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Blue-, Green- and Non-luminescent Crystals from One Reaction. Isolation and Structural Characterization of a Series of Gold(I)-Siver(I) Heterometallic Complexes Utilizing a Gold Carbene Metalloligand Containing Free Amino Groups

Daniel Rios, Marilyn M. Olmstead, and Alan L. Balch*

Department of Chemistry, University of California Davis, One Shields Avenue, Davis, California 95616

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The metalloligand $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]Cl$, **1**, has been prepared by the reaction of ethylenediamine with $[Au(CNMe)_2]Cl$. Compound **1** crystallized as a luminescent dimer with a Au···Au separation of 3.0224(4) Å. It reacted in solution with silver hexafluorophosphate to form the coordination polymer, $\{[Au\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag(NCMe)](PF_6)_2\}_n$, **2**. The structure of **2** involves a chain of alternating gold(I) and silver(I) ions with a Au···Ag distance of 2.9694(4) Å. The reaction of the metalloligand, **1**, with silver tetrafluoroborate yielded three products: the green luminescent coordination polymer, $\{[Au\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag\text{-}(NCMe)](BF_4)_2\}_n$, **3**, which is analogous to **2**; the non-luminescent binuclear complex, $[Au\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag](BF_4)_2$, **4**; and the blue luminescent complex, $[\{\mu\text{-}C(NHMe)NHCH_2CH_2NH(MeHN)C\}Au_2\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag](BF_4)_{3}\cdot 3(MeCN)$, **5**. Compound **5** involves a bent Au···Ag···Au cation with two different Au···Ag distances (2.9165(8) Å and 3.1743(8) Å). This cation self-associates through a Au···Au interaction of 3.0275(5) Å, which allows the formation of an extended zigzag chain of cations in **5**.

Introduction

Heterobinuclear complexes involving Au(I) and another closed shell or pseudoclosed shell metal ion form a new class of luminescent materials that are gaining attention.[1,2] Suitable metal ions that produce luminescent complexes of this sort include the d^{10} ions, Ag(I) and Hg(II), the d^8 ions Pt(II), Pd(II), Ir(I), and Rh(I), and the s^2 ion Tl(I). The attractive metallophillic interactions that develop between the Au(I) ion and these heterometal ions result from a combination of correlation and relativistic effects.[3]

To obtain new examples of heterobinuclear complexes of Au(I) we have chosen to modify the colorless cation $[Au\{C(NHMe)_2\}_2]^+$, [4] whose structure is shown in Chart 1, in such a fashion that interactions with a second metal center are facilitated. Solutions of $[Au\{C(NHMe)_2\}_2]^+$ are not luminescent at room temperature but become intensely luminescent when frozen in a liquid N_2 bath.[5] Salts of $[Au\{C(NHMe)_2\}_2]^+$ with various anions are also luminescent both at room temperature and at low temperatures.[6,7] The luminescence from these salts and frozen solutions has been attributed to the self-association of the cation through aurophilic interactions that place the gold ions in close proximity. The self-association of a pair of such d^{10} complexes involves the interaction of the filled d_{z^2} orbitals to form a fully occupied set of $\sigma(d_{z^2})$ and $\sigma^*(d_{z^2})$ molecular orbitals, where the z axis falls along the Au···Au vector. [8−10] Additionally, there is a collinear interaction of the p_z orbitals to form a set of empty $\sigma(p_z)$ and $\sigma^*(p_z)$ molecular orbitals. Symmetry-allowed mixing of the filled $\sigma(d_{z^2})$ and $\sigma^*(d_{z^2})$ MOs with the empty $\sigma(p_z)$ and $\sigma^*(p_z)$ MOs stabilizes the filled $\sigma(d_{z^2})$ and $\sigma^*(d_{z^2})$ orbitals. As a result, a net bonding interaction exists between the two metal centers.

The cation $[Au\{C(NHMe)_2\}_2]^+$ is readily prepared by adding methylamine to a solution of the methyl isocyanide complex, $[Au\{CNMe)_2]^+$.[4] By replacing methyl amine with aminoethanol, we have recently reported the formation of the cation, $[Au\{C(NHMe)(NHCH_2CH_2OH)\}_2]^+$.[11] In a related vein, Espinet and co-workers prepared gold carbene

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*To whom correspondence should be addressed. E-mail: albalch@ucdavis.edu.

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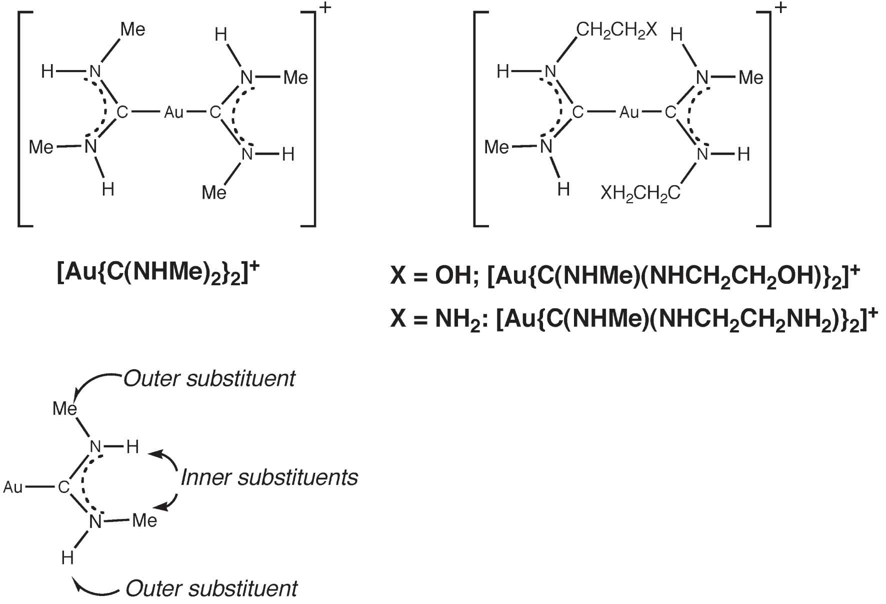
Chart 1. Gold(I) Carbene Complexes



$[Au\{C(NHMe)_2\}_2]^+$

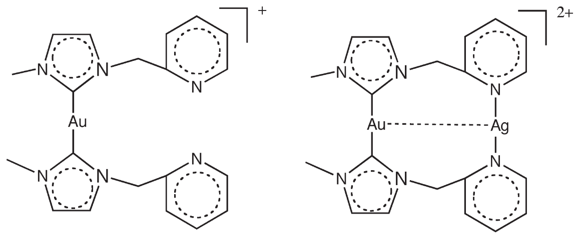
X = OH; $[Au\{C(NHMe)(NHCH_2CH_2OH)\}_2]^+$

X = NH_2: $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]^+$

complexes bearing external pyridyl substituent through the reaction of amines with gold complexes of 2-isocyanopyridine.[12] Here, we utilize the reaction between $[Au\{CNMe)_2]^+$ and ethylenediamine to form $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]^+$. Complexes such as $[Au\{C(NHMe)(NHCH_2CH_2OH)\}_2]^+$ and $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]^+$ are particularly attractive precursors for the formation of luminescent materials since the ligands attached to gold do not absorb light in the visible and near UV regions and are not the source of luminescence. Hence, any luminescence observed will result exclusively from the interactions between the metal ions.

