DALTON
FULL PAPER

Aurophilic attractions: one cation, $[Au\{C(OMe)NMeH\}_2]^+$, but three different structural arrangements in the solid state salts

Feilong Jiang, Marilyn M. Olmstead and Alan L. Balch*

Department of Chemistry, University of California, Davis, California 95616, USA.
E-mail: albalch@ucdavis.edu

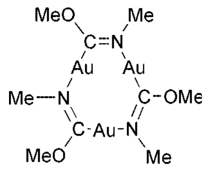
Received 13th July 2000, Accepted 13th September 2000
First published as an Advance Article on the web 25th October 2000

Three salts of the cation $[Au\{C(OMe)NMeH\}_2]^+$, formed by protonation of the solvoluminescent gold(I) trimer $[Au_3(MeN{=}COMe)_3]$, have been prepared and spectroscopically and structurally characterized. Each crystallizes as a unique form with varying aurophilic interactions between the linear, two-coordinate cations. Thus, the chloroform solvate, $[Au\{C(OMe)NMeH\}_2][C_7Cl_2NO_3]\cdot CHCl_3$, (where $[C_7Cl_2NO_3]^-$ is an anion obtained by hydrolysis of 2,3-dichloro-4,5-dicyano-1,4-benzoquinone, DDQ), contains the cation as an isolated monomer, while unsolvated $[Au\{C(OMe)NMeH\}_2][C_7Cl_2NO_3]$ contains pairs of cations that are linked by a single Au · · · Au interaction with a 3.1955(3) Å separation between the gold centers. In $[Au\{C(OMe)NMeH\}_2][O_2CCF_3]$ the cations associate to form infinite, nearly linear (Au · · · Au · · · Au angle, 172.209(7)°) chains that have the gold centers only 3.27797(15) Å apart. The luminescent behavior of $[Au\{C(OMe)NMeH\}_2][O_2CCF_3]$ is reported.

Introduction

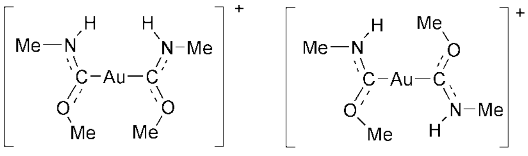
Two-coordinate gold(I) complexes with linear coordination are known to self associate though short Au · · · Au contacts. Such aurophilic interactions between these closed shell, d^{10} metal centers play an important role in determining the solid state structures of many gold(I) complexes as noted by Jones, Schmidbaur, and others.[1–3] Thus, in the solid state, two-coordinate gold(I) complexes experience attractive aurophilic interactions if the Au · · · Au separations are less than 3.6 Å.[4,5] This weakly bonding interaction has been examined in a number of theoretical studies and shown by Pyykkö and co-workers to be the result of correlation effects that are enhanced by relativistic effects.[6–8] Under certain conditions these aurophilic interactions are sufficiently strong to persist in solution[9] and to play a role in determining chemical reactivity.[9] Based on experimental studies of rotational barriers, the strength of this attractive aurophilic interaction has been shown to be comparable to that of hydrogen bonding, *i.e. ca.* 7–11 kcal mol^{-1}.[10,11]

As part of studies in this laboratory designed to probe the chemical and physical properties of the solvoluminescent trimer $[Au_3(MeN{=}COMe)_3]$[12–14] we have been examining its chemical reactivity along with that of related trimeric molecules.[15–17] The trimer emits yellow light when crystals that have previously been irradiated with near UV light make contact with solvents like dichloromethane and chloroform. The process has been termed solvoluminescence, since the intensity of the emission, which is readily detected by the human eye, is greatest for those organic liquids which are the best solvents for the trimer. The solvoluminescence appears to be associated with the unique solid state structure of $[Au_3(MeN{=}COMe)_3]$, which consists of trigonal prismatic columns of the trimers that are associated through aurophilic interactions. In this structure each gold atom within a trimer interacts with two gold centers in two adjacent trimers in the prismatic columns.



$\{Au_3(MeN{=}COMe)_3\}$

Here we report on reactions that result in the conversion of the trimer into the cation $[Au\{C(OMe)NMeH\}_2]^+$. The carbene ligands in this type of complex are constrained to planarity about the N–C(Au)–O core due to the restricted rotation of the C–O and C–N bonds. Such ligands generally adopt amphi structures with the methyl groups in alternate "in" and "out" locations.[18] If both ligands reside within the same plane then the *cis* and *trans* ligand orientations shown below are possible. The structures of three salts of this cation are reported. These salts differ in the nature of the aurophilic interactions found in the solid state. This work originated in our studies of the interactions of $[Au_3(MeN{=}COMe)_3]$ with electron acceptors such as nitro-9-fluorenones and 2,3-dichloro-4,5-dicyano-1,4-benzoquinone, DDQ.[19]



