Spectroscopic Evidence for Argentophilicity in Structurally Characterized Luminescent Binuclear Silver(I) Complexes

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Abstract: A spectroscopic and structural investigation of binuclear silver(I) complexes supported by aliphatic phosphine ligands, namely $[Ag(PCy_3)(O_2CCF_3)]_2$ (**1**), $[Ag_2(\mu\text{-dcpm})_2]X_2$ (X = CF_3SO_3, **2**; PF_6, **3**; dcpm = bis(dicyclohexylphosphino)methane), and $[Ag_2(\mu\text{-dcpm})(\mu\text{-}O_2CCF_3)_2]$ (**4**), is described. X-ray structural analyses of **1**−**4** reveal Ag−Ag separations of 3.095(1), 2.948 (av), 2.923 (av), and 2.8892(9) Å, respectively. Due to the optical transparency of the phosphine ligands, the UV−vis absorption band at 261 nm in CH_3CN for **2** and **3** is assigned to a $4d\sigma^* \rightarrow 5p\sigma$ transition originating from Ag(I)−Ag(I) interactions. The argentophilic nature of this band is verified by the resonance Raman spectrum of **2** with 273.9 nm excitation, where virtually all of the Raman intensity appears in the Ag−Ag stretch fundamental (80 cm^{-1}) and overtone bands. Complexes **2** and **3** exhibit photoluminescence in the solid state at room temperature.

Introduction

The propensity for aggregation of formally closed-shell d^{10} metal ions in polynuclear coordination compounds and solid-state lattices has long been recognized and exploited in, inter alia, supramolecular assembly and the design of molecules with rich photophysical properties.[1] Model spectroscopic studies of $d^{10}-d^{10}$ interactions in binuclear species, such as $[Au_2(dppm)_2]^{2+}$ (dppm = bis(diphenylphosphino)methane),[2] have established the occurrence of a low-energy $nd\sigma^* \rightarrow (n+1)p\sigma$ transition that is absent in the mononuclear two-coordinate counterparts.[3] This type of transition was originally observed in the related d^8-d^8 systems for Rh(I) and Pt(II) species by Gray and co-workers,[4] and is considered to be reliable evidence of weak metal−metal interaction in the ground state (and strong interaction in the excited state). While aurophilic attraction between gold(I) ions is widely acknowledged,[5] the development of silver−silver bonding interactions, or argentophilicity, remains in its infancy. Reports by Jansen of extended silver(I) aggregates in the ionic lattices of ternary silver(I) oxides and halides appeared over 10 years ago.[1a] More recently, silver nanoparticles with unique optical and electronic properties have been investigated in the emerging field of nanoscale materials.[6] For coordination compounds, accounts of ligand-unsupported Ag−Ag contacts based on structural determinations are scarce.[7,8] Short Ag(I)−Ag(I) separations (<3.4 Å, sum of van der Waals radii[9]) in bi- and polynuclear complexes are typically maintained by bridging ligands, but whether this constitutes the existence of $d^{10}-d^{10}$ interactions is yet to be resolved.[10,11] We now present the first unequivocal spectroscopic evidence for argentophilicity in binuclear silver(I) complexes bearing aliphatic phosphine ligands.

Experimental Section

General Procedures. All reagents were obtained from commercial sources and all solvents used for reactions were of analytical grade and purified according to conventional methods. Details of solvent treatment for photophysical studies, instrumentation, and emission measurements have been provided earlier[12] and are given in the Supporting Information. $[Ag_2(\mu\text{-dmpm})_2](PF_6)_2$ (dmpm = bis(dimethylphosphino)methane) was prepared by the literature method.[13] $[Ag(PR_3)_2]ClO_4$ (R = Me, Cy) was synthesized by interaction of the phosphine with $AgClO_4$ and characterized by elemental analyses, ^{31}P NMR, and FAB mass spectroscopy. The resonance Raman apparatus and methods have previously been described in detail,[14] and a summary is given here. The second anti-stokes Raman shifted line of the third

