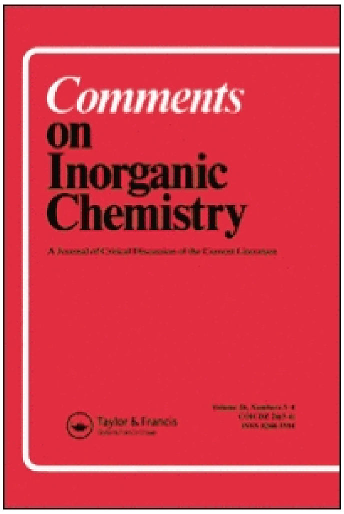

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CYCLIC TRINUCLEAR GOLD(I) COMPOUNDS: SYNTHESIS, STRUCTURES AND SUPRAMOLECULAR ACID-BASE π-STACKS

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Trinuclear 9-membered rings can be formed by gold(I) ions with exobidentate C,N or N,N monoanionic ligands. They are generally slightly irregular and puckered unless the metallocycle is imposed by intramolecular crystallographic symmetry. Gold-gold intramolecular interactions are always present and the complexes exhibit a roughly D_{3h} symmetry. Crystal structures of these trinuclear complexes show individual complexes, dimers supramolecular columnar packing or more complex supramolecular aggregates. Dimers and supramolecular structures are held together by aurophilic intermolecular gold-gold interactions. Bulky substituents on the ligands can prevent intermolecular metal-metal interactions or the formation of supramolecular architectures. It is well established that the Au(I) center in many linear 2-coordinate Au(I) complexes displays electrophilic tendencies in reaction chemistry while also often accepting electron donors to expand the coordination. Trinuclear Au(I) pyrazolates, carbeniates and benzylimidazolates are well known and undergo electron loss through oxidative addition forming first Au(I,III) mixed valence species and ultimately (with the carbeniates, TR(carb), the

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benzylimidazolates, TR(bzim) and the chlorinated pyrazolate TR(Cl-pz) trinuclear Au(III) species. Surprisingly, these Au(I) carbeniates and benzylimidazolates also are excellent bases for the metals cations Tl(I) and Ag(I). The acidic, neutral $[Hg(C_6F_4)_3]_3$ interacts with TR(carb) and TR(bzim) as seen by X-ray solid state and solution NMR measurements. Recently it has been shown that the neutral pi acids C_6F_6 and TCNQ also form stacked pi-acid, pi-base solid state products with TR(carb) and TR(bzim). The TR(bzim) and TR(carb) products are luminescent as solids but C_6F_6 intercalation quenches the luminescence of the p-tol, ethoxy TR(carb), which is a dimer in the solid state. It is interesting that pi-acid, pi-base stacking can involve either a ABAB pattern or an ABBABBA pattern of the molecules, where B is base, TR(carb) or TR(bzim). The B units are aurophilically bonded to each other by two Au...Au linkages. DFT calculations demonstrate that the basicity of the BB dimer is increased relative to the molecular species.

INTRODUCTION

A triangular arrangement of metal atoms is very common in cluster chemistry and a great variety of examples have been described.[1] Trinuclear complexes with metal atoms arranged in a triangle, cyclic trinuclear complexes, CTCs, are expected for group 11 and other ions with predominantly linear coordination, e.g. Hg(II) complexes.[2] Metal-metal interactions reach a maximum for the gold compounds where theoretical studies have shown that these aurophilic interactions result from a combination of correlation and relativistic effects.[3] It has been suggested, based on dynamic NMR measurements, that an aurophilic interaction energy of 10–30 $\mathrm{KJ\,mol^{-1}}$ occurs. This is analogous to the energy of hydrogen bonding and occurs when the Au...Au separation is less than 3.6 Å.[4] Here we report an overview of the synthesis, structural investigations, reactivity, and supramolecular aggregation of cyclic trinuclear gold(I) complexes, Table 1.

