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LUMINESCENT SILVER(I) CLUSTER. SYNTHESIS, SPECTROSCOPIC PROPERTIES AND X-RAY CRYSTAL STRUCTURE OF $[Ag_3(C{\equiv}CPh)_2(dppm)_3]Cl \cdot 4Et_2O \cdot H_2O$ {dppm = bis(diphenylphosphino)methane}

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Abstract—The $[Ag_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]^+$ complex {dppm = bis(diphenylphosphino)methane} was prepared by reacting $[(RC{\equiv}C)Ag]_\infty$ with dppm in CH_2Cl_2. The X-ray crystal structure of $[Ag_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]Cl \cdot 4Et_2O \cdot H_2O$ has been determined. The complex has an isosceles triangular array of Ag atoms and with two asymmetric phenylacetylide caps. The intramolecular $Ag^{(I)} \cdots Ag^{(I)}$ separations are 2.866(2) and 2.983(1) Å. Extended-Hückel molecular-orbital calculation reveals that the HOMO comprises of contributions from Ag(I) and phenylacetylide whereas the LUMO is largely the π^* of phenylacetylide. The complex shows a solid-state emission at 555 nm with a lifetime of 0.4 μs at room temperature.

There has been a considerable interest in alkynylmetal complexes of d^{10}[1–4] and d^8[5] metal ions, owing to their intriguing luminescent properties. Recent studies showed that the phenylacetylide complexes of gold(I),[1] and copper(I)[4] and platinum(II)[5,6] show long lived and emissive excited states in solution at room temperature.

The alkynyl complexes of Ag(I) should also have interesting structural and photoredox properties. However, studies on the photoluminescence of polynuclear silver(I) complexes are sparse.[7] Herein is described the synthesis, crystal structure and emission properties of a trinuclear Ag(I) cluster $[Ag_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]Cl$ {dppm = bis(diphenylphosphino)methane}. Its electronic structure has also been studied by EHMO calculation.

EXPERIMENTAL

Materials

$[(PhC{\equiv}C)Ag]_\infty$ complex was prepared by a published method.[8] The dppm ligand was obtained from Aldrich and used without further purification. All reagents and solvents were of analytical grade.

$[Ag_3(C{\equiv}CPh)_2(dppm)_3]Cl$

This was prepared by stirring a suspension of $[(PhC{\equiv}C)Ag]_\infty$ (0.1 g) and dppm (0.19 g) in dichloromethane (25 cm^3) for 20 min. A pale yellow solution was obtained. This was filtered and was evaporated to dryness. The solid residue was redissolved in a minimum amount of ethanol. Upon cooling in refrigerator for 1 day, pale yellow crystals were obtained. Yield = 87%. Found: C, 64.1; H, 4.6. Calc. for $C_9H_{76}P_6ClAg_3$: C, 63.7; H, 4.5%. IR,

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cm^{-1} (Nujol mull): 1970, 1900(vw) [ν(C≡C)]. ^1H-NMR ($CDCl_3$, Me_4Si) δ 3.0 (s, 6H), 6.90–7.38(m, 70H). Electrospray M-S: 1679.6(P^+).

Physical measurements and instrumentation

^1H NMR spectra were obtained from a JEOL 270 Fourier-transform-NMR spectrometer with tetramethylsilane as internal reference. Elemental analysis was performed at National Taiwan University. Electrospray-mass spectrum in acetonitrile was collected on a Finnigan MAT 95 high-resolution mass spectrometer. UV–vis spectra were obtained on a Perkin–Elmer Lambda 19 spectrophotometer. Time-resolved emission spectra were measured by an intensified-charge-couple-device(ICCD) connected with the Spectrometric Multi-channel Analyser system (CSMA) (a Princeton Applied Research (PAR) model). Lifetime measurements were conducted with a Quanta Ray DCR-3 Nd-YAG pulsed laser system. Sample solutions for photophysical experiments were degassed by at least four successive freeze-pump–thaw cycles.

