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Argento-aurophilic bonding in organosulfur complexes. The molecular and electronic structures of the heterobimetallic complex AgAu(MTP)₂

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It is a pleasure to help celebrate the career of Professor Andrew Wojcicki, a long time friend and a superb organometallic chemist.

Abstract

The heterobimetallic complex $AgAu(MTP)_2$, (1), was obtained from the reaction of $PPN[Au(MTP)_2]$ with $AgNO_3$ (MTP = diphenylmethylenethiophosphinate; PPN = bis(triphenyl-phosphoranylidene)ammonium). Compound 1 was found to be isomorphous with but not isostructural to the previously reported compounds $Au_2(MTP)_2$, (2) and $Ag_2(MTP)_2$, (3). Surprisingly, 1 has a very short intramolecular Ag-Au distance (2.912 Å), which is much shorter than the intramolecular metal-metal distances in $\mathbf{2}$ and 3 (~3.0 Å in both). The three compounds form extended one-dimensional chain structures in the solid state. The intermolecular interactions in 1 were found to be Ag-Au interactions (3.635 Å), as opposed to Au-Au and Ag-Ag interactions. Density-functional theory (DFT) calculations were used to study the stability of the geometrical isomers with different coordination modes of the MTP ligand in models of 1-3. Isomers with Ag-C bonds were found much higher in energy than those with Au-C bonds, which explains the stability of 1 and 2, which have Au-C bonds, relative to 3, which has two Ag-C bonds. Dilute solutions of the three compounds showed virtually identical absorption spectra in which the lowest-energy band is due to a $\pi - \pi^*$ intraligand transition. The electronic spectra for concentrated solutions and the solid state show lower energy bands due to intermolecular interactions. The relative energies of the absorption edge followed the order $Au_2 \ll AgAu < Ag_2$. DFT calculations demonstrate that monomer models cannot describe this trend. However, DFT calculations for dimer and trimer models of the three compounds give excellent agreement with the experimental results, as the HOMO-LUMO gap follows the same order as the absorption edge. The importance of intermolecular metal-metal interactions is further manifested by the presence of emission bands in the visible region for the three compounds. Crystal data for AgAu(CH₂P(S)Ph₂)₂: monoclinic, space group C2/c; Z = 8; a = 24.384(2) Å; b = 6.5472(6) Å; c = 6.5472(6) Å; c = 6.5472(6)16.4884(18) Å; $\beta = 113.356(5)^{\circ}$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Electronic structures; Silver complexes; Gold complexes; Bimetallic complexes

1. Introduction

Coordination compounds of gold(I) are well known to have *aurophilic bonding*, namely closed-shell $(d^{10}-d^{10})$ interactions between monovalent gold atoms. This phenomenon has been observed in a variety of mononuclear and multinuclear Au(I) compounds and is described in both experimental and theoretical reviews [1,2]. Evidence for an analogous *argentophilic bonding* has been presented recently based on Raman spectroscopy, which showed Ag–Ag vibrations that correlate with the short Ag–Ag distances in the crystal structures of mononuclear [3] and binuclear [4] Ag(I) compounds. Closed-shell interactions in homometallic complexes of Cu(I) [2,5] are also known, but this has been based mostly on structural studies of Cu–Cu distances without evidence based on vibrational and theoretical studies that might show a bonding character for the Cu(I)– Cu(I) interactions [6]. On the other hand, mixed-metal heterometallic complexes of Group 11 elements are very scarce [7,8]. A meaningful comparison of $d^{10}-d^{10}$

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interactions between complexes of different metals requires that the metals are coordinated to identical ligands and have identical coordination number, geometry, counterions (in ionic complexes), and space group. The rare satisfaction of these conditions in isomorphous Au(I) and Ag(I) compounds has allowed Schmidbaur and co-workers to discover that gold is smaller than silver, contrary to what was believed prior to these studies [9]. Here we present a study of Au(I)– Au(I), Ag(I)–Ag(I), and Ag(I)–Au(I) bonding in three isomorphous binuclear compounds of the same ligand.

Synthetic, structural, and spectroscopic characterization of organosulfur complexes of transition metals, especially those with a closed-shell electronic configuration has long been studied in the Fackler group [10,11]. Included in this work has been the synthesis of homoand hetero-bimetallic and trimetallic complexes of the ligand diphenylmethylenethiophosphinate (MTP), which coordinates to the metal atom through sulfur and/or carbon [10]. To date, a significant number of transition metal complexes of the MTP ligand have been synthesized and characterized by X-ray crystallography [10-13]. An important subset of this class includes complexes of Au(I) and Ag(I). The homobimetallic complexes $M_2(MTP)_2$ (M = Au; Ag) have been reported earlier [12,13]. Heterobimetallic complexes of MTP with two different monovalent coinage metal ions were previously unknown. The reported heterobimetallic and heterotrimetallic complexes of MTP contain Au(I) with the ions Pt(II), Tl(I), Pb(II), or Hg(II) [10,11].