1.1. Synthesis

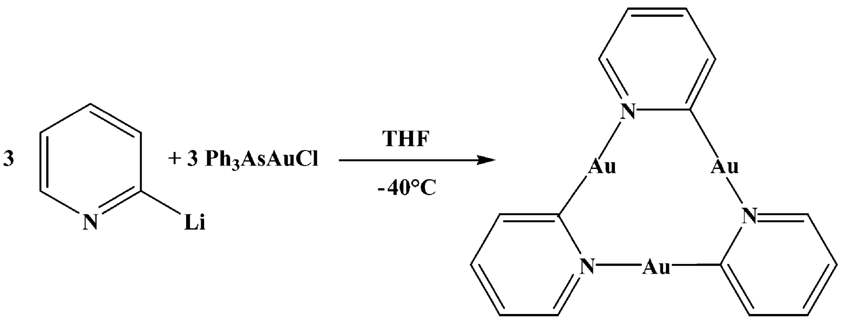
The first CTC gold(I) compound was reported by Vaughan in 1970.[5] The complex $[\mu\text{-}N^1,C^2\text{-pyAu}]_3$, 1, was obtained in a very good yield by adding triphenylarsine gold(I) chloride to a THF solution of 2-pyridyllithium at -40°C, Scheme 1.

Some other CTC gold(I) pyridine complexes were obtained by the same procedure using various substituted pyridines.[5] All the complexes

Table 1. Trimeric cyclic gold(I) compounds of special interest in this review[a]

Number	Complex	Ref
1	$[\mu\text{-N}^1,\text{C}^2\text{-pyAu}]_3$	5,12
2	$[\mu\text{-C(OMe)=N(C}_6\text{H}_{11}\text{)Au}]_3$	6
3	$[\mu\text{-C(OMe)=N(Me)Au}]_3$	7a, 11
4	$[\mu\text{-C(OEt)=N(C}_6\text{H}_4p\text{-Me)Au}]_3$	7b, 11
5	$[\mu\text{-N}^3,\text{C}^2\text{-bzimAu}]_3$	8
6	$[\mu\text{-N,N-3,5-Ph}_2\text{pzAu}]_3$	9c
7	$[\mu\text{-N,N-3,5-(CF}_3)_2\text{pzAu}]_3$	9f, 13
8	$[\mu\text{-N,N-3,5-(4}'\text{MeOPh)}_2\text{pzAu}]_3$	9d, 14
9	$[\mu\text{-N,N-pzAu}]_3$	15
10	$[\mu\text{-N,N-4-MepzAu}]_3$	15

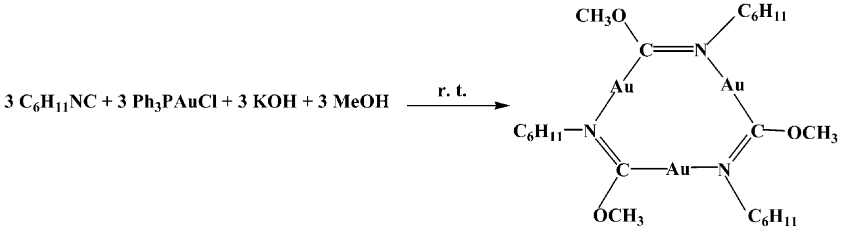
[a] py = pyridinate; bzim = 1-benzylimidazolate; pz = pyrazolate.



1

Scheme 1

have a very low solubility in common organic solvents. Except for 1, they are indefinitely stable in light. In 1972, the synthesis of another CTC gold(I) complex $[\mu\text{-C(OCH}_3\text{)=N(C}_6\text{H}_{11}\text{)Au}]_3$, **2**, was reported. The complex was obtained by the reaction of chloro(triphenylphosphine) gold(I) with cyclohexyl isocyanide in a methanolic potassium hydroxide solution, Scheme 2.[6] In following years, using the same or similar synthetic approaches, many other analogous carbeniate cyclic gold(I) complexes were described.[7] They have the general formula $[\mu\text{-C,N-carbAu}]_3$ (carb is C(OR)=NR$'$) where R$'$ is an aliphatic alicyclic, alkyl aromatic or aromatic group. This class of CTCs is colorless, rather stable and sparingly soluble in organic solvents.

