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Synthesis, spectroscopy and crystal structures of [Au₂{µ-Ph₂PN(Et)PPh₂}₂][SbF₆]₂ and [Au₃Cl₂{µ-Ph₂PN(Et)PPh₂}₂]PF₆*

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Abstract—Treatment of $[Au(MeCN)_2]SbF_6$ in acetonitrile with bis(diphenylphosphino)ethylamine (dppa) afforded a colourless crystalline material characterised as $[Au_2(\mu-dppa)_2][SbF_6]_2$. An X-ray diffraction study confirmed that the two ligands bridge the two gold atoms with a Au…Au separation of 2.838(2) Å. The electronic absorption spectrum exhibits a band at 298 nm (ϵ_{max} , *ca*. 17000 dm³ mol⁻¹ cm⁻¹) attributable to a $p_{\sigma} \leftarrow d_{\sigma}^*$ transition. The compound luminesces strongly in acetonitrile ($\lambda_{max} = 500$ nm). Treatment of HAuCl₄.2H₂O with 2,2'-thioethanol in methanol followed by the ligand afforded a colourless crystalline material characterised as $[Au_3Cl_2(\mu-dppa)_2]PF_6$. A crystal structure determination revealed a cation of C_2 symmetry, comprising a bent chain of three gold atoms (Au…Au…Au = 167.5(8)°, Au…Au = 3.037(1) Å), with each pair of adjacent gold atoms bridged by a diphosphazane ligand and with the coordination at the outer gold atoms completed by a chloride ligand. This compound luminesces extremely weakly in acetonitrile but does emit strongly at 485 nm when irradiated in the solid state. The luminescence displayed by both compounds is attributed to the presence of a substantial intramolecular interaction between the gold atoms, but ligand effects appear to be more important in determining the emissive energies. © 1998 Elsevier Science Ltd. All rights reserved

Homoleptic digold(I) complexes, in which the gold atoms are bridged by two symmetric diphosphine ligands and in which each gold atom is two-coordinate, have been shown to be photoluminescent [1]. The best studied examples are salts of the dppm $(dppm = Ph_2PCH_2PPh_2)$ ligand-bridged digold(I) cation, $[Au_2(\mu-dppm)_2]^{2+}$. The BF₄ salt is strongly phosphorescent in acetonitrile solution, the emission being observed at 593 nm at room temperature with a lifetime of 21 μ s and a quantum yield of 0.31 [2]. The ClO₄ salt also exhibits phosphorescence at room temperature in acetonitrile solution, but at 570 nm with a lifetime of 18 μ s and a quantum yield of 0.15 [3, 4]. The

room temperature emission spectrum of the BH₃CN⁻ salt has been recorded in the solid state, since this species decomposes on irradiation in solution; emission occurs at 490 nm in this case [2, 5]. In contrast, mononuclear bisphosphine complexes such as [Au(P- Ph_{3}_{2}]BPh₄ are not luminescent [6]. This has led to the conclusion that the loss of centrosymmetric structure, brought about by the presence of an Au---Au interaction in the dinuclear species, is in some way responsible for the luminescence displayed by compounds of this type [6]. However, the intermetallic separation does not appear to play a significant role in determining the energy of the emission. For instance, Fackler et al. have shown that there is no direct correlation between the Au-Au separation and the emission wavelength (recorded in the solid state) for the following series of luminescent ligand-bridged compounds: $[Au_2(\mu-dppm)_2][BH_3CN]_2$, digold(I) $[Au_2(\mu-dppm)_2]Cl_2, \quad [Au(CH_2)_2PPh_2]_2,$ $[n-\mathrm{Bu}_4\mathrm{N}]_2$

^{* (}Dedicated to our friend and colleague, Jack Lewis, on the occasion of his 70th birthday)

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 $[Au(S_2C=C(CN)_2)]_2$, $[Au(CH_2P(S)Ph_2)]_2$, and [Au $(S_2CNEt_2)]_2$ [2]. It has been suggested that this lack of correlation may be as a consequence of the HOMO having some ligand character and not being a purely metal orbital, with ligand changes affecting the energy of the HOMO, either directly or indirectly [2]. This being the case, the emissive properties of diphosphine ligand-bridged digold(I) complexes of the $[Au_2(\mu$ $dppm)_2]^{2+}$ type may be more the property of the diphosphine ligand and, in particular, of the AuP₂ unit rather than of the intergold separation [1]. The diphosphazane ligand Ph2PN(Et)PPh2 (dppa) is closely related to the dppm ligand, the only difference being the presence of an ethylamino, rather than a methylene group, between the two phosphorus atoms. It was therefore of interest to compare the structure and emissive properties of the diphosphazane ligandbridged chromophore, $[Au_2(\mu-dppa)_2]^{2+}$, with those of the $[Au_2(\mu-dppm)_2]^{2+}$ species. Accordingly, the SbF₆ salt of the $[Au_2(\mu-dppa)_2]^{2+}$ cation has been synthesised, its structure determined by means of Xray diffraction, and its absorption and emission spectra in acetonitrile recorded.