cis *trans*

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

Results

Synthetic and spectroscopic studies

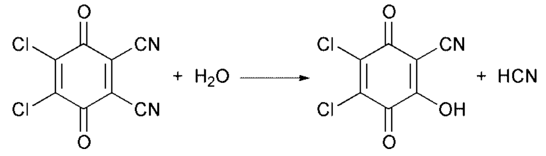
Treatment of $[Au_3(MeN{=}COMe)_3]$ with trifluoroacetic acid in dichloromethane solution results in the rupture of the trinuclear framework and the formation of the cation $[Au\{C(OMe)NMeH\}_2]^+$ *via* the disproportionation shown in eqn. (1).

$$2\,[Au_3(MeN{=}COMe)_3] + 6\,HX \longrightarrow 3\,[Au\{C(OMe)NMeH\}_2]^+ 3\,[AuX_2]^- \qquad (1)$$

The cation has been isolated as the light yellow crystalline salt $[Au\{C(OMe)NMeH\}_2][O_2CCF_3]$. The ^1H NMR spectrum of this salt in chloroform-*d* solution consists of a singlet at δ 4.24 due to the methoxy protons and a doublet at δ 2.90 with $J = 5.0$ Hz due to the methyl protons of the NMeH group. In contrast, under similar conditions [$Au_3(MeN{=}COMe)_3$] displays two equally intense resonances at δ 4.02 (MeO resonance) and at 3.00 (NMe resonance). The unique NH proton of [Au{C(OMe)NMeH}$_2$]$^+$ produces a broad quartet resonance at δ 1.21. The infrared spectrum of this solid shows N–H stretching vibrations at 3330m and 3127m cm^{-1}. Other infrared spectral data are given in the Experimental section.

The UV/vis absorption spectrum of [Au{C(OMe)NMeH}$_2$][O_2CCF_3] in dichloromethane solution shows bands at 276 (7820) and 300 nm (3530 M^{-1} cm^{-1}). At room temperature, solutions of [Au{C(OMe)NMeH}$_2$][O_2CCF_3] show an emission band at 405 nm with excitation maxima at 288 and 301 nm which coincide with the absorption bands of the solution. Solid [Au{C(OMe)NMeH}$_2$][O_2CCF_3] displays intense greenish yellow emission at room temperature. The emission spectrum displays a maximum at 520 nm with an excitation profile with a maximum at 301 nm. The difference in the luminescent properties of [Au{C(OMe)NMeH}$_2$][O_2CCF_3] in solution and in the solid state can readily be attributed to differences in the aurophilic interactions which are extensive in the solid but non existent in solution.

Addition of a yellow solution of DDQ to a colorless solution of [$Au_3(MeN{=}COMe)_3$] in dichloromethane results in the immediate formation of a blue solution. The UV/vis absorption spectrum of this solution shows new absorbances at 458, 574, and 614 nm which we believe are due to the formation of charge transfer complexes between DDQ and the trimer. However, such solutions are unstable and gradually turn red. Evaporation of this solution over time produces a red, crystalline solid, [Au{C(OMe)NMeH}$_2$][$C_7Cl_2NO_3$]. The anion involved in this salt is readily formed from DDQ *via* hydrolysis, as seen in eqn. (2),[20] and subsequent deprotonation. The red color of this salt is due to the anion, which has an absorption centered at 486 nm.



(2)

Conducting the same reaction with DDQ in chloroform produces red crystals of the solvated salt, [Au{C(OMe)NMeH}$_2$][$C_7Cl_2NO_3$]·$CHCl_3$. The ^{1}H NMR spectra of this salt and of [Au{C(OMe)NMeH}$_2$][$C_7Cl_2NO_3$] are nearly identical to the spectrum obtained from [Au{C(OMe)NMeH}$_2$][O_2CCF_3], as expected for salts with a common cation in each.