There have been several related efforts that have utilized carbene ligands to bridge silver and gold. Catalano and coworkers have prepared several N-heterocyclic carbene complexes of gold that have pyridyl groups attached and allow coordination to a second metal ion.[13-17] Chart 2 shows some relevant structures. While luminescence is observed from the binuclear silver and gold complexes utilizing these N-heterocyclic carbene ligands as bridges, the ligands themselves are luminescent. Consequently, it is difficult to distinguish between metal-based and ligand-based luminescence in complexes with the sort of N-heterocyclic carbene ligand shown in Chart 2.

Chart 2. Gold N-Heterocyclic Carbene Complexes



$[Au(MeimCH_2py)_2]^+$ $[Au(MeimCH_2py)_2Ag]^{2+}$

Results and Discussion

Preparation and Characterization of the Metalloligand, $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]Cl$, 1. The colorless, luminescent salt $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]Cl$, **1**, was readily synthesized by the addition of dry 1,2-diaminoethane to a solution of $[Au(CNMe)_2]Cl$ that had been formed from a mixture of AuCl(tht) (tht = tetrahydrothiophene) and methyl isocyanide in dry acetonitrile as shown in Scheme 1. The product, which was obtained in 52% yield, is air stable and soluble in polar solvents like methanol and acetonitrile.

This complex crystallizes in the tetragonal space group, $I4_1/acd$, with one-half of the cation and one-half of the chloride anion residing in the asymmetric unit. Crystal data are given in Table 1. Figure 1 shows the structure of the cation as well as the interactions between two cations and the associated chloride ions. The atom numbering for the cation is given in Supporting Information, Figure SI-1. The Au1−C2 distance is 2.040(5) Å and the C2−Au1−C2C angle is 177.6(2)°. The $H_2NCH_2CH_2$- group on the planar carbene ligand is situated in an outer position and extends away from the adjacent cation. The two carbene ligands in the cation are not parallel as they are in many other gold carbene complexes;[5-7] the dihedral angle between them is 52.40(5)°.

As Figure 1 shows, two of the cations form a dimer that is held together by both aurophilic interactions and hydrogen bonding. Within this dimer, the Au1A···Au1B distance is quite short, 3.0224(4) Å. The chloride anions form four intradimer hydrogen bonds to the N−H group of both cations with N−H···Cl distances of 2.29(3) Å. The chloride anions also bridge one dimer to two others via another set of hydrogen bonds to the NH_2 groups with an N−H···Cl

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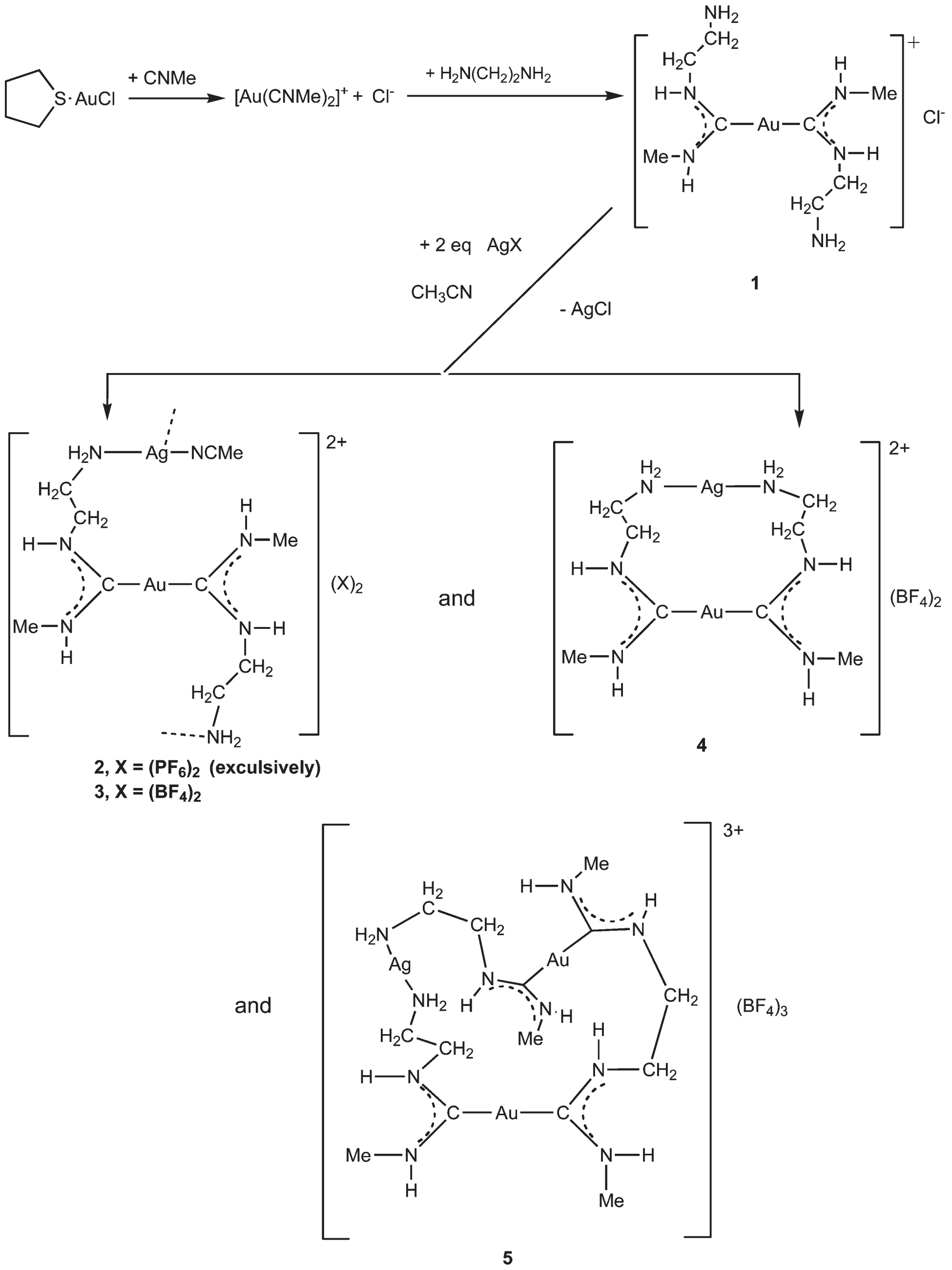
Scheme 1. Preparation of Gold(I) Compounds