Trigold(I) complexes stabilised by bidentate bridging ligands have received less attention, especially with regard to their photophysical properties. However, the syntheses and crystal structures of the [AuCl(C₆F₅)₃]⁻ and chloride salts of the [Au₃Cl₂(μ dppm)₂]⁺ cation have been reported [7, 8]. In contrast to [Au₂(μ -dppm)₂]²⁺, this cation does not appear to luminesce in solution, the authors only reporting the existence of an intense emission at 485 nm in the solid state for the chloride salt [8].

To establish whether $[Au_3Cl_2(\mu-dppa)_2]^+$ has similar luminescent properties, its synthesis as the hexa-fluorophosphate salt was effected and its crystal structure and emission properties determined.

RESULTS AND DISCUSSION

Treatment of an acetonitrile solution of $[Au(MeCN)_2]^+$ with a molar equivalent of the solid Ph₂PN(Et)PPh₂ (dppa) ligand afforded a yellow solution from which $[Au_2(\mu-dppa)_2][SbF_6]_2$ could be isolated in good yield as a colourless microcrystalline solid by precipitation with diethylether. Elemental analysis, the infrared spectrum recorded as a KBr pellet and the ¹H NMR spectrum are all consistent with the formulation of the compound as $[Au_2(\mu$ dppa)₂][SbF₆]₂, as subsequently confirmed by means of a single crystal structure determination (see below). The ${}^{31}P{}^{1}H$ NMR spectrum recorded in CD₃CN exhibits a single sharp peak at 100.25 ppm, indicative of a phosphorus atom bonded to a gold atom; the phosphorus atoms of the free ligand resonate at 60.60 ppm. Interestingly, the phosphorus atoms of the diphosphazane ligand are considerably deshielded relative to those of the dppm ligand, the latter resonating at ca. 35 ppm in $[Au_2(\mu-dppm)_2][ClO_4]_2$ [4]. This is to be expected in view of the stronger electronwithdrawing properties of the ethylamino as opposed to the methylene group. The compound is stable in the solid state but, if left to stand in solution in the presence of oxygen, it slowly degrades.

The procedure used for the preparation of $[Au_3Cl_2(\mu-dppa)_2]PF_6$ is similar to one of two methods employed by Lin et al. for the preparation of $[Au_3Cl_2(\mu$ -dppm)₂]Cl [8]. Thus, the compound is obtained in good yield by reacting HAuCl₄.2H₂O with 2,2'-thioethanol in methanol before treating it with a slight excess of ligand. Isolation of the compound as a colourless microcrystalline solid was achieved by addition of NH₄PF₆ and crystallisation from the methanol solution. Elemental analysis, the infrared spectrum recorded as a KBr pellet and the ¹H NMR spectrum are all consistent with the formulation of the compound as $[Au_3Cl_2(\mu-dppa)_2]PF_6$, as subsequently confirmed by means of a single crystal structure determination (see below). The ${}^{31}P{}^{1}H{}$ NMR spectrum recorded in CD₃CN exhibits a well-defined AA'BB' pattern with the multiplets centred at 103.61 and 83.11 ppm. Such a pattern is also observed for the $[Au_3Cl_2(\mu$ -dppm)₂]⁺ cation in its $[AuCl(C_6F_5)_3]^-$ salt [7]. On the other hand the ${}^{31}P{}^{1}H{}$ spectrum for the chloride salt is complicated by an exchange process driven by the reaction of the chloride counterion with the trinuclear gold cation. In this case, a AA'BB' pattern is only observed in the presence of added AgBF₄, *i.e.*, when the potentially coordinating chloride counterion is replaced by the non-coordinating tetrafluoroborate anion [8]. As expected, the phosphorus atoms in the diphosphazane ligand-bridged trigold cation are deshielded relative to those in the analogous dppm ligand-bridged species; Uson et al. report an AA'BB' pattern for [Au₃Cl₂(µ-dppm)₂][Au- $Cl(C_6F_5)_3$ with the multiplets centred at 37.1 and 29.0 ppm [7]. As with the dinuclear diphosphazane ligand-bridged species, the trinuclear complex $[Au_3Cl_2(\mu-dppa)_2]PF_6$ is stable in the solid state but, if left to stand in solution in the presence of oxygen, it slowly degrades.