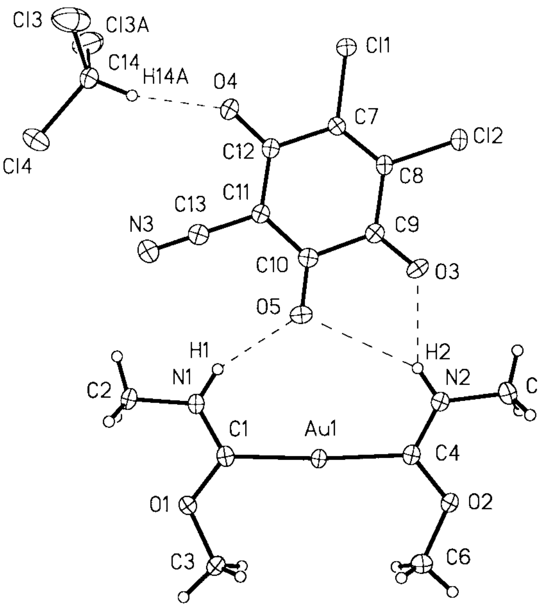


Fig. 1 A drawing that shows the hydrogen bonding interactions (shown as dashed lines) between the individual components of [Au{C(OMe)NMeH}$_2$][$C_7Cl_2NO_3$]·$CHCl_3$ with 50% thermal contours. Distances involving hydrogen bonding are: N1···O5, 2.988(3); N2···O5, 3.577(4); N2···O3, 2.932(3); C14···O4, 3.131(4) Å.

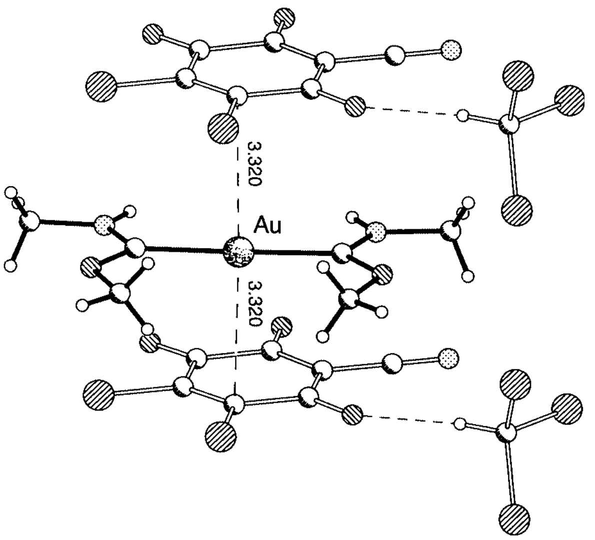


Fig. 2 A drawing of the structure of [Au{C(OMe)NMeH}$_2$][$C_7Cl_2NO_3$]·$CHCl_3$ that shows the isolated [Au{C(OMe)NMeH}$_2$] ion which is sandwiched between two [$C_7Cl_2NO_3$] anions.

Crystallographic studies

[Au{C(OMe)NMeH}$_2$][$C_7Cl_2NO_3$]·$CHCl_3$. Fig. 1 shows a drawing of the cation, the anion, and the chloroform molecule as they are arranged in the crystal. Each of these components lies on a crystallographic mirror plane. Selected bond distances and angles in the cation are given in Table 1 where they may be compared to the dimensions of the cation in other salts. The three components are linked by four hydrogen bonds which also lie in the mirror plane.

In addition to the crystallographic symmetry the cation has effective C_{2v} symmetry. The gold ion is nearly linearly coordinated with a C1–Au–C4 angle of 176.40(11)°. The Au–C distances, 2.027(3) and 2.033(3) Å, are nearly equal and are similar to those found in related compounds. For example in [bis(1,3-bis(hexadecyl)benzimidazol-2-ylidene)gold(I)] bromide the Au–C distance is 2.03(2) Å,[21] and the Au–C distance is slightly shorter when *trans* to a chloride ligand as in bis(1,3-dimethylbenzimidazol-2-ylidene)gold(I) chloride [1.985(11) Å][22] and in [AuCl{C(OEt)NHC$_6H_4CO_2C_6H_4OC_2H_5$)}] where the Au–C distance is 1.985(7).[23]

There are no aurophilic interactions in crystalline [Au{C(OMe)NMeH}$_2$][$C_7Cl_2NO_3$]·$CHCl_3$. Fig. 2 shows a drawing that demonstrates that each cation in the solid is sandwiched between two of the anions. The gold ion is 3.320 Å away from the nearest carbon atoms of the anions. The dimensions of the anion, [$C_7Cl_2NO_3$]$^-$, are similar to those found for this unit in different environments.[19]

[Au{C(OMe)NMeH}$_2$][$C_7Cl_2NO_3$]. Fig. 3 shows a drawing of the asymmetric unit which consists of a cation and an anion which lie in a common plane. The cation and anion are joined by four hydrogen bonds, one of which is long. While the cation has no crystallographically imposed symmetry, it does have virtual C_{2v} symmetry. The dimensions of the cation are similar to those found for the other salts of [Au{C(OMe)NMeH}$_2$]$^+$ as seen in Table 1.