distance of 2.42(3) Å. The hydrogen-bonding environment of each chloride ion is a distorted tetrahedron. Colorless [Au{C(NHMe)$_2$}$_2$]Cl·H$_2$O forms a similar dimer but with a longer Au···Au separation of 3.1231(3) Å.[6] The short Au···Au separation in **1** may be facilitated by the interactions of the chloride ion and the NH groups of the two adjacent cations. This interaction brings the two cations into close proximity through neutralization of the charges on the adjoining cations and through hydrogen bond formation. In [Au{C(NHMe)$_2$}$_2$]Cl·H$_2$O the chloride ions form hydrogen bonds to NH groups within a single cation. In contrast, colorless [Au{C(NHMe)(NHCH$_2$CH$_2$OH)}$_2$] Cl consists of widely separated cations with no aurophilic interactions.

Solutions of **1** in methanol are colorless and nonemissive, as are solutions of [Au{C(NHMe)$_2$}$_2$]Cl·H$_2$O and [Au{C(NHMe)(NHCH$_2$CH$_2$OH)}$_2$]Cl. However, crystals of **1** are strongly emissive as seen in the spectra presented in Figure 2. At 298 K, crystalline **1** has an emission maximum at 377 nm with a corresponding excitation maximum at 330 nm and there are only minor changes observed upon cooling to 77 K. The corresponding dimer in [Au{C(NHMe)$_2$}$_2$]Cl·H$_2$O emits at 391 nm with an excitation maximum at 245 nm at 298 K. In these dimers, the interaction between cations involves the overlap of the filled d_{z^2} orbitals and empty p_z orbitals (with the z axis defined by the Au···Au vector) on the gold ions. Thus, the excitation involves a transition from the filled gold $\sigma^*(d_{z^2})$ molecular orbital (the highest occupied molecular orbital,

Table 1. Crystal Data and Data Collection Parameters

	1	2	3	4	5
formula	$C_8H_{22}AuClN_6$	$C_{10}H_{25}AuAgP_2F_{12}N_7$	$C_{10}H_{25}AuAgB_2F_8N_7$	$C_8H_{22}AuAgB_2F_8N_6$	$C_{20}H_{43}Au_2AgB_3F_{12}N_{13}$
formula weight	434.74	838.15	721.83	680.78	1227.91
T, K	90(2)	90(2)	90(2)	90(2)	90(2)
color and habit	colorless needle	light yellow needle	light yellow needle	colorless block	colorless block
crystal system	tetragonal	monoclinic	monoclinic	triclinic	monoclinic
space group	$I4_1/acd$	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$
a, Å	15.2281(2)	18.210(7)	17.536(3))	8.8011(12)	11.8897(8)
b, Å	15.2281(2)	15.601(6)	14.669(2)	9.2949(13)	22.3111(14)
c, Å	25.0483(4)	9.930(5)	10.0644(16)	11.8449(16)	14.3346(9)
α, deg	90	90	90	103.588(2)	90
β, deg	90	120.707(6)	122.378(7)	92.960(2)	97.244(2)
γ, deg	90	90	90	102.064(2)	90
V, Å^3	5808.58(14)	2425.5(18)	2186.4(6)	915.9(2)	3772.2(4)
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
(λ, Å)	(0.71073)	(0.71073)	(0.71073)	(0.71073)	(0.71073)
Z	16	4	4	2	4
d_{calcd}, g cm^{-3}	1.988	2.295	2.193	2.461	2.162
μ, mm^{-1}	10.302	7.086	7.675	9.151	8.367
unique data	2223	2788	2507	4390	9011
restraints	2	0	0	0	6
params. refined	83	155	136	237	464
R1^a	0.027	0.036	0.029	0.024	0.050
wR2^b	0.076	0.101	0.080	0.060	0.114

^{a}For data with $I > 2\sigma I$, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b}For all data. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

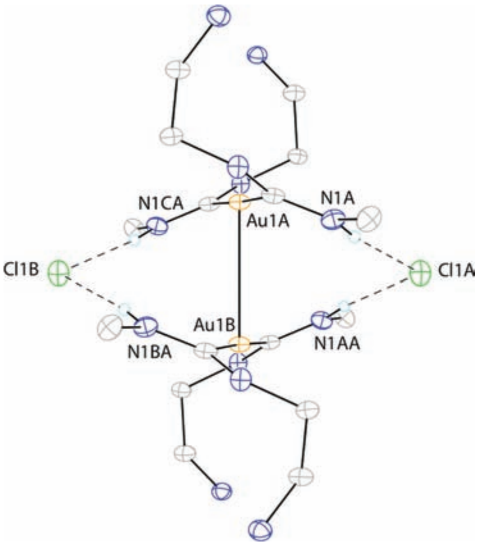


Figure 1. Drawing of **1**, showing the formation of a dimer and the four interactions of the N−H groups and chloride ions within the dimer. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown for clarity. Relevant interatomic distances are Au1A···Au1B = 3.0224(4) Å, N1A···Cl1a = 3.158(4) Å. Atom colors used in all figures are as follows: C, gray; N, blue; Au, orange; Cl, green; Ag, violet; B, red.

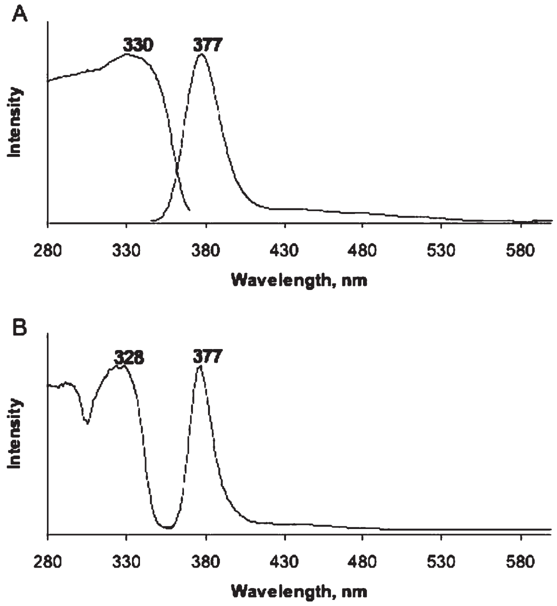


Figure 2. Emission (right) and excitation (left) spectra from colorless crystals of the metalloligand **1**. Panel A shows the emission and excitation at 298 K. Panel B shows the emission and excitation at 77 K.

