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Polymorphs and Aurophilic Interactions in Colorless Crystals of Au_2(μ-1,2 bis-(diphenylarsino)ethane)X_2, (X = Cl, Br, I)

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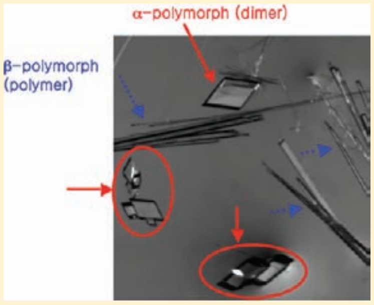
S *Supporting Information*

ABSTRACT: Solutions containing the components Au^+, dpae (dpae is 1,2 bis-(diphenylarsino)ethane), and X^- (X is Cl, Br, or I) can produce two different types of crystals with the composition $Au_2(\mu\text{-dpae})X_2$: colorless blocks and colorless needles. Crystallographic studies of these crystals show that they are polymorphs with different structural motifs. In the α-polymorphs, which are isostructural, individual molecules of $Au_2(\mu\text{-dpae})X_2$ form discrete dimers through two identical Au⋯Au contacts. In the β-polymorphs, which each have unique crystallographic parameters, the $Au_2(\mu\text{-dpae})X_2$ molecules assemble into polymeric chains through aurophilic interactions. The Au⋯Au contacts in the α-polymorph (3.1163(2), 3.1064(3), and 3.0842(2) Å for Cl, Br, I, respectively) are somewhat shorter than those in the β-polymorph (3.1668(3), 3.1042(8), and 3.1046(2) for Cl, Br, I respectively). The systematic study we now report shows an increase in the strength of this aurophilic interaction for the α-form in the series X = Cl < Br < I, which is in good agreement with theoretical studies by Pyykkö and his co-workers.



■ INTRODUCTION

Crystallization of two-coordinate d^{10} and four-coordinate d^8 transition metal complexes can result in self-association through the formation of weak bonds between the metal centers.[1,2] In the case of two-coordinate gold(I) complexes, a combination of relativistic and correlation effects can induce an attractive interaction between two gold(I) ions.[3,4] Such aurophilic interactions have been shown to have a bond strength that is comparable to a hydrogen bond.[5,6] In metallic gold the distance between adjacent gold atoms is 2.89 Å, while the separation between two gold(I) ions that may be expected from their van der Waals radii is about 3.6 Å.[7,8] Consequently, if the Au⋯Au separation is 3.6 Å or less, some degree of aurophilic interaction may be involved, and numerous compounds show the effects of aurophilic interactions in their structures and physical properties.[9]

In the absence of bridging ligands that force the proximity of two gold(I) ions, it is the crystallization process itself that produces the aurophilic interactions through self-association. Crystallization of some substances can be complicated by the existence of different polymorphs, isomers at the single crystal level in which the packing of the component molecules and their interactions with one another differ.[10] A number of gold(I) complexes that exhibit aurophilic interactions in the solid state form polymorphs. As outlined below, many of these polymorphs are luminescent and show interesting variations in their emission that depends upon the particular polymorph examined.[1]

The salt $[(C_6H_{11}NC)_2Au^I](PF_6)$ crystallizes in two polymorphic forms: yellow crystals with green emission and colorless crystals with blue luminescence.[11] The colorless polymorph forms in the monoclinic space group $P2_1/c$ and produces extended, strictly linear stacks of cations with a Au⋯Au distance of 3.1822(3) Å. The yellow polymorph crystallizes in the orthorhombic space group $P2_12_12_1$. There are four cations in the asymmetric unit that form a bent chain. The Au⋯Au distances between these cations are unusually short: Au---Au, 2.9803(6), 2.9790(6), 2.9651(6), and 2.9643(6) Å.

The neutral complex $(Me_2PhP)Au^ICl$ self-associates in two different fashions to produce two polymorphs.[12] In one polymorph two molecules associate to form a dimer with a Au---Au separation of 3.230(2) Å, while in the other polymorph a trimer forms with somewhat shorter Au---Au separations of 3.091(2) and 3.120(2) Å.. These two polymorphs show different luminescent behavior.[13]

The cyclic trimers $Au^I_3(RN{=}COMe)_3$ (where R = *n*-Pent or Me) also form polymorphs with varying types of aurophilic interactions between the three gold ions in the 9-membered ring.[14] Three different polymorphic forms of $Au^I_3(MeN{=}COMe)_3$ have been crystallized. One of these polymorphs shows the unusual property of solvoluminescence and has a remarkably long-lived excited state.[15,16] This polymorph has the cyclic trimers arranged into two types of columns: well-ordered, trigonal prismatic stacks and hexagonally disordered stacks. None of the other polymorphs of the cyclic trimers $Au^I_3(RN{=}COMe)_3$ have such stacks, and none have the long-lived emission required for solvoluminescence.

Crystals of $[\mu_3\text{-S}(Au^ICNC_7H_{13})_3](SbF_6)$ undergo an unusual polymorphic phase change upon cooling. In these crystals, the trimer self-associates to produce a pseudo-octahedral arrangement of gold ions that interact through both intra- and

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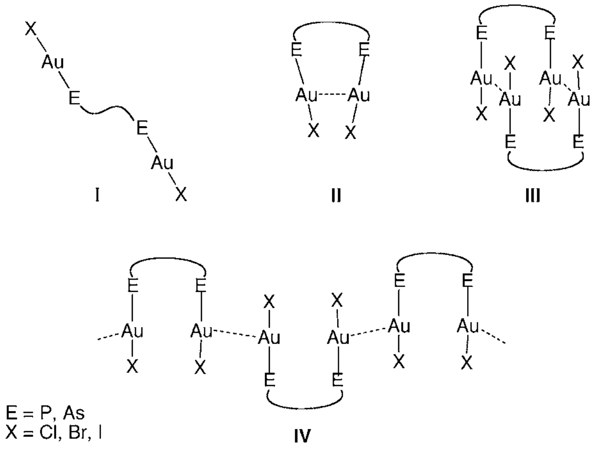
interionic interactions.[17] Cooling the crystal results in a reversible, polymorphic phase change at about 150 K that produces lengthening of the aurophilic interactions between one pair of cations, while inducing shortening of the aurophilic contacts between the other pair of cations. The phase change is accompanied by changes in the luminescence of the cluster.