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Table 1. Crystal Data

	1	2	3	4
formula	$C_{40}H_{66}O_4Ag_2F_6P_2$	$C_{52}H_{92}O_6Ag_2F_6P_4S_2$	$C_{50}H_{92}Ag_2F_{12}P_6$	$C_{29}H_{46}O_4Ag_2F_6P_2$
fw	1002.63	1331.04	1322.84	850.35
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	$P2_1/c$	$P2_1/a$ (No. 14)	*P*2/*n* (No. 13)
color	colorless	colorless	colorless	colorless
crystal size, mm	0.40 × 0.20 × 0.10	0.35 × 0.25 × 0.15	0.25 × 0.20 × 0.08	0.30 × 0.25 × 0.15
a, Å	27.074(3)	22.873(3)	18.572(4)	13.205(3)
b, Å	9.649(2)	16.540(3)	14.758(3)	9.109(3)
c, Å	18.948(3)	17.502(4)	22.858(4)	14.327(3)
β, deg	119.34(2)	110.05(2)	108.14(2)	92.76(2)
V, Å^3	4314(1)	6220(2)	5953(1)	1721.4(6)
T, K	301	298	301	301
Z	4	4	4	2
D_c (g cm^{-3})	1.543	1.421	1.476	1.640
μ, cm^{-1}	10.43	8.59	8.87	12.91
F(000)	2064	2768	2736	860
$2\theta_{max}$, deg	52	44	51	50
R,[a] R_w[b]	0.067, 0.091	0.055, 0.084	0.066, 0.108	0.033, 0.042
residual ρ, e Å^{-3}	+1.05, −0.85	+1.38, −1.54	+1.07, −1.04	+0.76, −0.41

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

harmonic of a Nd:YAG laser provided the excitation frequency for the resonance Raman experiment. The laser beam was loosely focused onto the sample using ~130° backscattering geometry and reflective optics were used to collect the Raman scattered light and image it through a depolarizer and entrance slit of a 0.5 m spectrometer. The grating of the spectrometer dispersed the Raman light onto a liquid nitrogen cooled CCD detector. Accumulations of about 1 min were acquired from the CCD and about 30 of these scans were added up to find the resonance Raman spectrum. Known acetonitrile solvent bands and Hg lamp emission lines were used to calibrate the Raman shifts of the resonance Raman spectrum. Appropriately scaled solvent and quartz cell background spectra (accumulated simultaneously with the sample spectra on a different part of the CCD) were subtracted to remove the solvent bands, the Rayleigh line, and the quartz cell background signal from the resonance Raman spectrum.

Syntheses. (a) [Ag(PCy$_3$)(O$_2$CCF$_3$)]$_2$ (1). A CH_2Cl_2 solution (30 mL) of $Ag(O_2CCF_3)$ (0.10 g, 0.45 mmol) and tricyclohexylphosphine (0.13 g, 0.45 mmol) was stirred at room temperature for 6 h. A white solid was afforded upon precipitation by *n*-hexane. Recrystallization from a mixture of CH_2Cl_2/*n*-hexane yielded colorless rods. Yield: 0.19 g, 85%. Mp 177−178 °C. MS-FAB (+ve, *m*/*z*): 1003 (M^+), 501 (M^+/2). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 30.4 (dm, J = 580 Hz). FT-IR (KBr, cm^{-1}): 2988s, 1712s, 1450m, 1418m, 1021s, 950m, 761m, 691s, 600m, 555s. Anal. Calcd for $C_{40}H_{66}O_4Ag_2F_6P_2$: C, 47.92; H, 6.63. Found: C, 47.85; H, 6.54.

(b) [Ag$_2$(μ-dcpm)$_2$](CF$_3$SO$_3$)$_2$ (2). Bis(dicyclohexylphosphino)-methane (0.16 g, 0.40 mmol) and a suspension of $Ag(CF_3SO_3)$ (0.10 g, 0.39 mmol) in dichloromethane (30 mL) was stirred for 6 h. A white solid was afforded upon precipitation by diethyl ether. Recrystallization by diffusion of diethyl ether into an acetonitrile solution gave colorless crystals. Yield: 0.23 g, 90%. Mp 210−212 °C. MS-FAB (+ve, *m*/*z*): 1033 (M^+). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 33.9 (dm, J = 660 Hz). FT-IR (KBr, cm^{-1}): 2989s, 1480m, 1423m, 1008s, 948s, 725m, 633m, 501s. Anal. Calcd for $C_{52}H_{92}O_6Ag_2F_6P_4S_2$: C, 46.92; H, 6.97. Found: C, 46.98; H, 6.89.

