

Synthesis and Optical Properties of a Nitrate Anion Bridging Tetranuclear Silver(I) Complex. X-Ray Crystal Structure of $\text{Ag}_4(\mu_2\text{-dppm})_2(\mu\text{-NO}_3)_4 \cdot 0.5\text{H}_2\text{O}$

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Though the polynuclear d^{10} metal complexes were discovered a long time ago, the study on photophysical and photochemical characters of polynuclear d^{10} metal complexes has attracted much attention and developed rapidly in the last decades of last century.¹ With the development of the computer hardware and software, theoretical studies on polynuclear d^{10} metal systems can be more accurate and efficient.² However, there are a number of difficulties to be overcome in the design of this kind of complexes with bridging and ancillary ligands, such as bis(diphenylphosphino)methane (dppm). Dppm ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$) is not only a very excellent bridging ligand for bonding two metal atoms to form stable eight-membered ring $[\text{M}(\mu_2\text{-dppm})_2\text{M}]^3$ which are well known with many structural and applied studies,⁴ but also sometimes act as mono-dentate ligand.⁵ Dppm can also form a number of trinuclear complexes $[\text{M}_3(\mu\text{-dppm})_3]$ with late transition metal ions, especially, d^{10} metals ions. When $\text{M} = \text{Cu}(\text{I})$ or $\text{Ag}(\text{I})$, a capping ligand always accompanies the $[\text{M}_3(\mu\text{-dppm})_3]$ core by the coordination mode of μ_3 -bridging. Moreover, the $\text{M}\cdots\text{M}$ [$\text{M} = \text{Cu}(\text{I}), \text{Ag}(\text{I})$] interactions have been a driving force for the self-assemble of $\text{Cu}(\text{I})$, or $\text{Ag}(\text{I})$ aggregates and played an important role in polynuclear complexes containing phosphorous ligand or pyridine.⁶⁻⁹ Yam and co-workers make use of the phosphorous d^{10} metal complexes as precursor to synthesize complexes containing acetylide group.¹⁰ Besides, the $\text{M}\cdots\text{M}$ interactions also have a very important effect on the luminescence properties of these d^{10} systems.¹¹

By exclusion of all traces of oxygen, a new tetranuclear silver(I) complex using dppm ligand has been synthesized and isolated, in which the metal atoms are bridged by dppm and NO_3 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. THF, diethyl ether, were purified by standard procedures¹² and distilled under nitrogen atmosphere prior to use. Dppm was obtained from Acros Corporation

and used directly as supplied commercially. The IR spectrum was recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellets in the range $4000\text{-}400\text{ cm}^{-1}$. Elemental analysis was carried out on a Vario EL III elemental analyzer. The complex dissolved in DMF as sample was recorded on a Hewlett-Packard 8452A (PE Corporation) spectrophotometer with a 1-cm quartz cuvette for electronic absorption spectrum measurement. The electronic emission and excitation spectra recorded at room temperature were obtained on an Edinburgh FL/FS 920 TCSPC fluorescence spectrophotometer.

Synthesis of $\text{Ag}_4(\mu\text{-dppm})_2(\mu\text{-NO}_3)_4 \cdot 0.5\text{H}_2\text{O}$. AgNO_3 (0.034 g, 0.20 mmol) in distilled water was dropwise to a solution of dppm (0.151 g, 0.39 mmol) in THF (5 mL). The reaction mixture was heated at 323 K for 6 h. The white suspension was filtered and the filtrate layered with diethyl ether was placed carefully in refrigerator at about 277 K. Yield based on dppm: 0.617 g, 54%. Elemental analysis (%), Found (calcd): C, 41.05 (41.02); H, 3.00 (3.03); N, 3.81 (3.83). IR data (in KBr, cm^{-1}): 1478 (w), 1434 (m), 1384 (s), 1272 (s), 780 (w), 740 (m), 690 (w), 516 (w), 478 (w).

X-ray crystallography. A colorless prism crystal with approximate dimensions of $0.18 \times 0.22 \times 0.25\text{ mm}^3$ was carefully selected and mounted on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.7107\text{ \AA}$) radiation for subsequent X-ray diffraction studies with ω scan mode in the range of $4.21 < \theta < 25.03^\circ$ at 293(2) K. A total of 19295 reflections were collected, of which 4934 reflections with $I > 2\sigma(I)$ out of 5152 unique reflections ($R_{\text{int}} = 0.0243$) were considered as observed. The intensity data was reduced using CrystalClear program.¹³ The structure was solved by direct methods using SHELXTLTM package of crystallographic software¹⁴ 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. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 3.3247P]$ where $P = (F_o^2 + 2F_c^2)/3$. 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-238224). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44