Crystal structure and photophysical properties of $[Au_2(\mu-dppa)_2][SbF_6]_2$

Crystals of the compound consist of well-separated $[Au_2(\mu\text{-dppa})_2]^{2+}$ cations and SbF_6^- anions, there being no unusual intermolecular contact distances. Figure 1 shows an ORTEP drawing of the cation, while selected interatomic distances and angles for the cation are given in Table 1.

The two gold atoms are bridged by the two diphosphazane ligands such that there is a crystallographically imposed centre of symmetry midway between them. The coordination at each gold atom is only approximately linear, as evidenced by a P(1)– Au-P(2') angle of 167.5(8)°. As illustrated in Fig. 1, the deviation from linearity apparently results from Synthesis, spectroscopy and crystal structures



Fig. 1. ORTEP drawing of the $[Au_2(\mu-dppa)_2]^{2+}$ cation in $[Au_2(\mu-dppa)_2][SbF_6]_2$. The carbon atoms are drawn as spheres of arbitrary radius and the remaining atoms as 20% probability ellipsoids.

Au…Au′	2.838(2)		Au-P(1)	2.313(6)
Au–P(2')	2.298(5)		P(1)–N	1.70(2)
P(1)-C(1)	1.75(3)		P(1)-C(7)	1.79(3)
P(2)–C(13)	1.75(3)		P(2)-C(7)	1.79(3)
P(2)–C(19)	1.82(3)		P(2)–C(19)	1.82(3)
P(1)-Au- $P(2')$		167.5(7)	Au-P(1)-N	115.4(8)
Au-P(1)-C(1)		106.4(10)	Au– $P(1)$ – $C(7)$	114.3(9)
N-P(1)-C(1)		110.1(13)	N-P(1)-C(7)	104.7(12)
C(1) - P(1) - C(7)		106(2)	Au'-P(2)-N	111.3(8)
Au'-P(2)-C(13)		115.5(9)	Au'-P(2)-C(19)	105.6(9)
N–P(2)–C(13)		107.5(12)	N-P(2)-C(19)	105.4(12)
C(13)–P(2)–C(19)		111.2(14)	P(1)-N-P(2)	117.0(11)
P(1)–N–C(25)		121.5(7)	P(2)-N-C(25)	116.9(7)

Table 1. Selected interatomic distances (Å) and angles (°) for [Au₂(µ-dppa)₂][SbF₆]₂

the two gold atoms being pulled towards each other by a substantial Au-Au interaction. This is reflected in an Au…Au distance of 2.838(2) A that is significantly shorter than the Au-Au distances in $[Au_2(\mu-dppm)_2][BH_3CN]_2 \cdot 2CH_2Cl_2 \quad (2.982 \text{ \AA})$ [9], $[Au_2(\mu-Me_2PCH_2PMe_2)_2][ClO_4]_2$ [10], (3.028 A) [10], $[Au_2(\mu-Me_2PCH_2PMe_2)_2]Br_2.H_2O$ (3.023 Å) [Au₂(µ-Me₂PCH₂PMe₂)₂]Cl₂.H₂O (3.010 Å) [11] and [Au₂(µ-Cy₂PCH₂PCy₂)₂][PF₆]₂ (2.935 Å) [12]. It is also shorter than the Au. Au distance of 2.962 Å reported for $[Au_2(\mu-dppm)_2]Cl_2$, but this comparison is not strictly valid since the gold atoms in the latter compound are formally three-coordinate, due to the close approach of the chloride anions [13]. In fact, the core structure of the $[Au_2(\mu-dppa)_2]^{2+}$ cation is very similar in all respects to that observed for the other digold(I) ligand bridged species listed above, there being no evidence of a tendency for the gold atom to become three-coordinate by associating with the fluoride of the SbF₆⁻ anion. There is a slight twisting of the bridging ligands about the Au··Au vector, as reflected by a P(1)–Au···Au'–P(2) torsion angle of 12.4°. The Au–P bond lengths of 2.314(5) and 2.297(5) Å are somewhat shorter than the value of 2.400 Å given for eight compounds of the closely related dppm ligand with gold [14], but are very similar to the Au–P distance of

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Fig. 2. Absorption and emission (340 nm excitation) spectra in CH₃CN of [Au₂(µ-dppa)₂][SbF₆]₂.

