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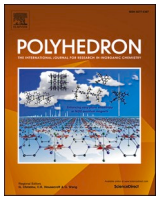

Aurophilic interactions in luminescent, box-like or partial helical cations formed from bis(2-diphenylphosphinoethyl)phenylphosphine (Triphos) and gold(I) ions

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ABSTRACT

Two luminescent salts, $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) and $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**) where Triphos is bis(2-diphenyl-phosphinoethyl)phenylphosphine have been prepared from non-luminescent precursors. The luminescence in each salt results from aurophilic interactions between two or three gold(I) ions. Crystals of $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) contain a box-like structure with an $[Au(CN)_2]^-$ ion suspended between two gold(I) ions in the box. Crystals of $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**) contain a partial helical structure with pairs of gold(I) ions closely connected and surrounded by helical $Ph_2PCH_2CH_2PPh$-units from two Triphos ligands.

1. Introduction

Luminescent compounds are important components of sensors, displays, and optoelectronic devices [1–4]. The construction of luminescent molecular containers, molecules with a well-defined inside and outside, has attracted considerable attention [5–8]. Utilizing a luminescent molecule as a ligand is one means of obtaining such a luminescent molecular cage [5,9]. Luminescent cages can also be obtained from non-luminescent components as outlined below.

Multidentate phosphine ligands are useful building blocks for the construction of complex metal ion-containing structures with various geometric shapes [10–12]. For example, bridging diphosphines, $R_2P(CH_2)_nPR_2$, can be used to place two metal ions in close proximity [13,14] or to position them further apart [15–17]. They can also be used to build large molecules including a chiral ring of sixteen gold(I) ions [18]. Multidentate phosphine ligands have also been used to form molecular containers, three dimensional molecules with a defined inside and outside. For example, a prismatic cage incorporating three metal ions has been synthesized using tris(diphenylphosphine)-cyclohexane [19]. Similarly, the tetrahedral cage, $[M_4(1,3,5\text{-tris}((diphenylphosphino)ethynyl)benzene)_4]^{4+}$, has been prepared using a tridentate phosphine [20].

As shown in Figs. 1 and 2, the non-luminescent, tridentate ligand, bis(2-diphenylphosphinoethyl)phenylphosphine (Triphos), can be used to construct an array of luminescent gold(I)-containing complex cations. These cations may be categorized as helical moieties as seen in Fig. 1, or box-like units as seen in Fig. 2. While the gold ions in the helical complexes are located close to one another, consistent with aurophilic interactions, the six gold ions in these box-like structures are too widely spaced to undergo aurophilic interactions. Aurophilic interactions are attractive interactions between gold ions that have a bond strength similar to a hydrogen bond [21–24]. The sum of the van der Waals radii for two gold(I) ions is about 3.6 Å [23].Two gold ions are believed to experience an aurophilic interaction when the separation between them 3.5 Å or less [23]. The helical ions shown in Fig. 1 are luminescent due to the aurophilic bonding between the three gold ions, which are held in close proximity by the bridging Triphos ligands [25]. The box-like cations are luminescent because of the interaction of two of the gold(I) ions with the ionic unit at the center of the box, but no aurophilic interactions are present in these cations. These box-like ions have been found to host a single chloride or bromide ion [26,27], two bromide ions and two water molecules, or a (CuX_2)- (X=Cl or Br) unit [28]. The chloro- and bromo-box salts are mechanochromic [29–31] and are converted into the halo-bridged helicates shown in Fig. 1 upon grinding.[17] A

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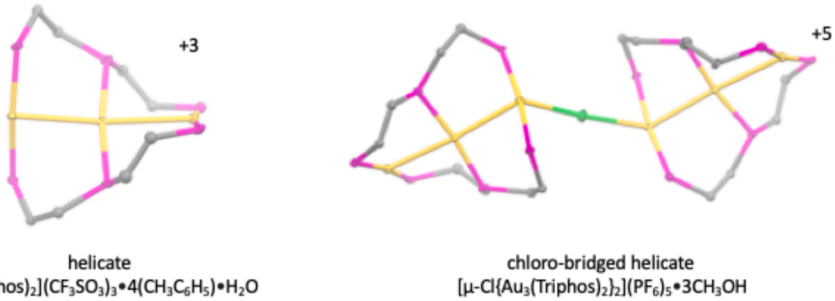

Fig. 1. Structures of the helicate and chloro-bridged helicate cations. Hydrogen atoms and phenyl groups are omitted for clarity. Color scheme: gold, yellow; phosphorus, pink; carbon, grey; chlorine, green. Drawn from data in Ref. [26].