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Table 1. Crystallographic Data

empirical formula	C ₅₀ H ₄₄ Ag ₄ N ₄ O ₁₃ P ₄
formular weight	1464.25
crystal system	Orthorhombic
Space group	<i>Aba</i> 2
crystal size (mm)	0.18 × 0.22 × 0.25
<i>a</i> (Å)	18.564(6)
<i>b</i> (Å)	18.906(6)
<i>c</i> (Å)	17.821(6)
<i>V</i> (Å ³)	6255(3)
<i>Z</i>	4
<i>D</i> _{calcd} (Mgm ⁻³)	1.555
<i>μ</i> (mm ⁻¹)	1.393
<i>F</i> (000)	2896
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ ^a = 0.0383, <i>wR</i> ₂ ^b = 0.1061
Goodness of fit on <i>F</i> ²	1.021
Largest difference peak and hole/eÅ ⁻³	0.646, -0.312
Largest and Mean Δσ	0.001, 0.000

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

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Results and Discussion

Description of the structure. The selected bond distances and bond angles 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

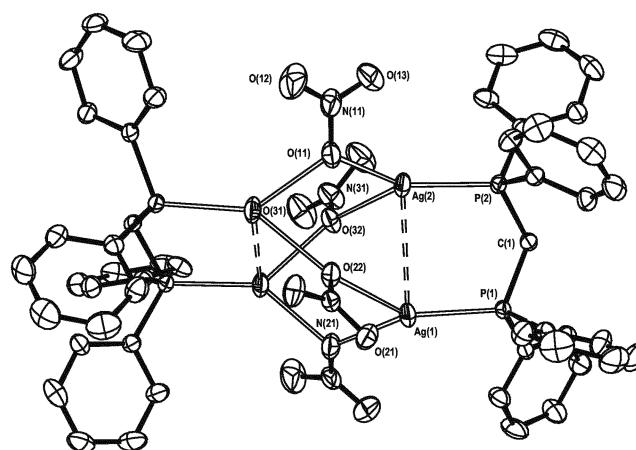


Figure 1. The molecular structure of the complex Ag₄(μ₂-dppm)₂(μ-NO₃)₄·0.5H₂O. H hydrogen atoms are omitted for clarity.

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⁻¹¹⁵)

The title complex crystallizes in space group *Aba*2. As shown in Figure 1, the complex is best described as two [Ag₂(dppm)] subunits bridged by four nitrate anions with a C₂ axis passing through the atoms N(21), O(22), N(31) and O(32). Each silver atom is three-coordinated by one phosphorous atom of dppm and two oxygen atoms of two nitrate anions to form a coplanar triangle. Each nitrate anion

Table 2. Selected Bond Distances (Å) and Angles (°) for Ag₄(μ-dppm)₂(μ-NO₃)₄·0.5H₂O

Bond Distance (Å)					
Ag(1)-O(11)#1	2.315(4)	Ag(2)-P(2)	2.3527(10)	N(11)-O(12)	1.197(6)
Ag(1)-P(1)	2.3627(10)	Ag(2)-O(32)	2.3747(16)	N(21)-O(22)	1.232(7)
Ag(1)-O(22)	2.4631(14)	P(1)-C(1)	1.841(4)	N(21)-O(21)	1.231(5)
Ag(1)-Ag(2)	3.1974(8)	P(2)-C(1)	1.843(3)	N(31)-O(31)	1.227(6)
Ag(2)-O(11)	2.310(4)	N(11)-O(13)	1.218(8)	N(11)-O(11)	1.262(6)
Bond Angle (°)					
O(11)#1-Ag(1)-P(1)	140.89(10)	C(21)-P(2)-Ag(2)	111.65(13)		
O(11)#1-Ag(1)-O(22)	75.39(10)	N(31)-O(32)-Ag(2)	108.49(11)		
P(1)-Ag(1)-O(22)	142.50(3)	O(12)-N(11)-O(13)	122.9(6)		
O(11)#1-Ag(1)-Ag(2)	110.16(10)	O(12)-N(11)-O(11)	120.0(6)		
P(1)-Ag(1)-Ag(2)	89.76(3)	O(13)-N(11)-O(11)	117.0(5)		
O(22)-Ag(1)-Ag(2)	61.67(8)	N(11)-O(11)-Ag(2)	114.1(4)		
O(11)-Ag(2)-P(2)	140.03(10)	N(11)-O(11)-Ag(1)#1	125.0(3)		
O(11)-Ag(2)-O(32)	83.46(11)	Ag(2)-O(11)-Ag(1)#1	113.91(15)		
P(2)-Ag(2)-O(32)	136.50(5)	O(21)-N(21)-O(21)#1	121.3(6)		
O(11)-Ag(2)-Ag(1)	112.66(11)	O(21)-N(21)-O(22)	119.3(3)		
P(2)-Ag(2)-Ag(1)	88.00(3)	Ag(2)-O(32)-Ag(2)#1	143.0(2)		
O(32)-Ag(2)-Ag(1)	67.95(7)	Ag(1)#1-O(22)-Ag(1)	152.7(2)		
C(41)-P(1)-Ag(1)	114.72(13)	C(1)-P(2)-Ag(2)	115.41(11)		
C(11)-P(1)-Ag(1)	113.09(12)	N(21)-O(22)-Ag(1)	103.67(12)		
C(1)-P(1)-Ag(1)	115.42(11)	O(31)-N(31)-O(31)#1	121.6(8)		
C(31)-P(2)-Ag(2)	115.28(12)	O(31)-N(31)-O(32)	119.2(4)		