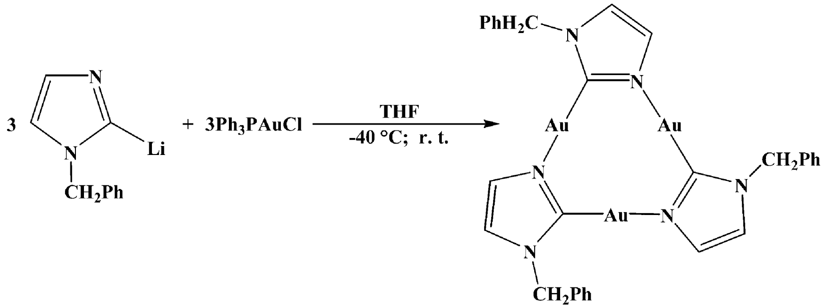


2

Scheme 2

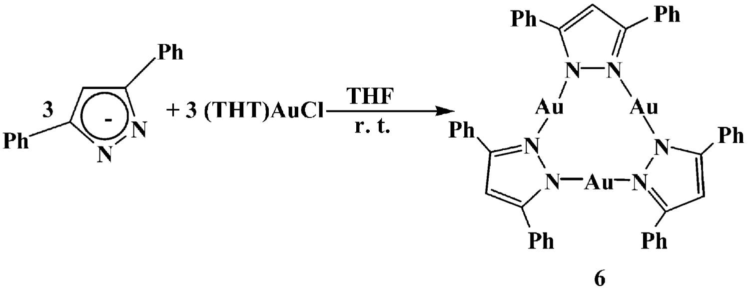
Another family of gold(I) CTCs, having a C-Au-N environment, was described in which the bridging ligand between gold atoms is an alkyl-2-imidazolate anion (alkyl group = CH_3 or CH_2Ph).[8] A typical reaction is carried out at $-40\,^{\circ}C$ in THF solution using Vaughan's method (Scheme 3), but in this case the crude brown solid was extracted overnight at room temperature with hexane. In this work-up, the phosphine ligand goes into the hexane and the gold CTC is formed as a light ivory precipitate. The crude CTC is then crystallized from CH_2Cl_2/hexane. The reaction can be carried out using $(CH_3)_2SAuCl$ as a starting material instead of Ph_3PAuCl, in this way the CTCs **4** and **5** are immediately formed in a good yield, but the reaction is delicate, and often colloidal gold(0) is formed. Complex **5** and its analogous methyl complex are colorless. Light and air stable and quite soluble in the common organic solvents.

Gold(I) CTCs having a N-Au-N environment are also known and have the general formula [μ-N, N-pzAu]$_3$ (pz = pyrazolate or variously ring substituted pyrazolates).[9] In these compounds the bidentate anion



5

Scheme 3



Scheme 4

ligands bridging the gold atoms are obtained by deprotonation of a pyrazole ring with a base such as KOH or NaH. An example of a pyrazolate gold trimer synthesis, [μ-N, N-3,5-$Ph_2pzAu]_3$, is presented in Scheme 4.[9c]

The gold(I) pyrazolate CTCs are colorless, quite stable and soluble in common organic solvents. It is noteworthy that when Na[3,5-Ph_2pz] and AgO_2CPh are added to a THF solution of Ph_3PAuCl a hexanuclear gold cycle having a 18-atom ring is formed, Figure 1.[9c]

1.2. Structure Determination

The structures of the gold(I) CTCs originally were suggested based on the coordination requirements of gold(I), IR spectroscopy and M.W. determinations. The definitive confirmation of the cyclic trimeric nature of these gold complexes was obtained few years later when the structure of **4** was reported (Figure 2).[10] This structure is a 9-membered ring formed by the three carbeniate groups bridging the gold atoms through the N and C atoms with gold(I) atoms two coordinate. The ring is rather irregular and puckered with Au-N distances of 2.018(22), 2.037(23) and 2.045(21) Å Au-C distances of 1.953(28), 1.953(25) and 1.975(26) Å and C-Au-N angles of 173.1(9), 176.0(11) and 176.19(9)°. The deviation of the C-Au-N angles from the linearity as well as the puckering of the ring are due to the presence of intramolecular (average Au...Au = 3.272(1) Å) and intermolecular gold-gold interactions. Only two short Au...Au contacts of 3.244(1) Å are found between the two CTCs, and the dimer of CTCs is arranged in the crystal structure to give a characteristic Au_6 chair (Figure 3). The packing diagram of **4** (Figure 3b) shows additional weak aurophilic interactions at 3.824 Å.