2.314(2) Å in $[Au_2(\mu-Cy_2PCH_2PCy_2)_2]^{2+}$ [12] and the Au–P distances of 2.311(4) and 2.317(4) Å in $[Au_2(\mu-dppm)_2][BH_3CN]_2 \cdot 2CH_2Cl_2$ [9].

The room temperature UV/vis absorption spectrum of $[Au_2(\mu-dppa)_2][SbF_6]_2$ in acetonitrile is shown in Fig. 2. A very intense absorption band is observed as a shoulder at 226 nm which can be attributed to transitions within the phenyl rings [2]. Also observed are bands at 267 nm (ϵ_{max} , ca. 23000 dm³ mol⁻¹ cm⁻¹) and at 298 nm (ϵ_{max} , ca. 17000 dm³ mol⁻¹ cm⁻¹) while some lower energy and weaker absorptions are observed in the region 330-370 nm. Thus, the bands in the 250-400 nm region appear at positions very similar to those observed in the absorption spectrum of $[Au_2(\mu\text{-dppm})_2][ClO_4]_2$ recorded in acetonitrile [4], but with differences in the relative intensities of the bands and a generally lower resolution of the peaks in the absorption spectrum of $[Au_2(\mu-dppa)_2][SbF_6]_2$. On this basis, we tentatively assign the absorption band at 298 nm to the spin-allowed $p_{\sigma} \leftarrow d_{\sigma}^*$ transition, the equivalent band in the dppm-bridged cation being at 290 nm for the ClO_4^- salt [4] and at 293 nm for the BF_4^- salt [2]. Figure 2 also shows the emission spectrum of the $[Au_2(\mu-dppa)_2]^{2+}$ cation measured at room temperature in acetonitrile, an intense and asymmetric emission band being observed at 500 nm. Thus, the $[Au_2(\mu-dppm)_2]^{2+}$ and $[Au_2(\mu-dppa)_2]^{2+}$ chromophores have in common the fact that they both emit strongly on irradiation in solution. This is unusual, as most ligand-bridged digold(I) species do not generally emit in solution, only displaying luminescence in the solid state [2]. For example, the diphosphine ligand-bridged species $[Au_2(\mu-Cy_2PCH_2)]$ $PCy_2)_2]^{2+}$ does not emit at room temperature, only luminescing at 489 nm in the solid state at 77 K [12].

The emission maximum of 500 nm, recorded at room temperature in acetonitrile for the $[Au_2(\mu$ dppa)₂]²⁺ cation, occurs at a considerably lower wavelength, compared to the wavelengths recorded for the emission maxima observed under the same conditions for the $[Au_2(\mu\text{-dppm})_2]^{2+}$ cation; these occur at 570 and 593 nm for the ClO_4^- [3, 4] and BF_4^- salts [2] respectively. The difference of 23 nm in the emission wavelengths for the latter two salts has been ascribed to medium effects [1], but these seem unlikely to account for the decrease in emission wavelength of \geq 70 nm observed for the dppa ligand-bridged species. The emissive state for the dppm ligand-bridged cation is generally accepted as being phosphorescent [2-4], with the excited state being assigned as either ${}^{3}A_{u}(d\sigma^{*})(p\sigma)$ [2–4] or ${}^{3}B_{1u}(d\delta^{*})(p\sigma)$ [3, 4]. Assuming that one of these two assignments also applies to the dppa ligand-bridged chromophore, the expectation would be that a decrease in the Au---Au distance would lead to an increase in the interaction between the gold atoms and, hence, an increase in the emission wavelength. Exactly the opposite trend is observed when the Au…Au distances of the two cations are compared. Thus, although the Au-Au distance of 2.838(2) Å observed for $[Au_2(\mu-dppa)_2]^{2+}$ is significantly shorter than the value of 2.982(2) Å reported for the BH₃CN⁻ salt of the $[Au_2(\mu$ $dppm)_2]^{2+}$ cation [9], the wavelength of the emission is substantially shorter. It seems certain that effects intrinsic to the bridging ligands are responsible for the large difference in emission energy observed for the $[Au_2(\mu-dppm)_2]^{2+}$ and $[Au_2(\mu-dppa)_2]^{2+}$ chromophores. Such an effect could be caused by replacing a CH₂ group in the dppm ligand with an electronwithdrawing N(Et) group to give the dppa ligand,

resulting in less electron density on the donor phosphorus atoms in the dppa as compared to the dppm ligand. However, we are not in a position to quantify such an effect on the relative energies of the HOMO and LUMO in species of this type and, hence, to fully explain the differences in emission energy.