An important feature of many of the MTP complexes of closed-shell metals is their extended linear chain structures. Linear chain transition metal complexes have attracted the interest of experimental and theoretical chemists and physicists for many years due to their fascinating chemical and photophysical properties [14,15]. Recent examples include the development of a vapochromic light emitting diode from a linear chain Pt(II) complex, [16] the synthesis of an Au(I) dithiocarbamate complex that possesses a luminescent linear chain structure only in the presence of vapors of organic solvents, [17] and a trinuclear Au(I) complex whose extended chain structure is responsible for its storage of energy and releasing it as long-lived orange phosphorescence, 'solvoluminescence', upon contact with solvent [18]. We have recently reported that colorless trinuclear Au(I) compounds that do not form extended-chain structure by themselves can produce brightly-colored complexes by sandwiching naked Tl⁺ and Ag⁺ ions to form linear chain complexes with fascinating luminescence properties that include luminescence thermochromism [7]. Recent results have demonstrated that the electron-rich trinuclear Au(I) complexes can interact with neutral inorganic [19] and organic [20] Lewis acids to produce infinite linear chain complexes. The influence of the extended-chain molecular structure on the electronic structure is paramount, as suggested from the electronic spectra and semi-empirical calculations for coordination compounds possessing such a structure. Here we demonstrate this concept by modern computational methods based on density-functional theory (DFT) calculations for models containing up to six metal ions, the results of which were correlated with the experimental spectroscopic results for the three isomorphous bimetallic complexes 1-3.

We report here the synthesis, crystal structure, and electronic absorption and luminescence spectra of the new heterobimetallic complex $AgAu(MTP)_2$, (1). The molecular and electronic structures are compared with the related homobimetallic complexes $Au_2(MTP)_2$, (2) and $Ag_2(MTP)_2$, (3). The intramolecular and intermolecular metal-metal bonding in the three compounds are compared based on X-ray crystallography and DFT calculations. The various coordination possibilities, for the MTP ligand to the Ag and Au atoms, in models of the three compounds are analyzed based on their DFT energies. Finally, the absorption and luminescence properties for solutions and solids of the three complexes are studied and related to the extended-chain structure.

2. Experimental

2.1. General procedures

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques [21]. All solvents were freshly distilled and de-aerated prior to use. PPN[Au(MTP)₂], Au₂(MTP)₂ and Ag₂(MTP)₂ were prepared according to published procedures [10–13]. AgNO₃ and PPNCl were purchased from Aldrich and used without further purification.

¹H and ³¹P NMR measurements were carried out using a Unity Plus 300 spectrometer operating at 300 MHz for proton spectra. Absorption spectra were carried out using a Hewlett–Packard model HP 8452 UV–Vis spectrophotometer. The absorption spectra were obtained for solutions of the compounds in freshly-distilled reagent grade CH₂Cl₂. Luminescence spectra were obtained on an SLM/AMINCO Model 8100 spectrofluorometer using a 150 W xenon lamp. Low temperature luminescence measurements were made by placing crystalline solids in a cryostat of local design. Liquid nitrogen was used to obtain the 77 K data.

2.2. Synthesis of $AgAu(MTP)_2$ (1)

A 390 mg sample of PPN[Au(MTP)₂] (0.33 mmol) was dissolved in 10 ml of CH_2Cl_2 . To this CH_2Cl_2 solution, 55 mg of AgNO₃ (0.33 mmol) were added. A

white precipitate started to form after 15 min of stirring at ambient temperature. The mixture was stirred for 1 h and then the solid was filtered and washed with CH₃OH and diethyl ether. The product was dried under reduced pressure for 1 h and then weighed (90% yield). Compound 1 was recrystallized from CH₂Cl₂ at -20 °C. The white solid is stable in air and room light and has a melting point (m.p.) of 165 °C (dec.). ¹H NMR (CDCl₃-TMS): 1.80 ppm, d, CH₂, $J_{P-H} = 12$ Hz; $\delta =$ 7.3–7.9 ppm, m, C₆H₅. ³¹P{¹H} NMR 52.17 ppm relative to a 85% H₃PO₄ in D₂O standard. No Ag–P coupling was detected by ³¹P NMR even at -80 °C (CDCl₃) or in the solid-state. Calc. for C₂₆H₂₄P₂S₂AuAg: C, 40.70; H, 3.15; S, 8.36%. Found: C, 40.41; H, 3.07; S, 8.25%.