Some salts of the linear anion, $[Au(CN)_2]^-$ exist in polymorphic forms with varying interactions between the anions. Thus, $Zn[Au(CN)_2]_2$ forms four polymorphs, three of which are luminescent.[18] The coordination polymer, $Cu[Au(CN)_2]_2 \cdot 2$(dimethyl sulfoxide), forms both a blue and a green polymorph with the copper ions in five and six-coordinate environments, respectively.[19]

Here we report the formation of a series of polymorphs involving complexes of the type $Au_2(\mu\text{-dpae})X_2$ (dpae is 1,2 bis(diphenylarsino)ethane). Molecules of this sort with a somewhat flexible bridging ligand can form a variety of different structures as outlined in Scheme 1.[20,21] In the simplest of cases (form **I**) there may be no aurophilic interactions whatsoever. If the ligand bridge permits, an internal aurophilic interaction may occur as shown in form **II**. Self-association through aurophilic interactions may lead to the creation of a dimer (form **III**) or to an extended polymer (form **IV**).[17−22] For example, $Au_2(\mu\text{-cis-dppee})X_2$, where dppee is cis-bis(diphenylphosphine)ethylene, has an internal aurophillic interaction (form **II**) because the rigid backbone holds the two gold ions close together with an Au1---Au2 distance of 3.05(1) Å (for X = Cl)[23] or 2.9526(5) (for X = I).[24,25] On the other hand, in $Au_2(\mu\text{-trans-dppee})Cl_2$ the trans nature of the ligand forces the two gold ions within the molecule to be widely separated, with an intramolecular Au---Au separation of 7.742(1) Å.[26] However, $Au_2(\mu\text{-trans-dppee})X_2$ self-associates to produce a polymer (form **IV**) through aurophilic interactions, Au---Au, 3.043(1) Å (for X = Cl)[26] or 3.2292(7) Å (for X = I).[24] In $Au_2(\mu\text{-dpae})X_2$ the ligand backbone is more flexible, and the opportunities to form different structures is greater than in the case of $Au_2(\mu\text{-cis (or trans)-dppee})Cl_2$.

Scheme 1. Aurophilic Interactions in Ligand-Bridged Binuclear Gold Complexes



■ RESULTS

Synthesis and Crystal Growth. The two polymorphic forms of dpae-bridged digold halide complexes were synthesized from the simple reaction of Au(tht)Cl, Au(tht)Br, or AuI with dpae. For each halide the α- and β-polymorphs crystallized concomitantly from dichloromethane/diethyl ether. These polymorphs had very distinct crystal morphologies as shown in Figure 1 for a representative example, $Au_2(\mu\text{-dpae})I_2$. The α-polymorph was present as colorless blocks, while the β-polymorph invariably grew as colorless needles. Individual crystals of each polymorph were obtained by manual separation. The infrared spectra of these compounds in both polymorphic forms are given in the Experimental Section. There are very few differences in these spectra. The melting points of the six crystalline phases are also recorded in the Experimental Section. In general, the α-polymorph melts at a temperature that is 7 to 10 °C higher than the corresponding β-polymorph. Attempts to obtain mass spectra directly from individual crystals were unsuccessful. However, positive ion mode MALDI mass spectra obtained from evaporated solutions of the crystals revealed the presence of the $[Au_2(\mu\text{-dpae})X]^+$ ion in the gas phase.

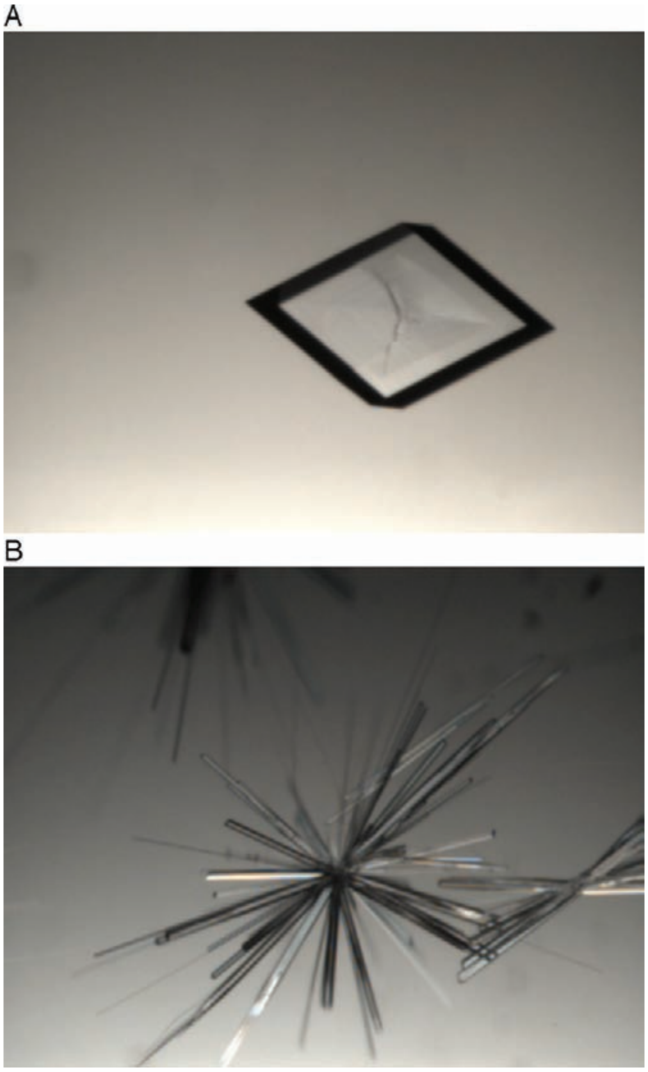


Figure 1. Photographs of crystals of $Au_2(\mu\text{-dpae})I_2$. (**A**) A block of the α-polymorph. (**B**) Needles of the β-polymorph.