(c) [Ag$_2$(μ-dcpm)$_2$](PF$_6$)$_2$ (3). A suspension of $AgPF_6$ (0.10 g, 0.40 mmol) in dichloromethane (40 mL) and bis(dicyclohexylphosphino)-methane (0.16 g, 0.40 mmol) was stirred at 40 °C for 5 h. Upon concentration and addition of diethyl ether, a white crystalline solid was obtained. Recrystallization by diffusion of diethyl ether into a dichloromethane solution afforded colorless crystals. Yield: 0.24 g, 92%. Mp 236−237 °C. MS-FAB (+ve, *m*/*z*): 1033 (M^+). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 36.3 (dm, J = 690 Hz). FT-IR (KBr, cm^{-1}): 3001s, 1475m, 1401m, 1004vs, 977s, 745m, 622m. Anal. Calcd for $C_{50}H_{92}Ag_2F_{12}P_6$: C, 45.40; H, 7.01. Found: C, 45.56; H, 6.95.

(d) [Ag$_2$(μ-dcpm)(μ-O$_2$CCF$_3$)$_2$] (4). A suspension of $Ag(O_2CCF_3)$ (0.15 g, 0.68 mmol) and bis(dicyclohexylphosphino)methane (0.14 g, 0.34 mmol) in dichloromethane was stirred for 5 h. Removal of volatile components yielded a white crystalline solid. The crude product was recrystallized by vapor diffusion of diethyl ether into a dichloromethane solution to afford colorless crystals. Yield: 0.21 g, 73%. Mp 222−223 °C. MS-FAB (+ve, *m*/*z*): 850 (M^+). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 35.0 (dm, J = 660 Hz). FT-IR (KBr, cm^{-1}): 2990s, 1701s, 1469m, 1420m, 1010s, 930s, 752m, 603m, 543s. Anal. Calcd for $C_{29}H_{46}O_4Ag_2F_6P_2$: C, 40.96; H, 5.45. Found: C, 40.79; H, 5.59.

X-ray Crystallography. Crystal data and details of collection and refinement are summarized in Table 1. For **1**/**3** respectively, a total of 4085/10929 unique reflections were collected on a MAR diffractometer with a 300 nm image plate detector [λ(Mo Kα) = 0.71073 Å]. The structures were solved by direct methods (SIR92[15]), expanded using Fourier techniques, and refined by full-matrix least squares using the TeXsan[16] software package for 3012/6074 reflections with $I > 3\sigma(I)$ and 244/599 parameters. For **2**/**4** respectively, a total of 8069/3248 unique reflections were collected on a Nonius CAD4/Rigaku AFC7R diffractometer [λ(Mo Kα) = 0.71073 Å, $\omega - 2\theta$ scans]. The structures were solved by Patterson[17]/direct[15] methods, expanded using Fourier techniques, and refined by full-matrix least squares using the TeXsan[16] software package for 5838/2267 absorption-corrected (transmission 0.91−1.00/0.85−1.00) reflections with $I > 3\sigma(I)$ and 649/195 parameters.

