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Bridging 1,2-Bis(diphenylphosphino)methane Ligands Facilitate the Formation of Binuclear Complexes with Both Two-Coordinate and Three-Coordinate Gold(I) Ions

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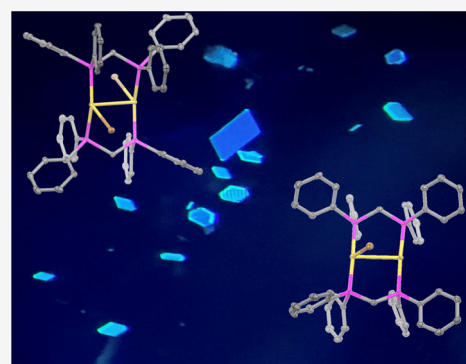
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ABSTRACT: Five new crystalline gold(I) complexes β -Au₂(μ -dppm)₂Br₂·2CH₂Cl₂ (1), [Au₂(μ -dppm)₂Br]Br·2CH₂Cl₂ (2), [Au₂(μ -dppm)₂Br](PF₆) (3), [Au₂(μ -dppm)₂Cl](BPh₄)·3CH₂Cl₂ (4) and [Au₂(μ -dppm)₂]Cl(AsF₆)·2CH₂Cl₂ (5) (where dppm is bis(diphenylphosphino)methane) have been prepared and structurally characterized by single crystal X-ray diffraction. Colorless β -Au₂(μ -dppm)₂Br₂·2CH₂Cl₂ (1) has centrosymmetric structure with two three-coordinate gold(I) ions held in close proximity by the dppm ligands. Crystals of [Au₂(μ -dppm)₂Br]Br·2CH₂Cl₂ (2), [Au₂(μ -dppm)₂Br](PF₆) (3), and [Au₂(μ -dppm)₂Cl](BPh₄)·3CH₂Cl₂ (4) have a cation with an unusual arrangement that binds a two-coordinate gold(I) ion to a three-coordinate gold(I) ion through an aurophilic interaction. Whereas Au₂(μ -dppm)₂Cl(BPh₄)·3CH₂Cl₂ (4) has a chloride ion bound to only one of the gold ions in the complex, [Au₂(μ -dppm)₂]Cl(AsF₆)·2CH₂Cl₂ (5) has an ion paired chloride ion that is symmetrically disposed between the two gold ions at a rather long distance. Each complex displays luminescence under UV irradiation.



INTRODUCTION

Frequently gold(I) complexes form colorless crystals, but many crystalline gold(I) compounds become luminescent under UV irradiation and can produce colors ranging from blue to red.^{1–5} This luminescent behavior makes gold(I) complexes promising candidates for the development of various electro-optical devices and sensors.^{6–10}

Individual two-coordinate, linear gold(I) complexes are generally not luminescent unless one of the ligands involved is emissive itself.³ However, two-coordinate gold(I) complexes can become luminescent upon aggregation due to aurophilic interactions. Thus, the two-coordinate cation, [(cyclohexylNC)₂Au]⁺, is not luminescent when it is surrounded by two large tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anions.¹¹ However, this cation becomes luminescent due to assembly into extended chains with close Au...Au contacts when smaller anions like hexafluorophosphate are the counterions.^{10,12–15} In contrast, monomeric, three-coordinate gold(I) complexes are usually luminescent.^{16–18} Consequently, luminescence cannot be utilized to identify cases where three-coordinate gold(I) complexes associate through aurophilic interactions.

The aurophilic interactions responsible for the aggregation of two-coordinate gold(I) complexes result from a combination of London dispersion forces and relativistic effects,^{19,20} and have been used to assist in the construction of various supramolecular arrays.^{8,21,22} The aurophilic interaction between two closed-shell, d¹⁰ gold(I) ions has a bond strength comparable to a hydrogen bond.²³

While the aggregation of cationic, anionic, and neutral two-coordinate gold(I) complexes is well established, much less is known about the ability of three-coordinate gold(I) complexes to participate in aurophilic interactions. There is only one example of self-association of a three-coordinate gold(I) complex that we have found. The planar cations in crystals of [(bipyridine)Au(2,6-dimethylphenylisocyanide)](N-{SO₂CF₃})₂ pack around centers of symmetry to form dimers connected by a Au...Au bond at a distance of 3.2201(6) Å.²⁴ Computational analysis indicates that the strength of this bond is 6.3 kcal/mol. Nothing has been reported about the absorption and possible emission spectra of this compound.

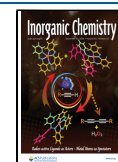
As shown in structure A of Scheme 1, diphosphine ligands of the type R₂P(CH₂)_nPR₂ can be used to form binuclear metal complexes with varying spacings between metal centers.^{25–29} When *n* is 3 or greater, the metal centers are generally far apart. For example, in Au₂(μ -Ph₂P(CH₂)₃PPh₂)₂I₂ the gold ions are separated by 5.0671(6) Å, well beyond the point where aurophilic interactions occur, and the distance between the gold(I) ions is even larger as *n* increases. However, for crystals of the accordion-like dimers, Au₂(μ -dppe)₂X₂ (where dppe is

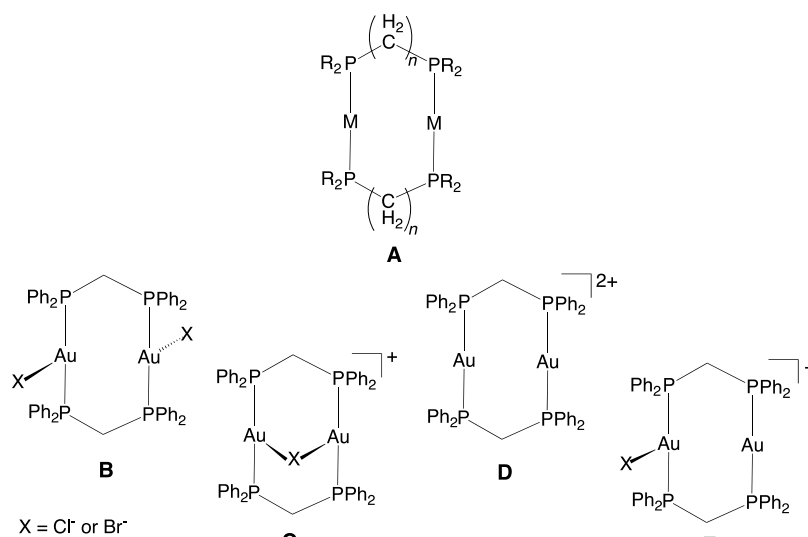
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Scheme 1. (A) Binuclear Complexes Bridged by Two Diphosphine Ligands. (B–E) Ligand Dispositions in Gold(I) Dimers Bridged by dppm


bis(diphenylphosphino)ethane and X is I or Br), the separations between the two gold ions varied depending upon the solvate molecules incorporated into the crystals. For X = I the separation between the gold(I) ions varied from 3.192(1) to 3.7866(3) Å,^{30,31} while for X = Br the separation ranged from 3.0943(2) to 3.8479(3) Å.³² While the short end of these ranges suggest that aurophilic interactions are present, computational studies indicate that aurophilic interactions are not a significant contributor to the bonding within Au₂(μ-dppe)₂I₂ unless the Au...Au distance shrunk down to 2.987 Å.³¹ Such a short Au...Au distance was not found in any of the solvated forms of three-coordinate Au₂(μ-dppe)₂X₂, but can be found in the dimeric dication [Au₂(μ-dppe)₂]²⁺ with two-coordinate gold(I) ions.³¹