Molecular and Supramolecular Structures of the α-Polymorphs. The α-polymorphs of $Au_2(\mu\text{-dpae})X_2$, where X = Cl, Br, and I, are isostructural. Crystallographic data are presented in Table 1, while selected bond lengths and angles are listed in Table 2. The structure of a representative example,

Table 1. Crystal Data and Structure Refinement for $Au_2(\mu\text{-dpae})X_2$

	α-$Au_2(\mu\text{-dpae})Cl_2$	α-$Au_2(\mu\text{-dpae})Br_2$	α-$Au_2(\mu\text{-dpae})I_2$
formula	$C_{26}H_{24}As_2Au_2Cl_2$	$C_{26}H_{24}As_2Au_2Br_2$	$C_{26}H_{24}As_2Au_2I_2$
formula weight	951.12	1040.03	1134.03
T, K	90(2)	90(2)	90(2)
color and habit	colorless block	colorless block	colorless block
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	12.7185(5)	12.8317(7)	13.0586(4)
b, Å	11.2726(5)	11.4253(6)	11.7775(4)
c, Å	19.1425(7)	19.4144(9)	19.7245(5)
α, deg	90	90	90
β, deg	109.766(2)	110.402(3)	111.741(2)
γ, deg	90	90	90
V, Å^3	2582.77(18)	2667.7(2)	2817.80(15)
Z	4	4	4
d_{calc}, g cm^{-3}	2.446	2.589	2.673
μ, mm^{-1}	14.110	16.457	14.936
unique data	5954	6134	6484
restraints	0	0	0
params.	289	289	289
R1^a	0.0174	0.0225	0.0151
wR2^b	0.0366	0.0445	0.0333
	β-$Au_2(\mu\text{-dpae})Cl_2$	β-$Au_2(\mu\text{-dpae})Br_2$	β-$Au_2(\mu\text{-dpae})I_2$
formula	$C_{26}H_{24}As_2Au_2Cl_2$	$C_{26}H_{24}As_2Au_2Br_2$	$C_{26}H_{24}As_2Au_2I_2$
formula weight	951.12	1040.03	1134.03
T, K	90(2)	90(2)	90(2)
color and habit	colorless needle	colorless needle	colorless needle
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	11.4453(6)	11.5476(11)	11.5408(7)
b, Å	11.5553(6)	15.3861(14)	12.1003(8)
c, Å	21.0671(11)	30.518(3)	12.3726(8)
α, deg	85.9628(7)	90	115.888(2)
β, deg	80.4396(7)	100.319(2)	93.849(2)
γ, deg	69.7158(7)	90	111.803(2)
V, Å^3	2576.9(2)	5334.5(9)	1387.78(15)
Z	4	8	2
d_{calc}, g cm^{-3}	2.452	2.590	2.714
μ, mm^{-1}	14.143	16.459	15.163
unique data	15503	12289	6371
restraints	0	0	0
params.	578	547	289
R1^a	0.0278	0.0407	0.0164
wR2^b	0.0605	0.1022	0.0409

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for α-$Au_2(\mu\text{-dpae})X_2$

	α-$Au_2(\mu\text{-dpae})Cl_2$	α-$Au_2(\mu\text{-dpae})Br_2$	α-$Au_2(\mu\text{-dpae})I_2$
	Distance, Å		
Au1---Au2A intermolecular	3.1163(2)	3.1064(3)	3.0842(2)
Au1---Au2 intramolecular	6.5120(3)	6.5613(4)	6.6714(3)
Au1−As1	2.3384(3)	2.3452(5)	2.3571(3)
Au2−As2	2.3397(3)	2.3453(4)	2.3590(3)
Au1−X1	2.2978(8)	2.4060(5)	2.5585(2)
Au2−X2	2.2893(8)	2.4104(4)	2.5608(2)
	Angles, deg		
As1−Au1−X1	176.18(2)	176.08(2)	175.50(1)
As2−Au2−X2	172.52(3)	171.30(2)	168.93(1)

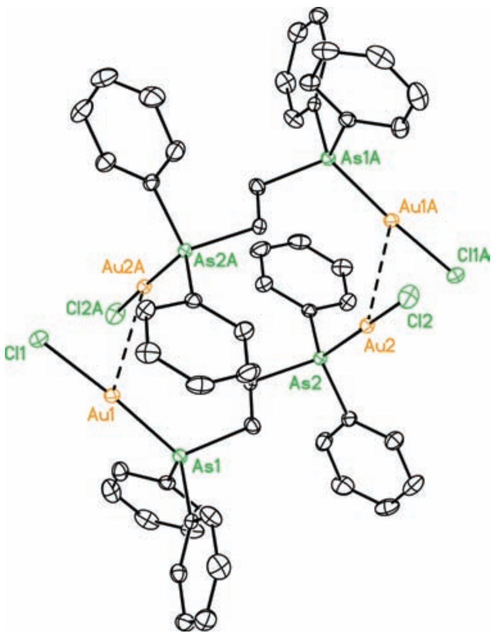


Figure 2. Structure of a pair of molecules in the α-polymorph of $Au_2(\mu\text{-dpae})Cl_2$. Thermal ellipsoids are shown at the 50% probability level in this and all subsequent figures. Hydrogen atoms are omitted for clarity in all figures.