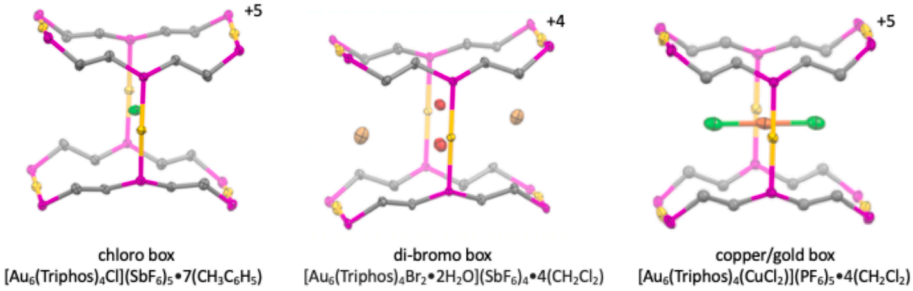

Fig. 2. Structures of the cations in the chloro-box, di-bromo box and copper/gold-box salts. Hydrogen atoms and phenyl groups are omitted for clarity. Color scheme: gold, yellow; phosphorus, pink; carbon, grey; chlorine, green; bromine, brown; oxygen, red; copper, orange. Drawn from data in Ref. [26–28].

mechanism for this process that involves only the breaking of two Au-P bonds has been proposed [17]. The di-bromo box and the copper/gold box are not mechanochromic.

In addition to the cations shown in Figs. 1 and 2, Triphos also forms the linear complexes, $TriphosAu_3X_3$ (Cl^-, Br^-, I^-), in which an AuX unit is bonded to each phosphorus atom of Triphos [32,33] Unfortunately, nothing has been reported about the luminescence of these compounds.

The preparation of the gold/copper box utilized a reaction between the helicate trication, $[Au_3(Triphos)_2]^{3+}$, and the anion $[CuX_2]^-$ to create the new box [28]. Here, we report extension of that chemistry to the preparation and structural characterization of two new luminescent cations built from Triphos that contain six or seven gold(I) ions and involve novel aurophilic interactions between some, but not all, the gold ions.

2. Experimental

2.1. Preparation of compounds

The gold helicate $[Au_3(Triphos)_2](CF_3SO_3)_3$ and (tht)AuCl were synthesized as previously reported [25,26]. Bis(2-diphenylphosphinoethyl)phenylphosphine (Triphos), methanol, toluene, and dichloromethane were purchased from Sigma-Aldrich Co. LLC. Chloroauric acid, Potassium dicyanoaurate, and thallium triflate were purchased from Strem Chemicals, Inc. Thallium salts are toxic and should be handled carefully. Ammonium hexafluorophosphate was purchased from Alfa Aeser, Inc. Solids were used as received. Solvents were used as received, and all reactions were conducted on the bench top open to the atmosphere.

2.2. Synthesis of $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (1)

A 124.4 mg (0.059 mmol) portion of the helicate, $[Au_3(Triphos)_2](CF_3SO_3)_3{\cdot}4(CH_3C_6H_5){\cdot}H_2O$, was dissolved into 7 mL dichloromethane. To this solution, 10.4 mg (0.036 mmol) quantity of $K[Au(CN)_2]$ was added directly under heavy agitation, resulting in a green suspension. At this point, 5 mL of methanol was added, resulting in the suspension clearing without a color change, but ultraviolet irradiation displayed orange luminescence. After two hours of stirring, the solution was filtered, then allowed to evaporate to dryness (122.2 mg, 96 % yield). The product was a yellow solid that displayed yellow luminescence. The product was then dissolved in a minimum volume of dichloromethane and recrystallized by slow diffusion of toluene. Colorless lathes crystallized from this solution and were collected and used for the crystallographic and spectroscopic studies.

Infrared spectrum (cm^{-1}): 3055 (w), 2914 (w), 2132 (w), 2020 (w), 1619 (w), 1586 (w), 1575 (w), 1483 (m), 1436 (s), 1407 (m), 1336 (w), 1312 (w), 1276 (m), 1251 (m), 1224 (s), 1183 (m), 1164 (w), 1105 (s), 1071 (w), 1028 (m), 999 (m), 924 (w), 898 (w), 885 (m), 845 (w), 818 (w), 730 (vs), 689 (vs), 651 (vs), 573 (w), 510 (s), 478 (s), 437 (m). Major peaks correlating to the Triphos ligand: 3055, 2914, 1586, 1575, 1483, 1312, 1183, 1105, 1071, 1028, 999, 924, 845, 730, and 689 cm^{-1}. The major peak correlating to $Au(CN)_2^-$: 2132 and 437 cm^{-1}. The major peaks correlating to the anion $(CF_3SO_3)^-$: 1619, 1312, 1276, 655, and 581 cm^{-1}.