2.3. Crystal structure determination of 1 by X-ray diffraction

Single crystals of 1 were grown by recrystallizing a warm CH_2Cl_2 solution at -20 °C. Good quality block crystals that proved suitable for X-ray crystallography were obtained after ~24 h of storage at -20 °C. The structure was determined using direct methods (SHELXL-97, Sheldrick, 1997). Details of the crystal data, parameters for data collection, the solution and refinement of the structure are given in Table 1.

2.4. Computational details

All calculations were performed with the GAUSSIAN 98 suite of programs for molecular models of 1, 2, and 3 shown in Schemes 1 and 2. The calculations were at the DFT level, [22] using the Becke three parameter [23]

Table 1 Crystal data and structure refinement for AgAu(MTP)₂

Chemical formula	C. H. Ag Au PS
	C131112Ag0.50Au0.501 5
Formula weight	383.0/
Crystal system	monoclinic
Space group	C2/c
Temperature (K)	110(2)
Wavelength (Å)	0.71073
Unit cell dimensions	
a (Å)	24.384(2)
b (Å)	6.5472(6)
c (Å)	16.4884(18)
β (°)	113.356(5)
V (Å ³)	2416.6(4)
Ζ	8
$\rho_{\rm calc} ({\rm mg}\;{\rm m}^{-3})$	2.109
$\mu ({\rm mm}^{-1})$	7.193
$R_1^{a} [I > 2\sigma(I)]$	0.0450
$wR_2^{b} [I > 2\sigma(I)]$	0.1077
R_1^{a} (all data)	0.0572
wR_2 ^b (all data)	0.1155

^a $R_1 = \Sigma ||F_0| - F_c||/|F_0|.$

⁶
$$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}.$$



Scheme 1. Structures of **1**, **2**, and **3**. The R groups are phenyl groups in the crystal structures. In the molecular models used, the R groups were phenyl, methyl, and hydrogen, depending on the calculations type (text).



Scheme 2. Alternative bonding modes considered in the molecular structure models of 1, 2, and 3.

hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) [24]. A Huzinaga/Dunning basis set [25] of a double-zeta quality was used for carbon and hydrogen atoms. A double-zeta basis set plus one polarization function on the P and S atoms was used, in order to properly describe the hypervalent character of phosphorous and sulfur compounds. A small-core effective core potential (ECP) developed by Hay and Wadt [26] was used for gold atoms to represent the 60 core electrons $(1s^2 2s^2 2p^6... 4d^{10} 4f^{14})$ with a double-zeta basis set for the 19 outer electrons from the atomic $5s^2$ $5p^6$ $5d^{10}$ $6s^1$ shells. The ECP for gold incorporates two relativistic effects for the core electrons, mass velocity and Darwin, and thus represents the dominant relativistic contributions to the behavior of the outer electrons. Single point energy and geometry optimization calculations were carried out on the model systems with geometries taken directly from their X-ray crystal structures.

3. Results and discussion

3.1. Molecular structure

Crystallographic data for 1 are shown in Table 1. The molecular structure of the unit cell of 1 is shown in Fig. 1. The Ag and Au atoms are bridged by the MTP ligand. The Au atom is coordinated linearly to two carbon atoms; $C-Au-C = 179.1(6)^{\circ}$. On the other hand, the Ag



Fig. 1. Molecular structure of $AgAu(MTP)_2$ showing 40% thermal ellipsoids.

atom is coordinated to two sulfur atoms with a significant deviation from linearity; $S-Ag-S = 171.71(13)^\circ$. The monoclinic space group C2/c determined for 1 renders the compound isomorphous with the previously reported compounds $Au_2(MTP)_2$, (2) [12] and $Ag_2(MTP)_2$, (3) [13] although the compounds are not isostructural since 2 and 3 have a molecular center of symmetry. The coordination of the MTP ligand to the metal atoms in the three compounds is shown in Scheme 1. Selected interatomic distances and bond angles are given in Table 2 for 1. The Au-C and Ag-S distances of ~ 2.07 Å and 2.44 Å in 1 are similar to the corresponding distances in 2 and 3.

The intramolecular Ag–Au distance is 2.912 Å. This distance is surprisingly very short, compared with the intramolecular metal-metal distances in the compounds 2 and 3 (\sim 3.0 Å in both). It is interesting to note that the deviation from linearity in the S-Ag-S coordination is such that the Ag atom is directed toward the Au atom (Fig. 1), thus suggesting that the intramolecular Ag–Au bonding in 1 is inherent and little influenced by the ligand geometry. Fig. 2 shows that 1 packs as an infinite linear chain with intermolecular metal-metal interactions. It is interesting that these metal-metal interactions are Ag-Au intermolecular interactions, as opposed to possible Au-Au and Ag-Ag interactions. The intermolecular Ag–Au distance is 3.635 Å, appreciably longer than the Au-Au and Ag-Ag intermolecular distances in 2 and 3 (about 3.2 Å in both). The Ag–Au···Ag and Au···Ag–Au angles are both 180° , a consequence of the symmetry of the space group.