$Au_2(\mu\text{-dpae})Cl_2$, is shown in Figure 2. Within the $Au_2(\mu\text{-dpae})Cl_2$ molecule, the Au---Au separation is quite long, 6.5120(3) Å. However, as Figure 2 shows, individual molecules of $Au_2(\mu\text{-dpae})Cl_2$ self-associate through two identical aurophilic interactions (Au1---Au2A, 3.1163(2) Å) to form well-defined dimers of the form **III** in Scheme 1. While the individual molecules do not possess any crystallographically imposed symmetry, the dimer is formed by the packing of two molecules about a center of symmetry.

Within the isostructural series, α-$Au_2(\mu\text{-dpae})X_2$, where X = Cl, Br, and I, the intermolecular Au1---Au2A distance decreases as the halide changes from Cl to Br to I, and the Au−X and Au−As distances increase. The intramolecular separations between gold centers are 6.5120(3), 6.5613(4), and 6.6714(3) for the Cl, Br, and I forms, respectively.

Molecular and Supramolecular Structures of the β-Polymorphs. While the three α-polymorphs are isostructural, none of the three β-polymorphs are isostructural, as the data in Table 1 show. Nevertheless, the β-polymorphs all possess similar features in both their molecular and their supramolecular structures. All form extended polymers through aurophilic interactions that correspond to form **IV** in Scheme 1. Selected bond distances and angles are given in Table 3, and certain torsional angles are found in Table 4.

β-$Au_2(\mu\text{-dpae})Cl_2$. The structure of the β-polymorph of $Au_2(\mu\text{-dpae})Cl_2$ is the most complex of the three β-polymorphs. The asymmetric unit of β-$Au_2(\mu\text{-dpae})Cl_2$ consists

Table 3. Selected Bond Distances (Å) and Angles (deg) for β-Au$_2$(μ-dpae)X$_2$

	β-Au$_2$(μ-dpae)Cl$_2$	β-Au$_2$(μ-dpae)Br$_2$	β-Au$_2$(μ-dpae)I$_2$
	Distance, Å		
Au1---Au2 intermolecular	3.1668(3)	3.1042(8)	3.1046(2)
Au3---Au4 intermolecular	3.0821(3)	3.1486(7)	
Au1---Au1A intramolecular	7.6733(4)	7.6408(8)^a	7.6070(4)
Au2---Au2A intramolecular	7.7448(9)		
Au3···Au3A intramolecular	8.3509(4)	7.6839(8)^b	7.7002(4)
Au4---Au4A intramolecular	7.7052(4)		
Au1–As1	2.3448(5)	2.3506(13)	2.3635(3)
Au2–As2	2.3448(4)	2.3508(13)	2.3691(3)
Au3–As3	2.3320(5)	2.3438(12)	
Au4–As4	2.3430(5)	2.3460(13)	
Au1–X1	2.2978(8)	2.4132(13)	2.5650(3)
Au2–X2	2.2893(8)	2.4204(13)	2.5680(2)
Au3–X3	2.2842(11)	2.4113(12)	
Au4–X4	2.2945(11)	2.4052(13)	
	Bond Angles, deg		
As1–Au1–X1	175.13(3)	170.47(5)	166.430(10)
As2–Au2–X2	170.51(3)	169.97(5)	167.840(10)
As3–Au3–X3	177.71(3)	172.71(5)	
As4–Au4–X4	170.30(3)	171.53(5)	

[a] Au1---Au4. [b] Au2---Au3.

of four separate half-molecules. The other half of each molecule is generated by a crystallographic inversion center. These inversion centers coincide with the midpoints of the H$_2$C–CH$_2$ bonds in the dpae ligands. Within each molecule, the two gold atoms are widely separated (Au1---Au1A, 7.6733(4); Au2---Au2A, 7.7448(9) Å, Au3---Au3A, 8.3509(4); Au4---Au4A, 7.7052(4) Å).

The four molecules are arranged into two separate polymeric strands. In each strand the molecules are linked through aurophilic interactions. Figure 3 shows drawings of portions of each of the two strands. The Au---Au distances that connect the individual molecules are Au1---Au2, 3.1668(3) Å; Au3---Au4, 3.0821(3) Å. These distances are similar to the Au---Au separation (3.1163(2) Å) in the α-polymorph.

β-Au$_2$(μ-dpae)Br$_2$. This polymorph contains two complete molecules with no crystallographic symmetry in the asymmetric unit. The individual molecules are twisted so that the two gold ions in each molecule are widely separated: Au1---Au4, 7.6408(8) Å; Au2---Au3, 7.6839(8) Å. As seen in Figure 4, these molecules are connected through aurophilic interactions into a chain in which the two different molecules alternate. The resulting chain closely resembles the two strands found in β-Au$_2$(μ-dpae)Cl$_2$. The Au---Au distances (Au1---Au2, 3.1042(8) Å; Au3---Au4, 3.1486(7) Å) are similar to the Au1---Au2 distance (3.1064(3) Å) in the corresponding α-polymorph.

β-Au$_2$(μ-dpae)I$_2$. In this polymorph, there are two half molecules in the asymmetric unit. The other half of each molecule is generated by reflection through a center of symmetry at the middle of a H$_2$C–CH$_2$ bond. However, despite the relative simplicity of the asymmetric unit, the individual molecules resemble those in the other two β-polymorphs with the two gold ions widely separated: Au1---Au1A, 7.6070(4) Å; Au2---Au2A, 7.7002(4) Å. These two molecules are arranged into strands in which they alternate and are connected through aurophilic interactions (Au1---Au2, 3.1046(2) Å) as seen in Figure 5.