2.3. Synthesis of $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (2)

An initial solution of CuCl was made in acetonitrile by dissolving 68.5 mg of CuCl (0.692 mmol) into 22 mL acetonitrile (0.031 mmol/mL). Two mL of this solution was measured by pipet and diluted to 10 mL of acetonitrile. Separately, a 97.0 mg (0.181 mmol) portion of Triphos was dissolved in 20 mL dichloromethane, then added to the acetonitrile solution with heavy agitation. Then, 86.7 mg (0.270 mmol) of tetrahydrothiophene gold(I) chloride was dissolved in 5 mL dichloromethane and added to the stirring solution and allowed to stir for two hours. At this point, 529.2 mg (3.247 mmol) of ammonium hexafluorophosphate was added directly as a solid. The solution rapidly displayed a color change to green. The solution grew cloudy and displayed blue luminescence upon ultraviolet irradiation. The mixture was stirred for 1 h, then allowed to settle and the supernatant liquid was

Table 1
Crystal data for complexes.

	$[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**)	$[Au_6(Triphos)_4PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**)
color/habit	colorless lathe	colorless lathe
chemical formula	$C_{136}H_{132}Au_6Cl_{11}F_{15}O_{15}P_{12}S_5$	$C_{136}H_{132}Au_6Cl_3F_{36}OP$
formula weight	4872.42	4931.92
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
a (Å)	16.3281(9)	19.1780(17)
b (Å)	17.6728(10)	20.4594(18)
c (Å)	18.0800(10)	27.346(3)
α (deg)	109.835(2)	84.431(3)
β (deg)	102.720(2)	74.801(3)
γ (deg)	106.873(2)	65.123(3)
V (Å^3)	4392.3(4)	9392.5(15)
Z	1	2
T (K)	90(2)	100(2)
λ (Å)	0.71073	0.71073
ρ (g/cm^3)	1.842	1.744
μ (mm^{-1})	6.232	4.951
R_1 (obsd data)[a]	0.0402	0.0570
wR_2 (all data, F^2 refinement)[b]	0.1029	0.1400

[a] $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$.
[b] $wR_2 = ((\Sigma[w(F_o^2 - F_c^2)^2])/\Sigma[w(F_o^2)^2])^{1/2}$.

decanted, then the volume was reduced by rotary evaporation to approximately 10 mL. One 5 mL aliquot was transferred to a separate flask and toluene was added in mL increments until the saturation point was identified by persistent cloudiness, at which point a 10:7 DCM/toluene mixture was added until the solution was clear, and additional toluene was layered over the top. The mixture was allowed to crystallize by slow diffusion.

Infrared spectrum (cm^{-1}): 3060(w), 1612(w), 1585(w), 1574(w), 1783(m), 1436 (s), 1402(m), 1334(w), 1312(w), 1274(w), 1188(w), 1173(w), 1127(w), 1100(s), 1027(w), 999(m), 919(w), 875(m), 829 (vs), 737(s), 709(m), 704(m), 689(vs), 659(m), 614(w), 556(vs), 515 (vs), 495(s), 478(m), 437(w), 397(m), 384(m). The major peaks