Crystal structure and photophysical properties of $[Au_3Cl_2(\mu-dppa)_2]PF_6$

Crystals of the compound consist of well-separated $[Au_3Cl_2(\mu-dppa)_2]^+$ cations and PF_6^- anions, there being no unusual intermolecular contact distances. Figure 3 shows an ORTEP drawing of the cation while selected interatomic distances and angles for the cation are given in Table 2.

The cation comprises a bent chain of three gold atoms, each pair of adjacent gold atoms being bridged by a diphosphazane ligand and with the coordination at the two outer gold atoms being completed by a chloride ligand. Overall, the cation has C_2 symmetry. The deviation of the chain of gold atoms from linearity is reflected by a Au(2)···Au(1)···Au(2') angle of 163.8(2)°. This is in marked contrast to the arrangement of gold atoms in $[Au_3Cl_2(\mu-dppm)_2]^+$, where the Au···Au···Au angles are 74.2 and 74.6° for the $[AuCl(C_6F_5)_3]^-$ and Cl⁻ salts respectively [7, 8]. Each diphosphazane ligand is considerably twisted, as reflected by a P(1)–Au(1)···Au(2)–P(2) torsion angle of 46.9°. The equivalent torsion angles in the dppmbridged trigold(I) cation are somewhat smaller, being

15.4 and 26.7° in the $[AuCl(C_6F_5)_3]^-$ salt and 23.6° in the chloride salt. It has been previously shown that diphosphazane ligands are very flexible in terms of twisting about the metal-metal vector which they bridge [15] and it may be that this is, in some way, responsible for the adoption of a near linear arrangement of gold atoms in the $[Au_3Cl_2(\mu-dppa)_2]^+$ cation. The central gold atom is symmetrically coordinated by the phosphorus atoms of trans disposed diphosphazane ligands with a P(1)-Au(1) P(1') angle of 175.4(6)°. The outer two gold atoms are asymmetrically coordinated, being bonded to the phosphorus atom of a diphosphazane ligand and to a chloride ligand; the P(2)–Au(2)–Cl angle of $177.1(1)^{\circ}$ shows only a small deviation from linearity. The Au(1)…Au(2) distance of 3.037(1) Å is somewhat shorter than the Au…Au distances observed for the $[Au_3Cl_2(\mu$ -dppm)₂]⁺ cation, these being 3.067 and 3.164 Å for the $[AuCl(C_6F_5)_3]^-$ salt and 3.076 Å for the chloride salt [7, 8]. This trend is consistent with the shorter Au···Au distance observed for the $[Au_2(\mu$ $dppa)_2]^{2+}$ cation as compared to that reported for the $[Au_2(\mu$ -dppm)₂]²⁺ cation (see above). The Au(1)–P(1) bond length of 2.313(2) Å is significantly longer than the Au(2)-P(2) bond length of 2.228(2) Å, presumably because of the greater trans influence of the diphosphazane as opposed to the chloride ligand. As might be expected, the Au–P(1) distance of 2.313(2) Å agrees well with that of 2.316 Å found for [Au(P- $MePh_2)_2$ ⁺ [16] since, in both cases, the gold atom is symmetrically coordinated by phosphorus donor



Fig. 3. ORTEP drawing of the $[Au_3Cl_2(\mu-dppa)_2]^{2+}$ cation in $[Au_3Cl_2(\mu-dppa)_2]PF_6$. The carbon atoms are drawn as spheres of arbitrary radius and the remaining atoms as 50% probability thermal ellipsoids.

$Au(1)\cdots Au(2)$	3.037(1)		Au(1) - P(1)	2 313	(2)
Au(2)-Cl	2.282(2)		Au-P(2)	2.228	(2)
P(1)-N	1.709(6)		P(1)-C(1)	1.807	(7)
P(1)-C(7)	1.797(7)		P(2)-N	1.683	66)
P(2)-C(13)	1.780(13)	P(2)-C(19)	1.809(7)	
N–C(25)	1.490(9)				
Au(2)…Au(1)…	··Au(2′)	163.8(2)	P(1)-Au(1)-P	(1')	175.4(6)
P(2)-Au(2)-Cl		177.1(1)	Au(1) - P(1) - N	[109.4(2)
Au(1) - P(1) - C(1)	(1)	112.8(2)	Au(1)–P(1)–C	(7)	113.3(2)
N-P(1)-C(1)		104.5(3)	N-P(1)-C(7)		107.6(3)
C(1)-P(1)-C(7) Au(2)-P(2)-C(13)		108.7(3)	Au(2)-P(2)-N		110.8(2)
		110.4(2)	Au(2)–P(2)–C	Au(2) - P(2) - C(19)	
N-P(2)-C13		107.7(3)	N-P(2)-C(19)		104.5(3)
C(13)-P(2)-C(19)	106.2(3)	P(1) - N - P(2)		117.5(3)
P(1)-N-C(25)		123.3(5)	P(2)–N–C(25) 1		119.1(5)