Molecular orbital calculations

Extended-Hückel Molecular Orbital (EHMO) calculations were carried out by using the *ICON8* program.[9] The geometric parameters were obtained from the X-ray diffraction data. A total of 491 orbitals of 176 atoms were employed. The parameters of Cu and Ag were taken from the literature whilst the others were acquired from the program.[10]

X-ray crystal structure

$[Ag_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]Cl \cdot 4Et_2O \cdot H_2O$, $Ag_3P_6C_{99}H_{104}O_5Cl$. M = 1868.02, monoclinic, space group $C2/m$, $a = 27.424(3)$, $b = 22.140(5)$, $c = 14.971(2)$ Å, $\beta = 93.60(8)°$, $U = 9072.2(2)$ Å^3, $Z = 4$, $D_{calc} = 1.394$ g cm^{-3}, μ(Mo-Kα) = 8.147 cm^{-1}, crystal dimensions 0.13×0.45×0.70 mm; $F(000) = 3752$. X-ray diffraction data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer (graphite-monochromatized Mo-Kα radiation, $\lambda = 0.7107$ Å) using the ω–2θ scan mode with $2\theta_{max} = 45.0°$. The data were corrected for absorption. All data reduction and structure refinement were performed using the NRCC-SDP-VAX packages. The structures were solved by the Patterson method and refined by least squares. The last least squares cycle was calculated with 115 atoms, 472 parameters and 4407 reflections ($|I_0| > 2.0\sigma|I_0|$) out of 6066 unique reflections giving $R_F = 0.049$, $R_w = 0.065$ and GoF = 1.33. The final difference Fourier map showed residual extrema in the range of 1.17 to −0.670 e Å^{-3}.

Selected bond lengths and angles are listed in Table 1.

RESULTS AND DISCUSSION

Previous studies showed the reaction of $[Cu_2(\mu\text{-}dppm)_2(NCCH_3)]^{2+}$[11] and $[Cu(PPh_3)_2][BF_4]$[12] with KC≡CPh lead to the formation of tri- and tetranuclear copper(I)–phenylacetylide complexes, respectively. In this work, the reaction of $[RC{\equiv}CAg]_\infty$ with dppm give the titled complex. Similar reaction of $[PhC{\equiv}CCu]_\infty$ with dppm has been found to give $[Cu_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2$

Table 1. Selected bond distances (Å) and angles (°)

Ag(1)—Ag(2)	2.983(1)	Ag(2)—Ag(1)—Ag(2′)	57.42(3)
Ag(2)—Ag(2′)	2.866(2)	Ag(2)—Ag(1)—P(1)	88.23(6)
Ag(1)—P(1)	2.469(3)	Ag(2′)—Ag(1)—P(1)	144.57(7)
Ag(1)—C(1)	2.635(1)	Ag(2)—Ag(1)—C(1)	50.1(2)
Ag(1)—C(9)	2.321(1)	Ag(2)—Ag(1)—C(9)	54.7(3)
Ag(2)—P(2)	2.477(3)	Ag(1)—Ag(2)—Ag(2′)	61.29(2)
Ag(2)—P(3)	2.464(2)	Ag(1)—C(1)—Ag(2)	72.5(4)
Ag(2)—C(1)	2.401(1)	Ag(1)—C(1)—C(2)	102.2(1)
Ag(2)—C(9)	2.506(1)	Ag(2)—C(1)—C(2)	142.3(3)
C(1)—C(2)	1.18(2)	C(1)—C(2)—C(3)	177.6(2)
C(2)—C(3)	1.48(2)	Ag(1)—C(9)—Ag(2)	76.2(3)
C(9)—C(10)	1.19(2)	Ag(2)—C(9)—Ag(2′)	69.7(4)
C(10)—C(11)	1.44(2)	Ag(1)—C(9)—C(10)	136.4(1)
		Ag(2)—C(9)—C(10)	135.6(6)
		C(9)—C(10)—C(11)	177.2(1)