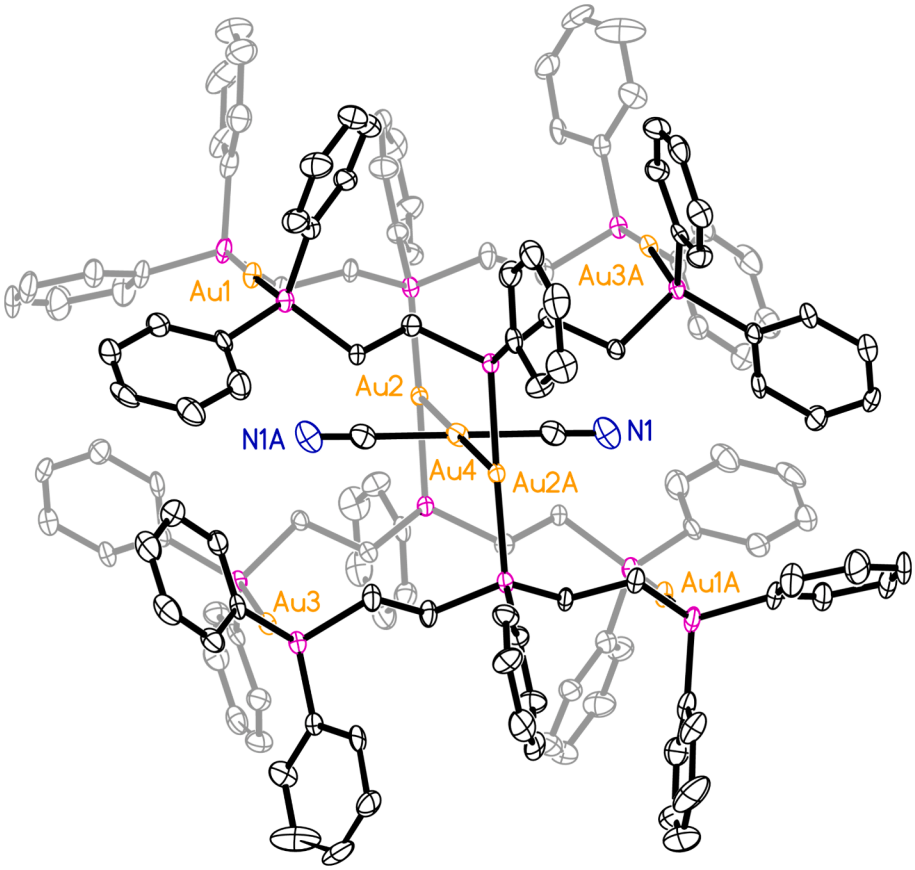

Fig. 3. Structure of the pentacation in $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) with hydrogen atoms removed for clarity. Only the major site is shown for the one disordered phenyl ring. Thermal contours are displayed at the 30 % probability level. Color scheme: gold, orange; phosphorus, pink; carbon, black; nitrogen, blue.

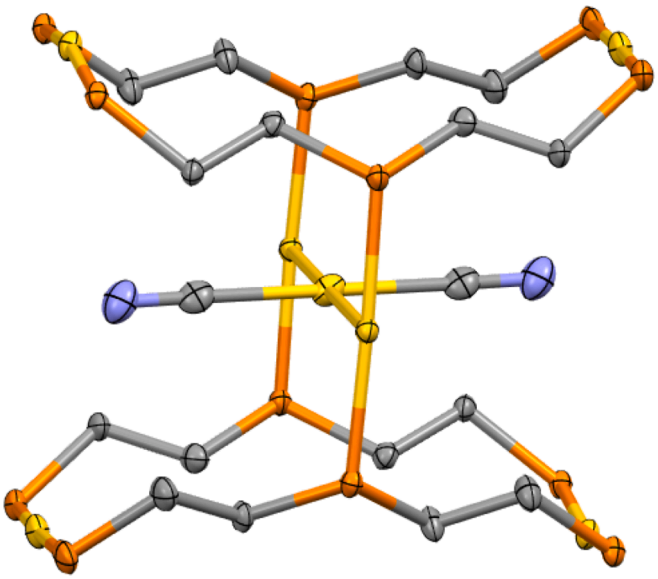

Fig. 4. Skeletal structure of the pentacation in $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) with phenyl groups and hydrogen atoms removed for clarity. Color scheme: gold, yellow; phosphorus, orange; carbon, grey; nitrogen, blue.

correlating to the Triphos ligand: 3060, 1585, 1574, 1312, 1188, 1173, 1100, 1027, 999, 919, 875, 737, 709 and 689 cm^{-1}. The major peaks correlating to the anion $(PF_6)^-$: 1435, 829, 556 cm^{-1}.

2.4. Physical measurements

IR spectra were recorded on a Bruker Alpha FT-IR spectrometer using attenuated total reflectance (ATR). Excitation and emission spectra were recorded on a PerkinElmer LS50B luminescence spectrophotometer. To prevent solvate evaporation and the crystal crumbling, spectra were taken quickly and several times with crystals from the same source that had been crystallographically identified as the correct material. In the process, the crystals were exposed to the dioxygen in air.