To examine the flexibility of interactions of three-coordinate gold(I) ions in close proximity, we turned to compounds bridged by bis(diphenylphosphino)methane (dppm).³³ Au₂(μ-dppm)₂Br₂ and Au₂(μ-dppm)₂Cl₂ were known to possess a face-to-face structure shown as (B) in Scheme 1 and [Au₂(μ-dppm)₂(μ-I)]⁺ was shown to have an A-frame structure^{34–36} shown as (C) in Scheme 1, but the possible luminescence of these compounds had not been examined.^{37–39}

RESULTS AND DISCUSSION

Formation and Structure of the β-Polymorph of Au₂(μ-dppm)₂Br₂·2CH₂Cl₂ (1) and [Au₂(μ-dppm)₂Br]Br·2CH₂Cl₂ (2). Treatment of a solution of dppm with a suspension of gold(I) bromide in dichloromethane and a solution of potassium bromide in dichloromethane/methanol produced a yellow solid. Colorless crystals were obtained by diffusion of diethyl ether into a dichloromethane solution of the product. Examination of the crystals under a microscope using UV light revealed the presence of two types of crystals that had grown concomitantly as shown in Figure 1. The blue luminescent plates were crystallographically identified as a new polymorph of molecular β-Au₂(μ-dppm)₂Br₂·2CH₂Cl₂ (1), while the teal luminescent blocks were found to be ionic [Au₂(μ-dppm)₂Br]Br·2CH₂Cl₂ (2). The proportion of the molecular compound, β-Au₂(μ-dppm)₂Br₂·2CH₂Cl₂ (1), could be enhanced when carefully dried dichloromethane was used as



Figure 1. Photograph of crystalline plates of blue luminescent β-Au₂(μ-dppm)₂Br₂·2CH₂Cl₂ (1) and teal luminescent blocks of ionic [Au₂(μ-dppm)₂Br]Br·2CH₂Cl₂ (2) taken under UV irradiation.

solvent, while the fraction of the ionic compound, [Au₂(μ-dppm)₂Br]Br·2CH₂Cl₂ (2), could be increased by using dichloromethane that had been saturated with water to provide a more polar environment. Occasionally crystals of the α-polymorph of Au₂(μ-dppm)₂Br₂·2CH₂Cl₂ were found along with crystals of molecular β-Au₂(μ-dppm)₂Br₂·2CH₂Cl₂ (1) and ionic [Au₂(μ-dppm)₂Br]Br·2CH₂Cl₂ (2). However, we were unable to reliably produce enough of the α-polymorph of Au₂(μ-dppm)₂Br₂·2CH₂Cl₂ to collect spectroscopic data on these crystals. The original report on the α-polymorph of Au₂(μ-dppm)₂Br₂·2CH₂Cl₂ did not indicate how the crystal were grown.³⁶ Consequently, we limit further discussion to the β-polymorph of Au₂(μ-dppm)₂Br₂·2CH₂Cl₂ (1).

The structure of the β-polymorph of Au₂(μ-dppm)₂Br₂·2CH₂Cl₂ has been determined by single crystal X-ray diffraction. Crystal data are given in Table 1 and selected

Table 1. Crystal Data for Gold(I) Complexes

| | β -Au ₂ (μ -dppm) ₂ Br ₂ · 2CH ₂ Cl ₂ (1) | α -Au ₂ (μ -dppm) ₂ Br ₂ · 2CH ₂ Cl ₂ ^c | [Au ₂ (μ -dppm) ₂ Br]Br · 2CH ₂ Cl ₂ (2) |
|--|---|---|--|
| color/habit | colorless plate | pale yellow | colorless block |
| chemical formula | C ₅₂ H ₄₈ Au ₂ Br ₂ Cl ₄ P ₄ | C ₅₂ H ₄₈ Au ₂ Br ₂ Cl ₄ P ₄ | C ₅₂ H ₄₈ Au ₂ Br ₂ Cl ₄ P ₄ |
| formula weight | 1492.32 | 1492.33 | 1492.33 |
| crystal system | triclinic | triclinic | orthorhombic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P2_12_12_1$ |
| <i>a</i> (Å) | 10.1292(12) | 10.970(2) | 13.6747(5) |
| <i>b</i> (Å) | 11.0548(14) | 11.332(1) | 14.5276(6) |
| <i>c</i> (Å) | 12.9356(16) | 12.343(1) | 25.8882(10) |
| α (deg) | 71.338(2) | 109.54(1) | 90 |
| β (deg) | 86.797(2) | 107.81(1) | 90 |
| γ (deg) | 67.197(2) | 97.88(1) | 90 |
| <i>V</i> (Å ³) | 1261.2(3) | 1326.81(1) | 5143.0(3) |
| <i>Z</i> | 1 | 1 | 4 |
| <i>T</i> (K) | 90(2) | 298 | 90(2) |
| λ (Å) | 0.71073 | | 0.71073 |
| ρ (g/cm ³) | 1.965 | 1.868 | 1.927 |
| μ (mm ⁻¹) | 7.769 | | 7.620 |
| <i>R</i> ₁ (obsd data) ^a | 0.0183 | 0.0535 | 0.0160 |
| <i>wR</i> ₂ (all data, <i>F</i> ² refinement) ^b | 0.0389 | | 0.0359 |
| | [Au ₂ (μ -dppm) ₂ Br](PF ₆) (3) | [Au ₂ (μ -dppm) ₂ Cl](BPh ₄) · 3CH ₂ Cl ₂ (4) | [Au ₂ (μ -dppm) ₂ Cl](AsF ₆) · 2CH ₂ Cl ₂ (5) |
| color/habit | colorless block | yellow block | colorless block |
| chemical formula | C ₅₀ H ₄₄ Au ₂ BrF ₆ P ₅ | C ₇₇ H ₇₀ Au ₂ BCl ₇ P ₄ | C ₅₂ H ₄₈ AsAu ₂ Cl ₅ F ₆ P ₄ |
| formula weight | 1387.54 | 1772.11 | 1556.89 |
| crystal system | monoclinic | triclinic | monoclinic |
| space group | $P2_1/n$ | $P\bar{1}$ | $C2/c$ |
| <i>a</i> (Å) | 18.6625(10) | 12.0702(4) | 27.274(7) |
| <i>b</i> (Å) | 13.3339(7) | 16.8803(6) | 20.4594(18) |
| <i>c</i> (Å) | 20.1402(10) | 20.5697(7) | 15.035(4) |
| α (deg) | 90 | 69.1994(18) | 90 |
| β (deg) | 105.504(3) | 71.2565(18) | 92.187(4) |
| γ (deg) | 90 | 90 | 90 |
| <i>V</i> (Å ³) | 94829.4(4) | 3636.9(2) | 5357(2) |
| <i>Z</i> | 4 | 2 | 4 |
| <i>T</i> (K) | 90(2) | 90(2) | 90(2) |
| λ (Å) | 0.71073 | 0.71073 | 0.71073 |
| ρ (g/cm ³) | 1.908 | 1.618 | 1.930 |
| μ (mm ⁻¹) | 7.120 | 4.417 | 6.510 |
| <i>R</i> ₁ (obsd data) ^a | 0.0433 | 0.0288 | 0.0177 |
| <i>wR</i> ₂ (all data, <i>F</i> ² refinement) ^b | 0.1185 | 0.0720 | 0.0783 |