HOMO) to the empty $\sigma(p_z)$ molecular orbital (the lowest unoccupied molecular orbital, LUMO).[8,18−20] Since 1 has a shorter Au···Au interaction than $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$, the HOMO−LUMO gap is lower in **1** than in $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$. As a consequence the excitation energy observed for **1** is lower than the excitation energy for $[Au\{C(NHMe)_2\}_2]Cl\cdot H_2O$.

The structure of $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]Cl$, **1**, in solution has been examined by ^{13}C and ^1H NMR spectroscopy. The ^{13}C NMR spectrum in dimethyl sulfoxide-d_6 consists of a major set of four resonances at 203.7 ppm for the carbene carbon atom resonance, 52.3 and 43.6 ppm for the methylene carbon atom resonances, and 29.5 ppm for the methyl resonance. These resonances are assigned to the isomeric structure A shown in Chart 3. In this isomer the methyl group is in an inner position and the -$NHCH_2CH_2NH_2$ substituent is in an outer position as found in the crystal structure. These positions for the methyl group and -$NHCH_2CH_2NH_2$ substituent are also consistent with the available data for

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(18) The bonding scheme is analogous to that seen for other binuclear gold(I) complexes such as $[Au^I_2(Ph_2PCH_2PPh_2)_2]^{2+}$,[7,8] and for d^8 metal complexes: $[Rh^I(CNR)_4]_n^{n+}$[9,10] and $[Pt^{II}_2(\mu\text{-}P_2O_5H_2)_4]^{4+}$.[11,12]

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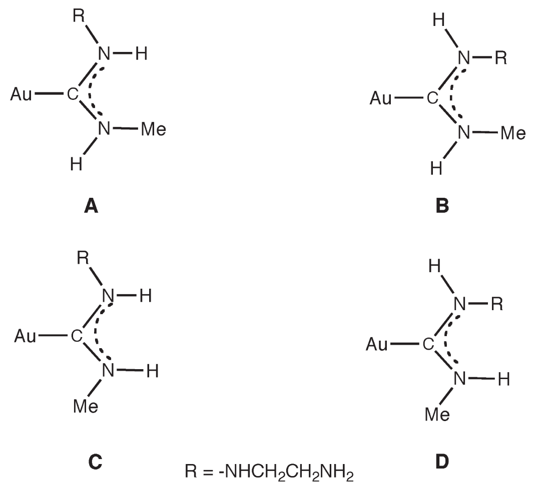
(20) Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1976**, *98*, 2354.

Chart 3. Ligand Isomers in [Au{C(NHMe)(NHCH2CH2NH2)}2]Cl, **1**



$[Au\{C(NHMe)_2\}_2]^+$, for which the isomer with one inner and one outer methyl group (as shown in Chart 1) is the dominant species in solution.[4−7] Additional lower intensity resonances indicate that the three other isomers B, C, and D are also present in solution. Thus, there are three low intensity resonances at 203.8, 204.1, and 204.5 ppm that arise from the carbene carbon atoms of isomers B, C, and D. The 300 MHz ^{1}H NMR spectrum is most informative in the region from 8 to 9 ppm where the clearly resolved carbene N−H resonances occur. The major isomer A produces two equally intense resonances: a quartet at 8.52 ppm with J = 17 Hz due to the N−H group bound to a methyl group and a broadened triplet at 8.17 ppm due to the N−H moiety adjacent to the $CH_2CH_2NH_2$ substituent. Additionally, in this region there are three quartets at 8.46, 8.60, and 8.40 ppm and three triplets at 8.38, 8.41, and 8.90 ppm that arise from the isomers B, C, and D. Isomer A produces a methyl doublet at 2.61 ppm with J = 17 Hz with overlapping doublets due to the minor isomers at 2.65 and 2.7 ppm. A complex set of overlapping methylene resonances is seen in the 2.9−3.5 ppm region.

The laser desorption mass spectrum of $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]Cl$, **1**, in the positive ion mode shows an intense peak at 399.12 m/z (calcd. 399.16 m/z) due to the cation.

Preparation and Characterization of the Coordination Polymer, $\{[Au\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag(NCMe)](PF_6)_2\}_n$, 2. Addition of silver hexafluorophosphate to a suspension of **1** in acetonitrile afforded nearly colorless needles of **2** as the only crystalline product in 47% yield, as shown in Scheme 1.

This complex crystallizes with half of Au1, Ag1, one carbene ligand, a hexafluorophosphate ion, and an acetonitrile molecule in the asymmetric unit. Figure 3 shows the extended polymeric nature of the complex. The atomic numbering in the asymmetric unit is given in Supporting Information, Figure SI-2. The gold ion is situated on a center of symmetry. Thus, the core of the cation, which is composed of atoms C1N1C2AuN2C3 and their centrosymmetrically generated counterparts, is planar. The Au−C2 distance is 2.090(5) Å and the C2−Au1−C2′ angle is 180°. The silver ion (Ag1) is coordinated to N3

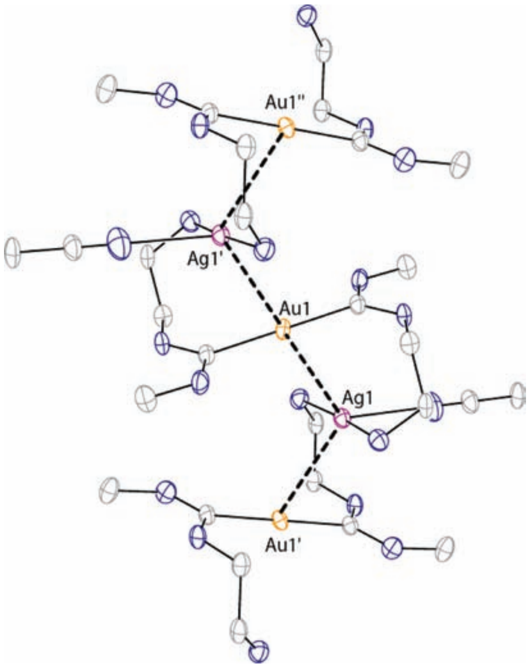


Figure 3. Drawing of a chain of metalloligands bonding to silver atoms in compound **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown for clarity.

with an Ag1−N3 distance of 2.247(4) Å and to an acetonitrile molecule with a much longer Ag1−N4 distance of 2.612(8) Å. The N3−Ag1−N3′ angle is 173.1(2)° and the N3−Ag1−N4 angle is 93.43(11)°. The sum of the N3−Ag1−N3′, N3−Ag1−N4, and N3′−Ag1-N4 angles is 360.0°; thus the AgN3N3′N4 unit is planar. The Au1···Ag1 distance is 3.0141(11) Å, and there is an extended chain of alternating two-coordinate gold and three-coordinate silver ions that runs throughout the crystal. In this chain, the Ag···Au···Ag portion is strictly linear, while the Au···Ag···Au portion is bent at an angle of 110.90(4)°. The anion is hydrogen-bonded to the outer H−N group of the carbene ligand with an N1···F2 distance of 2.936(5) Å and to the inner N−H groups with an N2···F4 distance of 3.154 Å.