Results and Discussion

Synthesis and Structural Characterization. Reaction of stoichiometric amounts of $Ag(O_2CCF_3)$ with tricyclohexylphosphine (PCy_3) in CH_2Cl_2 afforded colorless crystals of [Ag(PCy$_3$)(O$_2$CCF$_3$)]$_2$ (**1**, 85%) upon recrystallization from CH_2Cl_2/*n*-hexane. Similarly, treatment of AgX (X = O_3SCF_3 and PF_6) with bis(dicyclohexylphosphino)methane (dcpm) in CH_2Cl_2 gave [Ag$_2$(μ-dcpm)$_2$]X$_2$ as colorless solids [X = CF_3SO_3 (**2**, 90%), PF_6 (**3**, 87%)] which can be recrystallized from CH_3CN/Et_2O for **2** and CH_2Cl_2/Et_2O for **3**, respectively. The bis(trifluoroacetate) species [Ag$_2$(μ-dcpm)(μ-O$_2$CCF$_3$)$_2$] (**4**, 73%) was formed by interaction of 2 molar equiv of $Ag(O_2CCF_3)$ with dcpm. All four complexes displayed distinctive doublets of multiplets in their $^{31}P\{^1H\}$ NMR spectra at δ 30−36 in $CDCl_3$.

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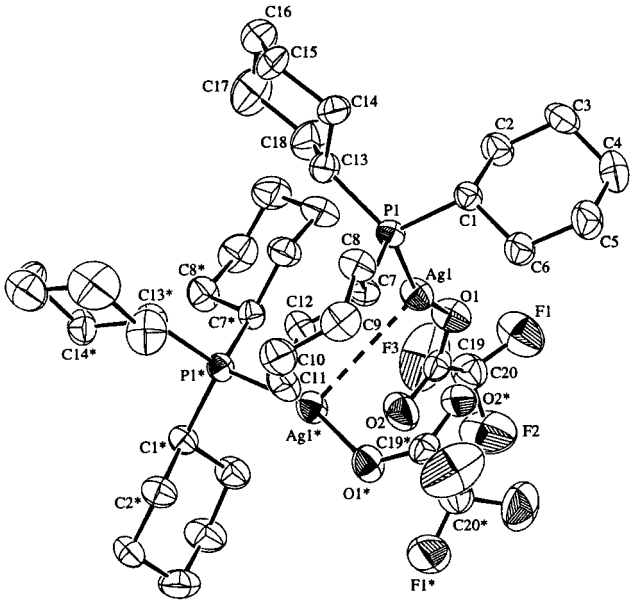

Figure 1. Perspective view of $[Ag(PCy_3)(O_2CCF_3)]_2$, **1** (40% thermal ellipsoids). Selected bond distances (Å) and angles (deg): Ag(1)−Ag(1*) 3.095(1), Ag(1)−O(1) 2.173(5), Ag(1)−O(2*) 2.509(6), Ag(1)−P(1) 2.377(2), O(1)−C(19) 1.202(9); Ag(1*)−Ag(1)−O(1) 85.4(1), Ag(1*)−Ag(1)−P(1) 110.57(5), P(1)−Ag(1)−O(1) 160.7(2), Ag(1)−O(1)−C(19) 123.7(5).

Compounds **1**−**4** have been characterized by X-ray crystallography. Complex **1** crystallizes in a dimeric form, with two $[(Cy_3P)Ag(O_2CCF_3)]$ units (P−Ag−O = 160.7(2)°) held together by an Ag−Ag contact of 3.095(1) Å (Figure 1). The PCy_3 and trifluoroacetate ligands are in a syn configuration, with Ag−O(acetate) distances of 2.173(5) and 2.509(6) Å. The crystal structure of the phosphine-bridged derivative $[Ag_2(\mu\text{-dcpm})(\mu\text{-}O_2CCF_3)_2]$ (**4**, Figure 3) also reveals short and long Ag−O(acetate) separations (2.191(3) and 2.446(4) Å respectively), plus a silver−silver distance of 2.8892(9) Å.

The molecular structures of **2** and **3** (Figure 2) contain $Ag_2P_4C_2$ cores that adopt chair conformations. The silver−silver separations of 2.936(1) and 2.960(1) Å in **2** and 2.907(1) and 2.938(1) Å in **3**, plus those in **1** and **4**, are typical for polynuclear Ag(I) derivatives with proposed d^{10}−d^{10} interactions.[7,8,18] A slightly longer Ag−Ag distance of 3.041(2) Å was reported for the analogous complex $[Ag_2(\mu\text{-dmpm})_2](PF_6)_2$.[13] Close cation−anion contacts are evident in the crystal lattices of **2** (e.g. Ag(1)···O(3) 2.692(7) Å) and **3** (e.g. Ag(1)···F(2′) 2.64(5) Å), but intriguingly, such interactions are not apparent in the X-ray structure[19] of the gold(I) congener $[Au_2(\mu\text{-dcpm})_2](ClO_4)_2$ (closest Au···$OClO_3$ 3.36(2) Å).