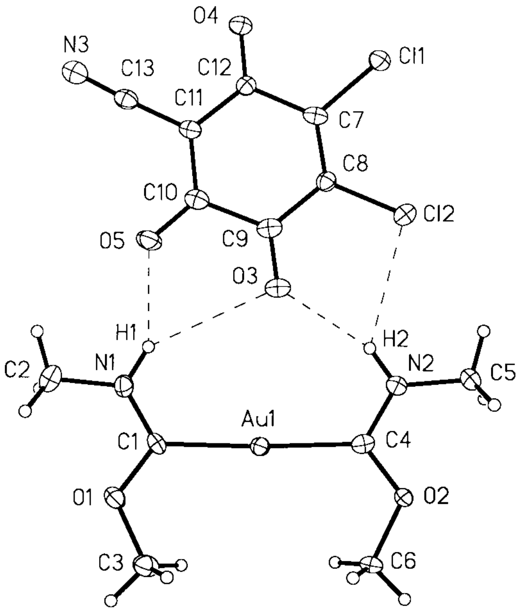


Fig. 3 A drawing that shows the hydrogen bonding interactions (shown as dashed lines) between the individual components of $[Au\{C(OMe)NMeH\}_2][C_7Cl_2NO_3]$ with 50% thermal contours. Distances relevant to the hydrogen bonding between the cation and anion are: N1 · · · O3, 3.577(5); N1 · · · O5, 2.909(5); N2 · · · O3, 3.042(4); N2 · · · Cl2, 3.421(4) Å.

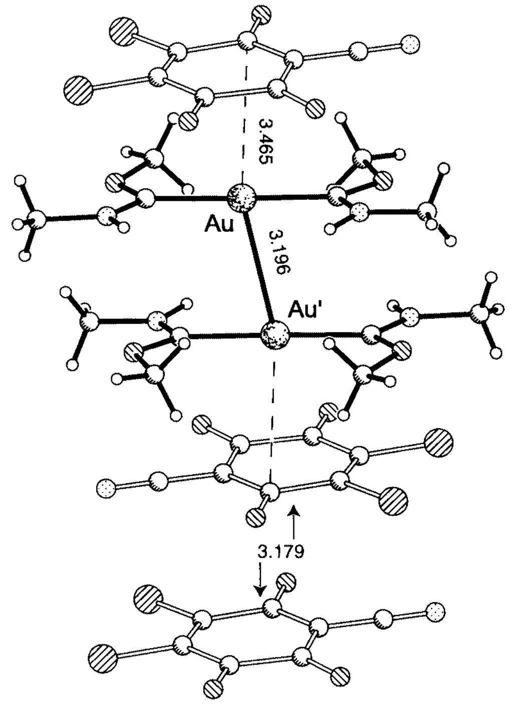


Fig. 4 A drawing of the structure of $[Au\{C(OMe)NMeH\}_2][C_7Cl_2NO_3]$ which shows the orientation of the dimeric cation formed by aurophilic attraction and its location with respect to the anions that surround it on top and bottom.

The cations in $[Au\{C(OMe)NMeH\}_2][C_7Cl_2NO_3]$ self associate through aurophilic interactions to form discrete, centrosymmetric dimers as seen in Fig. 4. The separation between the two gold centers is only 3.1955(3) Å, which is clearly indicative of an significant aurophilic attraction that must overcome Coulombic repulsion between these cations. In contrast, the separations between neighboring gold centers in the similarly sized and bonded salt $[Au\{CNMe\}_2][O_3SCF_3]$ are significantly longer, 3.611 and 3.624 Å.[24] The pairs of cations are arranged so that the ligands on adjacent cations eclipse one another. Within a pair of cations the C(1)–Au–Au′ and C(4)–Au–Au′ angles are 99.32(11) and 83.20(10)°, respectively. Consequently Au′ is not centered above the adjacent C(1)–Au–C(4) unit but is slightly displaced to one side. These pairs of cations in $[Au\{C(OMe)NMeH\}_2][C_7Cl_2NO_3]$ are sandwiched between anions to form columnar units (see Fig. 4). The closest gold to carbon contact between the cation and the anion is 3.465 Å. Within the columnar structure, pairs of anions also make face-to-face contact with a 3.179 Å interplanar separation between them.

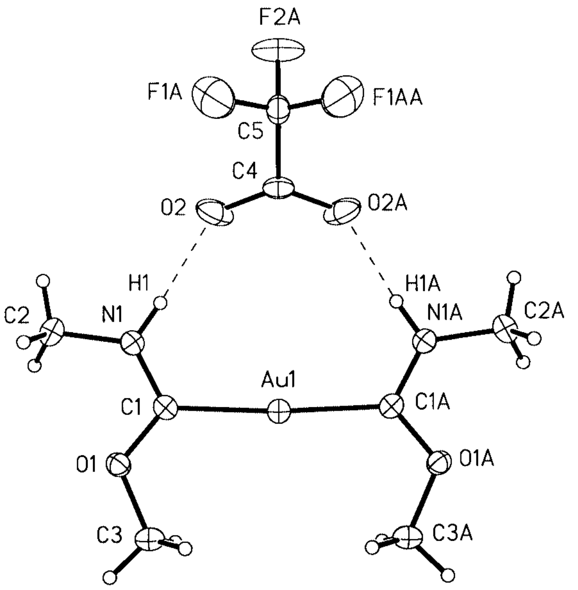


Fig. 5 A drawing that shows the hydrogen bonding interactions (shown as dashed lines) between the individual components of $[Au\{C(OMe)NMeH\}_2][O_2CCF_3]$ with 50% thermal contours. The N1 · · · O2 distance is 2.770(3) Å.