The polymeric structure of **2** is related to the structure of several coordination polymers prepared by Catalano and co-workers using gold complexes of N-heterocyclic carbene ligands shown in Chart 2[14−17] Thus, for example $\{[AuAg(NCMe)(MeimCH_2py)_2](BF_4)_2\}_n$ crystallizes to form a chain of alternating three-coordinate silver and two-coordinate gold ions with Au···Ag separations (2.9239(6), 2.8912(6), 2.8633(6), and 2.8873(6) Å)[16] that are even shorter than the value of 3.0141(11) Å seen in **2**. However, the angular arrangement in **2** differs significantly from that in $\{[AuAg(NCMe)(MeimCH_2py)_2](BF_4)_2\}_n$. While in **2**, the Ag···Au···Ag portion is linear, and the Au···Ag···Au portion is bent, in $\{[AuAg(NCMe)(MeimCH_2py)_2](BF_4)_2\}_n$ the Ag···Au···Ag part is bent with angles of 144.06(3) and 135.20(2)° as is the Au···Ag···Au portion with angles of 175.37(3) and 166.85(2)°.

Crystals of **2** are strongly luminescent. They produce a green luminescence at room temperature, but, upon cooling to 77 K, the color of the emission becomes blue. Figure 4 shows relevant spectra. At 298 K the emission consists of a single band at 507 nm. At 198 K, there are two emission bands at 406 and 476 nm. Upon cooling to 77 K the low energy emission band loses intensity relative to the emission band at 413 nm, which dominates the spectrum. The dual emission features seen best at 198 K are attributed to fluorescence at 406 nm and phosphorescence at 476 nm.

Compound **2** dissolves only slightly in methanol, acetonitrile, or acetone with sonocation to give colorless, nonluminescent solutions. It is likely that the polymeric nature of **2** is disrupted when the compound dissolves in these potentially coordinating solvents and that these solutions contain the component ions.

Formation of Three Products from the Reaction of the Metalloligand, 1, with Ag(BF_4). In contrast to the reaction of **1** with Ag(PF_6), which produces only the coordination polymer **2**, the reaction of **1** with Ag(BF_4) yields three products. Figure 5 shows photographs of crystalline products that form in acetonitrile solution after removal of silver chloride and layering of diethyl ether over the acetonitrile. The photograph on the left shows the sample under ambient light. A number of nearly colorless crystals are readily seen. The photograph on the right shows the sample under irradiation with UV light. The crystals at the bottom display a blue luminescence, while the crystals a bit further up in the tube show a green luminescence. The crystals at the top of the photograph are not emissive. The green-glowing crystals of compound **3** were separated from the non-luminescent crystals of compound **4** and the blue-glowing crystals of compound **5** by careful washing with acetonitrile, which dissolved compounds **4** and **5**. Samples of each type of crystal could also be manually separated and were characterized by single crystal X-ray diffraction.

Coordination Polymer, {[Au{μ-C(NHMe)($NHCH_2CH_2NH_2$)}$_2$Ag(NCMe)](BF_4)$_2$}$_n$, 3. The green-glowing crystals of compound **3** contain the coordination polymer, {[Au{μ-C(NHMe)($NHCH_2CH_2NH_2$)}$_2$Ag(NCMe)](BF_4)$_2$}$_n$, that is an analogue of **2**. As the data in Table 1 show, crystals of compound **3** are nearly isostructural with those of compound **2**. Thus, both contain chains of alternating two-coordinate gold and three-coordinate silver ions. Table 2 allows comparison of the key structural parameters in the two polymers. The Au1···Ag1 distance is shorter in **3** (2.9694(4) Å) than in **2** (3.0139(11)), and the Au1···Ag1···Au1′ angle is wider in **3** (115.850(19)°) than in **2** (110.91(4)°).

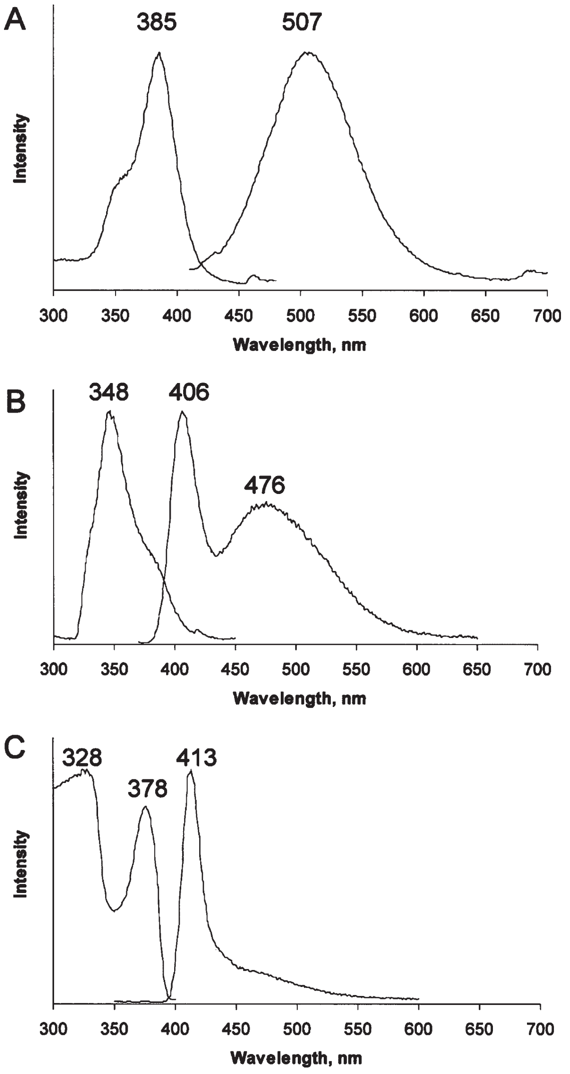


Figure 4. Emission (right) and excitation (left) spectra from light yellow crystals of compound **2**. Panel A at 298 K; panel B at 198 K; and panel C at 77 K.