Spectroscopic Characterization. Previous assignments of the metal-centered $4d\sigma^* \rightarrow 5p\sigma$ transition in polynuclear silver(I) compounds with bridging arylphosphine ligands are problematic because the intraligand transitions of free arylphosphines usually occur in a similar energy region. In this work, the aliphatic PCy_3 and dcpm ligands are optically transparent in the UV region $\lambda \geq 250$ nm. It is therefore feasible to probe the $4d\sigma^* \rightarrow 5p\sigma$ transition originating from Ag(I)−Ag(I) interactions in the ground and excited states. In CH_2Cl_2, an intense UV−vis absorption band is observed for **2** and **3** at λ_{max} 266 nm ($\epsilon = 2.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}), and for **4** at λ_{max} 243 nm ($\epsilon = 1.3 \times 10^4$ dm^3 mol^{-1} cm^{-1}; see Supporting Information).

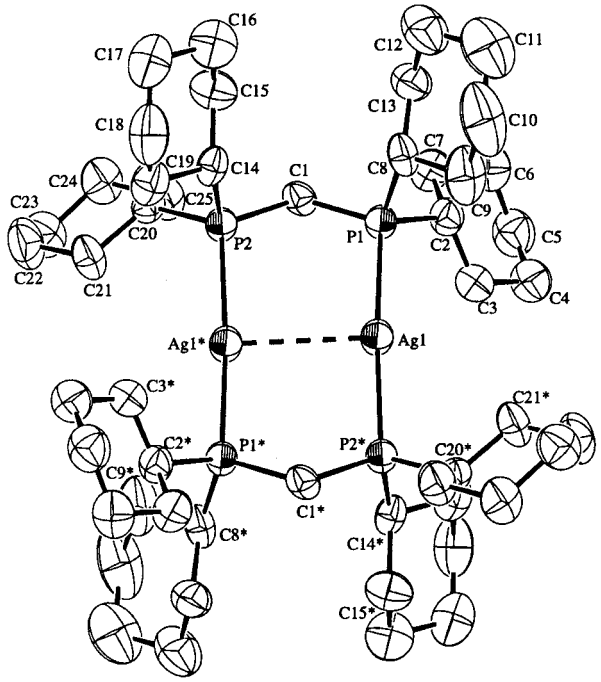

Figure 2. Perspective view of cation 1 in $[Ag_2(\mu\text{-dcpm})_2](PF_6)_2$, **3** (40% thermal ellipsoids). Selected bond distances (Å) and angles (deg): Ag(1)−Ag(1*) 2.938(1), Ag(1)−P(1) 2.405(2), Ag(1)−P(2*) 2.405(2); Ag(1*)−Ag(1)−P(1) 92.89(5), Ag(1*)−Ag(1)−P(2*) 90.69(5), P(1)−Ag(1)−P(2*) 172.37(8), Ag(1)−P(1)−C(1) 111.9(2), P(1)−C(1)−P(2) 114.5(4).