^a*R*₁ = ($\sum ||F_o| - |F_c||$) / $\sum |F_o|$. ^b*wR*₂ = (($\sum [w(F_o^2 - F_c^2)^2]$) / $\sum [w(F_o^2)^2]$)^{1/2}. ^cFrom data in ref 39.

bond distances and angles are presented in Table 2. A view of the β -Au₂(μ -dppm)₂Br₂ molecule is shown in Figure 2. The dimer is located on a crystallographic center of symmetry, which lies at the midpoint of the bond between the two gold ions. The Au...Au distance is 3.0771(4) Å, which is suggestive of an aurophilic interaction between the two gold ions. Each gold ion is in a nearly planar, three-coordinate geometry, which is quite similar to the coordination environment found in the various solvates of Au₂(μ -dppe)₂Br₂.³² The Au–Br distance is 2.8978(5) Å, which is a bit longer than the range of Au–Br distances (2.7115(11)–2.8848(3) Å) in the solvates of Au₂(μ -dppe)₂Br₂ and quite a bit longer than the Au–Br distance (2.625(2) Å) in Au(PPh₃)₂Br.⁴⁰ The Au–P distances, 2.3060(7) and 2.3390(7) Å, fall near the range of Au–P distances (2.2995(6)–2.3205(6) Å) observed in the solvates of Au₂(μ -dppe)₂Br₂. As usual with complexes of this sort, the P–Au–P angle (159.06(3)°) is much larger than the P–Au–Br angle (96.46(1)°). The Au...Au–Br angle is 96.46(1)°, and the bromide ion is quite far (4.4580(5) Å) from the adjacent,

nonbonded gold(I) ion. As can be seen from the data in Table 2, the bond distances and angles in β -Au₂(μ -dppm)₂Br₂ · 2CH₂Cl₂ (1) are similar to those in α -Au₂(μ -dppm)₂Br₂ · 2CH₂Cl₂.³⁶ Drawings comparing these two polymorphs can be found in the Supporting Information, Figures SI-1 and 2.

The structure of the cation in the other product from this reaction, [Au₂(μ -dppm)₂Br]Br · 2CH₂Cl₂ (2), is shown in part A of Figure 3. This cation contains an unusual combination of a three-coordinate gold(I) ion and two-coordinate gold(I) ion. The distance between the two gold(I) ions is 2.9475(5) Å, which is indicative of an aurophilic bond between the two ions. The coordinated bromide ion is displaced toward the adjacent gold(I) ion so that the Au...Au–Br angle is 66.68(1)° and the distance to the other gold(I) ion is 3.2223(6) Å. The remaining bromide ion is quite far (8.9378(6), 10.3285(6) Å) from either gold(I) ion.

Preparation and Structure of [Au₂(μ -dppm)₂Br](PF₆) (3). Colorless crystals of Au₂(μ -dppm)₂Br(PF₆) (3) were obtained by mixing dppm, gold(I) bromide, and ammonium

Table 2. Selected Bond Distances and Angles for Gold(I) Complexes

| complex | β -[Au ₂ (μ -dppm) ₂ Br ₂]·2CH ₂ Cl ₂ (1) | α -[Au ₂ (μ -dppm) ₂ Br ₂]·2CH ₂ Cl ₂ ^a | [(Au ₂ (μ -dppm) ₂ Br)Br]·2CH ₂ Cl ₂ (2) |
|-------------------|--|--|--|
| | Distances (Å) | | |
| Au···Au | 3.0771(4) | 3.015(2) | 2.9475(5) |
| Intraligand P···P | 3.0580(8) | 3.049(5) | 3.057(1)(P1–P2) 3.053(2)(P3–P4) |
| Au1–P1 | 2.3060(7) | 2.312(4) | 2.318(1) |
| Au1–P4 | 2.3390(7) | 2.354(4) | 2.313(1) |
| Au2–P2 | 2.3060(7) | 2.354(4) | 2.304(1) |
| Au2–P3 | 2.3390(7) | 2.312(4) | 2.305(1) |
| Au1–X1 | 2.8978(5) | 2.869(2) | 2.9148(7) |
| Au2–X1 | | | 3.2223(6) |
| Au2–X2 | 2.8978(5) | 2.869(2) | |
| | Angles (deg) | | |
| P1–Au1–P4 | 159.06(3) | 156.50(1) | 169.65(4) |
| P2–Au2–P3 | 159.06(3) | 156.50(1) | 166.40(4) |
| Au1···Au2–X1 | 96.46(1) | 102.68(6) | 66.68(1) |
| Au1···Au2–X2 | 96.46(1) | 102.68(6) | |
| | Torsional Angles (deg) | | |
| P2–Au2···Au1–P1 | 20.73(2) | 23.4(1) | 0.61(4) |
| P3–Au2···Au1–P4 | –20.73(2) | –23.4(1) | 4.15(4) |
| complex | [(Au ₂ (μ -dppm) ₂ Br)](PF ₆) (3) | [(Au ₂ (μ -dppm) ₂ Cl)](BPh ₄)·3CH ₂ Cl ₂ (4) | [(Au ₂ (μ -dppm) ₂ Cl)](AsF ₆)·2CH ₂ Cl ₂ (5) |
| | Distances (Å) | | |
| Au···Au | 2.9435(3) | 2.9522(4) | 2.9968(8) |
| Intraligand P···P | 3.081(2)(P3–P4) 3.059(2)(P1–P2) | 3.068(1)(P1–P2) 3.053(1)(P3–P4) | 3.068(1) |
| Au1–P1 | 2.328(2) | 2.3042(9) | 2.311(1) |
| Au1–P4 | 2.301(2) | 2.307(1) | 2.311(1) |
| Au2–P2 | 2.321(2) | 2.3042(9) | 2.134(1) |
| Au2–P3 | 2.317(2) | 2.3040(9) | 2.134(1) |
| Au1–X1 | 2.9687(7) | 3.0220(7) | 3.1035 |
| Au2–X1 | 3.4461(7) | 2.8956(9) | 3.1035 |
| Au2–X2 | | | |
| | Angles (deg) | | |
| P1–Au1–P4 | 159.12(5) | 177.59(3) | 175.87(3) |
| P2–Au2–P3 | 169.80(5) | 175.75(3) | 175.87(3) |
| Au1···Au2–X1 | 71.31(2) | 62.22(2) | 61.13 |
| Au1···Au2–X2 | | | |
| | Torsional Angles (deg) | | |
| P2–Au2···Au1–P1 | –8.03(5) | –1.18(3) | 7.61(3) |
| P3–Au2···Au1–P4 | 2.84(5) | –4.26(3) | 7.61(3) |