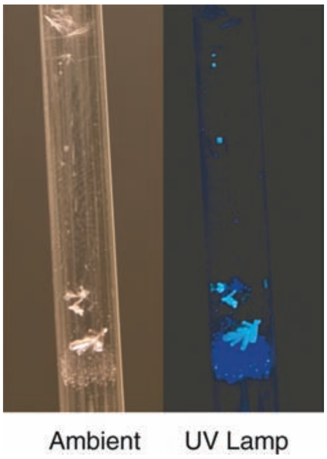


Figure 5. Photographs of a tube containing the products from the reaction of the metalloligand, **1**, with Ag(BF_4). The photograph on the left shows the sample taken under room light. The photograph on the right shows emission from the sample under UV irradiation. Notice the fine, non-emissive crystals at the top of the tube photographed under ambient light.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Coordination Polymers **2** and **3**

	2	3
Bond Distances (Å)		
Au1···Ag1	3.0139(11)	2.9694(4)
Au1−C2	2.092(5)	2.044(5)
Ag1−N3	2.247(4)	2.194(4)
Ag1−N4	2.621(8)	2.714(4)
Bond Angles (deg)		
Ag1···Au1···Ag1′	180	180
Au1···Ag1···Au1′	110.91(4)	115.850(19)
C2−Au1−C2′	180	180
N3−Ag1−N3′	173.2(2)	176.7(2)
C2′−Au1−Ag1	112.07(12)	109.55(12)
C2−Au1−Ag1	67.93(12)	70.45(12)

The luminescence from **3** at 298 K arises from an emission band at 545 nm, which has an excitation maximum at 390 nm. Thus, the excitation and emission behavior of **3** at 298 K is similar to that of **2**. However, on cooling to 77 K the emission maximum of **3** shifts only slightly to 540 nm. The marked changes in luminescence seen for **2** in Figure 5 are absent for **3**.

Binuclear Complex, $[Au\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag](BF_4)_2$, 4. Crystallographic results for the non-luminescent crystals of compound **4** reveal that it is the binuclear complex, $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag](BF_4)_2$. Figure 6 shows a drawing of the complex. Both amino arms of the metalloligand bind the same silver ion in a chelating fashion to produce a binuclear cation. The Au1···Ag1 distance is 3.1049(5) Å. The C2−Au1−C6 angle (172.53(14)°) is slightly bent. The N3−Ag1−N6 angle (169.84(12)°) is more strongly bent.

The structure of $[Au\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag](BF_4)_2$, **4**, is related to that of the binuclear complex, $[Au(MeimCH_2py)_2Ag]^{2+}$, shown in Chart 2. In $[Au(MeimCH_2py)_2Ag]^{2+}$ the Au···Ag separation is 3.0318(5) Å, while in $[Au\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag](BF_4)_2$, **4**, it is a bit longer, 3.1049(5) Å.

In $[Au\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag](BF_4)_2$, **4**, one anion is hydrogen bonded to the N−H groups of the carbene ligands with N1···F8 and N4···F6 distances of 2.916(4) Å and 2.900(4) Å, respectively. The other anion is hydrogen bonded to the amino arm NH_2 group with N3···F1 and N3···F2 distances of 3.077(4) Å and 3.146 (4) Å, respectively.

Figure 7 shows the interactions between two binuclear complexes. The two complexes pack about a center of symmetry. There is a weak interaction between a silver atom of one unit and a fluorine atom of another unit with an Ag1−F7 distance of 2.939(4) Å.

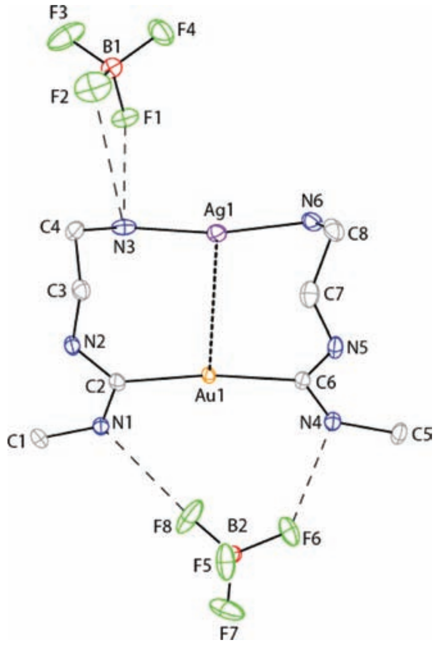


Figure 6. Drawing that shows the incorporation of a silver atom to the metalloligand and its interaction with adjacent anions in compound **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown for clarity. Relevant interatomic distances are as follows: Au1···Ag1 = 3.1049(5) Å, N1···F8 = 2.916(4) Å, N3···F1 = 3.077(4) Å, N3···F2 = 3.146(5) Å, N4···F6 = 2.909(4) Å.

Although the binuclear complex **4** is non-emissive at room temperature, it does become emissive upon cooling. At 77 K, the crystals show emission centered at 365 nm with excitation maxima at 300 and 275 nm. The emission spectrum resembles that of the crystals of **1**. Thus, the emission characteristics of **1** and **4** reflect the similar characteristics of the Au···Au and Au···Ag interactions.

Blue Luminescent Complex, $[\{\mu\text{-}C(NHMe)NHCH_2CH_2NH(MeHN)C\}Au_2\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}Ag](BF_4)_3\cdot 3(MeCN)$, 5. The structure of this complex, which contains two gold ions and one silver ion, three anions, and three uncoordinated acetonitrile molecules, is shown in Figure 8. Remarkably, compound **5** contains a bridging dicarbene ligand that connects the two gold ions. We presume that this bridging dicarbene ligand was formed by nucleophilic attack of an amino arm of **1** upon a carbene ligand of another cation with the subsequent release of methylamine. Each gold ion is coordinated by two carbene ligands in nearly linear fashion (angles: C2−Au1−C6, 174.3(4); C12−Au2−C9, 176.4(4)°), while the silver ion is coordinated to NH_2 groups from the amino arms of carbene ligands on each of the two gold ions. The Ag1−N3 and Ag1−N10 distances are 2.167(7) and 2.180 (8) Å, respectively, and the N3−Ag1−N10 angle is 157.0 (3). The Au1···Ag1 distance (2.9165(8) Å) is significantly shorter than the Au2···Ag1 distance (3.1743(8) Å). Au1 and Au2 are separated by 4.981 Å. The Au1···Ag1···Au2 angle is 93.00(2)°. The three tetrafluoroborate ions are connected by hydrogen bonds to the outer N−H groups of the three different carbene ligands in the complex.