Luminescence. These compounds are only feebly luminescent, but the α- and β-polymorphs do show clear differences in their emission spectra. Thus, at room temperature α-Au$_2$(μ-dpae)Cl$_2$ exhibits an emission at 591 nm with an excitation maximum at 365 nm, while β-Au$_2$(μ-dpae)Cl$_2$ shows an emission maximum at 569 nm with an excitation maximum at 360 nm. Similarly, α-Au$_2$(μ-dpae)I$_2$ exhibits an emission maximum at 655 nm with an excitation maximum at 369 nm, while β-Au$_2$(μ-dpae)I$_2$ shows an emission maximum at 640 nm with an excitation maximum at 362 nm. The emission from

Table 4. Torsional Angles (deg) for α-Au$_2$(μ-dpae)X$_2$ and β-Au$_2$(μ-dpae)X$_2$

	α-Au$_2$(μ-dpae)Cl$_2$	α-Au$_2$(μ-dpae)Br$_2$	α-Au$_2$(μ-dpae)I$_2$
	Angle, deg		
X1–Au1---Au2A–X2A	110.28(10)	100.52(10)	99.65(10)
As1–Au1---Au2A–As2A	98.35(10)	97.13(10)	94.15(10)
As1–C–C–As2	173.93(15)	172.55(19)	170.71(13)
X1–Au1---Au2–X2	61.5(1)	61.1(1)	61.5(1)
	β-Au$_2$(μ-dpae)Cl$_2$	β-Au$_2$(μ-dpae)Br$_2$	β-Au$_2$(μ-dpae)I$_2$
	Angle, deg		
X1–Au1---Au2A–X2A	112.99(4)	118.59(4)	
As1–Au1---Au2A–As2A	114.454(17)	117.56(5)	119.970(19)
X3–Au3---Au4A–X4A	122.89(4)	118.48(10)	114.293(14)
As3–Au3---Au4A–As4A	122.23(17)	118.51(10)	
X1–Au1~Au1A–X1A or Br1–Au1~Au4–Br4	180	176.0	180
X2–Au2~Au2A–X2A or Br2–Au2~Au3–Br3	180	175.7	
Cl3–Au3~Au3A–Cl3A	180		
Cl4–Au4~Au4A–Cl4A	180		
As1–C–C–As1A	180	179.4(6) As1,As4	180
As2–C–C–As2A	180	177.5(6) As2, As3	180
As3–C–C–As3A	180		
As4–C–C–As4A	180		

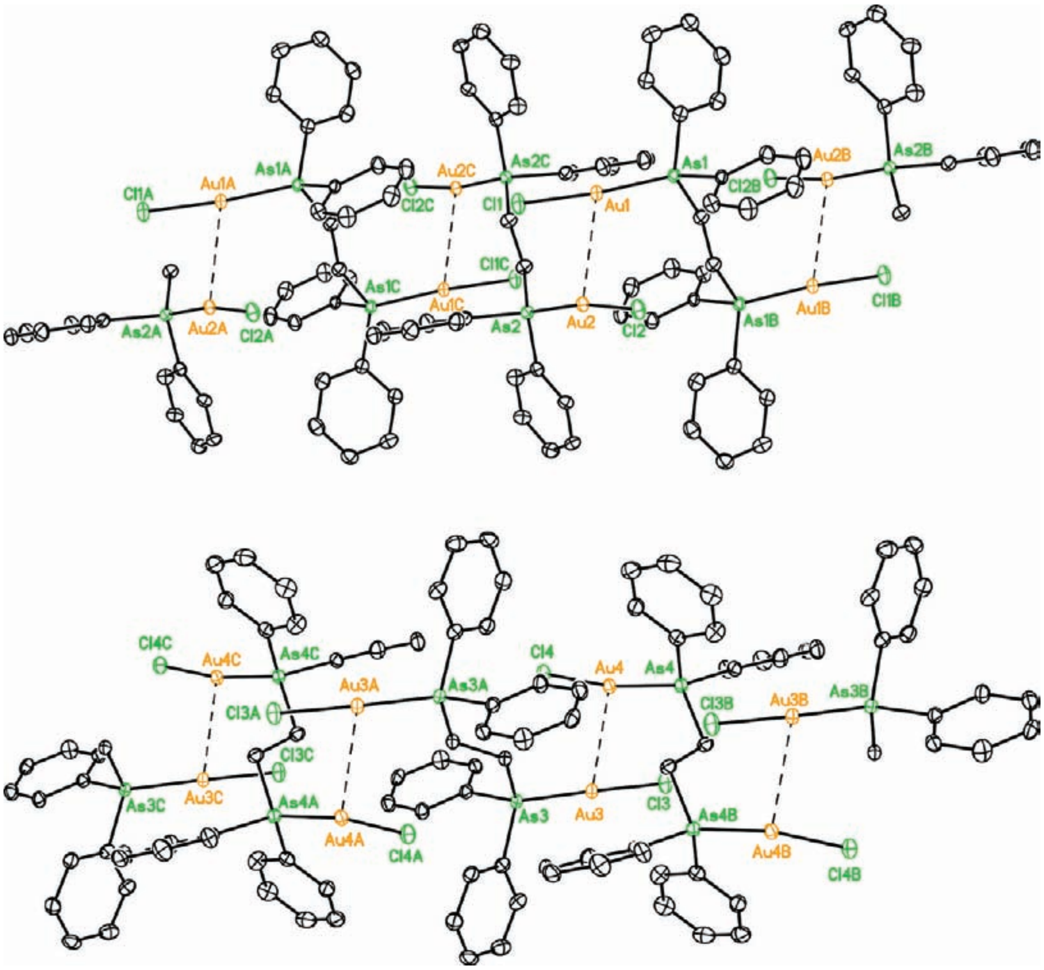


Figure 3. Portions of the two distinct polymeric strands in the β-polymorph of $Au_2(\mu\text{-dpae})Cl_2$.