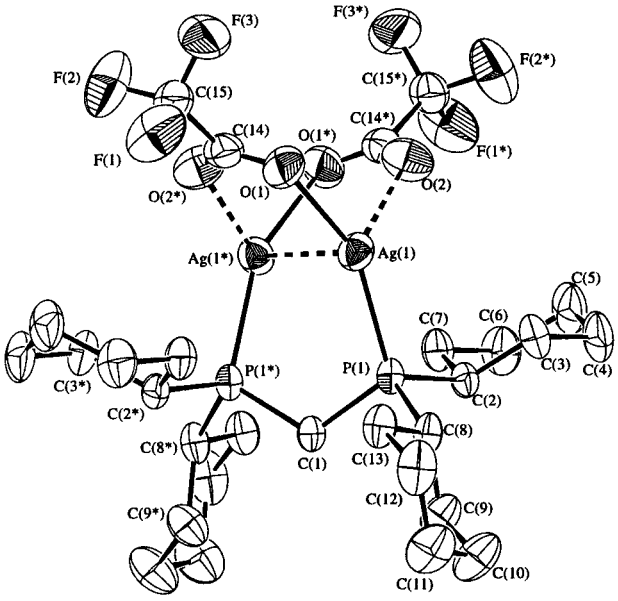

Figure 3. Perspective view of $[Ag_2(\mu\text{-dcpm})(\mu\text{-}O_2CCF_3)_2]$, **4** (40% thermal ellipsoids). Selected bond distances (Å) and angles (deg): Ag(1)−Ag(1*) 2.8892(9), Ag(1)−O(1) 2.191(3), Ag(1)−O(2) 2.446(4), Ag(1)−P(1) 2.354(1), O(1)−C(14) 1.240(6); Ag(1*)−Ag(1)−O(1) 90.0(1), Ag(1*)−Ag(1)−O(2) 74.4(1), Ag(1*)−Ag(1)−P(1) 88.96(3), P(1)−Ag(1)−O(1) 152.3(1), P(1)−Ag(1)−O(2) 113.5(1).

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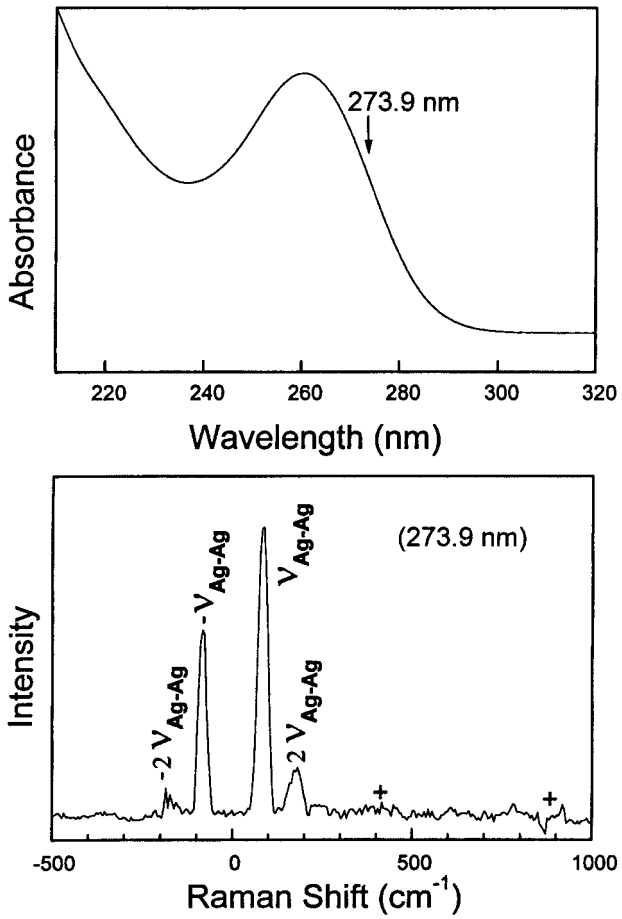

Figure 4. UV−vis absorption (top) and resonance Raman (bottom) spectra for $[Ag_2(\mu\text{-dcpm})_2](CF_3SO_3)_2$ (**2**) in acetonitrile (solvent subtraction artifacts marked by +).