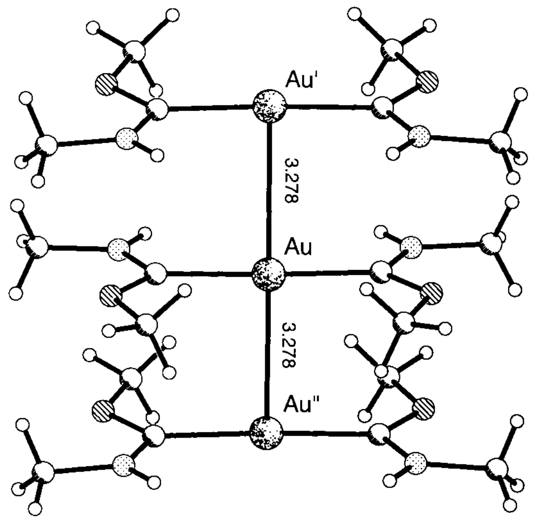


Fig. 6 A drawing of the structure of $[Au\{C(OMe)NMeH\}_2][O_2CCF_3]$ which shows the set of three cations connected by aurophilic interactions. These cations are only a portion of an infinite linear chain within the crystal.

$[Au\{C(OMe)NMeH\}_2][O_2CCF_3]$. The cation and the anion are bisected by a crystallographic mirror plane as seen in Fig. 5. There are hydrogen bonds from each NH group of the cation to oxygen atoms of the trifluoroacetate anion. The cation has the usual virtual C_{2v} symmetry and linear gold coordination.

The cations self associate about centers of symmetry in this solid to form infinite chains. A portion of this chain that consists of three adjacent cations is shown in Fig. 6. Within the chain the gold centers are only 3.27797(15) Å apart. This separation is somewhat longer than that observed (3.1955(3) Å)

Table 1 Selected interatomic distances (Å) and angles (°) in $[Au\{C(OMe)NMeH\}_2]^+$ salts

	$[Au\{C(OMe)NMeH\}_2]$-$[C_7Cl_2NO_3]\cdot CHCl_3$ **1**	$[Au\{C(OMe)NMeH\}_2]$-$[C_7Cl_2NO_3]$ **2**	$[Au\{C(OMe)NMeH\}_2]$-$[O_2CCF_3]$ **3**
Au–C	2.027(3)	2.025(4)	2.031(3)
	2.033(3)	2.029(4)	
O–C(carb)	1.333(3)	1.332(5)	1.330(3)
	1.326(3)	1.321(5)	
N–C(carb)	1.302(4)	1.293(5)	1.306(3)
	1.302(4)	1.312(5)	
Au···Au		3.1955(3)	3.27797(15)
C–Au–C	176.40(11)	175.99(17)	175.39(11)
C–Au–Au′		99.32(11)	89.67(6)
C–Au–Au″		83.20(10)	90.02(6)
Au–C(carb)–O	126.5(2)	125.7(3)	127.67(16)
	126.8(2)	126.2(3)	
Au–C(carb)–N	121.2(2)	121.7(3)	119.75(17)
	120.6(2)	121.5(3)	
N–C(carb)–O	112.4(2)	112.6(4)	112.6(2)
	112.6(2)	112.3(4)	
Au···Au···Au			172.209(7)

in the dimers in $[Au\{C(OMe)NMeH\}_2][C_7Cl_2NO_3]$ but is significantly shorter than the separations (3.611 and 3.624 Å) seen in $[Au\{CNMe\}_2][O_3SCF_3]$.[24] Comparison with $[Au_3(MeN{=}COMe)_3]$, which also contains an infinite chain of gold centers with a 3.346(1) Å separation between gold centers in the chain, is also relevant here.[13] The infinite chain in $[Au\{C(OMe)NMeH\}_2][O_2CCF_3]$ is nearly linear with an Au···Au···Au angle of 172.209(7)°, while the chains in $[Au_3(MeN{=}COMe)_3]$ are strictly linear. The cations within the chains are arranged so that the gold atoms on adjacent cations are centered over the C(1)–Au–C(1A) portion with C(1)–Au–Au′ and C(1)–Au–Au″ angles of 89.67(6) and 90.02(6)° respectively. Thus the offset seen in $[Au\{C(OMe)NMeH\}_2][C_7Cl_2NO_3]$ (see Fig. 4) is not present in $[Au\{CNMe\}_2][O_3SCF_3]$.