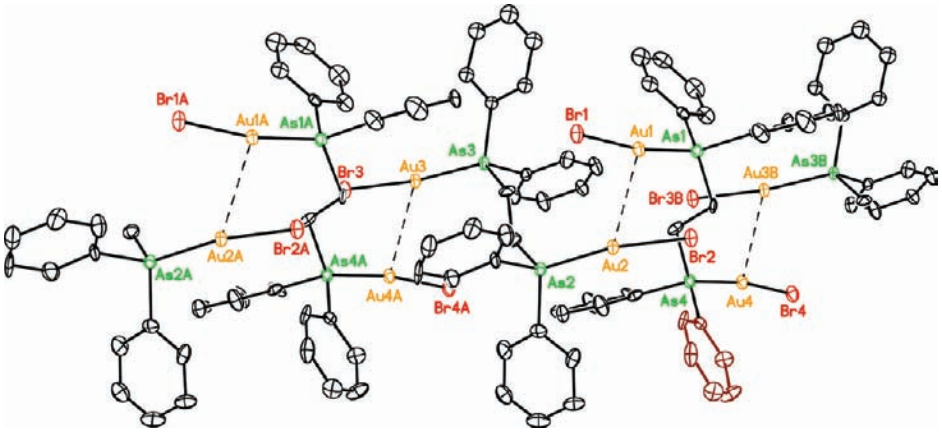


Figure 4. Portion of the polymeric chain in the β-polymorph of $Au_2(\mu\text{-dpae})Br_2$.

either form of $Au_2(\mu\text{-dpae})Br_2$ was too weak for us to measure a spectrum.

■ DISCUSSION

Polymorphs of molecular substances usually involve differences in molecular conformation, molecular orientation, or crystal packing.[10,27,28] Rarely do polymorphs have variations in the bonding interactions of their components; however, when such changes occur, especially if the changes involve metal−metal interactions, they can have profound effects on the materials' structural, spectroscopic, and physical properties.

There are several examples of two-coordinated gold(I) compounds of the type $(R_3E)AuX$ (E = P, As; X = Cl, Br, I) that form polymorphs, but that do not involve the sort of aurophilic interactions seen for $Au_2(\mu\text{-dpae})X_2$. $(Ph_3As)AuCl$ is a particularly relevant example, which exists in two different forms: colorless needles and colorless prisms.[29] Both forms crystallize in the orthorhombic space group $P2_12_12_1$ with structures that differ mainly in the torsional angles of the

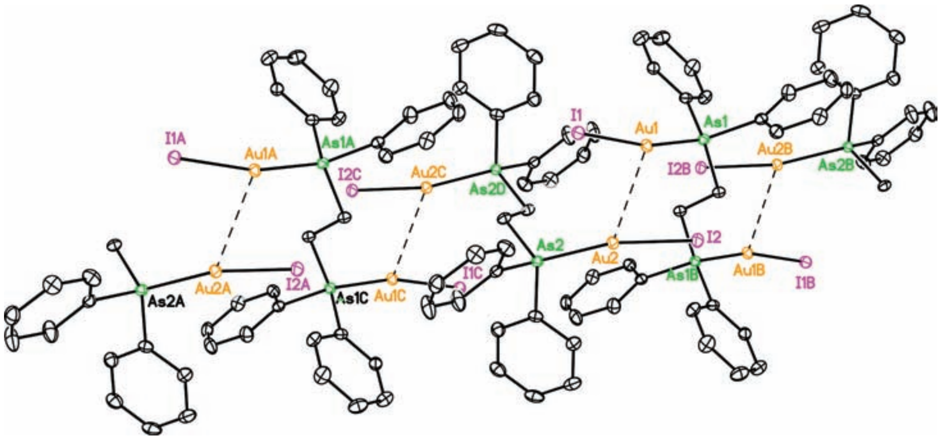


Figure 5. Portion of the polymeric chain in the β-polymorph of $Au_2(\mu\text{-dpae})I_2$.

phenyl rings about the phosphorus atom and in the intermolecular packing. There are no close Au···Au contacts in either polymorph. The shortest Au---Au separation is 5.916(1) Å for the needles, and 6.913(1) Å for the prismatic crystals. $Au(PCy_3)I$ (Cy is cyclohexyl) also crystallizes in two different polymorphic forms, triclinic and orthorhombic.[30] Neither form shows any close interactions between the gold(I) ions. $Au_2(\mu\text{-dppe})Cl_2$ (dppe is bis(diphenylphosphino)ethane) forms pseudopolymorphs, a nonsolvated form and a solvate, $Au_2(\mu\text{-dppe})Cl_2\cdot 0.4CH_2Cl_2$.[31,32] These do exhibit aurophilic interactions, and the nonsolvated form is isostructural with α-$Au_2(\mu\text{-dpae})Cl_2$.

The α-polymorphs of $Au_2(\mu\text{-dpae})X_2$ are isostructural, and consequently, it is not surprising that their molecular and supramolecular structures are similar. However, each of the β-polymorphs crystallizes in a unique fashion, yet there are many similarities in their structures as well. Thus, all three β-polymorphs self-associate to form very similar polymeric chains, as seen in Figures 3–5. Additionally, the aurophillic interactions in the β-polymorphs are also closely allied. The Au---Au distances span a narrow range, 3.08 to 3.18 Å, and the X—Au—Au—X and As—Au—Au—As torsional angles fall in another small range from 113 to 123°. The range of Au---Au distances in the α-polymorphs is similar, 3.08 to 3.12, but the X—Au—Au—X and As—Au—Au—As torsional angles in the α-polymorphs fall into a different range, 94 to 111°.

Figure 6 shows a comparison of the molecular structures in α- and β-polymorphs of $Au_2(\mu\text{-dpae})I_2$, which are representative examples for the other halide compounds as well. The conformations of these two monomers are quite different. As the torsional angles in Table 4 show, As—C—C—As units in both the α- and the β-polymorphs are nearly planar. For the α-polymorph the AsAuI units project out on the same side of this plane, while they project on opposite sides for the β-polymorph as shown in Figure 6. This arrangement in the β-polymorph does not allow the two arms to interact to produce a dimer, but does allow a polymer to form. However, the conformation of α-polymorph allows the two gold(I) ions in the monomer to hug a second molecule of $Au_2(\mu\text{-dpae})I_2$ to yield the dimeric structure.

