag(2A)	57.579(6)	I(1)-Ag(2)-Ag(1)	56.763(6)
P(1)-Ag(1)-Ag(2)	91.114(14)	Ag(1A)-Ag(2)-Ag(1)	112.103(8)
I(2A)-Ag(1)-Ag(2)	123.406(8)	C(1)-P(1)-Ag(1)	112.69(5)
I(1)-Ag(1)-Ag(2)	56.558(6)	C(31)-P(1)-Ag(1)	117.89(6)
Ag(2A)-Ag(1)-Ag(2)	67.897(8)	C(11)-P(1)-Ag(1)	110.00(6)
P(2)-Ag(2)-I(1A)	112.600(14)	C(21)-P(2)-Ag(2)	118.75(5)
P(2)-Ag(2)-I(2)	122.696(13)	C(41)-P(2)-Ag(2)	110.75(5)
I(1A)-Ag(2)-I(2)	102.508(7)	C(1)-P(2)-Ag(2)	113.27(5)
P(2)-Ag(2)-I(1)	111.011(13)		

Symmetry code for the complex: A -x+1, -y, -z+1.

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Results and Discussion

Description of crystal structure. The selected bond distances and bond angles are listed in Table 2. The molecular structure of the title complex is shown in Figure 1.

It is important that the greatest care should be taken to exclude any traces of air and the procedure of reaction must be processed under nitrogen atmosphere in order to avoid the ligand oxidation. The structural analysis and IR spectroscopic data for the title complex show that there is no evidence for P=O bond formation (ν (P=O) bands are normally shown in the range of 1120-1280 cm^{-1}).⁸

The complex consists of discrete neutral tetranuclear silver units with a crystallographic inversion center and is best described as being based on a parallelogram of four silver atoms. Atom set Ag(1)-Ag(2)-Ag(1A)-Ag(2A) constitutes an ideal coplanar parallelogram. The molecular structure of the title complex is similar to those found in the centrosymmetric chair-like $[\text{Ag}_4(\text{PPh}_3)_2\text{I}_4]$, $[\text{Ag}_4(\text{dppm})_2\text{Cl}_4]$,^{2b} $[\text{Cu}_4(\text{dppm})_2\text{Cl}_4]$,¹⁰ $[\text{Cu}_4(\text{PPh}_3)_2\text{Br}_4]$,¹¹ $[\text{Cu}_4(\text{PPh}_3)_2\text{I}_4]$.¹² Atom Ag(1) is three-coordinated by one phosphorus atom of a bridging dppm and two iodine atoms to form a triangle with maximum deviation of Ag(1) from the best least-squares

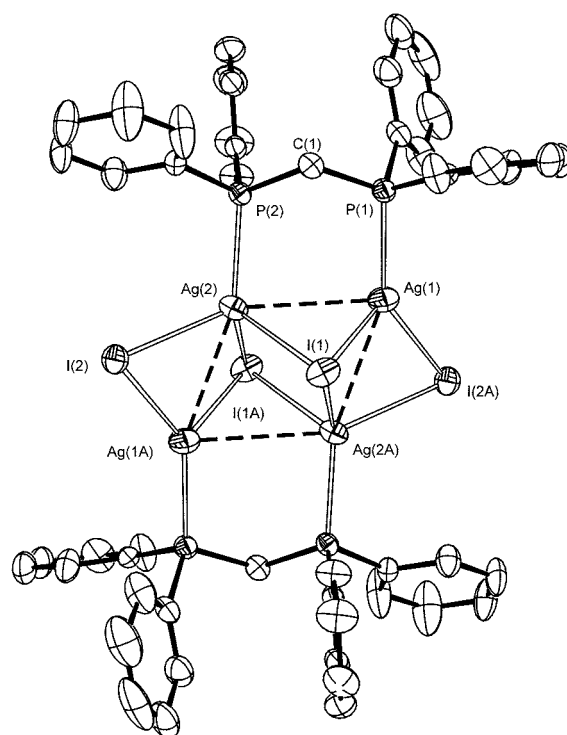


Figure 1. The molecular structure of the complex $[\text{Ag}_4(\text{dppm})_2(\mu_3\text{-I})_2(\mu_2\text{-I})_2]$ with thermal ellipse at the 30% probability level. Hydrogen atoms are omitted for clarity.

plane being 0.1343 Å. Atom Ag(2) is four-coordinated by one phosphorus atom, two μ_3 -iodine atoms and one μ_2 -iodine atom to yield a distorted-tetrahedral formation, which can be reflected by the angles around the Ag(2) atoms ranging from 99.533(7) to 122.696(13)°. On each of the long edges of the parallelogram, two silver atoms are chelated by a dppm ligand with the Ag-P bond distances being Ag(1)-P(1) = 2.4060(5) and Ag(2)-P(2) = 2.4462(5) Å, respectively. The Ag-P bond distance for the four-coordinated silver atom is slightly longer than that for three-coordinated one. The Ag-P bond distances in the title compound are shorter than those found in $[\text{Ag}_3(\text{dppm})_2\text{I}_2]$,¹³ but longer than those found in $[\text{Ag}_4(\text{dppm})_2\text{Cl}_4]$.^{2b} On the other short edges, the silver atoms are asymmetrically bridged by a μ_2 -iodine atom with I(2)-Ag(2) = 2.8905(3) and I(2)-Ag(1A) = 2.6839(3) Å, respectively. The Ag-I bond distances for four-coordinated silver atoms are 0.21 Å longer than those for three-coordinated silver atoms. The average Ag-I = 2.8668 Å in the present complex is shorter than that in $[\text{Ag}_3(\text{dppm})_2\text{I}_2]$ ¹³ (2.973(9) Å). The dihedral angle between the Ag(1A)-Ag(2)-I(2) plane and the plane of parallelogram is 22.85°. The I(1) atom and its symmetry-related I(1A) atom lie above and below the plane of parallelogram and capping-bridge three silver atoms with I(1)-Ag(2A) = 2.8923(3), I(1)-Ag(2) = 2.9303(3), and I(1)-Ag(1) = 2.9372(3) Å, respectively, yielding two face-sharing tetrahedra.