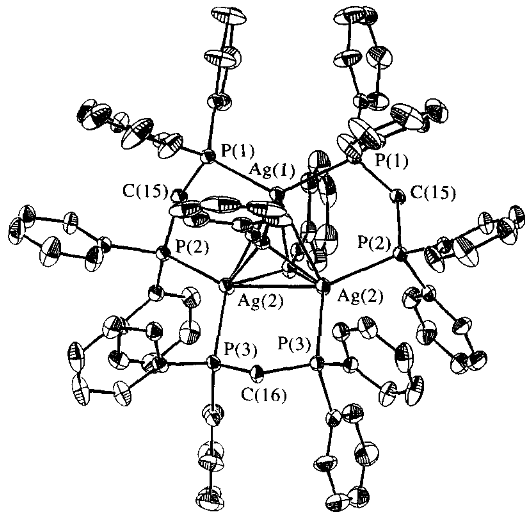

Fig. 1. The ORTEP drawing of $[Ag_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]^+$ with selected numbering, H atoms omitted for clarity. Symmetry operation : $x, -y, z$.

$(dppm)_3]Cl$, which has been characterized by an X-ray crystal analysis.[13] The presence of chloride was not observed in the starting materials. Thus, the chloride ion of the $[M_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]Cl$ is proposed to come from the reaction of CH_2Cl_2 with $[RC{\equiv}CM]_\infty$ by an undetermined pathway, during the formation of $[M_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]^+$.

The titled complex crystallizes in a monoclinic cell which contains 16 diethyl ether and four water molecules. The structure of complex cation, shown in Fig. 1, is nearly isostructural to its Cu^I analogue. The bridging mode of the alkynyl group is asymmetric with the Ag—C distances ranging from 2.321(12) to 2.635(2) Å and the bond angles between the alkynyl group and each Ag^I (∠P—Ag—C) being 135.6(6)–136.4(11)°. The measured $Ag^I \cdots Ag^I$ distances of 2.983(1) and 2.866(2) Å are comparatively longer than that of $Cu^I \cdots Cu^I$ distances [2.691(1) and 2.573(1) Å] in the related $[Cu_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]^+$ analogue.[13] The difference in the intramolecular $M \cdots M$ distances ($\Delta(M \cdots M) = 0.293$ Å), however, is smaller than the difference of ionic radius of these two coinage ions (*ca* 0.34 Å). The result of Extended-Hückel molecular-orbital calculation (EHMO) also reveals that the Mülliken $Ag^I \cdots Ag^I$ and $Cu^I \cdots Cu^I$ bond order are 0.0315 and 0.0347, respectively.

The electronic structure of the two isostructural $[M_3(dppm)_3(PhC{\equiv}C)_2]^+$ (M = Cu, Ag) have been investigated by EHMO calculations. The energies and the composition of the near frontier molecular orbitals are listed in Table 2. The LUMO of both complexes are predominately the π^* of the phenylacetylide. On the other hand, the HOMO have substantial contributions from both the metal and phenylacetylide. It should be noted that the Cu(4*p*) and Ag(5*p*) orbital are much higher in energy than the LUMO, suggesting that the $M(3d/4s) \rightarrow M(4p)$ is unlikely to be the lowest energy dipole-allowed transition. With reference to the results of EHMO calculation, we suggest that the lowest energy dipole-allowed transition has parentage of the intraligand $\pi \rightarrow \pi^*$ of phenylacetylide and $d_{\sigma^*}(M \cdots M) \rightarrow \pi^*(PhC{\equiv}C^-)$. Figure 2 shows the absorption spectrum of the $[Ag_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]^+$ complex in acetonitrile, which is featureless. The intense absorption around 274 nm, which appears as a shoulder, is tentatively

Table 2. (a) % distribution of the molecular-orbitals of complex $[Ag_3(C{\equiv}CPh)_2(dppm)_3]Cl$