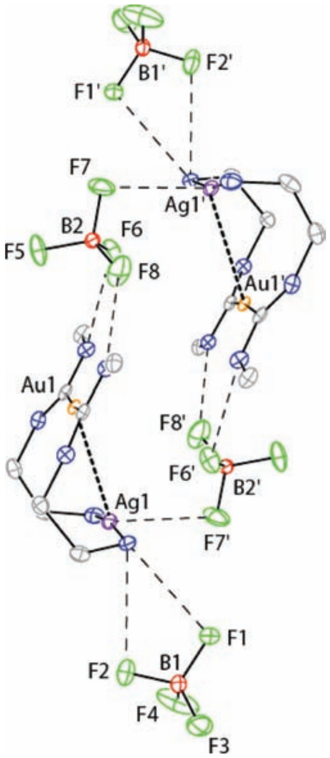


Figure 7. Illustration that shows the extended network of hydrogen bonding between asymmetric units and anions in compound **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown for clarity. Relevant interatomic distances are Ag1···F7 = 2.939(3) Å.

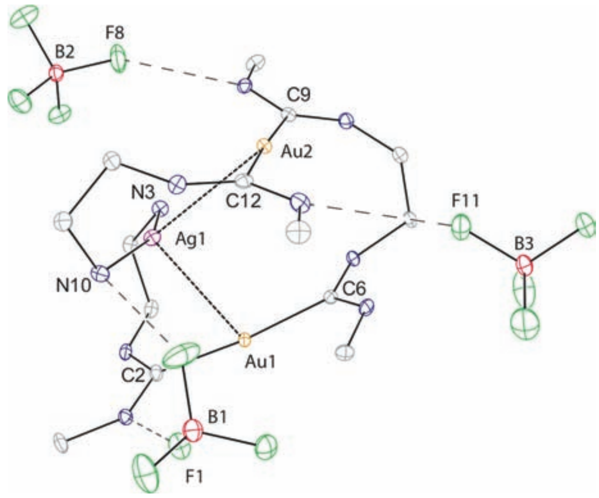


Figure 8. Drawing showing the bonding of a silver atom and hydrogen bonding to two anions in compound **5**. Thermal ellipsoids are shown at the 50% probability level. For clarity, hydrogen atoms are not shown.

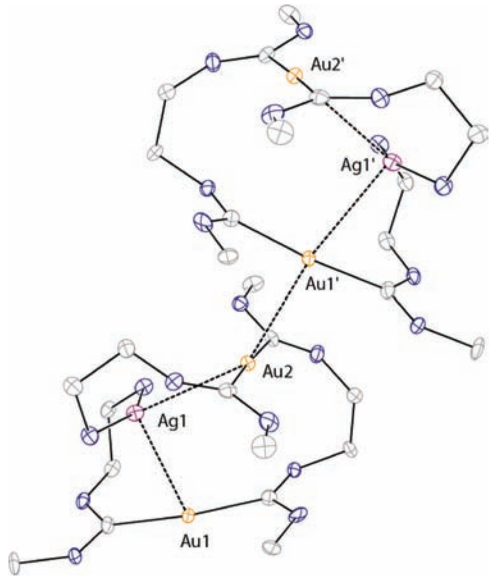


Figure 9. Illustration showing the aurophillic interaction between two cations in compound **5**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are not shown for clarity.

To add to the complexity of this structure, the unit shown in Figure 8 self-associates through Au1′···Au2 interactions to form extended chains. Figure 9 shows the interaction between two of the [{μ-C(NHMe)NHCH$_2$CH$_2$NH(MeHN)C}Au$_2${μ-C(NHMe)-(NHCH$_2$CH$_2$NH$_2$)}Ag]$^{3+}$ ions. The Au1′···Au2 distance is 3.0275(5) Å. Figure 10 shows the extended chain of metal ions that extends through the crystal and gives some of the dimensions in this portion **5**.

Crystals of **5** are emissive and produce a broad band at 449 nm with an excitation maximum at 356 nm as seen in the spectra in Figure 11. The emission spectrum is essentially the same at 298 and 77 K except for the anticipated narrowing of the emission band. The low energy observed for this emission and its excitation relative to the binuclear Au···Au and Au···Ag units in **1** and **4** is likely to result from the extended chain of metal ions producing a narrowing of the gap between the filled d and empty p orbitals that are involved in the extensive set of metallophillic interactions in compound **5**.

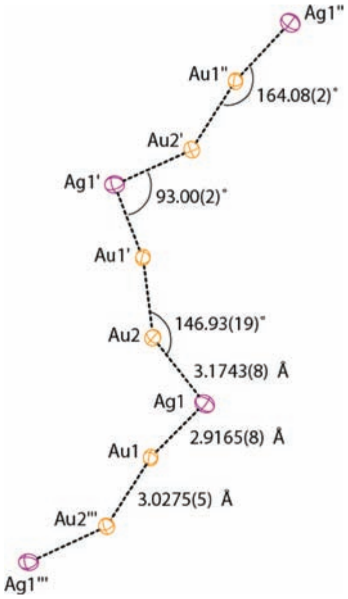


Figure 10. Drawing showing the metallic interactions and angles in compound **5**. Thermal ellipsoids are shown at the 50% probability level.

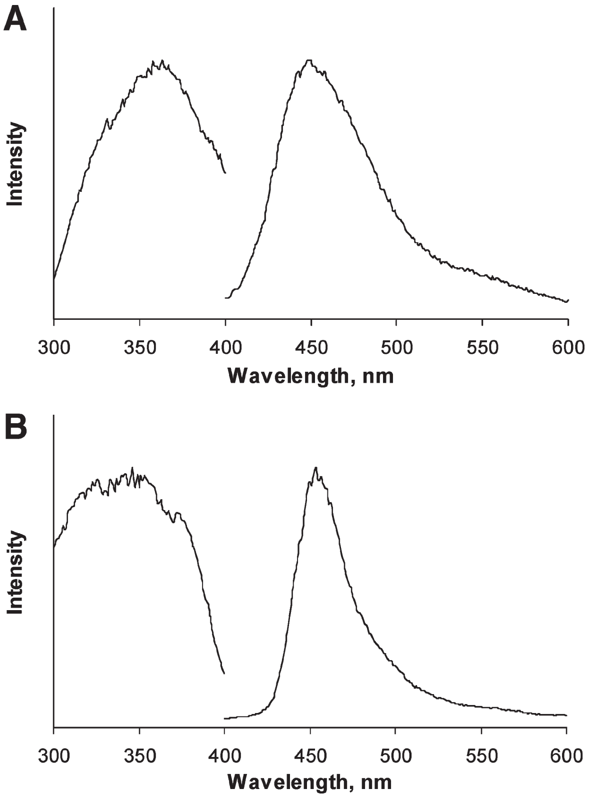


Figure 11. Emission (right) and excitation (left) spectra from colorless crystals of compound **5**. Panel A at 298 K; panel B at 77 K.