^aFrom data in ref 39.

hexafluorophosphate in dichloromethane/methanol as outlined in the [Experimental Section](#). The structure of the cation in [Au₂(μ -dppm)₂Br](PF₆) (3) is shown in part B of [Figure 3](#). While the structures of the two cations shown in [Figure 3](#) are similar as are the Au···Au distances (2.9475(5) Å in (2), 2.9435(3) Å in (3)), there also some significant differences. For example, in [Au₂(μ -dppm)₂Br](PF₆) (3) the P–Au–P angle (159.12(5)°) at the three-coordinate gold center is more acute than the corresponding angle (169.65(4)°) in [Au₂(μ -dppm)₂Br]Br·2CH₂Cl₂ (2). In [Au₂(μ -dppm)₂Br]Br·2CH₂Cl₂ (2), the two methylene groups reside on the same side of the Au₂P₄ group as the bromide ligand. However, in [Au₂(μ -dppm)₂Br](PF₆) (3) one methylene group is on the same side as the bromide ligand while the other one is on the opposite side. Otherwise, [Au₂(μ -dppm)₂Br]Br·2CH₂Cl₂ (2) and [Au₂(μ -dppm)₂Br](PF₆) (3) have similar structures and similar bonding.

Preparations and Structures of [Au₂(μ -dppm)₂Cl]-(BPh₄)·3CH₂Cl₂ (4) and [Au₂(μ -dppm)₂Cl](AsF₆)·2CH₂Cl₂

(5). These salts were produced by mixing (tetrahydrothiophene)gold(I) chloride with dppm in dichloromethane followed by the addition of either sodium tetraphenyl borate or sodium hexafluoroarsenate as outlined in the [Experimental Section](#). The structure of the cation in [Au₂(μ -dppm)₂Cl](BPh₄)·3CH₂Cl₂ (4), as determined by single crystal X-ray diffraction, is shown in [Figure 4A](#). This cation has a structure that is similar to those of the bromo analogs found in [Au₂(μ -dppm)₂Br]Br·2CH₂Cl₂ (2); and [Au₂(μ -dppm)₂Br](PF₆) (3) shown in [Figure 3](#). [Au₂(μ -dppm)₂Cl]-(BPh₄)·3CH₂Cl₂ (4), has a three-coordinate gold(I) ion as well as a two-coordinate gold(I) ion connected by two bridging dppm ligands. The distance between the two gold(I) ions is 2.9522(4) Å, which suggests that there is an aurophilic interaction between the two ions. The Au–Cl bond distance is 2.8956(9) Å, which is significantly longer than the known Au–Cl distance (2.533(4) Å) in Au(PPh₃)₂Cl or the Au–Cl distance (2.500(4) Å) in Au(PPh₃)₂Cl·0.5(C₆H₆).³⁷ The coordinated chloride ion is displaced toward the adjacent

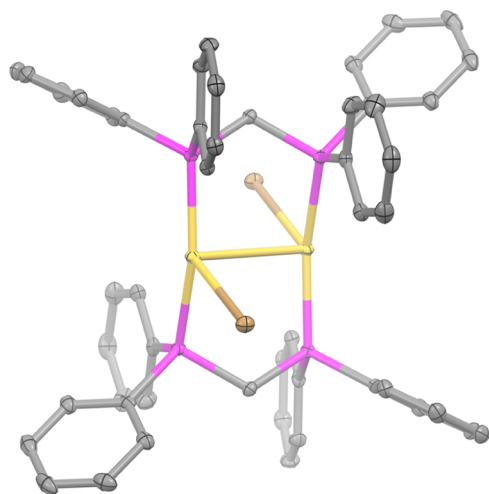


Figure 2. Structure of $\text{Au}_2(\mu\text{-dppm})_2\text{Br}_2$ in the β -polymorph of $\text{Au}_2(\mu\text{-dppm})_2\text{Br}_2 \cdot 2\text{CH}_2\text{Cl}_2$ (1). Hydrogen atoms and solvate molecules are not shown for clarity. Drawn with thermal contours at the 30% probability level. Color code: gold, yellow; phosphorus, pink; bromine, brown; carbon, gray.

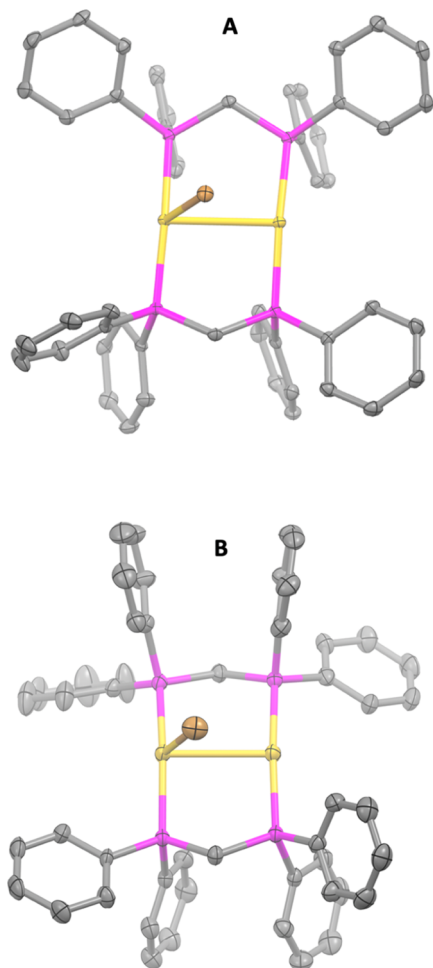


Figure 3. Structures of the cations in (A) $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}]\text{Br} \cdot 2\text{CH}_2\text{Cl}_2$ (2); and (B) $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}](\text{PF}_6)$ (3). Hydrogen atoms are not shown for clarity. Drawn with thermal contours at the 30% probability level. Color code: gold, yellow; phosphorus, pink; bromine, brown; carbon, gray.