In contrast, the absorption spectra of **1** (monomeric in solution) and mononuclear $[Ag(PR_3)_2]ClO_4$ (R = Me, Cy) show ϵ values below 10^2 at $\lambda \geq 250$ nm. The high ϵ values and profiles of the prominent absorptions are similar to the $5d\sigma^* \rightarrow 6p\sigma$ transitions of $Au_2(P{-}P)_2^{2+}$ (P−P = dppm,[2] dcpm[20]), which exhibit weak Au(I)−Au(I) interactions in the ground state. Significantly, the intense band for **2** and **3** displays a slight blue shift to 261 nm in acetonitrile ($\epsilon = 1.7 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[21] We suggest that weak solvent (CH$_3$CN)···Ag contacts can disrupt the intramolecular Ag−Ag interaction, which would consequently affect the $4d\sigma^* \rightarrow 5p\sigma$ transition. Previous reports have demonstrated that coordination of N-donor molecules, including acetonitrile, to the $[Cu_2(\mu\text{-dppm})_2]^{2+}$ moiety results in very long Cu···Cu interactions (>3.7 Å).[22]

The 261 nm UV band for **2** in CH$_3$CN has been examined using resonance Raman spectroscopy, which confirms that it is metal-centered in nature. Figure 4 shows the 261 nm absorption and a resonance Raman spectrum obtained with 273.9 nm excitation: virtually all of the Raman intensity appears in the Ag−Ag stretch fundamental and overtone bands. It is evident that the transition is predominantly localized on the Ag−Ag bond. The depolarization ratio for the Stokes and anti-Stokes fundamentals of the Ag−Ag stretch was measured. A value of 0.40 was obtained, which approaches the theoretical value of 0.33 for a $nd\sigma^* \rightarrow (n{+}1)p\sigma$ transition. The observed $\nu(Ag_2)$ at 80 cm^{-1} provides experimental support for that proposed for $[Ag_2(dmpm)_2](PF_6)_2$ (76 cm^{-1})[23] and $Tl[Ag(CN)_2]$ (~88 cm^{-1})[8b] using nonresonant Raman techniques. The $\nu(Au_2)$ value for the analogous $Au_2(dcpm)_2^{2+}$ species (88 cm^{-1})[20] is comparable to $\nu(Ag_2)$ for **2** despite the higher atomic mass of gold. This is consistent with the fact that gold(I) has a greater tendency to undergo homoatomic attraction. The energy of the $4d\sigma^* \rightarrow 5p\sigma$ transition for **2** and **3** also accounts for the difficulty in locating the corresponding transition in previous spectroscopic studies of polynuclear silver(I) compounds,[24] since the bridging or ancillary ligands in most instances absorb in a similar UV region. We note that the $4d\sigma^* \rightarrow 5p\sigma$ transition for $[Ag_2(\mu\text{-dmpm})_2]^{2+}$ appears at 256 nm ($\epsilon = 1.3 \times 10^4$ dm^3 mol^{-1} cm^{-1}) in CH$_3$CN; this minor blue shift compared to **2** and **3** is in accordance with a slightly longer Ag−Ag separation in $[Ag_2(\mu\text{-dmpm})_2](PF_6)_2$ (3.041(2) Å).[13]

The force constant $F(Ag_2)$ estimated from the 80 cm^{-1} $\nu(Ag_2)$ value for **2** assuming a pure Ag_2 stretch mode is 0.203 mdyn Å^{-1}.[25] For nine binuclear Ag_2 compounds, Harvey and co-workers[26] observed a good linear correlation between the Ag_2 bond distance and ln $F(Ag_2)$ [$r(Ag_2) = -0.284 \ln F(Ag_2) + 2.53$]. Our values for **2** fit very closely to the curve of the Harvey correlation, and provide further support for assignment of the resonance Raman bands of **2** to a Ag−Ag stretch. In addition, a resonance Raman intensity analysis study of **2** shows that the resonance Raman and absorption data can only be simulated accurately using a high excited-state frequency of ca. 180 cm^{-1} and a bond length change of ca. 0.20 Å.[27] The apparent change to a substantially larger frequency reflects the expected Ag−Ag single bonded excited state for a $nd\sigma^* \rightarrow (n{+}1)p\sigma$ transition. This is in agreement with previous studies by Omary and Patterson,[28] who proposed Ag−Ag bonded excited states to account for the solid-state photoluminescence of $[Ag(CN)_2]^-$ systems.