2.5. X-ray crystallography and data collection

Crystals of each of the two salts along with some mother liquor were placed on a microscope slide and coated immediately with a hydrocarbon oil. Suitable crystals of $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) and $[(Triphos)_4Au_6](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**) were mounted in the 90 K nitrogen cold stream provided by a Cryo Industries low-temperature apparatus on the goniometer head of a Bruker APEX II sealed-tube diffractometer and CCD detector. The diffraction data were collected with the use of MoKα (Λ = 0.71073 Å) radiation. A multi-scan absorption correction was applied with the program SADABS [34]. The structure was solved by a dual space method, (SHELXT) [35] and refined by full-matrix least-squares on F^2 (SHELXL-2017) [35]. Crystal data are given in Table 1. Disorder in $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) was treated as follows. Two of the phenyl rings in the pentacation are disordered and modeled in two different positions. This crystal contains large spaces that are loosely occupied by the anions and solvate molecules with significant disorder. Within these spaces two sites are partially occupied by triflate anions or dichloromethane molecules. Another site is partially occupied by a triflate ion or a toluene molecule. One of the dichloromethane molecules is badly disordered and two of the toluene solvates are disordered. Disorder in $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**) was treated as follows. One of the phenyl rings of the hexacation is disordered over two positions. Two of the hexafluorophosphate ions are disordered with one site involving three positions and the other two positions. One of the toluene solvate molecules is disordered as is one of the dichloromethane solvate molecules.

3. Results and discussion

3.1. Preparation and structure of $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (1)

Colorless crystals of the box-like compound, $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) were obtained by addition of solid $K[Au(CN)_2]$ to a dichloromethane solution of the helicate, $[Au_3(Triphos)_2](CF_3SO_3)_3{\cdot}4(CH_3C_6H_5){\cdot}H_2O$, followed by the addition of

Table 2
Selected Bond Distances and Angles.

$[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**)		$[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$(**2**)		$[Au_6(Triphos)_4Au(CuCl_2)](PF_6)_5{\cdot}4CH_2Cl_2$	(from ref. [28])
Bond Length (Å)		Bond Length (Å)		Bond Length (Å)	
Au2-Au4	3.1305(3)	Au1-Au2	2.9562(5)	Cu1-Au2	3.1646(10)
Au1-P1	2.2939(19)	Au5-Au6	2.9690(5)	Au1-P1	2.300(3)
Au1-P4	2.2934(18)	Au1-P1	2.305(2)	Au1-P6	2.305(3)
Au2-P2	2.3040(16)	Au1-P4	2.307(2)	Au2-P2	2.304(2)
Au2-P5	2.3017(16)	Au2-P2	2.305(2)	Au2-P5	2.305(3)
Au3-P3	2.3040(16)	Au2-P5	2.303(2)	Au3-P3	2.301(3)
Au3-P6	2.3008(16)	Au3-P3	2.313(3)	Au3-P4	2.297(3)
Au4-C69	2.008(7)	Au3-P7	2.312(2)	Cu1-Cl1	2.104(4)
N1-C69	1.146(8)	Au4-P6	2.292(2)		
Au2···Au2A (width)	6.2610(6)	Au4-P10	2.294(3)	Au2···Au2A (width)	6.329
Au1···Au3 (length)	8.3422(6)	Au5-P8	2.9690(5)	Au1···Au3 (length)	8.357
Au1···Au3A (depth)	7.3408(6)	Au5-P11	2.302(2)	Au1···Au3A (depth)	7.386
		Au6-P9	2.320(2)		
		Au6-P12	2.321(3)		
Bond Angle (deg)		**Bond Angle (deg)**		**Bond Angle (deg)**	
P1-Au1-P4	177.60(6)	P1-Au1-P4	169.20(8)	P1-Au1-P6	173.65(9)
P2-Au2-P5	177.73(6)	P2-Au2-P5	177.84(8)	P2-Au2-P5	177.41(7)
P3-Au3-P6	167.54(5)	P3-Au3-P6	172.75(8)	P3-Au3-P6	175.68(8)
		P6-Au4-P10	170.24(9)		
		P8-Au5-P11	173.99(8)		
		P9-Au6-P12	173.18(9)		