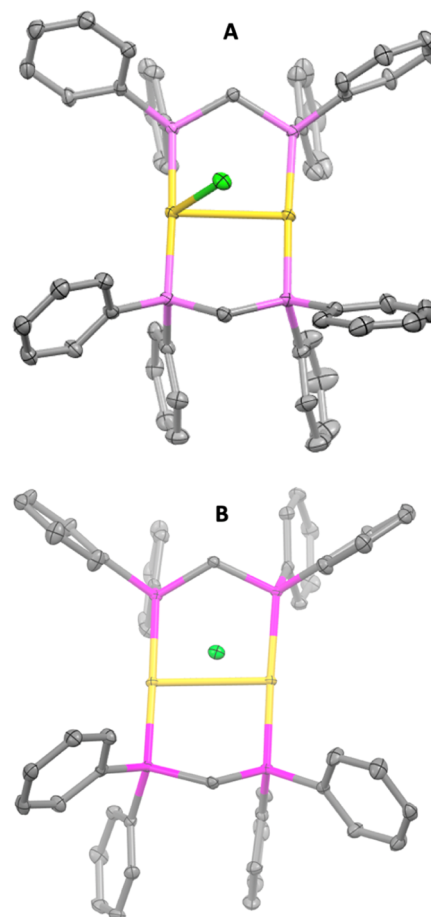


Figure 4. Structures of the cations in (A), $[\text{Au}_2(\mu\text{-dppm})_2\text{Cl}](\text{BPh}_4) \cdot 3\text{CH}_2\text{Cl}_2$ (4), and (B) $[\text{Au}_2(\mu\text{-dppm})_2]\text{Cl}(\text{AsF}_6) \cdot 2\text{CH}_2\text{Cl}_2$ (5). Hydrogen atoms are not shown. Thermal contours are at the 30% probability level. Color code: gold, yellow; phosphorus, pink; chlorine, green; carbon, gray.

gold(I) ion so that the $\text{Au} \cdots \text{Au} - \text{Cl}$ angle is $62.22(2)^\circ$. The distance from the chloride ion to the adjacent two-coordinate gold(I) ion is $3.0220(7)$ Å.

The structure of the cation and the loosely associated chloride ion in $[\text{Au}_2(\mu\text{-dppm})_2]\text{Cl}(\text{AsF}_6) \cdot 2\text{CH}_2\text{Cl}_2$ (5) is shown in Figure 4B. The asymmetric unit consists of one-half of the cation, which resides on a mirror plane that bisects the two methylene carbon atoms and the midpoint of the $\text{Au} \cdots \text{Au}$ bond. In addition, the asymmetric unit contains half of an ordered hexafluoroarsenate ion that resides on a mirror plane and is disordered over two orientations, and a disordered dichloromethane molecule in a general position. In the cation, the $\text{Au} \cdots \text{Au}$ distance, $2.9968(8)$ Å, is similar to the $\text{Au} \cdots \text{Au}$ distance ($2.9522(4)$ Å) in $[\text{Au}_2(\mu\text{-dppm})_2\text{Cl}](\text{BPh}_4) \cdot 3\text{CH}_2\text{Cl}_2$ (4). The loosely associated chloride ion is symmetrically positioned 3.1035 Å from either gold(I) ion in the dication. A similar situation occurs in $[\text{Au}_2(\mu\text{-dppm})_2]\text{Cl}_2 \cdot (\text{CH}_3)_2\text{CO} \cdot \text{H}_2\text{O}$, where there is a chloride ion in a similar position but closer to the gold(I) ions with $\text{Au} \cdots \text{Cl}$ distances of $2.9492(13)$ and $2.9776(12)$ Å.

We have identified three salts ($[\text{Au}_2(\mu\text{-dppm})_2\text{Br}]\text{Br} \cdot 2\text{CH}_2\text{Cl}_2$ (2), $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}](\text{PF}_6)$ (3), $[\text{Au}_2(\mu\text{-dppm})_2\text{Cl}](\text{BPh}_4) \cdot 3\text{CH}_2\text{Cl}_2$ (4)) that contain the unusual arrangement of a two-coordinate gold(I) ion connected to a

three-coordinate gold(I) through an aurophilic interaction. In looking for other such arrangements, we found that $[\text{Au}_2(\mu\text{-dcmp})_2\text{Cl}]\text{Cl}\cdot 0.25\text{CH}_3\text{OH}$ (where dcmp is bis(dicyclohexylphosphino)methane) also has a two-coordinate gold(I) ion connected to a three-coordinate gold(I) but in a somewhat different orientation with a nearly linear $\text{Cl}-\text{Au}\cdots\text{Au}$ unit and an $\text{Au}\cdots\text{Au}$ distance of 2.9925(2) Å as shown in (A) in Figure 5.⁴¹ That crystal also contained a second isomeric

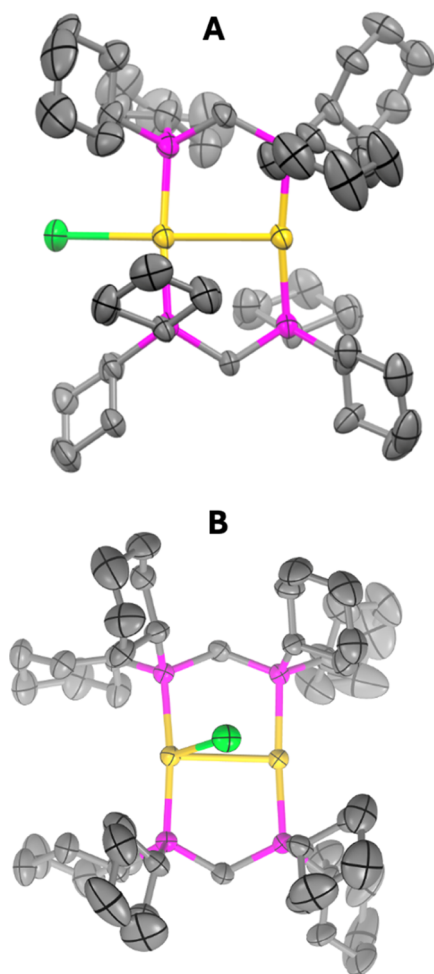


Figure 5. Structures of the cations in $[\text{Au}_2(\mu\text{-dcmp})_2\text{Cl}]\text{Cl}\cdot 0.25\text{CH}_3\text{OH}$ drawn from data in ref. 41. Selected dimensions. (A) Bond lengths; $\text{Au}\cdots\text{Au}$, 2.9925(2); $\text{Au}-\text{Cl}$, 2.7756(9) Å; bond angle, $\text{Cl}-\text{Au}\cdots\text{Au}$, 171.89(2)°. (B) Bond lengths; $\text{Au}\cdots\text{Au}$, 2.9445(2); $\text{Au}-\text{Cl}$, 2.8731(9) Å; bond angle, $\text{Cl}-\text{Au}\cdots\text{Au}$, 68.64(2)°. Hydrogen atoms are not shown. Thermal contours are at the 30% probability level. Color code: gold, yellow; phosphorus, pink; chlorine, green; carbon, gray.

cation shown in (B) in Figure 5 that was not mentioned in the original article. The cation shown in (B) is quite similar to the cation in $[\text{Au}_2(\mu\text{-dppm})_2\text{Cl}](\text{BPh}_4)\cdot 3\text{CH}_2\text{Cl}_2$ (4). Both cations have acute $\text{Cl}-\text{Au}\cdots\text{Au}$ angles (62.22(2)° for (4), 68.64(2)° for $[\text{Au}_2(\mu\text{-dcmp})_2\text{Cl}]\text{Cl}\cdot 0.25\text{CH}_3\text{OH}$), nearly equivalent $\text{Au}-\text{Cl}$ distances (2.8956(9) Å for (4), 2.8731(9) Å for $[\text{Au}_2(\mu\text{-dcmp})_2\text{Cl}]\text{Cl}\cdot 0.25\text{CH}_3\text{OH}$), and similar $\text{Au}\cdots\text{Au}$ distances (2.9522(4) Å for (4), 2.9445(2) Å for $[\text{Au}_2(\mu\text{-dcmp})_2\text{Cl}]\text{Cl}\cdot 0.25\text{CH}_3\text{OH}$).