At 298 K, compounds **2** and **3** exhibit photoluminescence in the solid state at λ_{max} 420 and 417 nm (lifetime ~0.5 μs, E_{ex} 270 nm), respectively.[29] The particularly large Stokes shifts of the solid emission maxima from the $4d\sigma^* \rightarrow 5p\sigma$ absorption band in acetonitrile (ca. 14500 cm^{-1}) indicate that the electronically excited [$d\sigma^*$, $p\sigma$] state may not be responsible for the luminescence. We have observed in our laboratory that changes in metal coordination, in both ground and excited states, can dramatically alter the emissions of related Au(I)[19] and Cu(I)[30] systems, while recent studies by Catalano and co-workers also

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(21) The perchlorate salt $[Ag_2(\mu\text{-dcpm})_2](ClO_4)_2$ was also prepared and displays identical UV−vis absorption data.

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(26) (a) Perreault, D.; Drouin, M.; Michel, A.; Harvey, P. D. *Inorg. Chem.* **1993**, *32*, 1903−1912. (b) Harvey, P. D. *Coord. Chem. Rev.* **1996**, *153*, 175−198.

(27) See supporting information for full details.

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(29) Complexes **2** and **3** display very weak emissions ($\phi \leq 10^{-4}$) at λ_{max} 380 (max) and ~590 (broad) nm in acetonitrile at 298 K.

(30) Details will be published in due course: Mao, Z.; Che, C. M.; Phillips, D. L.

(31) Catalano, V. J.; Kar, H. M.; Garnas, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1979−1982. Also see ref 24d.

demonstrated similar findings for tetranuclear Ag(I) clusters.[31] In this report, close metal−anion contacts are observed in the crystal lattices of **2** and **3** (see above), and we therefore suggest that weak metal−anion interactions may play a role in the solid state emissions.

Concluding Remarks. Our current studies on $[M_2(\mu\text{-dcpm})_2]^{2+}$ (M = Ag, Au[19,20]) afford a rare opportunity to directly compare Ag−Ag and Au−Au metallophilic bonding. Using the Raman-observed $\nu(M_2)$ values [M = Ag (80 cm^{-1}), Au (88 cm^{-1})], the force constant assuming a pure M_2 stretch mode is calculated[25] to be 0.203 mdyn $Å^{-1}$ for $F(Ag_2)$ and 0.449 mdyn $Å^{-1}$ for $F(Au_2)$. These results may therefore serve as a useful indicator for comparing the bond strengths of Ag−Ag versus Au−Au interactions.

It is also pertinent to compare the $nd\sigma^* \rightarrow (n+1)p\sigma$ transition energies of the $[Ag_2(dcpm)_2]^{2+}$ and $[Au_2(dcpm)_2]^{2+}$ complexes. The blue shift from 277 nm for Au_2 to 261 nm for Ag_2 is 2213 cm^{-1}, which approaches the corresponding value of 2200 cm^{-1} for the isoelectronic d^{10} $[M_2(dppm)_3]$ (M = Pd, Pt) pair.[3b] This similarity is interesting and can be qualitatively ascribed to the difference in the $nd \rightarrow (n+1)p$ energy gap of the free metal ions from second to third row transition metals. Quantitatively, this difference in energy gap is considerably more pronounced in the free metal ions (17200 cm^{-1} for Ag/Au[1a]). It is well documented that Au(I) species exhibit metal−metal interactions for both ground and excited states, and this is likely to be the situation for the Ag(I) system in view of the small energy difference between the $nd\sigma^* \rightarrow (n+1)p\sigma$ transitions. Our results for the Ag(I) system suggest that $nd\sigma^* \rightarrow (n+1)p\sigma$ excitation produces a silver−silver bonded excited state like for the Au(I) congener.[20] In summary, this article highlights the first spectroscopic verification for the existence of Ag(I)−Ag(I) attractive interactions in coordination compounds.

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Supporting Information Available: Details of solvent treatment for photophysical studies, instrumentation, and emission measurements; ORTEP diagrams and tables of crystal data, atomic coordinates, calculated hydrogen coordinates, anisotropic displacement parameters, and bond distances and angles for **1**−**4**; UV−vis absorption spectra for **1** and **4**; resonance Raman intensity analysis study for **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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