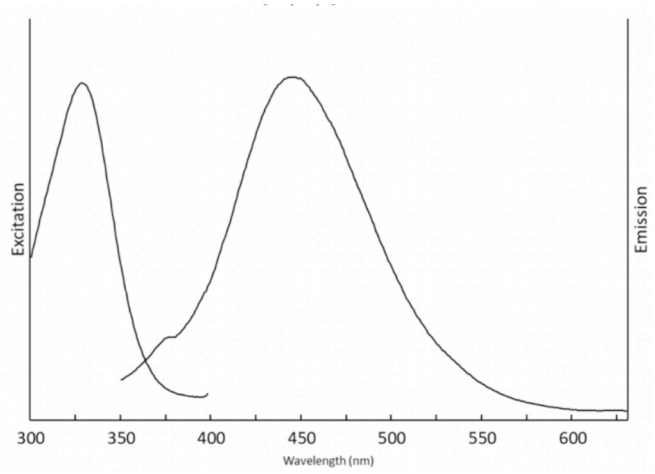

Fig. 5. Excitation spectrum (left) for emission at 445 nm and emission spectrum (right) for excitation at 323 nm from crystalline $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**).

methanol. After filtration, the resulting solution was evaporated to dryness. The residue was dissolved in dichloromethane and toluene was allowed to diffuse into the solution to produce colorless crystals of the product. These crystals are extremely fragile and readily lose dichloromethane once removed from the mother liquor. Thus, we were careful to protect these crystals to maintain their composition and structure, both for single crystal X-ray diffraction and spectroscopic measurements.

The structure of the pentacation in $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) as determined by X-ray diffraction is shown in Figs. 3 and 4. Some significant bond distances and angles are given in Table 2. The cation is centrosymmetric with Au4 residing on a crystallographic center of symmetry. The box is formed from six widely separated gold ions that are connected by the four bridging Triphos ligands to form four of the edges of the box. The shape of this pentacation is similar to the shape of the other box pentacations shown in Fig. 2 A strictly linear $Au(CN)_2^-$ unit resides at the center of the box. The Au2-Au4 distance is 3.1305(3) Å, which is indicative of aurophilic bonding between the Au $(CN)_2^-$ unit and two of the gold(I) ions on either side of the cage. The overall structure of the pentacation $[Au_6(Triphos)_4Au(CN)_2]^{5+}$ is similar to that of the copper/gold boxes shown in Fig. 2 and to $[Au_6(Triphos)_4(CuCl_2)]^{5+}$ in particular [28]. Some dimensions for $[Au_6(Triphos)_4(CuCl_2)]^{5+}$ are included in Table 2 for comparison purposes. The Au2-Au4 distance (3.1305(3) Å) is in the range where aurophilic interactions are expected and falls between the Cu-Au distances (3.0738(4) and 3.2172(4) Å) in $[Au_6(Triphos)_4(CuBr_2)](CF_3SO_3)_5{\cdot}3CH_2Cl_2{\cdot}3CH_3OH{\cdot}4(H_2O)$ and $[Au_6(Triphos)_4(CuCl_2)](PF_6)_5{\cdot}4(CH_2Cl_2)$ [28]. Significant metallophilic interactions within the Au-Cu-Au units in $[Au_6(Triphos)_4(CuBr_2)]^{5+}$ and $[Au_6(Triphos)_4(CuCl_2)]^{5+}$ have been identified in computational studies of these pentacations and similar aurophilic interactions are likely present in $[Au_6(Triphos)_4Au(CN)_2]^{5+}$. The Au2-Au4 distance in this pentacation is a bit longer than the Au-Au distances (3.0075(2), 2.95657(19) Å) in the helicate $[Au_3(Triphos)_2](CF_3SO_3)_3{\cdot}4(CH_3C_6H_5){\cdot}H_2O$ [26].

Colorless crystals of $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) display a blue luminescence. The excitation and emission spectra of these crystals at room temperature are shown in Fig. 5. The lifetime of the luminescence was 11 microseconds. Thus, the luminescence is due to phosphorescence as was the case for the closely related copper/gold boxes [19]. In the simplest terms, bonding within the central Au group involves construction of molecular orbitals using the three filled d_z2 orbitals and the three empty p_z orbitals, where the z axis lies along the axis of the Au_3 unit. For a relevant molecular orbital diagram, see Scheme 1 in Tran et al. [36] Excitation probably involves promotion of an electron from the highest filled MO constructed from the gold d_z2 orbitals into the lowest empty MO involving the p_z orbitals. Emission is likely to involve the reverse process after intersystem crossing to provide the excited triplet state.