Within the gold(I) dimers bridged by two dppm ligands, the $\text{Au}\cdots\text{Au}$ distances are confined to a rather narrow range (2.9475(5) to 3.0771(4) Å) for the five compounds reported here. In comparison, the variability of Au/Cl interactions is remarkable for compounds with a $\text{Au}_2(\mu\text{-dppm})_2^{2+}$ core. Molecular $\text{Au}_2(\mu\text{-dppm})_2\text{Cl}_2$ with the structure shown in (B) in Scheme 1 exists in two forms: an acetone solvate with an $\text{Au}-\text{Cl}$ distance of 2.771(4) Å,³⁴ and an acetonitrile solvate with a longer $\text{Au}-\text{Cl}$ distance of 2.951(4) Å.³⁵ In contrast, crystalline $[\text{Au}_2(\mu\text{-dppm})_2]\text{Cl}_2\cdot(\text{CH}_3)_2\text{CO}\cdot\text{H}_2\text{O}$, has an A-frame structure (C in Scheme 1) with a bridging chloride ions somewhat asymmetrically placed between the gold(I) ions with $\text{Au}-\text{Cl}$ distances of 2.9492(13) and 2.9776(12) Å while $[\text{Au}_2(\mu\text{-dppm})_2]\text{Cl}(\text{AsF}_6)\cdot 2\text{CH}_2\text{Cl}_2$ (5) contains a symmetrically positioned chloride ion that is 3.1035 Å away from either gold(I) ion.³⁶ Finally, $[(\text{Au}_2(\mu\text{-dppm})_2\text{Cl})](\text{BPh}_4)\cdot 3\text{CH}_2\text{Cl}_2$ (4) has a structure with a chloride ion connected to only one gold(I) ion with an $\text{Au}-\text{Cl}$ distance of 2.8956(9) Å. All of these binuclear compounds have $\text{Au}-\text{Cl}$ distances that are much longer than the $\text{Au}-\text{Cl}$ distance (2.533(4) Å) in monomeric $\text{Au}(\text{PPh}_3)_2\text{Cl}$.³⁸ It appears that this lengthening of the $\text{Au}-\text{Cl}$ bonds in these dimeric complexes may be a consequence of the aurophilic interactions.

Excitation and Emission Data. Each of the five crystalline complexes reported here is luminescent in the solid state. For solvated crystals, the loss of solvate molecules can affect the excitation and emission spectra.^{11,42} Consequently, we were particularly careful to obtain spectra on homogeneous samples that were protected to avoid solvate evaporation.

Table 3 contains the excitation and emission maxima for each compound. Figure 1 shows how we were visually able to differentiate $\beta\text{-Au}_2(\mu\text{-dppm})_2\text{Br}_2\cdot 2\text{CH}_2\text{Cl}_2$ (1) from $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}]\text{Br}\cdot 2\text{CH}_2\text{Cl}_2$ (2) based on differences in luminescence and crystal morphology. Figure 6 shows the excitation and emission spectra for these two compounds and for $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}](\text{PF}_6)$ (3). Crystalline $\beta\text{-Au}_2(\mu\text{-dppm})_2\text{Br}_2\cdot 2\text{CH}_2\text{Cl}_2$ (1) has its emission at 458 nm at room temperature, while $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}]\text{Br}\cdot 2\text{CH}_2\text{Cl}_2$ (2) shows emission at 472 nm under the same conditions. Notice that while the spectra are similar, there is enough difference to allow the two compounds to be identified.

For these compounds, the emission varies over a rather short-range, which is perhaps not surprising given the

Table 3. Excitation and Emission Data for Crystalline Solids

| complexes | room temperature (298 K) | | low temperature (77 K) | |
|--|--------------------------|---------------|------------------------|---------------|
| | excitation (nm) | emission (nm) | excitation (nm) | emission (nm) |
| $\beta\text{-Au}_2(\mu\text{-dppm})_2\text{Br}_2\cdot 2\text{CH}_2\text{Cl}_2$ (1) | 398 | 458 | 395 and 420 | 470 |
| $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}]\text{Br}\cdot 2\text{CH}_2\text{Cl}_2$ (2) | 380 | 472 | 375 | 472 |
| $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}](\text{PF}_6)$ (3) | 363 | 468 | 365 | 482 |
| $[\text{Au}_2(\mu\text{-dppm})_2\text{Cl}](\text{BPh}_4)\cdot 3\text{CH}_2\text{Cl}_2$ (4) | 371 | 467 | 355 | 474 |
| $[\text{Au}_2(\mu\text{-dppm})_2]\text{Cl}(\text{AsF}_6)\cdot 2\text{CH}_2\text{Cl}_2$ (5) | 358 | 464 | 363 | 454 |

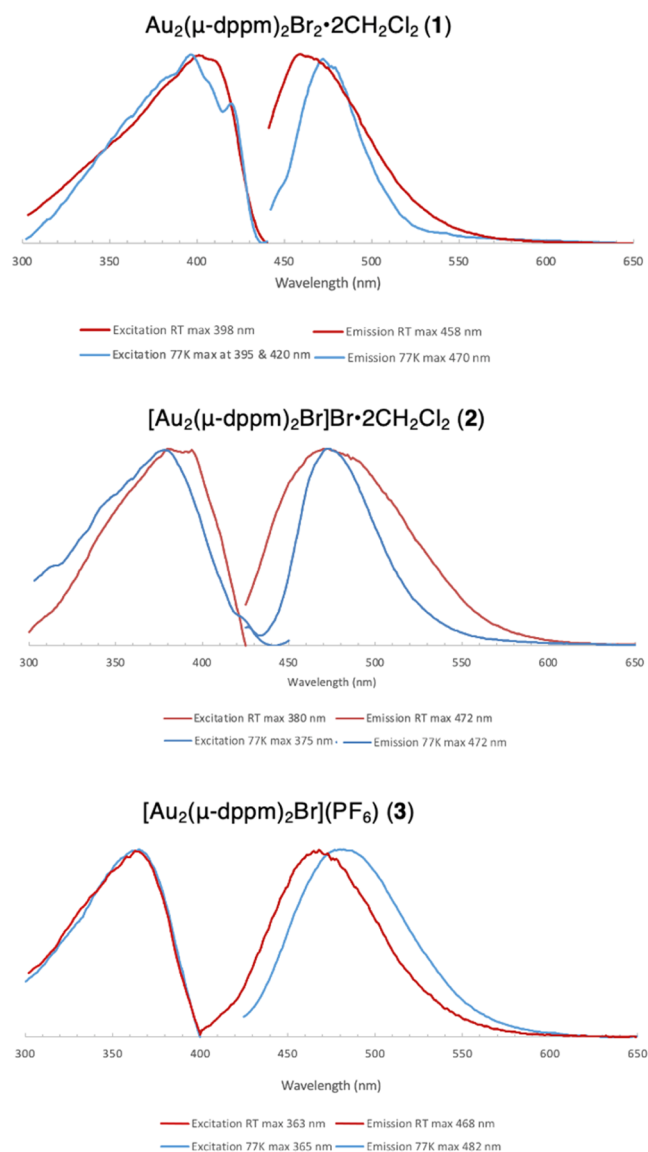


Figure 6. Excitation and emission spectra of crystalline samples of β - $\text{Au}_2(\mu\text{-dppm})_2\text{Br}_2\cdot 2\text{CH}_2\text{Cl}_2$ (1), $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}]\text{Br}\cdot 2\text{CH}_2\text{Cl}_2$ (2) and $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}](\text{PF}_6)_3$ (3) at room temperature and at 77 K.