Table 2. Selected interatomic distances (Å) and angles (°) for [Au₃Cl₂(µ-dppa)₂]PF₆

ligands. Similarly, the Au(2)–P(2) distance of 2.228(2) Å corresponds closely with the Au–P distance of 2.238(5) Å in [ClAu(dppm)AuCl] [17] since the coordination environments of the gold atoms are the same. The Au(2)–Cl bond length of 2.282(2) Å is very similar to that observed in [ClAu(dppm)AuCl] [17] (2.288 Å) and those reported for the [Au₃Cl₂(μ -dppm)₂]⁺ cation of 2.288 and 2.301 Å in the [AuCl(C₆F₅)₃]⁻ salt and 2.290 Å in the chloride salt. In summary, although the arrangements of the gold atoms in [Au₃Cl₂(μ -dppm)₂]⁺ and [Au₃Cl₂(μ -dppm)₂]⁺ cations are different, the immediate coordination environments of the gold atoms are very similar.

The room temperature UV/vis absorption spectrum of $[Au_3Cl_2(\mu$ -dppa)_2]PF_6 in acetonitrile is shown in Fig. 4. The band at 230 nm, which is observed as a shoulder on the very intense peak in the ultraviolet region, can be attributed to transitions within the phenyl rings [2]. Also observed are a band at 295 nm ($\epsilon_{max} = ca$. 20000 dm³ mol⁻¹ cm⁻¹) and a relatively weak absorption centred at 357 nm. The band at 295 nm is in a very similar position to that at 298 nm observed in the UV/vis spectrum of $[Au_2(\mu$ dppa)_2][SbF₆]_2 measured in acetonitrile Fig. 2. On this basis, and for the same reasons as those discussed above, it is also tentatively assigned to a $p\sigma \ll d\sigma^*$



Fig. 4. Absorption in CH₃CN and solid state emission (340 nm excitation) spectra of $[Au_3Cl_2(\mu$ -dppa)_2]PF_6.

transition. Irradiation of an acetonitrile solution of $[Au_3Cl_2(\mu\text{-}dppa)_2]PF_6$ at 340 nm only affords a very weak and indistinct emission band centred at about 560 nm. On the other hand, a powdered sample of the compound exhibits an intense blue emission as shown in Fig. 4 ($\lambda_{max} = 475$ nm). This emission is slightly blueshifted compared to the emission maximum of 485 nm recorded in the solid state for $[Au_3Cl_2(\mu-dppm)_2]Cl$ [8]. The origin of the emission is uncertain. However, solid [AuCl(PPh₃)] has only a slight bluish-white emission, due to $\pi - \pi^*$ transitions in the phenyl rings and bis(phosphine)gold(I) complexes such as [Au(P-Ph₃)₂]BPh₄ do not emit at all, neither in solution nor in the solid state [6]. It would therefore appear that the intramolecular gold-gold interactions present in the trinuclear $[Au_3Cl_2(\mu-L-L)_2]^{2+}$ cations (L-L=dppm or dppa) are, in some way, responsible for the intense emission observed in the solid state for these compounds.

EXPERIMENTAL

General considerations

All manipulations were performed under nitrogen using a combination of vacuum and Schlenk techniques. Solvents were purified and degassed by standard procedures [18]. Infrared data were recorded as KBr pellets on a Shimadzu FTIR-4300 spectrophotometer. ¹H NMR spectra were recorded on a Varian Gemini-200 spectrometer with chemical shifts referenced to SiMe₄. ${}^{31}P{H}$ NMR spectra were recorded on a Varian FT80A spectrometer, chemical shifts being quoted relative to 85% H₃PO₄ (external, ³¹P). Absorption spectra were recorded on a Shimadzu UV-2101PC UV-vis scanning spectrophotometer. Emission spectra were obtained on a Shimadzu RF-5000 recording spectrofluorophotometer. The C, H, and N analyses were performed by Galbraith Laboratories of Knoxville, Tennessee. The ligand Ph₂PN(Et)PPh₂ was prepared by a slight modification of the literature method [19].