Conclusions

The results presented here shows that the metalloligand **1** has been prepared and can be used to bind to silver(I) metals to make an interesting array of mixed gold−silver complexes with short gold(I)-to-silver(I) interactions. The products obtained depend upon the anion present. The luminescence of all of these complexes can be readily attributed to the metal–metal interactions present in the solids, since the monomeric parent gold carbene cation, $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]^+$, is non-emissive. The metalloligand **1** has the potential for forming bi and polynuclear complexes in several ways. As demonstrated in the formation of compounds **2**, **3**, and **4**, the free amino arm of the carbene ligand can directly coordinate to another metal center as it does here with silver. The free amino arm can also interact with other ligands as it does in forming **5**. In this case, a free amino arm of **1** has attacked another carbene ligand to produce an unusual bridging dicarbene ligand that binds two different gold ions. The free amino substituent in the metalloligand **1** should also readily undergo Schiff base condensations with aldehydes and ketones that can produce an array of new sites for metal ion coordination. Further work on the construction of polynuclear complexes utilizing the metalloligand **1** is in progress.

Experimental Section

Materials. Literature procedures were used for the preparation of methyl isocyanide[21] and AuCl(tht).[22] All solvents and 1,2-diaminoethane were dried before use.

Preparation of $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]Cl$, 1. A 0.100 g (0.312 mmol) portion of AuCl(tht) was dissolved in 300 mL of acetonitrile. Subsequently 100 μL of methyl isocyanide were added. The mixture was allowed to stir for 30 min. A 200 μL (2.99 mmol) portion of 1,2-diaminoethane was added, and a white precipitate formed. After stirring for an hour, the white solid was collected and washed with diethyl ether. Yield: 0.071 g (52.4%). Colorless needles suitable for X-ray diffraction were grown by slow diffusion of diethyl ether to a concentrated methanol solution of this complex in a 5 mm diameter glass tube. Infrared spectrum: 750 m, 823 m, 865 m, 972 m, 994 m, 1087 w, 1095 w, 1168 m, 1191 w, 1263 m, 1311 w, 1349 m, 1383 m, 1435 m, 1471 m, 1539 m, 1563 m, 2850 m, 2902 m, 2979 m, 3049 m, 3188 vs (N − H), 3255 vs (N − H), cm^{-1}.

Preparation of $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag(NCMe)](PF_6)_2$, 2. A 50 mL round-bottom flask was charged with a magnetic bar, 0.050 g (0.115 mmol) of $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]Cl$, 0.059 g (0.233 mmol) of silver hexafluorophosphate, and 30 mL of dry/degassed acetonitrile that was cooled in an ice–water bath. The mixture was stirred for 2 h at which point a colorless precipitate of silver chloride was present. The mixture was filtered through Celite, and the volume of the filtrate reduced to 2 mL. Slow diffusion of diethyl ether to the resulting clear solution afforded light yellow needles of **2**. Remarkably, this reaction only produces one product. Yield: 0.045 g (46.7%). Infrared spectrum: 673 w, 740 w, 815 sh, 917 w, 1015 w, 1025 w, 1047 w, 1067 w, 1124 w, 1167 w, 1206 w, 1321 w, 1351 w, 1394 w, 1437 w, 1462 w, 1525 w, 1581 m, 2843 w, 2936 w, 3314 w, 3360 vs (N − H), 3440 vs (N − H), cm^{-1}.

Reaction of $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]Cl$, 1, with Silver Tetrafluoroborate: Preparation of 3, 4, and 5. A 50 mL round-bottom flask was charged with a magnetic bar, 0.050 g (0.115 mmol) of $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]Cl$, 0.045 g (0.231mmol) of silver tetrafluoroborate, and 30 mL of dry/degassed acetonitrile, which was cooled in an ice–water bath. The mixture was stirred for 2 h at which point a colorless precipitate of silver chloride was present. The mixture was filtered through Celite, and the filtrate reduced in volume to 2 mL. Slow diffusion of diethyl ether to the resulting clear solution afforded crystals of **3**, **4**, and **5**. The relative yields are **4** > **3** > **5**. Crystals of compound **3** were isolated by careful addition of small quantities of acetonitrile to the mixture of all three products. The acetonitrile dissolves compounds **4** and **5** immediately and left compound **3** as a solid that was removed by filtration and washed with diethyl ether. The colorless crystals of compounds **4** and **5** are non-luminescent and blue luminescent, respectively. Small quantities of each of these two compounds were separated from the mixture of products manually under a microscope while using UV-light. During this procedure, adequate UV protection of the eyes is required. As a safety precaution only sufficient material for crystallographic and spectroscopic examination was separated in this fashion.

X-ray Crystallography and Data Collection. The crystals were removed from the glass tubes in which they were grown together with a small amount of mother liquor and immediately coated with a hydrocarbon oil on a microscope slide. A suitable crystal of each compound was mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker SMART CCD with graphite monochromated Mo Kα radiation at 90(2) K. Check reflections were stable throughout the data collection.

The structures were solved by direct methods and refined using all data (based on F^2) using the software SHELXTL 5.1. A semiempirical method utilizing equivalents was employed to correct for absorptions. Hydrogen atoms were added geometrically and refined with a riding model.

Physical Measurements. Infrared spectra were recorded as pressed KBr pellets on a Matteson Galaxie Series FTIR 3000 spectrometer. Fluorescence excitation and emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrophotometer.

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Supporting Information Available: Figures SI-1 and SI-2 showing the atomic labeling for compounds **1** and **2**. X-ray crystallographic files in CIF format for $[Au\{C(NHMe)(NHCH_2CH_2NH_2)\}_2]Cl$, **1**, $\{[Au\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2\text{-}Ag(NCMe)](PF_6)_2\}_n$, **2**, $\{[Au\{\mu\text{-}C(NHMe)\text{-}(NHCH_2CH_2NH_2)\}_2Ag(NCMe)](BF_4)_2\}_n$, **3**, $[Au\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag](BF_4)_2$, **4**, and $[\{\mu\text{-}C(NHMe)NHCH_2CH_2NH(MeHN)C\}Au_2\text{-}\{\mu\text{-}C(NHMe)(NHCH_2CH_2NH_2)\}_2Ag](BF_4)_3\cdot 3(MeCN)$, **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] Uson, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85.