structural similarities within this group of complex ions. Cooling the crystals results in a narrowing of the emission bands as expected for the reduction in vibrational motion. While $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}]\text{Br}\cdot 2\text{CH}_2\text{Cl}_2$ (2) and $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}](\text{PF}_6)_3$ (3) nominally contain a common cation, the structures of these cations differ as shown in Figure 3 and the emission spectra differ as well.

As seen in Table 3, the excitation and emission maxima for $[\text{Au}_2(\mu\text{-dppm})_2\text{Cl}](\text{BPh}_4)_3\cdot 3\text{CH}_2\text{Cl}_2$ (4), and $[\text{Au}_2(\mu\text{-dppm})_2]\text{Cl}(\text{AsF}_6)_2\cdot 2\text{CH}_2\text{Cl}_2$ (5) differ slightly but fall near the range seen for the bromo salts. Again, the effect of cooling the crystals results in only small changes with a narrowing of the emission bands be the most common feature. The spectra for these two salts can be found in the Supporting Information, Figure SI-3.

Solution Behavior. To better understand the solution behavior of these new gold(I) complexes, we examined their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Due to poor solubility, we were unable to obtain $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for $\beta\text{-Au}_2(\mu\text{-dppm})_2\text{Br}_2$

(1) or $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}]\text{Br}\cdot 2\text{CH}_2\text{Cl}_2$ (2). In acetonitrile solution, $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}](\text{PF}_6)_3$ (3) displayed a singlet at 31.5 ppm for the cation and a heptet at for the $(\text{PF}_6)^-$ ion. The spectrum for $[\text{Au}_2(\mu\text{-dppm})_2\text{Cl}](\text{BPh}_4)_3\cdot 3\text{CH}_2\text{Cl}_2$ (4) in chloroform solution consisted of a singlet at 32.1 ppm, while the spectrum for $[\text{Au}_2(\mu\text{-dppm})_2]\text{Cl}(\text{AsF}_6)_2\cdot 2\text{CH}_2\text{Cl}_2$ (5) displayed a singlet at 32.2 ppm in chloroform solution. Cooling the samples of each of these three compounds to 255 K produced some line broadening and shifting. These data suggest that the halide ions move about the cations in solution, but the actual identity of the species present in solution has not been ascertained. Additional evidence for the mobility of the halide ions in solution comes from the observation that $\beta\text{-Au}_2(\mu\text{-dppm})_2\text{Br}_2\cdot 2\text{CH}_2\text{Cl}_2$ (1) and $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}]\text{Br}\cdot 2\text{CH}_2\text{Cl}_2$ (2) crystallize from a single solution concomitantly. Consequently, we did not continue to investigate the solution properties of these complexes further and limited our studies to the crystalline state, where the structures of the complexes are well-established.

CONCLUSIONS

Unlike the situation in the flexible dppe-bridged dimers, $\text{Au}_2(\mu\text{-dppe})_2\text{X}_2$ and $[\text{Au}_2(\mu\text{-dppe})_2]^{2+}$, where the separation between the two gold(I) ions can vary from 2.8787(9) to 3.8479(3) Å,^{29–32} the dppm-bridged dimers reported here have short, intraionic Au...Au distances that fall in a narrow range from 2.9435(3) to 3.0771(4) Å. No interionic aurophilic interactions occur in these salts. The variability in the structures of these dppm-bridged dimers involves the bonding to the bromide or chloride ions, while all maintain aurophilic bonding. In the three cations $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}]\text{Br}\cdot 2\text{CH}_2\text{Cl}_2$ (2), $[\text{Au}_2(\mu\text{-dppm})_2\text{Br}](\text{PF}_6)_3$ (3) and $[\text{Au}_2(\mu\text{-dppm})_2\text{Cl}](\text{BPh}_4)_3\cdot 3\text{CH}_2\text{Cl}_2$ (4), the halide ion is clearly bonded only to only one gold(I) producing unusual complexes with a two-coordinate gold(I) ion connected to a three-coordinate gold(I) ion. In contrast, in $\beta\text{-Au}_2(\mu\text{-dppm})_2\text{Br}_2\cdot 2\text{CH}_2\text{Cl}_2$ (1) both bromine ions are coordinated to produce a face-to-face arrangement of two three-coordinate gold(I) ions, while in $[\text{Au}_2(\mu\text{-dppm})_2]\text{Cl}(\text{AsF}_6)_2\cdot 2\text{CH}_2\text{Cl}_2$ (5), the chloride ions is ion paired between the two gold(I) ions.

Each of the new compounds is luminescent in the crystalline state. This result is not surprising since dimers of two-coordinate gold are luminescent as are many three-coordinate gold(I) complexes, and these new compounds contain both structural elements. The excitation and emission maxima for these complexes show only small variations, which may reflect the fact that bromide or chloride coordination is rather weak. Thus, the luminescence may be attributed to transitions involving the interactions between the two gold ions, which has been discussed elsewhere.³⁸

Finally, this article reports three compounds in which the unusual combination of a three-coordinate gold(I) ion with a two-coordinate gold(I) ion are held together by bridging dppm ligands and aurophilic interactions. As shown in Figure 5, there are two possible positions for the X–Au bond in these complexes: nearly perpendicular to the Au–Au bond as found in the new compounds reported here or parallel to the Au–Au bond.

EXPERIMENTAL SECTION

Materials. Gold(I) bromide was purchased from Alfa Chemistry and dppm was purchased from Sigma-Aldrich. All solvents were reagent grade and used as received.

Preparation of Molecular β -Au₂(μ -dppm)₂Br₂·2CH₂Cl₂ (1) and Ionic [Au₂(μ -dppm)₂Br]Br·2CH₂Cl₂ (2). A 79.8 mg (0.208 mmol) portion of dppm was dissolved in 5 mL of dichloromethane, and an equivalent amount of AuBr (50.0 mg, 0.180 mmol) suspended in 4 mL of dichloromethane was added to the dppm solution under agitation. The solution was stirred for 5 min followed by the addition of KBr (34.1 mg, 0.287 mmol) dissolved in 4 mL of dichloromethane and 1 mL of methanol. The light yellow solution was stirred for 3 h and the crude mixture was evaporated to dryness. The resulting yellow solid was dissolved in a minimum amount of dichloromethane. The yellow solution was filtered using a filter pipet, and the filtrate was evaporated to dryness. A purified yield of 70.1 mg (29.5%) was obtained. The dried crude product was dissolved in dichloromethane. This solution was filtered into the bottom of an outer diameter of 5 mm glass tube and a few drops of dichloromethane were layered over this solution. Subsequently, diethyl ether was layered over the dichloromethane. As the solutions diffused together, colorless block crystals with blue luminescence and colorless parallelepiped crystals with teal luminescence formed. For spectroscopic measurements, the two types of crystals were manually separated.