Discussion

The results described here demonstrate that the solid state structures of the three salts of $[Au\{C(OMe)NMeH\}_2]^+$ display a marked variation in the nature of the aurophilic interactions present. No aurophilic interaction is found in $[Au\{C(OMe)NMeH\}_2][C_7Cl_2NO_3]\cdot CHCl_3$, but in $[Au\{C(OMe)NMeH\}_2][C_7Cl_2NO_3]$ the cation crystallizes as a dimer with a short (3.1955(3) Å) separation between the gold centers. Thus, the need to accommodate the presence or absence of a solvent molecule within the lattice alters the nature of the interaction between the cations. In $[Au\{C(OMe)NMeH\}_2][O_2CCF_3]$ the aurophilic attraction leads to the formation of an extended chain structure with a separation of only 3.27797(15) Å between gold centers in the extended chain. These results indicate that interactions between ionic gold(I) complexes are subject to manipulation by alteration of the counter ion. This structural feature should allow tuning of the properties, particularly the luminescence, of ionic gold(I) complexes. The aurophilic interactions found in neutral gold(I) complexes may also be subject to alteration through incorporation of solvent molecules into the lattice, by utilizing additional functionalities capable of hydrogen bond formation, or by the formation of polymorphs. Thus, solvent incorporation has been found by Eisenberg and co-workers to produce an orange, luminescent form of $[\{Au(S_2CN(C_5H_{11})_2\}_2]\cdot$dmso in which intermolecular Au···Au interactions are found, while the solvent free version of the same complex is colorless.[25] Hydrogen bond formation along with aurophilic interactions have been used in engineering the structures of gold(I) thiolate complexes.[26] Two polymorphs of $[\{(Me_2PhP)AuCl\}_n]$ have been found: one with a dimeric structure and a Au···Au distance of 3.230(2) Å and the other with a trimeric structure and a Au···Au distance of 3.091(2) Å.[27] The luminescence of these two forms shows significant differences.[28]

In each salt examined here, however, the individual cations themselves have remarkably similar structures as seen from the bond distance and angle information given in Table 1. Thus in all cases the Au–C distances fall in the narrow range 2.025–2.033 Å, the O–C(carbene) distances are slightly longer than the N–C(carbene distances), the angles about the carbene carbon atoms fall in the order Au–C–O > Au–C–N > N–C–O, and the cations have the *cis* structure which brings the two NH groups into the closest proximity. This arrangement of the two ligands is closely linked to the presence of hydrogen bonding interactions with the anions. In each structure these hydrogen bonding schemes lead to coplanarity or near coplanarity of the carbene ligands. Thus the *cis* structure is favored over the *trans* structure or a structure where the two carbene ligands would be perpendicular to one another. In the latter arrangement, π-back bonding from gold into the p orbital of the ligand carbon atom would be maximized, but such back bonding does not appear to play a significant role in determining the relative ligand orientations in these cations.

We attribute the luminescence differences seen for $[Au\{C(OMe)NMeH\}_2][O_2CCF_3]$ in solution and in the solid state to the presence of aurophilic interactions in the solid and their absence in solution. However, solvation effects and exciplex formation have also been identified as significant factors in understanding the visible light emission from binuclear gold complexes.[29,30] It is also possible that interactions of the solvent and the anions with $[Au\{C(OMe)NMeH\}_2]^+$ are significant factors in determining the differences in luminescence behavior. Further studies of the luminescence behavior of gold(I) carbene complexes are ongoing in this laboratory.

Experimental

Materials

Dichloromethane, chloroform, and diethyl ether were dried over molecular sieves. Trifluoroacetic acid and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were purchased from Aldrich and used as received. $[Au_3(MeN{=}COMe)_3]$ was prepared as described previously.[12]

Methods

^1H NMR spectra were recorded at 300 MHz on a Bruker QE 300-1 NMR spectrometer employing routine parameters, infrared spectra on a Mattson-Galaxy Series FTIR 3000 spectrophotometer, UV/vis spectra with a Hewlett Packard 8452A