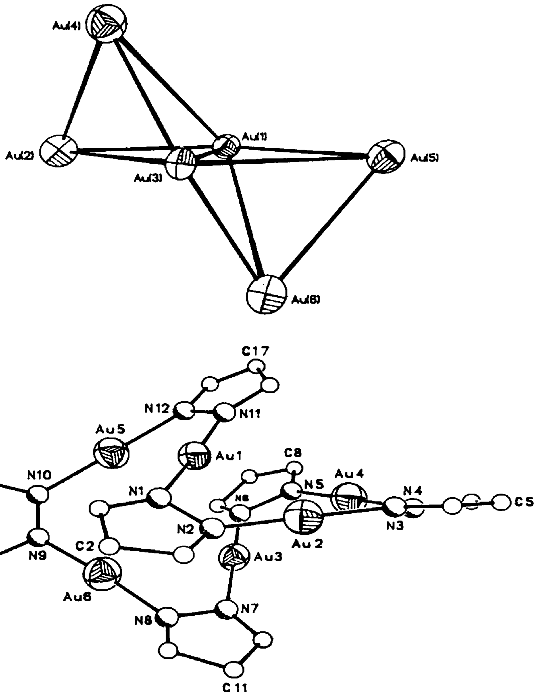


Figure 1. (top) Drawing of the bitetrahedra formed by the six gold atoms of the hexakis (μ-N,N′-3,-5-diphenylpyrazolato)hexagold(I). (bottom) 18-membered twisted ring of the hexanuclear gold(I) complex (phenyl groups are omitted). The thermal ellipsoids are drawn at the 50% probability level.

The structure of **3**, another gold carbeniate CTC, has been reported recently.[11] Although the structural arrangement is similar to that of complex **4**, the molecular and crystal structure are rather different, Figure 4. Here, the trinuclear complex is regular and planar. The C-Au and N-Au bond distances are 2.00(1) and 2.03(1) Å, respectively, and the C-Au-N angles are all 180°. The Au-Au distance of 3.308(2) Å is indicative of an intramolecular interaction between the metal atoms. The most important and unique feature of complex **3** is the ability of the CTCs to aggregate in the solid state along the *c* axis to form ordered and disordered columnar stacks. In each unit cell, the two types of stacks occur in a 2:1 ratio (Figure 5).

In the ordered stacks, the intermolecular Au…Au distance is 3.346(1) Å and the gold centers are arranged to form an infinite trigonal

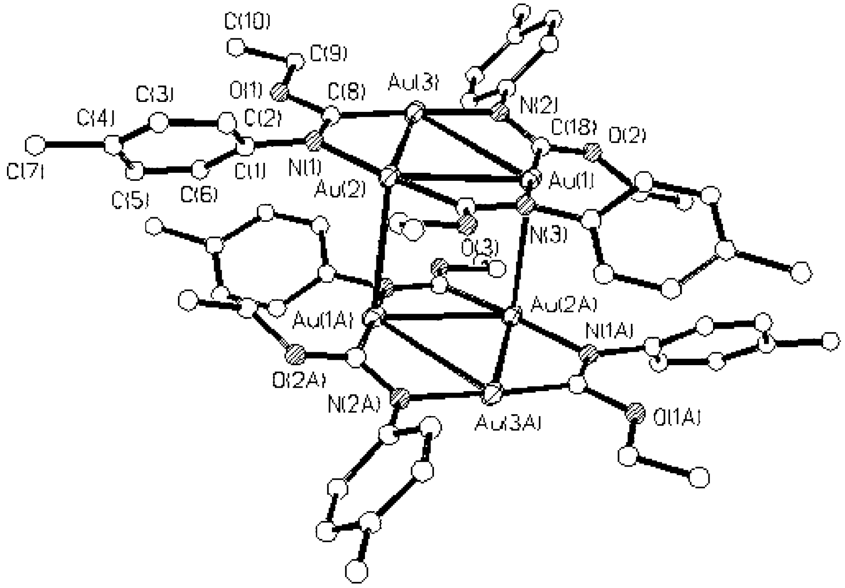


Figure 2. **View of the structure of the complex [μ-C(OEt) = N(C_6H_4Me)Au]$_3$, 4. Two CTCs are held together by autophilic intermolecular interactions with Au...Au, 3.422 Å.**

prismatic array. In the disordered stacks, there are two sets of positions for each gold triangle. The ability of complex **3** to aggregate through gold-gold intermolecular interactions forming these supramolecular arrays confers to it extraordinary luminescent properties described by Balch as solvoluminescence.