Theoretical studies by Pyykkö and co-workers for the dimerization of H_3PAuX predicted an increase in the strength of this aurophilic interaction in the series X = F < CH_3 < H < Cl < CN < Br < I < $-SCH_3$.[33] Previously, structural studies of the compounds Me_2PhAuX (X = Cl, Br, I) experimentally demonstrated that the Au(I)···Au(I) contacts decrease in the order Cl > Br > I.[34] A similar trend has been also seen for the pair of complexes (1,3,5-triaza-7-phospha-adamantane)AuX (X = Cl, Br).[35] We have also observed this trend in α form of $Au_2(\mu\text{-dpae})X_2$ where the Au(I)···Au(I) contacts decrease in the order Cl > Br > I. However, In β-$Au_2(\mu\text{-dpae})X_2$ the average gold—gold separations decrease in the order Cl ~ Br > I, but there are significant differences in the two different Au---Au contacts for X = Cl or Br.

Some polymorphs of d^{10} and d^8 metal complexes undergo temperature dependent phase changes that alter the metallophillic interactions within these crystals. For example, the Au---Au distances between individual trimers in crystals of $[\mu_3\text{-}S(Au^ICNC_7H_{13})_3](SbF_6)$ undergo both lengthening and contraction upon a phase change produced by cooling as mentioned in the Introduction.[17] The polymorphs of $Ir^I(CO)_2(OC(CH_3)CHC(CH_3)N(p\text{-tol}))$ also undergo alterations of the columnar stacking and Ir---Ir distances upon changing temperature.[36] However, crystals of both the α- and β-polymorphs of $Au_2(\mu\text{-dpae})X_2$ are stable to about 200 °C and then melt without any evident interconversion. Given the large differences in the geometry of the monomeric entities in the crystals as seen in Figure 6, it is not surprising that the two forms do not readily interconvert.

In conclusion, this study has identified the existence of two polymorphs of $Au_2(\mu\text{-dpae})X_2$ for X = Cl, Br, or I, determined their structures, and identified differences in their physical properties. Our observations indicate that examination of just one crystal structure or choosing only the most promising crystal (i.e., the block shown in **A** in Figure 1) is not sufficient to understand the nature of aurophillic interactions and the mode of self-association of two-coordinate gold(I) complexes.

■ EXPERIMENTAL SECTION

Materials. A previously reported procedure was used for the preparation of (tht)AuCl (tht = tetrahydrothiophene).[37] Bis(diphenylarsine)ethane (dpae) was purchased from Alfa Inorganics.

Preparation of α-$Au_2(\mu\text{-dpae})Cl_2$ and β-$Au_2(\mu\text{-dpae})Cl_2$. A 100 mg (0.312 mmol) portion of Au(tht)Cl was dissolved in 30 mL of dichloromethane and to this solution was added 90 mg (0.185 mmol) of dpae. After stirring for 2 h, the suspension became a clear solution. The solution was filtered, and then the solvent was removed in a vacuum. The white solid was collected and washed with diethyl ether: yield, 130 mg (87%). Recrystallization from methylene chloride/diethyl ether yielded concomitantly colorless blocks and colorless needles of α-$Au_2(\mu\text{-dpae})Cl_2$ and β-$Au_2(\mu\text{-dpae})Cl_2$, respectively.