Similar Ag–Au distances to the ones in 1 were reported for the non-classical multinuclear compounds $\{Ag([Au(\mu-C^2,N^3-bzim)]_3)_2\}BF_4 \cdot CH_2Cl_2; [7] \sim 2.8 \text{ Å}$

Table 2 Selected bond lengths (Å) and angles (°) for AgAu(MTP)₂

Bond lengths	
Ag(1) - S(1)	2.438(3)
Ag(1)-Au(1)	2.9124(13)
Au(1)-C(1)	2.069(13)
P(1)-C(1)	1.743(11)
P(1)-C(8)	1.788(13)
P(1)-C(2)	1.805(11)
P(1)-S(1)	2.005(4)
Bond angles	
$S(1)-Ag(1)-S(1)^{a}$	171.71(13)
S(1)-Ag(1)-Au(1)	94.14(7)
$C(1)-Au(1)-C(1)^{a}$	179.1(6)
C(1) - Au(1) - Ag(1)	90.5(3)
C(1)-P(1)-C(8)	109.7(5)
C(1)-P(1)-C(2)	109.3(5)
C(8) - P(1) - C(2)	103.3(5)
C(1)-P(1)-S(1)	114.4(4)
C(8) - P(1) - S(1)	109.0(4)
C(2)-P(1)-S(1)	110.6(4)
P(1)-S(1)-Ag(1)	101.25(15)
P(1)-C(1)-Au(1)	115.5(6)
C(3)-C(2)-C(7)	118.1(10)
C(3)-C(2)-P(1)	122.8(8)
C(7)-C(2)-P(1)	119.0(9)

^a Symmetry transformations used to generate equivalent atoms: -x, y, -z+1/2.



Fig. 2. The repeat structure of AgAu(MTP)₂.

and $[Au_2Ag_2(C_6F_5)_4(L)]$ (L = neutral weakly-coordinated solvent); 2.78–2.79 Å [8]. However, the Au–Ag interactions in these examples are mostly electrostatic in nature and are believed to form owing to the strong Lewis-base character of the neutral and anionic complexes $[Au(\mu-C^2,N^3-bzim)]_3$ [19] and $Au(C_6F_5)_2^{-1}$, [8], respectively, which interact with the Ag⁺ cation. The intermolecular interactions in both these cases are aurophilic interactions, not Au–Ag interactions. In 1, on the other hand, the intramolecular and intermolecular

cular Au(I)-Ag(I) interactions are dominantly closedshell metallophilic bonding interactions in a classical coordination compound and, in this vein, they are considered quite unusual and unprecedented in the literature of monovalent coordination compounds of Group 11. Nevertheless, because 1 is a heterobimetallic complex with an unsymmetrical metal core, one would expect some polarity for the molecule. Indeed, DFT calculations confirm this prediction. Calculations were performed for molecules of 1-3 without any approximation in the crystal structure (no atoms were omitted; no changes in the geometry were made). Single-point energy DFT calculations for the crystal structure of 1 shows that the molecule indeed possesses a dipole moment of 3.79 D, thus suggesting a significant polar character. In contrast, the dipole moments for 2 and 3 are 0.0133 and 0.0076 D, essentially zero as expected for the centrosymmetric structures found. The Mulliken atomic charge distribution from these calculations shows that the Ag atom in 1 carries a +0.15 partial charge while the Au atom carries a higher charge (+ 0.22). Both Au atoms in 2 have an identical charge of +0.06 while the Ag atoms in 3 also have an identical charge of +0.12, according to DFT calculations. These complexes have identical coordination at both metal centers. This is not true for 1. The strength of the Ag-Au bond in 1, therefore, is attributed to both metallophilic closed-shell interactions and polar interactions.

The symmetrical bonding of the Ag atom to two S atoms and of the Au atom to two C atoms in 1 is suggestive of the stronger stability of Au–C bonds than Ag–C bonds. This result is consistent with the vastly large number of organogold compounds reported to date in comparison with organosilver compounds [27]. It is also noted that 1 and 2, both having Au-C bonds, are very stable compounds while 3, which has Ag–C bonds, is extremely sensitive to air, light, and temperature, and decomposes rather easily and rapidly. Modern computational methods support the structural observations in this and other studies that point to the stability of Au-C bonds. The calculations also shed some light on the possibility for rearrangements in this class of organometallic complexes of Au(I) and Ag(I). A review of the structural aspects of this topic has been reported recently [28] but, to our knowledge, no modern theoretical studies have been reported.