Synthesis of $[Au_2(\mu-dppa)_2][SbF_6]_2$

Excess gold powder (0.238 g, 1.208 mmol) was added with stirring to a solution of NOSbF₆ (0.134 g, 0.504 mmol) in acetonitrile $(ca. 10 \text{ cm}^3)$ at room temperature. Stirring was continued overnight to allow oxidation of gold to gold(I). The excess gold powder was removed by filtration through glass microfibre filter paper affording a clear colourless solution. Solid Ph₂PN(Et)PPh₂ (0.208 g, 0.504 mmol) was added with stirring following which the ligand dissolved and the solution turned yellow. After *ca* 1 h, the volume of the solution was reduced *in vacuo* and diethylether added. The product, which separated from the solution as a colourless microcrystalline solid, was isolated by filtration, washed with diethylether and dried *in vacuo*. Yield: *ca.* 0.77 g (90%). Found: C, 36.7; H, 2.9; N, 1.7; Calc. for $C_{52}H_{50}Au_2F_{12}N_2P_4Sb_2$: C, 36.9; H, 3.0; N, 1.6%. IR data (KBr pellet, cm⁻¹): 658 (vs) (SbF $_{6}^{-}$). ¹H NMR (CD₃CN): δ 7.64 (m, 40H, C₆H₅); 3.12 (q, 4H, CH₂); 0.35 (t, 6H, CH₃). ³¹P{¹H} NMR (CD₃CN): δ 100.25.

Synthesis of $[Au_3Cl_2(\mu-dppa)_2]PF_6$

Thiodiglycol (2,2'-thiodiethanol) (ca. 0.2 cm³) was added, with stirring, to an orange-coloured solution of HAuCl₄.2H₂O (0.211 g, 0.560 mmol) in methanol $(ca. 15 \text{ cm}^3)$ at room temperature. A slight excess of solid Ph₂PN(Et)PPh₂ (0.232 g, 0.560 mmol) was then added with stirring. After a period of ca. 30 min the ligand had dissolved to afford a solution of red-brown colour which subsequently turned yellow. After standing overnight, the solution became colourless. An excess of solid NH₄PF₆ (0.185 g, 1.140 mmol) was added and the solution stirred for 3-4 h. During this time, the product precipitated from the solution as a colourless microcrystalline solid. This was isolated by filtration through glass microfibre paper, washed with water followed by ether and finally dried in vacuo. Yield: ca. 0.70 g (80%). Found: C, 38.5; H, 3.2; N, 1.8; Calc. for C₅₂H₅₀Au₃Cl₂F₆N₂P₅: C, 38.3; H, 3.1; N, 1.7%. IR data (KBr pellet, cm^{-1}): 840 (vs) (PF $\frac{1}{6}$). ¹H NMR (CD₃CN): δ 7.64 (m, 40H, C₆H₅); 3.12 (q, 4H, CH₂); 0.35 (t, 6H, CH₃). ³¹P{¹H} NMR (CD₃CN): δ 103.61 and 83.11 (AA'BB' pattern).

X-ray structure determinations of $[Au_2(\mu-dppa)_2]$ $[SbF_6]_2$ and $[Au_3Cl_2(\mu-dppa)_2]PF_6$

Crystal data, data collection and refinement parameters for $[Au_2(\mu-dppa)_2][SbF_6]_2$ and $[Au_3Cl_2(\mu-dppa)_2][SbF_6]_2$ $dppa)_2$]PF₆ are given in Table 3. Single crystals of the former compound were grown by slow diffusion of diethylether into a solution of the compound in dichloromethane, while single crystals of the latter compound were grown by slow diffusion of diethylether into an acetonitrile solution of the compound. Weissenberg photographs of the $[Au_2(\mu-dppa)_2]$ [SbF₆]₂ crystals showed that the reflections were generally weak and rather diffuse, but repeated attempts to grow crystals which gave a better-defined diffraction pattern were unsuccessful. Diffractometer data were collected at 295K with a Nonius CAD4 diffractometer using graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ A). Lattice parameters were obtained from the least-squares refinement of the setting angles of 25 reflections with $\theta > 12^{\circ}$. Reflection intensities were measured by the variable-speed ω -2 θ method in the range $3 \leq 2\theta \leq 46^{\circ}$. Examination of three standard reflections, monitored after every 60 min, showed no evidence for crystal deterioration for either compound. Both data sets were corrected for Lorentz-polarisation effects and were also corrected for absorption using the psi-scan method [20]