Infrared Spectrum, Molecular β -Au₂(μ -dppm)₂Br₂·2CH₂Cl₂ (1). 3051(w), 3013(w), 2968(w), 2928(w), 2854(w), 1965(w), 1884(w), 1818(w), 1773(w), 1586(w), 1573(w), 1484(m), 1435(s), 1369(w), 1360(w), 1321(w), 1310(w), 1266(w), 1186(m), 1158(w), 1090(w), 1097(m), 1070(w), 1028(m), 998(m), 918(w), 843(w), 750(m), 736(s), 688(vs), 615(w) cm⁻¹.

Infrared Spectrum, Ionic [Au₂(μ -dppm)₂Br]Br·2CH₂Cl₂ (2). 3055(w), 3022(w), 2949(w), 2875(w), 1483(w), 1435(m), 1359(w), 1265(w), 1149(w), 1099(m), 1070(w), 1026(w), 999(w), 783(s), 740(s), 721(s), 688(vs), 617(w) cm⁻¹.

Preparation of [Au₂(μ -dppm)₂Br](PF₆) (3). A 78.7 mg (0.205 mmol) portion of dppm was dissolved in 5 mL of dichloromethane, and an equivalent amount of AuBr (56.7 mg, 0.205 mmol) suspended in 4 mL of dichloromethane was added to the dppm solution under agitation. The solution was stirred for 5 min followed by the addition of NH₄PF₆ (31.9 mg, 0.205 mmol) dissolved in 4 mL of dichloromethane and 1 mL of methanol. The light yellow solution was stirred for 3 h and the crude mixture was evaporated to dryness. The resulting yellow solid was dissolved in a minimum amount of dichloromethane. The yellow solution was filtered using a filter pipet, and the filtrate was evaporated to dryness. A purified yield of 82.3 mg (28.9%) was obtained. The dried crude product was dissolved in dichloromethane. This solution was filtered into the bottom of an outer diameter of 5 mm glass tube, a few drops of dichloromethane was layered over that solution and then diethyl ether was layered over the mixture. Colorless blocks with blue luminescence grew as diffusion mixed the solutions.

Infrared spectrum: 3049(w), 3016(w), 2966(w), 2918(w), 2362(w), 2337(w), 1485(m), 1436(s), 1317(w), 1311(w), 1186(w), 1163(m), 1101(s), 1024(w), 999(m), 918(w), 837(vs), 742(s), 740(s), 721(s), 688(vs), 619(w) cm⁻¹.

Preparation of [Au₂(μ -dppm)₂Cl](BPh₄)·3CH₂Cl₂ (4). A 65.7 mg (0.169 mmol) portion of dppm was dissolved in 5 mL of dichloromethane, and an equivalent amount of tthAuCl (54.7 mg, 0.171 mmol) dissolved in 4 mL of dichloromethane was added to the dppm solution under agitation. The solution was stirred for 10 min followed by the addition of Na(BPh₄) (55.6 mg, 0.161 mmol) dissolved in 4 mL of dichloromethane and 1 mL of methanol. The light yellow solution was stirred for 3 h and the crude mixture was evaporated to dryness. The resulting light yellow solid was dissolved in a minimum amount of dichloromethane. The solution was filtered using a filter pipet, and the filtrate was evaporated to dryness. A purified yield of 202.1 mg (78.9%) was obtained. The dried product was dissolved in dichloromethane. This solution was filtered into the bottom of an outer diameter of 5 mm glass tube and a small amount

of dichloromethane was layered of the solution. Diethyl ether was then layered over this mixture. Yellow block crystals with blue luminescence were formed and were isolated.

Infrared spectrum: 3052(w), 2850(w), 1434(m), 1418(m), 1344(w), 1265(w), 1238(m), 1112(w), 1102(m), 1026(w), 996(w), 944(w), 869(w), 776(m), 705(s), 685(s), 571(w), 515(m), 471(w) cm⁻¹.

Preparation of [Au₂(μ -dppm)₂Cl](AsF₆)·2CH₂Cl₂ (5). A 69.9 mg (0.1818 mmol) portion of dppm was dissolved in 1 mL of dichloromethane and 1 mL of acetonitrile, and an equivalent amount of tthAuCl (58.9 mg, 0.1837 mmol) dissolved in 2 mL of dichloromethane was added under agitation. The solution was stirred for 5 min and then a solution of NaAsF₆ (194.63 mg, 0.9185 mmol) in 1 mL of dichloromethane and 1 mL of methanol was added. The colorless solution was stirred for 3 h and the crude mixture was evaporated to dryness. The resulting yellow solid was dissolved in a minimum amount of dichloromethane. The solution was filtered using a filter pipet, and the filtrate was evaporated to dryness. A yield of 29.6 mg (2.13%) was obtained. The dried product was dissolved in dichloromethane. This solution was filtered into the bottom of a 5 mm diameter glass tube and a small amount of dichloromethane was layered over it. Diethyl ether was subsequently layered over these solutions. This mixture was cooled to -20 °C and allowed to stand. Colorless block-like crystals with green luminescence formed and were isolated.

Infrared spectrum: 2929(w), 2922(w), 2854(w), 2355(w), 2331(w), 1481(w), 1437(m), 1352(w), 1311(w), 1263(w), 1184(w), 1159(w), 1107(m), 1068(w), 1029(w), 999(w), 850(w), 783(m), 744(s), 684(vs) cm⁻¹.

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 liquid nitrogen cold stream of a Bruker SMART CCD with graphite monochromated Mo K α radiation at 90(2) K.

Data collected were corrected for Lorentz and polarization effects and for absorption using Blessing's method and merged as incorporated with the program Sadabs. The SHELXTL program package was implemented to determine the probable space group and set up the initial files based upon system symmetry, systematic absences and intensity statistics. The structures were determined by SHELXT and structural refinements were performed with SHELXL. When necessary, the absolute structure parameters were determined. Hydrogen atoms were added geometrically and refined with a riding model.⁴⁵

Physical Measurements. Infrared spectra were recorded on a Bruker α FT-IR spectrometer. Excitation and emission spectra were recorded on a PerkinElmer LS50B luminescence spectrophotometer.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c03657>.

Figures comparing α -Au₂(μ -dppm)₂Br₂·2CH₂Cl₂ with β -Au₂(μ -dppm)₂Br₂·2CH₂Cl₂; emission and excitation spectra for [Au₂(μ -dppm)₂Cl](BPh₄)·3CH₂Cl₂ (4) and [Au₂(μ -dppm)₂Cl](AsF₆)·2CH₂Cl₂ (5) (PDF)

Accession Codes

CCDC 2379676–2379680 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: 44 1223 336033.

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Notes

The authors declare no competing financial interest.

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