We have examined the different coordination modes of the MTP ligand in the three compounds, shown in Schemes 1 and 2, by DFT calculations. Full geometry optimization was carried out for each model after replacing the phenyl groups with hydrogen atoms. The results are shown in Table 3. The crystallographic arrangement for the AgAu compound, model **1a**, is favored over the model with the Ag bonded to two carbon atoms, model **1b**, by nearly 16 kcal mol⁻¹. The model having each metal bonded asymmetrically to C and S atoms, model 1c, has an intermediate energy between the energies for models 1a and 1b. These results suggest that the Au–C bond has a much greater stability than the Ag–C bond. For isomers of the Au₂ compound, the crystallographically found arrangement, 2a, is favored by 3.3 kcal/mol over the model 2b. Interestingly, this is not the case for the Ag₂ compound, in which model 3b is favored, albeit very slightly (1.9 kcal/ mol), over the crystallographically observed arrangement, 3a.

3.2. Electronic structure

Solutions of 1, 2, and 3 in CH₂Cl₂ have absorption spectra that are dependent on concentration. Fig. 3 shows the absorption spectra for dilute solutions of 1, 2, and 3 in CH₂Cl₂ at ambient temperature. The three compounds have rather similar absorption spectra, with a band around 275 nm. The position of the band is independent of the identities of the metals in the complex. Therefore, the assignment of this band is not strongly metal based, because of the large differences in the energy levels of Ag(I) and Au(I) [29]. The most reasonable assignment is an intraligand transition. The large extinction coefficient ($\sim 10^4$ M⁻¹ cm⁻¹) is consistent with an allowed transition of this type such as a ligand π - π * transition.

Upon increasing the concentration, a gradual red shift in the absorption edge was observed for each of the three compounds. Fig. 4 shows the absorption spectra for solutions of 1, 2, and 3 in CH_2Cl_2 at ambient temperature with concentration near saturation. A 1mm quartz cuvette was used for these measurements in order to attenuate the strong absorbance of concentrated solutions by an order of magnitude. The absorption edge is shifted from the dilute solution absorption band (at ~ 275 nm) by about 7800, 14000, and 6500 cm^{-1} for 1, 2, and 3, respectively. The low absorption energies for concentrated solutions of the Au₂ compound, 2, is consistent with the dark-yellow color for the solid and concentrated solutions of the compound, while the AgAu and Ag₂ compounds are white and have colorless solutions. The shift of the absorption edge for each compound to lower energies is indicative of molecular aggregation as the concentration is increased. This is consistent with the extended-chain structures observed for the three solids, whose electronic bands are positioned at lower energies than those for the saturated solutions (vide infra).

Based upon these data we suggest that compounds 1-3 exist as discrete oligomers (e.g. dimers and trimers) in concentrated solutions, as opposed to the infinite chain structures for the solids. The absence of well-defined absorption bands in the low energy regions for the concentrated solutions precludes accurate calculations for the formation constants of oligomers of each

Model	δ (a.u.)	$E (\text{kcal mol}^{-1})$	M-M (Å)	M-C (Å)	M-S (Å)	P-C	P-S	
1a	- 395.631	0.0	3.038	2.133	2.508	1.801	2.045	
1b	- 395.606	+15.9	3.164	2.195	2.401	1.777	2.067	
1c	- 395.621	+6.0	3.156	2.189 (Ag); 2.103 (Au)	2.513 (Ag) 2.441 (Au)	1.783 (Ag) 1.809 (Au)	2.037 (Ag) 2.056 (Au)	
2a	-385.322	0.0	3.266	2.101	2.446	1.808	2.050	
2b	-385.317	+3.3	3.216	2.131	2.404	1.797	2.063	
3a	-405.917	0.0	3.131	2.182	2.499	1.787	2.045	
3b	-405.92	-1.9	3.049	2.187; 2.190	2.493; 2.495	1.769; 1.783	2.045; 2.049	

Table 3 Summary of DFT Calculations for Fully Optimized Models of **1**, **2**, and **3**

See Schemes 1 and 2 for the structures of the models used. The models represent the crystal structures but with hydrogen atoms replacing the phenyl groups.



Fig. 3. Absorption spectra for dilute solutions of $AgAu(MTP)_2$, $Au_2(MTP)_2$, and $Ag_2(MTP)_2$.

compound. Such calculations have been reported for other Au(I) and Ag(I) compounds that show well-defined oligomer bands [30]. Our focus here, therefore, will be limited to the qualitative trend showing that the absorption energies for the oligomers that are dominant near the saturation points for the three compounds follow the order $2 \ll 1 < 3$.