Molecular orbital		% Distribution		
bond	energy (eV)	3Ag	3dppm	2PhC≡C
$\pi^*(PhC{\equiv}C)$	−8.243	2.39	0.52	97.09
$\psi^*[p(Ag)+\pi(PhC{\equiv}C)]$	−8.270	49.85	24.74	25.41
$\pi^*(PhC{\equiv}C)$	−8.359	0.20	0.10	99.71
$\pi^*(PhC{\equiv}C)$	−8.799	8.93	0.58	90.49
$\pi^*(PhC{\equiv}C)$	−8.946	7.78	0.98	91.23
Energy gap is 2.96 eV				
$\psi[d_{\sigma^*}(Ag)+\pi(PhC{\equiv}C)]$	−11.905	36.17	2.45	61.38
$\psi[d_{\pi^*}(Ag)+\pi(PhC{\equiv}C)]$	−12.009	43.63	6.71	49.66
$\psi[d_{\pi^*}(Ag)+\pi(PhC{\equiv}C)]$	−12.180	51.27	18.44	30.29
$\psi[d(Ag)+\pi(dppm)]$	−12.186	44.37	7.12	48.51
$\psi[d_{\delta^*}(Ag)+\pi(PhC{\equiv}C)]$	−12.281	22.82	6.10	71.08

Table 2. (b) % distribution of the molecular-orbitals of complex $[Cu_3(C{\equiv}CPh)_2(dppm)_3]Cl$

Molecular orbital bond	energy (eV)	% distribution 3Cu	3dppm	2PhC≡C
$\psi^*[s(Cu)+\pi(PhC{\equiv}C)]$	−8.302	49.57	24.39	26.04
$\psi^*[p(Cu)+\pi(PhC{\equiv}C)]$	−8.308	47.18	23.20	29.62
$\pi^*(PhC{\equiv}C)$	−8.323	16.39	1.88	81.73
$\pi^*(PhC{\equiv}C)$	−8.603	3.85	0.23	95.92
$\pi^*(PhC{\equiv}C)$	−8.891	12.68	1.31	86.02
	Energy gap is 2.65 eV			
$\psi[d_{\sigma^*}(Cu)+\pi(PhC{\equiv}C)]$	−11.540	40.09	2.69	57.22
$\psi[d_{\pi^*}(Cu)+\pi(PhC{\equiv}C)]$	−11.707	55.05	8.55	36.40
$\psi[d_{\pi^*}(Cu)+\pi(PhC{\equiv}C)]$	−12.022	33.74	17.86	62.28
$\psi[d_{\delta^*}(Cu)+\pi(PhC{\equiv}C)]$	−12.083	49.53	1.62	32.79
$\pi(PhC{\equiv}C)$	−12.225	6.30	8.15	92.08

assigned to the intraligand transition of coordinated phenylacetylide. This is because the $\pi \rightarrow \pi^*$ transition of coordinated phenylacetylide in $[\{Au(C{\equiv}CPh)\}_2(dppe)]$ occurs at similar energy.[1] Unlike the $[Cu_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]^+$ complex,[4,13b] the absorption at wavelength greater than 300 nm is much less intense.

The titled complex is photoluminescent in fluid solution and in solid-state (Table 3). In acetonitrile, excitation at 300–360 nm gives a broad emission with λ_{max} at 450 nm (Fig. 2). However, the emission maximum red-shifts to 555 nm when the measurement was made with solid sample at room temperature. The solid-state emission spectrum recorded 100 ns after laser flash at room temperature is shown in Fig. 3. Electrospray mass spectral measurement indicated that the complex does not dissociate in acetonitrile since a parent molecular ratio ion with $m/z = 1679.6$ has been found. Thus, the large difference in emission maxima of the solid sample (Fig. 3) and acetonitrile solution (Fig. 2) is unlikely due to the decomposition of the complex in solution. Rather, this could be ascribed by dual emission behaviour. In solution, the $^3(\pi, \pi^*)$ emission of the dppm and/or the $PhC{\equiv}C^-$ dominates. In solid-state, the lowest energy emissive state is probably metal–metal $[d_{\sigma^*}(M \cdots M)]$ to ligand $[\pi^*(PhC=C^-)]$ charge-transfer in nature.