The Ag(2)⋯Ag(1) distances of 3.2247(3) Å in the parallelogram is larger than the other Ag(2)⋯Ag(1A) distance of 3.0640(3) Å, which are considerably longer than

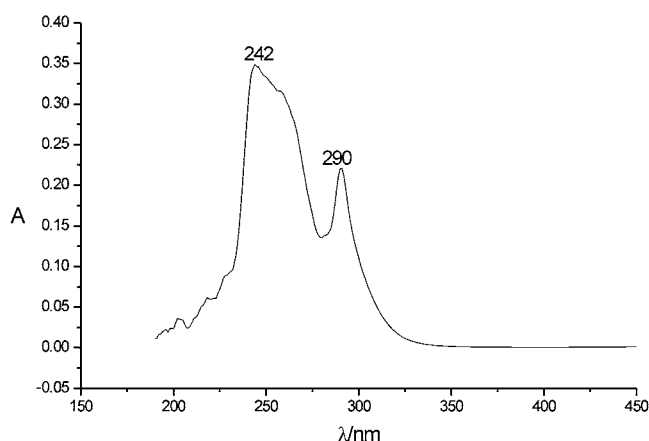


Figure 2. Electronic absorption spectrum of the title complex in THF solution at room temperature.

that in metallic silver (2.88 Å).¹⁴ The dppm bridging Ag...Ag distances of 3.2247(3) Å are comparable to those found in [Ag₄(dppm)₂Cl₄]^{2b} (3.254(1) Å), showing the Ag...Ag distances are mainly influenced by dppm ligand. However, the iodine bridging Ag...Ag distances are greatly shorter than those found in [Ag₄(dppm)₂Cl₄]^{2b} (3.374 Å) and [Ag₃(dppm)₂I]¹³ (av. 3.236(1) Å), which indicates stronger Ag...Ag interactions in the title complex. In comparison with Cl analog, the larger size of I atom, which has better overlap with valence orbitals on silver atom, and the π -acid character, which can make back-donation effect from the silver core, can reduce the antibonding nature of the d orbitals on the silver core to result in shortening of Ag...Ag distances.¹³

The bond distances and angles for dppm ligand in the present compound are similar to those found in other dppm complexes. There exist no π - π stacking interactions and hydrogen bonding interactions in the title compound, showing the packing force of crystal structure in the present compound should be very weak.

Optical studies. The electronic absorption spectrum of the title complex in THF solution at room temperature is shown in Figure 2. The intensive absorption peaks at 242 and 290 nm can be assigned to π - π^* or n - π^* orbital transition of the dppm ligand (intraligand IL transition), as the case found in the other dppm complexes containing other ligands, such as phen, bipy, py,¹⁵ but quite different from that of the complex [Ag₃(dppm)₂I] in MeCN with a high-energy absorption shoulder at 254 nm and a low-energy absorption tail at 335 nm.

The tetranuclear silver complex reported here shows luminescence features in the EtOH solution at room temperature as given in Figure 3. The title complex shows an emission at 415 nm, which can be assigned to originate predominantly from ligand-to-metal charge-transfer LMCT [$I^- \rightarrow Ag_4$] excited state,¹⁵ mixed with a metal-centred (ds/dp) state.¹⁶ While for [Ag₃(dppm)₂I] complex, there is a lower energy emission at 554 nm in DMF. The blue-shift from [Ag₃(dppm)₂I] to [Ag₄(dppm)₂(μ_3 -I)₂(μ_2 -I)₂] suggests that the emitting state is correlated to the metal-centred

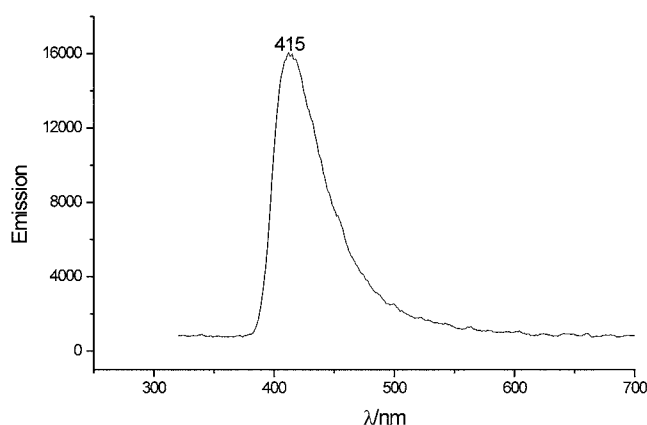


Figure 3. Emission spectrum of the title complex recorded in EtOH at room temperature with excitation wavelength of 349 nm.

excited state Ag(I) (4d⁹5s¹) which is modified by the Ag...Ag interaction.¹⁷ The blue-shift in emission spectrum is consistent with the shortening of Ag...Ag distances in [Ag₄(dppm)₂(μ_3 -I)₂(μ_2 -I)₂] (av. 3.1454(11) Å) as compared with that found in [Ag₃(dppm)₂I] (3.236(1) Å).

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