DFT calculations have been carried out for monomer, dimer, and trimer models of 1, 2, and 3. In order to reduce the computation time, the phenyl groups of the MTP ligand were replaced by methyl groups in these calculations. All bond lengths, bond angles, and dihedral angles in each model were maintained as in the crystal structures of the compounds. The value of the energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), i.e. the HOMO–LUMO gap, was calculated for each model. The results are summarized in Table 4.

It is noted that monomer models cannot describe the experimental trend for the relative energy of the absorption edge, which followed the order $Au2 \ll AgAu < Ag_2$ (Fig. 4). While monomer models for the DFT calculations are not consistent with these trends, DFT calculations for dimer and trimer models of the



Fig. 4. Absorption spectra for solutions of $AgAu(MTP)_2$, $Au_2(MTP)_2$, and $Ag_2(MTP)_2$ with concentrations near the saturation limit.

three compounds gave a qualitative agreement with the experimental results. The values of the HOMO–LUMO gap in Table 4 for dimer and trimer models followed the same order for the absorption edge for the concentrated solutions of 1-3 shown in Fig. 4 [31]. The large red shifts in the absorption energies upon increasing the concentration of solutions of 1-3 underscore the oligomerization of these species owing to closed-shell $d^{10}-d^{10}$ interactions. Similar spectral changes owing to Au(I)–Au(I) and Ag(I)–Ag(I) interactions have been reported in recent years and were attributed to aurophilic and argentophilic bonding, respectively [30]. The changes in the absorption spectrum of 1 with concentration are due to Au(I)–Ag(I) (as we demonstrated above) and hence, this represents the first example of such

Model	<i>E</i> (HOMO) (a.u.)	δ (LUMO) (a.u.)	H–L gap (a.u.)	H-L gap (10^3 cm^{-1})	
AgAu	-0.2096	-0.0101	0.1995	43.78	
2AgAu	-0.1943	-0.0125	0.1818	39.90	
3AgAu	-0.1873	-0.0150	0.1722	37.80	
1Au ₂	-0.2075	-0.0025	0.2050	44.99	
2Au ₂	-0.1809	-0.0021	0.1788	39.24	
3Au ₂	-0.1691	0.0000	0.1691	37.10	
$1Ag_2$	-0.2034	-0.0004	0.2030	44.55	
$2Ag_2$	-0.1861	0.0002	0.1863	40.89	
$3Ag_2$	-0.1786	0.0022	0.1808	39.68	

Table 4 HOMO-LUMO gaps for monomer, dimer, and trimer models of 1, 2, and 3 according to DFT calculations

The models represent the crystal structures but with methyl groups replacing the phenyl groups. All interatomic distances and bond and dihedral angles are the same as the crystallographic values.

spectral changes being due to *argento –aurophilic* bonding. While deviation from Beer's law due to oligomerization has also been reported recently for $[Au_2Ag_2(C_6F_5)_4(L)]$ species, [8c] Au(I)–Au(I) aurophilic bonding was responsible for those spectral changes. The calculations suggest this is unlikely to be responsible for the oligomerizations here for **1**.

Compounds 1-3 display photoluminescence in the solid state. Figs. 5-7 show the luminescence excitation



Fig. 5. Emission (thick lines) and excitation (thin lines) spectra of $AgAu(MTP)_2$ in the solid state (single crystals) at 77 K.



Fig. 6. Emission (thick lines) and excitation (thin lines) spectra of $Au_2(MTP)_2$ in the solid state at 77 K.



Fig. 7. Emission (thick lines) and excitation (thin lines) of $Ag_2(MTP)_2$ in the solid state at 77 K.

and emission spectra of 1-3, respectively, in the solid state at 77 K. It is noted that the excitation energies for the solids (Figs. 5-7) are somewhat lower than the absorption energies of the concentrated solutions (Fig. 4). This is obviously due to the expected lower band gap energy in the extended-chain species in the solid state, as opposed to the situation in oligomers of a few complexes in solution. Intermolecular $d^{10}-d^{10}$ bonding is a known reason for the existence of photoluminescence in linear two-coordinate complexes of coinage metal monovalent ions [32]. The emission energies are in the blue-green visible region ($\lambda_{max} = 424, 493$, and 466 nm for 1, 2, and 3, respectively). The observed site-selective excitation in 3 is at odds with the presence of only one crystallographically unique Ag site in the compound. Similar observations have previously been reported and attributed to the so-called self-trapped excitons, [33] but the case for 3 has not been established.