Table 2 Crystallographic data for compounds **1**–**3**

	1	**2**	**3**
Formula	$C_{14}H_{15}AuCl_5N_3O_5$	$C_{13}H_{14}AuCl_2N_3O_5$	$C_8H_{14}AuF_3N_2O_4$
M	679.51	560.14	456.18
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/m$	$P\bar{1}$	$Pnma$
a/Å	10.5702(8)	9.3330(5)	6.5408(3)
b/Å	6.6361(5)	9.4169(5)	13.5187(7)
c/Å	14.9708(11)	10.4907(6)	14.8583(8)
α/°		75.6230(10)	
β/°	91.221(3)	68.2100(10)	
γ/°		89.0390(10)	
V/Å^3	1049.89(14)	826.40(8)	1313.82(12)
Z	2	2	4
T/°C	89(2)	90(2)	89(2)
λ/Å	0.71073	0.71073	0.71073
μ/cm^{-1}	7.674	9.254	11.242
R1 (obs. data)	0.018	0.028	0.017
wR2 (all data, F^2 refinement)	0.045	0.051	0.041

diode array spectrophotometer and luminescence spectra on a Perkin-Elmer LS 50B spectrometer.

Preparations

[Au{C(OMe)NMeH}$_2$][O$_2$CCF$_3$]. Trifluoroacetic acid (57 mg, 0.5 mmol) was added to a colorless solution of [Au$_3$(MeN=COMe)$_3$] (81 mg, 0.1 mmol) in 50 mL of chloroform with stirring at room temperature. The mixture was stirred for one hour, and then filtered. The filtrate was allowed slowly to evaporate at room temperature for several days. The light yellow, needle-like crystals were forming during this period. The crystalline product was collected, washed with diethyl ether, and dried in vacuum to produce 59.0 mg (43%) of the desired product. In the solid state [Au{C(OMe)NMeH}$_2$][O$_2$CCF$_3$] displays a greenish yellow luminescence when irradiated with a UV lamp. ^{1}H NMR spectrum (300.1 MHz, 298 K, CDCl$_3$): δ 4.24 (6 H, s), 2.90 (6 H, d) and 1.21 (2 H, q). IR (KBr pellet cm^{-1}): 3330m, 3127m, 2971m, 2944m, 1688s, 1672vs, 1612s, 1496m, 1439m, 1397m, 1272s, 1202vs, 1185vs, 1171s, 1130s, 1102s, 1013w, 825m, 797m, 748m, 718s, 692s, 543m and 501m. UV/vis (dichloromethane solution): λ_{max}/nm (ε/M^{-1} cm^{-1}): 276 (7820) and 300 (3530).

[Au{C(OMe)NMeH}$_2$][C$_7$Cl$_2$NO$_3$]. A yellow solution of DDQ (34.1 mg, 0.15 mmol) in 30 mL of dichloromethane was added to a colorless solution of {Au$_3$(MeN=COMe)$_3$} (40.1 mg, 0.05 mmol) in 40 mL of dichloromethane. The reaction mixture was sonicated for a few minutes during which it become dark blue. After filtration of the sample, the filtrate was condensed under reduced pressure. Diffusion of diethyl ether into the sample for several days produced red needles of the product. This solid (yield 34.5 mg, 41%) was collected, washed with diethyl ether, and dried in vacuum. ^{1}H NMR spectrum (300.1 MHz, 298 K, CDCl$_3$): δ 4.27 (6 H, s), 2.97 (6 H, d) and 1.25 (2 H, q). IR (KBr pellet cm^{-1}): 3335s, 3250m, 2952m, 2925m, 2855w, 2216m, 1695m, 1979m, 1583s, 1576vs, 1456m, 1384w, 1265m, 1152w, 1010w, 884w, 823w and 797w. UV/vis (dichloromethane solution): λ_{max}/nm (ε/M^{-1} cm^{-1}): 290 (1170) and 486 (150).

[Au{C(OMe)NMeH}$_2$][C$_7$Cl$_2$NO$_3$]·CHCl$_3$. This red crystalline product was prepared in 40% yield and recrystallized from chloroform by use of the procedure described for [Au{C(OMe)NMeH}$_2$][C$_7$Cl$_2$NO$_3$]. The spectroscopic data for [Au{C(OMe)NMeH}$_2$][C$_7$Cl$_2$NO$_3$] and [Au{C(OMe)NMeH}$_2$]-[C$_7$Cl$_2$NO$_3$]·CHCl$_3$ are similar.

X-Ray data collection

Crystals of all three complexes were obtained by direct diffusion of diethyl ether into a saturated solution of the complex in dichloromethane or chloroform. All were coated with a light hydrocarbon oil and mounted on a glass fiber in the cold dinitrogen stream of the Siemens SMART CCD diffractometer, equipped with graphite monochromated Mo-Kα radiation. Lorentz and polarization corrections were applied. No decay was observed in 50 duplicate frames at the end of each data collection. An empirical absorption correction utilizing equivalents was employed.[31] Crystal data are given in Table 2.