Symmetry code: #1 -x+1, -y, z

acts as bidentate ligand bridging two silver atoms, whose μ -1,2 κ O coordination mode in metal-dppm complexes¹⁶⁻¹⁹ is unprecedented. Unlike to the $[\text{Ag}_4(\text{dppm})_4(\text{NO}_3)_2][\text{PF}_6]$ ¹⁶ in which the $[\text{Ag}_2(\text{dppm})_2]$ subunits are bridged by the nitrate anions with μ -1 κ O:2 κ O' coordination mode, it is worthy to note that the $[\text{Ag}_2(\text{dppm})]$ subunits bridged by the nitrate anions with μ -1,2 κ O coordination mode in title complex is found for the first time. To the best of our knowledge, though the transition metal complexes containing dppm ligand are well known, the metal-dppm complexes bridged by nitrate anion to form polynuclear compounds are rare.¹⁶⁻¹⁹

The average Ag-P bond distance is 2.358(1) Å [Ag(1)-P(1) = 2.363(1) Å, Ag(2)-P(2) = 2.353(1) Å]. And the average Ag-O bond distance is 2.401(4) Å [Ag(1)-O(11)#1 = 2.315(4) Å, Ag(1)-O(22) = 2.463(1) Å, Ag(2)-O(32) = 2.375(2) Å, Ag(2)-O(11) = 2.310(4) Å]. The average Ag-P and Ag-O bond distances are the shortest bond distances in the Ag-dppm complexes with bridging nitrate and comparable with those in the Ag-dppm complexes. However, Ag...Ag non-bonding distance of 3.1974(8) Å bridged by dppm is the longest in the nitrate bridging Ag-dppm complexes¹⁶⁻¹⁹ and longer than those in most silver(I)-dppm complexes.²⁰ The shortest distance between two neighbor phenyl rings is 18.564 Å, indicating no π - π stack interaction in the compound. The distances between the O(1w) and the atoms around O(1w) is larger than 7.0 Å, which indicates no hydrogen bonding interactions in the crystal structure. Hence, 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 DMF at room temperature was shown in Figure 2. The high-energy absorption band at *ca.* 267 nm is related to the dppm ligand, which is similar to the absorption spectrum of the free dppm. The absorption band can be assigned as intraligand π (dppm) transition.²¹

The tetranuclear complex reported here shows luminescence features by using the electronic emission spectrum in the DMF solution at room temperature as given in Figure 3. The title complex shows high-energy emission at *ca.* 444 nm, which is assigned to originate predominantly from ligand-to-metal charge-transfer LMCT [$\text{NO}_3^- \rightarrow \text{Ag}$].²²

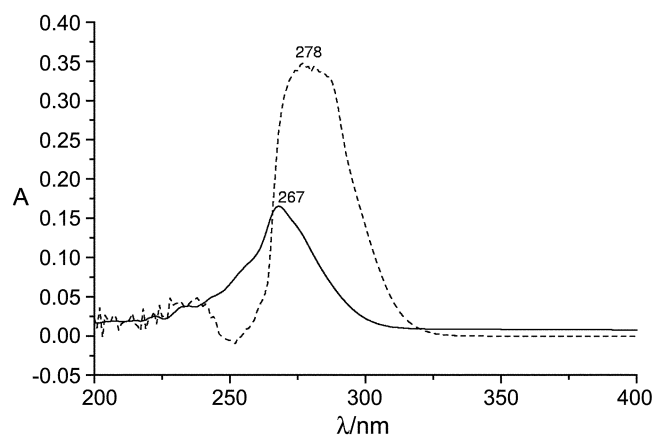


Figure 2. Electronic absorption spectrum of the complex (solid line) and dppm ligand (dash line) in DMF.

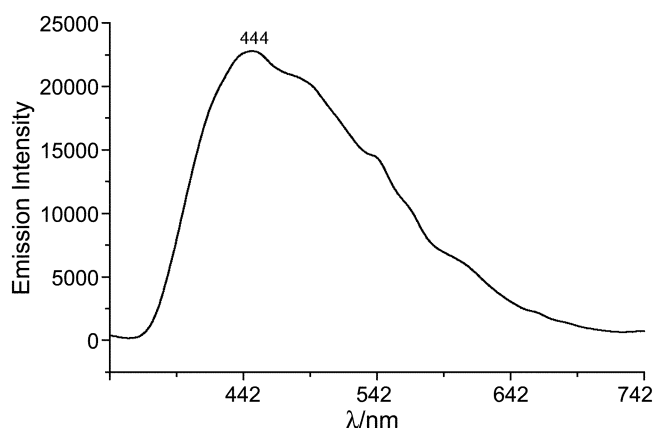


Figure 3. The electronic emission spectrum of the complex recorded at room temperature with excitation wavelength being at 396 nm.

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