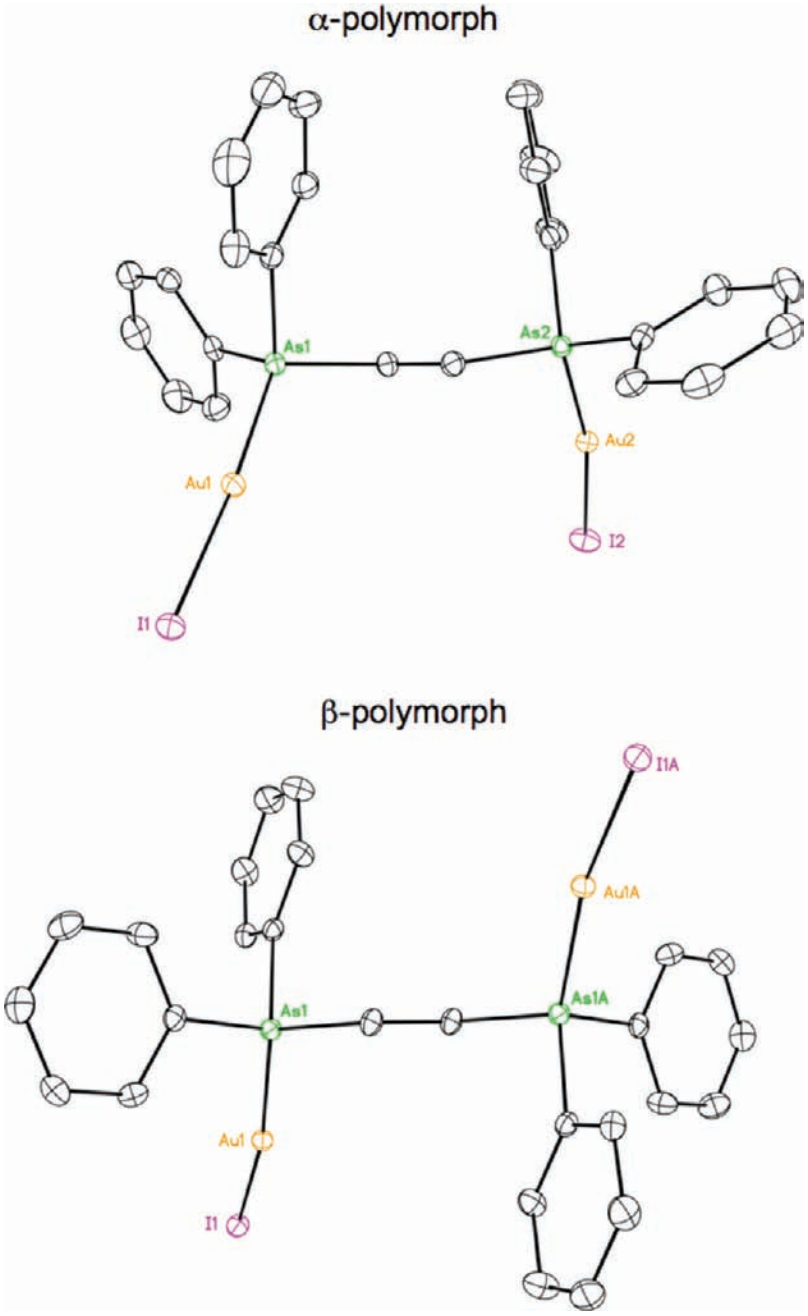


Figure 6. Comparisons of the molecular geometry of the $Au_2(\mu\text{-dpae})I_2$ molecule in the α (top) and β (bottom) polymorphs. In these views, the nearly planar As−C−C−As units are aligned horizontally.

MALDI mass spectrum (positive ion mode), 914.9 ($[Au_2(\mu\text{-dpae})Cl]^+$, ^{35}Cl), 915.9 ($[Au_2(\mu\text{-dpae})Cl]^+$, ^{37}Cl).

Melting point: 212−215° (α-form), 205−208° (β-form).

IR spectra: α-$Au_2(\mu\text{-dpae})Cl_2$: 3054w, 2913w, 1479 m, 1434s, 1410 m, 1333w, 1303w, 1149w, 1081 m, 1065 m, 1021w, 996 m, 849w, 734s, 709s, 688s, 614 m, 597 m, 456s.

β-$Au_2(\mu\text{-dpae})Cl_2$: 3045w, 2925w, 1574w, 1478 m, 1431s,1409 m, 1331w, 1302w, 1152w, 1077s, 1063 m, 1022w, 997 m, 968w, 732s, 709s, 687s, 616 m, 590 m, 469s, 461s.

Preparation of α-$Au_2(\mu\text{-dpae})Br_2$ and β-$Au_2(\mu\text{-dpae})Br_2$. A 100 mg (0.274 mmol) portion of Au(tht)Br was dissolved in 30 mL of dichloromethane and to this solution was added 85 mg (0.350 mmol) of dpae. After stirring for 2 h, the suspension became a clear solution. The solution was filtered, and then the solvent was removed in a vacuum. The white solid was collected and washed with diethyl ether: yield, 120 mg (84.2%). Recrystallization from methylene chloride/diethyl ether yields concomitantly colorless blocks and colorless needles of α-$Au_2(\mu\text{-dpae})Br_2$ and β-$Au_2(\mu\text{-dpae})Br_2$, respectively. MALDI mass spectrum (positive ion mode), 958.9 ($[Au_2(\mu\text{-dpae})Br]^+$, ^{79}Br), 9960.8 ($[Au_2(\mu\text{-dpae})Br]^+$, ^{81}Br).

Melting point: 216−218° (α-form), 209−212° (β-form).

IR spectra: α-$Au_2(\mu\text{-dpae})Br_2$: 3048w, 2916w, 1481 m, 1437s, 1408 m, 1335w, 1305w, 1151w, 1079 m, 1066 m, 1022w, 997 m, 851w, 735s, 711s, 689s, 614 m, 599 m, 458s.

β-$Au_2(\mu\text{-dpae})Br_2$: 3047w, 2928w, 1577w, 1479 m, 1434s,1411 m, 1330w, 1304w, 1153w, 1079s, 1064 m, 1020w, 999 m, 970w, 731s, 710s, 689s, 614 m, 592 m, 471s, 463s.

Preparation of polymorphs of α-$Au_2(\mu\text{-dpae})I_2$ and β-$Au_2(\mu\text{-dpae})I_2$. A 100 mg (0.309 mmol) portion of AuI was suspended in 30 mL of dichloromethane and to this suspension was added 90 mg (0.185 mmol) of dpae. After stirring for 2 h, the suspension became a clear solution. The solution was filtered, and then the solvent was removed in a vacuum. The white solid was collected and washed with diethyl ether: yield, 125 mg (71.3%). Recrystallization from methylene chloride/diethyl ether yields concomitantly colorless blocks and colorless needles of α-$Au_2(\mu\text{-dpae})I_2$ and β-$Au_2(\mu\text{-dpae})I_2$, respectively. MALDI mass spectrum (positive ion mode), 1006.9 ($[Au_2(\mu\text{-dpae})I]^+$, ^{127}I).

Melting point: 220–223° (α-form), 210–213° (β-form).

IR spectra: α-$Au_2(\mu\text{-dpae})I_2$: 3049w, 2916w, 1478 m, 1437s, 1411 m, 1335w, 1301w, 1147w, 1084 m, 1066 m, 1023w, 997 m, 848w, 731s, 708s, 687s, 616 m, 5978 m, 457s.

β-$Au_2(\mu\text{-dpae})I_2$: 3047w, 2921w, 1577w, 1476 m, 1434s,1412 m, 1334w, 1301w, 1151w, 1079s, 1064 m, 1020w, 996 m, 969w, 734s, 707s, 688s, 615 m, 592 m, 470s, 462s.

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 1000 CCD with graphite monochromated Mo Kα radiation at 90(2) K.

The structures were solved by direct methods and refined with 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.[38]

Physical Measurements. Infrared spectra were recorded on a Bruker ALPHA FT-IR spectrometer. Fluorescence excitation and emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrophotometer.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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