4. Conclusions

The present work presents an integrated structural/ theoretical/spectroscopic study of organosulfur coordination compounds of coinage metal cations. The studies underscore the significance of closed-shell, *argento* – *aurophilic* bonding, the polarity of which has led to surprisingly short Ag–Au distances.

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References

- [1] H. Schmidbaur, Chem. Soc. Rev. (1995) 391.
- [2] P. Pyykkö, Chem. Rev. 97 (1997) 599.
- [3] M.A. Omary, T.R. Webb, Z. Assefa, G.E. Shankle, H.H. Patterson, Inorg. Chem. 37 (1998) 1380.
- [4] C.M. Che, M.C. Tse, M.C.W. Chan, K.K. Cheung, D.L. Phillips, K.H. Leung, J. Am. Chem. Soc. 122 (2000) 2464.
- [5] (a) P.C. Ford, A. Vogler, Acc. Chem. Res. 26 (1993) 220;
 (b) O. Horváth, Coord. Chem. Rev. 135/136 (1994) 303.
- [6] In fact, evidence pointing to the contrary conclusion has been reported, see: F.A. Cotton, X. Feng, M. Matusz, R. Poli, J. Am. Chem. Soc. 110 (1988) 7077.
- [7] (a) A. Burini, R. Bravi, J.P. Fackler, Jr., R. Galassi, T.A. Grant, M.A. Omary, B.R. Pietroni, R. Staples, J. Inorg. Chem. 39 (2000) 3158;

(b) A. Burini, J.P. Fackler, Jr., R. Galassi, B.R. Pietroni, R.J. Staples, J. Chem. Soc., Chem. Commun. (1998) 95.

- [8] (a) R. Usón, A. Laguna, M. Laguna, P.G. Jones, G.M. Sheldrick, J. Chem. Soc., Chem. Commun. (1981) 1097;
 (b) R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones, G.M. Sheldrick, J. Chem. Soc., Dalton Trans. (1984) 285;
 (c) E.J. Fernández, M.C. Gimeno, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, P. Pyykkö, D. Sundholm, J. Am. Chem. Soc. 122 (2000) 7287.
- [9] (a) U.M. Tripathi, A. Bauer, H. Schmidbaur, J. Chem. Soc., Dalton Trans. (1997) 2865;
 (b) A. Bayler, A. Schier, G.A. Bowmaker, H. Schmidbaur, J. Am. Chem. Soc. 118 (1996) 7006.
- [10] J.P. Fackler, Jr., E. Galarza, G. Garzón, A.M. Mazany, H.H. Murray, M.A. Rawashdeh-Omary, R. Raptis, R.J. Staples, W.E. van Zyl, S. Wang, in: D. Coucouvanis (Ed.), Inorganic Synthesis, vol. 33, Wiley, New York, 2002.
- [11] (a) S. Wang, J.P. Fackler, Jr., Organometallics 9 (1990) 111;
 (b) S. Wang, J.P. Fackler, Jr., Organometallics 7 (1988) 2415;
 (c) S. Wang, J.P. Fackler, Jr., Inorg. Chem. 28 (1989) 2615;
 (d) H.H. Murray, D.A. Briggs, G. Garzón, R.G. Raptis, L.C. Porter, J.P. Fackler, Jr., Organometallics 6 (1987) 1992;
 (e) S. Wang, J.P. Fackler, Jr., C. King, J.C. Wang, J. Am. Chem. Soc. 110 (1988) 3308;
 (f) S. Wang, G. Garzón, C. King, J.C. Wang, J.P. Fackler, Jr., Inorg. Chem. 28 (1989) 4623;
 (g) T.F. Carkler, J.P. Fackler, Jr., P. Fackler, Jr., B. J. Staples, P.F. P. Winnenput.

(g) T.F. Carlson, J.P. Fackler, Jr., R.J. Staples, R.E.P. Winpenny, Inorg. Chem. 34 (1995) 426;

- (h) S. Wang, J.P. Fackler, Jr., Organometallics 8 (1989) 1578;
- (i) J.P. Fackler, Jr., Polyhedron 16 (1997) 1;

(j) C. King, D.D. Heinrich, G. Garzón, J.C. Wang, J.P. Fackler, Jr., J. Am. Chem. Soc. 111 (1989) 2300;

(k) D.D. Heinrich, R.J. Staples, J.P. Fackler, Jr., Inorg. Chim. Acta 229 (1995) 61.

[12] (a) A.M. Mazany, J.P. Fackler, Jr., J. Am. Chem. Soc. 106 (1984) 801;

(b) L.C. Porter, J.P. Fackler, Jr., Acta Crystallogr. Sect. C 43 (1987) 587.