	$[Au_2(\mu\text{-}dppa)_2][SbF_6]_2$	$[Au_3Cl_2(\mu\text{-dppa})_2]PF_6$	
Formula	$C_{52}H_{50}Au_{2}F_{12}N_{2}P_{4}Sb_{2}$	$C_{52}H_{50}Au_{3}Cl_{2}F_{6}N_{2}P_{5}$	
Formula weight	1646.37	1633.07	
Crystal size (mm)	$0.40 \times 0.25 \times 0.15$	$0.28 \times 0.25 \times 0.22$	
Crystal system	Monoclinic	Monoclinic	
a (Å)	12.160(4)	22.969(4)	
b (Å)	19.782(6)	15.781(3)	
<i>c</i> (Å)	11.395(4)	16.916(3)	
β (°)	99.29(3)	117.86(2)	
$V(Å^3)$	2705(2)	5420(2)	
Ζ	2	4	
Radiation, λ (Å)	0.71073	0.71073	
Space group	$P2_{1}/c$	C2/c	
ρ (calc.) (g cm ⁻³)	2.02	2.00	
μ (Mo– $K\alpha$) (cm ⁻¹)	67.61	86.26	
Unique intensities	2410 $[I > 3\sigma(I)]$	3257 $[I > 3\sigma(I)]$	
Weighting scheme	$1/[\sigma^2(F) + 0.0028F^2]$	$1/[\sigma^2(F) + 0.0009F^2]$	
No. of parameters	332	321	
$R = \Sigma (F_0 - F_c) / \Sigma F_0$	0.099	0.028	
$R_W = \Sigma_w^{1/2} (F_0 - F_c) / \Sigma_w^{1/2} F_0$	0.110	0.034	
$(\Delta/\sigma)_{ m max}$	0.055	0.057	
$\Delta \rho_{\rm max} ({\rm e}{\rm \AA}^{-3})$	4.18 (ca. 1 Å from Au)	1.10	

Table 3. Crystal and intensity collection data and details of refinement for $[Au_2(\mu-dppa)_2][SbF_6]_2$ and $[Au_3Cl_2(\mu-dppa)_2]PF_6$

(maximum and minimum transmission factors are 0.9999, 0.8936 and 0.9987, 0.8416 for $[Au_2(\mu-dppa)_2]$ [SbF₆]₂ and $[Au_3Cl_2(\mu-dppa)_2]PF_6$ respectively).

The structures of $[Au_2(\mu-dppa)_2][SbF_6]_2$ $[Au_3Cl_2(\mu-dppa)_2]PF_6$ were solved by standard Patterson methods using the program SHELXS 86 [21] and subsequently completed by Fourier recycling and refinement using the program SHELX 76 [21]. The full-matrix least-squares refinements were based on $|F_0|$. The ethyl groups of the diphosphazane ligands in $[Au_2(\mu-dppa)_2][SbF_6]_2$ are disordered such that they are not precisely related by the centre of symmetry midway between the two gold atoms. Various models for the disorder were tested but none gave a satisfactory solution. In the end, restrictions were placed on the N-C and C-C bond lengths with the methylene and methyl hydrogens not being included in the refinement. All the non-H atoms were assigned anisotropic temperature factors and the H-atoms a single common isotropic temperature factor; the latter were placed in calculated positions, except for the NEt hydrogens as noted above. Neutral-atom scattering factors were used with corrections for anomalous dispersion [22].

CONCLUSION

Two diphosphazane ligand-bridged complexes of gold have been synthesised, their crystal structures determined and their spectroscopic properties investigated, these being $[Au_2\{\mu-Ph_2PN(Et)PPh_2\}_2][SbF_6]_2$ and $[Au_3Cl_2\{\mu-Ph_2PN(Et)PPh_2\}_2]PF_6$. The cations of

these compounds have in common Au-Au distances which are sufficiently short to indicate a substantial interaction between the gold atoms. This interaction is believed to be, in some way, responsible for the luminescence exhibited by the compounds, in solution for the dinuclear species and in the solid state for the trinuclear complex. However, we have not been able to establish a correlation between the Au-Au separation and the energy of the emission and, thus, conclude that the emission wavelength is determined more by the properties of the ligand. This conclusion is borne-out by a comparison of the emission properties of the diphosphazane ligand-bridged compounds with those reported for salts of the bis(diphenylphosphino)methane ligand-bridged cations, [Au₂(µ- $Ph_2PCH_2PPh_2)_2]^{2+}$ and $[Au_3Cl_2(\mu-Ph_2PCH_2PPh_2)_2]^+$.

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