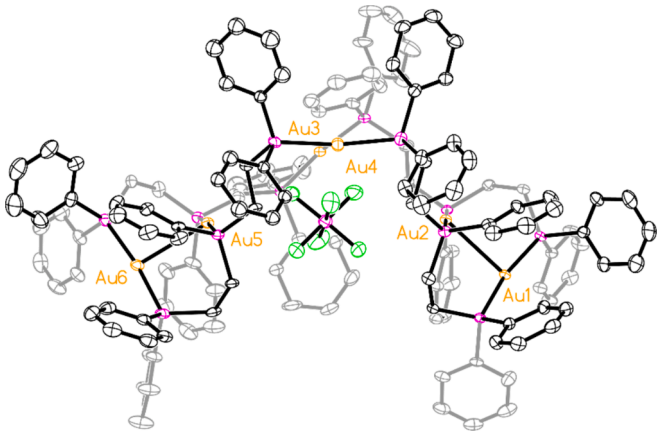

Fig. 6. Structure of the hexacation in crystalline $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**) with hydrogen atoms removed for clarity. Only the major positions are shown for the two disordered phenyl rings. Thermal contours are displayed at the 30 % probability level. Color scheme: gold, yellow; phosphorus, orange; carbon, grey.

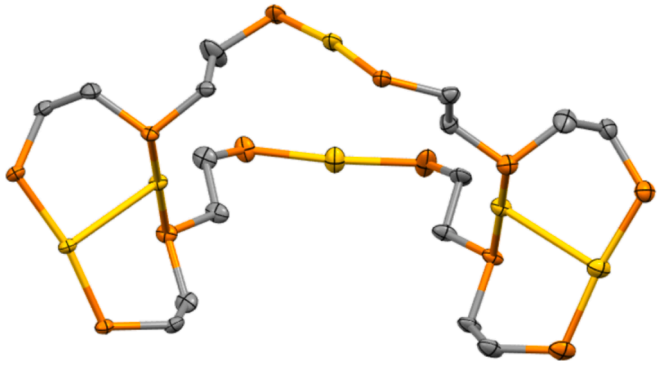

Fig. 7. Structure of the hexacation in crystalline $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**) with phenyl groups and hydrogen atoms removed. Color scheme: gold, yellow; phosphorus, orange; carbon, grey.

3.2. *Preparation and structure of $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (2)*

In an attempt to prepare the copper box, $[Au_6(Triphos)_4(CuCl_2)](PF_6)_5$ [19], we encountered another type of Triphos complex containing six gold(I) ions, $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**). Colorless crystals of $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**) formed out of a mixture of copper(I) chloride, Triphos, tetrahydrothiophene gold(I) chloride, and ammonium hexafluorophosphate in acetonitrile/dichloromethane mixture. These crystals were quite delicate and readily lost dichloromethane once separated from the mother liquor. Thus, precautions were taken to ensure the integrity of these crystals for crystallographic and spectroscopic measurements.

The structure of the hexacation in crystalline $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**) as determined by single crystal X-ray diffraction is shown in Figs. 6 and 7. Fig. 6 shows how the hexacation is wrapped about one of the six hexafluorophosphate ions in the solid. Fig. 7 shows a drawing of the hexacation with hydrogen atoms and phenyl groups removed so that the basic skeleton of the complex is readily viewed. The hexacation contains two helical segments in which two different gold(I) ions are bridged by two $Ph_2PCH_2CH_2PPh$ segments