- [13] S. Wang, J.P. Fackler, Jr., T.F. Carlson, Organometallics 9 (1990) 1973.
- [14] J.S. Miller (Ed.), Extended Linear Chain Compounds, vol. 1–3, Plenum Press, New York, 1981–1983.
- [15] R. Hoffmann, Angew. Chem., Int. Ed. Engl. 26 (1987) 846.
- [16] Y. Kunugi, K.R. Mann, L.L. Miller, C.L. Exstrom, J. Am. Chem. Soc. 120 (1998) 589.
- [17] M.A. Mansour, W.B. Connick, R.J. Lachicotte, H.J. Gysling, R. Eisenberg, J. Am. Chem. Soc. 120 (1998) 1329.
- [18] J.C. Vickery, M.M. Olmstead, E.Y. Fung, A.L. Balch, Angew. Chem., Int. Ed. Engl. 36 (1997) 1179.
- [19] A. Burini, J.P. Fackler, Jr., R. Galassi, T.A. Grant, M.A. Omary, M.A. Rawashdeh-Omary, B.R. Pietroni, R.J. Staples, J. Am. Chem. Soc. 122 (2000) 11264.
- [20] M.A. Rawashdeh-Omary, M.A. Omary, J.P. Fackler, Jr., R. Galassi, B.R. Pietroni, A. Burini, J. Am. Chem. Soc. 123 (2001) 9689.
- [21] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, second ed., Wiley, New York, 1986.
- [22] R.G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, 1989. Suite of programs used: GAUSSIAN 98, Revision A.6, M.J. Frisch et al., Gaussian Inc., Pittsburgh, PA, 1998.
- [23] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [24] (a) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785;
 (b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200.
- [25] T.H. Dunning, Jr., P.J. Hay, in: H.F. Schaefer, III (Ed.), Modern Theoretical Chemistry, vol. 3, Plenum, New York, 1976.
- [26] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270.
- [27] (a) J.P. Fackler, Jr., Silver organometallic chemistry, in: R.B. King (Ed.), Encyclopedia of Inorganic Chemistry, vol. 7, Wiley, New York, 1994, pp. 3829–3834;
 (b) I. Antes, S. Dapprich, G. Frenking, P. Schwerdtfeger, Inorg. Chem. 35 (1996) 2089;
 (c) Gmelin Handbuch der Anorganischen Chemie, vol. 61, eighth ed., Springer-Verlag, Berlin, 1975, Part B5;
 (d) A. Grohmann, H. Schmidbauer, in: G. Wilkinson, F.G.A. Stone (Eds.), Comprehensive Organometallic Chemistry, vol. 3, Pergamon Press, Oxford, UK, 1995.
 [28] S. Wang, J.P. Fackler, Jr., Rearrangement of gold and silver
- [28] S. Wang, J.P. Fackler, Jr., Rearrangement of gold and silver complexes, in: S. Patai, Z. Rappaport (Eds.), The Chemistry of Organic Derivatives of Gold and Silver, Wiley, New York, 1999, pp. 431–450.
- [29] (a) C.E. Moore, Atomic Energy Levels, vol. III, Natl. Bur. Stand., Washington, DC, 1958, Circ. 467;
 (b) L.E. Orgel, J. Chem. Soc. (1958) 4186.
- [30] (a) S.S. Tang, C.P. Chang, I.J.B. Lin, L.S. Liou, J.C. Wang, Inorg. Chem. 36 (1997) 2294;
 (b) M.A. Rawashdeh-Omary, M.A. Omary, H.H. Patterson, J. Am. Chem. Soc. 122 (2000) 10371.
- [31] One should realize that quantitative information should not be deduced from the HOMO-LUMO gaps to the absorption energies. Much higher levels of theory are needed to obtain such information, such as configuration interaction methods.
- [32] (a) J.M. Forward, J.P. Fackler, Jr., Z. Assefa, Photophysical and photochemical properties of gold(I) complexes, in: D.M. Roundhill, J.P. Fackler, Jr. (Eds.), Optoelectronic Properties of Inorganic Compounds (Chapter 6), Plenum Press, New York, 1999;

(b) M.A. Rawashdeh-Omary, M.A. Omary, H.H. Patterson, J.P. Fackler, Jr., J. Am. Chem. Soc. 123 (2001) 11237.
[33] (a) H. Yersin, J. Chem. Phys. 68 (1978) 4707;

(b) M.A. Rawashdeh-Omary, C.L. Larochelle, H.H. Patterson,

Inorg. Chem. 39 (2000) 4527;

(c) We cannot rule out heterogeneity in **3**, because the compound is not stable and single crystals of high optical purity are hard to obtain.