Solution and structure refinement. Calculations for the structures were performed using SHELXS 97 and SHELXL 97.[32] Tables of neutral atom scattering factors, f' and f'', and absorption coefficients were from a standard source.[33] For [Au{C(OMe)NMeH}$_2$][C$_7$Cl$_2$NO$_3$] three reflections were omitted due to extinction, while for [Au{C(OMe)NMeH}$_2$]-[C$_7$Cl$_2$NO$_3$]·CHCl$_3$ one (001) was omitted for the same reason. The structures were all solved *via* direct methods. All atoms except hydrogen atoms were refined anisotropically. All hydrogen atoms were located in Fourier difference maps and included through the use of a riding model, free refinement or fixed. Three hydrogen atoms were affixed on each of the methyl carbon atoms to provide tetrahedral geometry about these carbon atoms.

CCDC reference number 186/2184.

See http://www.rsc.org/suppdata/dt/b0/b005684g/ for crystallographic files in .cif format.

Acknowledgements

We thank the U. S. National Science Foundation (Grant 9610507 and CHE 0070291) for support and Johnson Matthey for a loan of chloroauric acid.

References

1 P. G. Jones, *Gold Bull.*, 1981, **14**, 102.
2 H. Schmidbaur, *Chem. Soc. Rev.*, 1995, 391.
3 P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597.
4 S. S. Pathaneni and G. R. Desiraju, *J. Chem. Soc., Dalton Trans.*, 1993, 319.
5 H. Schmidbaur, *Interdisip. Sci. Rev.*, 1992, **17**, 213.
6 P. Pyykkö, J. Li and N. Runeberg, *Chem. Phys. Lett.*, 1994, **218**, 133.
7 P. Pyykkö, N. Runeberg and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1451.
8 P. Pyykkö and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1458.
9 A. L. Balch, E. Y. Fung and M. M. Olmstead, *J. Am. Chem. Soc.*, 1990, **112**, 5181.
10 H. Schmidbaur, W. Graf and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 417.
11 D. E. Harwell, M. D. Mortimer, C. B. Knobler, F. A. L. Anet and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1996, **118**, 2679.

12 J. E. Parks and A. L. Balch, *J. Organomet. Chem.*, 1974, **71**, 453.
13 J. C. Vickery, M. M. Olmstead, E. Y. Fung and A. L. Balch, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 1179.
14 E. Y. Fung, M. M. Olmstead, J. C. Vickery and A. L. Balch, *Coord. Chem. Rev.*, 1998, **171**, 151.
15 A. L. Balch and D. J. Doonan, *J. Organomet. Chem.*, 1977, **131**, 137.
16 J. C. Vickery and A. L. Balch, *Inorg. Chem.*, 1997, **36**, 5978.
17 A. L. Balch, M. M. Olmstead and J. C. Vickery, *Inorg. Chem.*, 1999, **38**, 3494.
18 J. M. Miller and A. L. Balch, *Inorg. Chem.*, 1972, **11**, 2069.
19 M. M. Olmstead, F. Jaing and A. L. Balch, submitted for publication.
20 P. Bruni, G. Tosi and G. Valle, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 1022.
21 K. M. Lee, C. K. Lee and I. J. B. Lin, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 1850.
22 H. M. J. Wang, C. Y. L. Chen and I. J. B. Lin, *Organometallics*, 1999, **18**, 1223.
23 S.-W. Zhang, R. Ishii and S. Takahashi, *Organometallics*, 1997, **16**, 20.
24 W. Schneider, A. Sladek, A. Bauer, K. Angermaier and H. Schmidbaur, *Z. Naturforsch.*, *Teil B*, 1997, **52**, 53.
25 M. A. Mansour, W. B. Connick, R. J. Lachicotte, H. J. Gysling and R. Eisenberg, *J. Am. Chem. Soc.*, 1998, **120**, 1329.
26 B.-C. Tzeng, A. Schier and H. Schmidbaur, *Inorg. Chem.*, 1999, **38**, 3978.
27 D. V. Toronto, B. Weissbart, D. S. Tinti and A. L. Balch, *Inorg. Chem.*, 1996, **35**, 2484.
28 B. Weissbart, D. V. Toronto, A. L. Balch and D. S. Tinti, *Inorg. Chem.*, 1996, **35**, 2490.
29 W.-F. Fu, K.-C. Chan, V. M. Miskowski and C.-M. Che, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2783.
30 K. H. Leung, D. L. Phillips, M.-C. Tse, C.-M. Che and V. M. Miskowski, *J. Am. Chem. Soc.*, 1999, **121**, 4799.
31 SADABS (G. M. Sheldrick) based on a method of R. H. Blessing, *Acta Crystallogr.*, *Sect. A*, 1995, **51**, 33.
32 G. M. Sheldrick, SHELXL 97, crystal structure refinement program, University of Göttingen, 1997.
33 *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, vol. C.