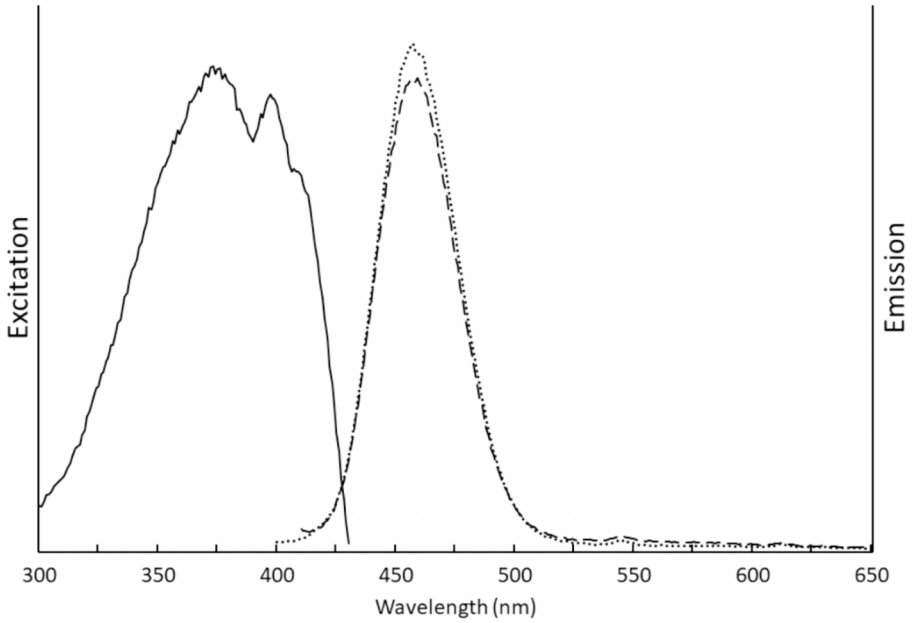

Fig. 8. Excitation (left, solid line for emission at 458 nm) and emission (right, dotted line for excitation at 373 nm, dashed line for excitation at 397 nm) spectra of crystals of $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**) at room temperature.

of the two Triphos ligands. Within these helical units the Au···Au distances are 2.9562(5) and 2.9690(5) Å and are indicative of aurophilic interactions between the two gold(I) ions. These helical unit resemble the binuclear dication, $[Au_2(\mu\text{-dppe})_2]^{2+}$, which has Au···Au distances ranging from 2.8787(9) to 2.9593(5)Å depending on the anion present [37]. The remaining $CH_2CH_2PPh_2$ units that extend away from the helical domain, are bonded to two different gold(I) ions, Au3 and Au4. The distance between Au3 and Au4 is quite large, 8.1924(9) Å. The overall cyclic structure of the cation is best seen in the skeletal drawing in Fig. 7.

Crystals of $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ display a blue luminescence. The excitation and emission spectra of these crystals are shown in Fig. 8. A single symmetric emission band is seen when excitation is set at 373 or 397 nm. The emission lifetime is 20 microseconds, which is indicative of phosphorescence. For the pairs of gold(I) ions in close proximity in this hexacation, excitation likely involves promotion of an electron from the antibonding $d\sigma_z$ orbital to the empty, bonding $p\sigma_z$ orbital, where the z axis lines along the Au-Au bond as has been established for other dinuclear gold(I) complexes [38]. Emission likely involves the reverse process after intersystem crossing. Other dimeric complexes with two gold(I) centers in close proximity show similar photophysical properties. For example, crystals of $[Au_2(\mu\text{-dppe})_2](PF_6)_2.CHCl_3$ produced emission at 474 upon excitation at 378 nm [23].

4. Conclusions

The complexity of compounds formed from four Triphos ligands and six gold(I) ions has been extended to two new complex cations, which contain aurophilic interactions. The box, $[Au_6(Triphos)_4Au(CN)_2]^{5+}$, and the partial helix, $[Au_6(Triphos)_4Au(CN)_2]^{6+}$, have been isolated as crystalline salts. Crystals of $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) contain a box-like moiety with an $[Au(CN)_2]^-$ unit suspended between two gold(I) ions of the box to form a linear chain of three gold(I) ions connected by aurophilic interactions. Crystals of the partial helix, $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**), contain a hexacation in which pairs of gold(I) ions are bridged by two Triphos ligands, The remaining PPh_2 unit on each of these ligands connects to two other, widely spaced gold ions to yield the complex ring structure shown in Figs. 6 and 7. Colorless crystals of $[Au_6(Triphos)_4Au(CN)_2](CF_3SO_3)_5{\cdot}5CH_2Cl_2{\cdot}C_6H_5CH_3$ (**1**) and $[Au_6(Triphos)_4](PF_6)_6{\cdot}2CH_2Cl_2{\cdot}6C_6H_5CH_3{\cdot}H_2O$ (**2**) are luminescent due to the aurophilic interactions in these cations. Within the Au_3 and Au_2 units in the cations the excitations involve transitions from the highest filled d_z molecular orbital to the lowest empty p_z molecular orbital where the z axis is located on the bonds connecting the gold(I) ions.

CRediT authorship contribution statement

Daniel T. Walters: Writing – review & editing, Writing – original draft, Investigation, Data curation. **Sarah Costa:** Writing – review & editing, Validation, Methodology, Investigation, Data curation. **Reza Babadi Aghakhanpour:** Investigation, Data curation, Conceptualization. **Marilyn M. Olmstead:** Investigation, Funding acquisition, Formal analysis, Data curation. **Alan L. Balch:** Writing – review & editing, Writing – original draft, Resources, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

CCDC 2359819–2359820 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_req

uest@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2024.117140.

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