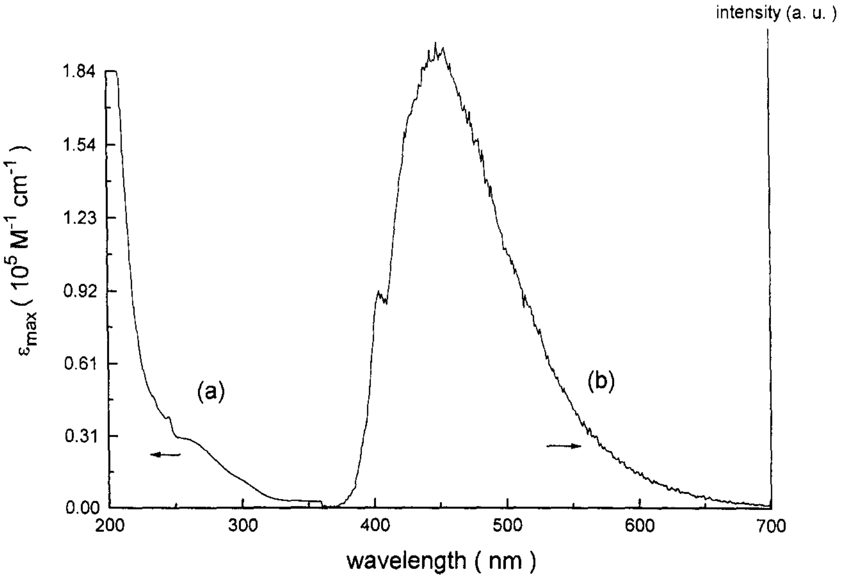

Fig. 2. (a) The UV–vis absorption and (b) the steady emission spectrum of $[Ag_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]^+$ in CH_3CN.

Table 3. Spectroscopic and photophysical data of Cu(I) and Ag(I) complexes in different degassed solvents

Complex	Medium (temp in K)	UV–vis absorption λ_{max} (nm)/ε_{max} (10^{-4} M^{-1} cm^{-1})	Emission λ_{max} (nm)[a]	Lifetime τ_0 (μs)	Quantum yield
$[Cu_3(C{\equiv}CPh)_2(dppm)_3]PF_6$[b]	acetonitrile(298)	260/5.00, 320(*sh*)/3.20	494	6.5	
	solid(298)		493	14	
	solid(77)		485, 525	14	
$[Ag_3(C{\equiv}CPh)_2(dppm)_3]Cl$	acetonitrile(298)	274/3.95	440	<50 ns	3.0×10^{-2}
	dichloromethane(298)	274/4.00	440	<50 ns	1.8×10^{-2}
	solid(298)		440	0.43	
	solid(10)		555, 600(*sh*)	0.46	

[a] All the complexes excited at >350 nm.
[b] Ref. 4.

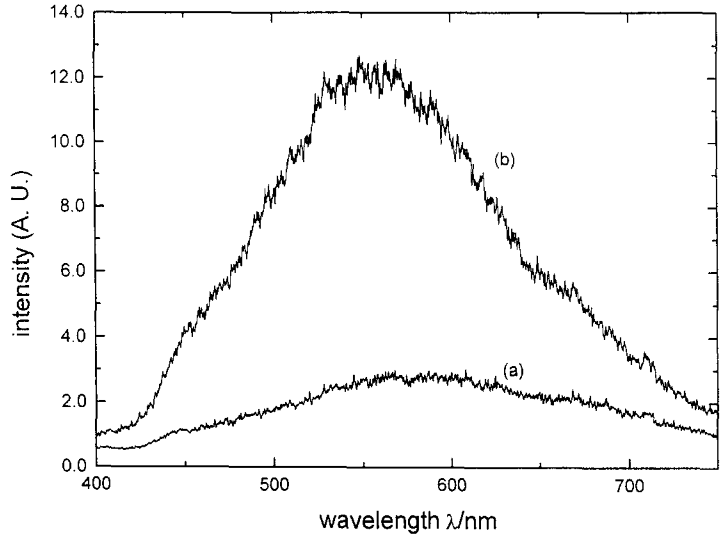

Fig. 3. The solid-state emission spectra of $[Ag_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(dppm)_3]^+$ in solid-state at (a) 291 K and (b) 10 K after 100 ns delay.

We note that the isostructural Cu^I complex also shows emission at 550–600 nm, which has been ascribed to transition of similar electronic origin.[4] Interestingly, the solid-state emission lifetime of the titled complex has been found to be insensitive to temperature, being virtually the same at 298 (0.43 μs) and at 10 K (0.46 μs).

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