A renewed interest in the chemistry of gold CTCs encouraged Balch's group to determine the crystal structure of Vaughan's CTC.[12] This is another 9-membered ring having a C-Au-N environment. In the asymmetric unit of Balch's structure of **1** there are two independent half molecules. Figure 6 shows a view of this molecule with disordered coordinating carbon and nitrogen atoms.

In Balch's structure of **1** the [μ-N^1,C^2-pyAu]$_3$ is located on a crystallographic mirror plane that lies perpendicular to the molecular plane and passes through Au(2). Each CTC is planar with the following bond distances and angles: Au(1)-N(1), 2.07(2) Å; Au(1)-C(2), 2.11(2) Å Au(2)-N(3), 2.03(3) Å; N(1)-Au(1)-C(2), 174.8(9)°; N(3)-Au(2)-C(3′), 174.3(3)°. The gold-carbon distances are slightly longer than those found in the carbeniate CTCs and the N-Au-C angles deviate from linearity due

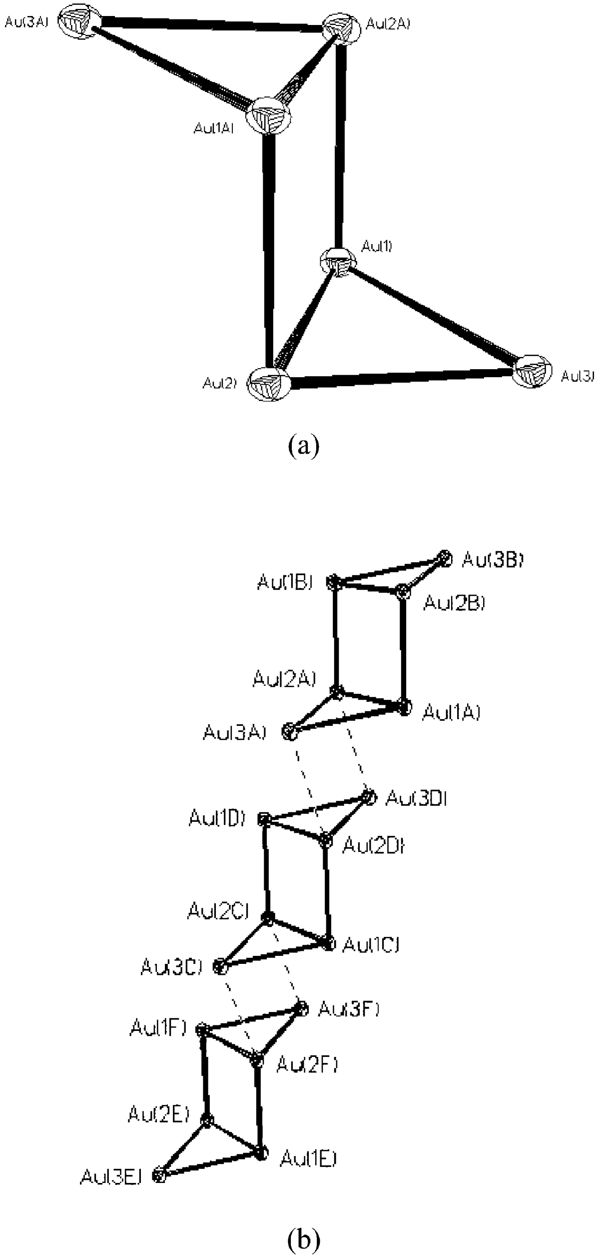


Figure 3. (a) The characteristic Au_6 "chair" observed in complex **4**. (b) Packing diagram of complex **4**.

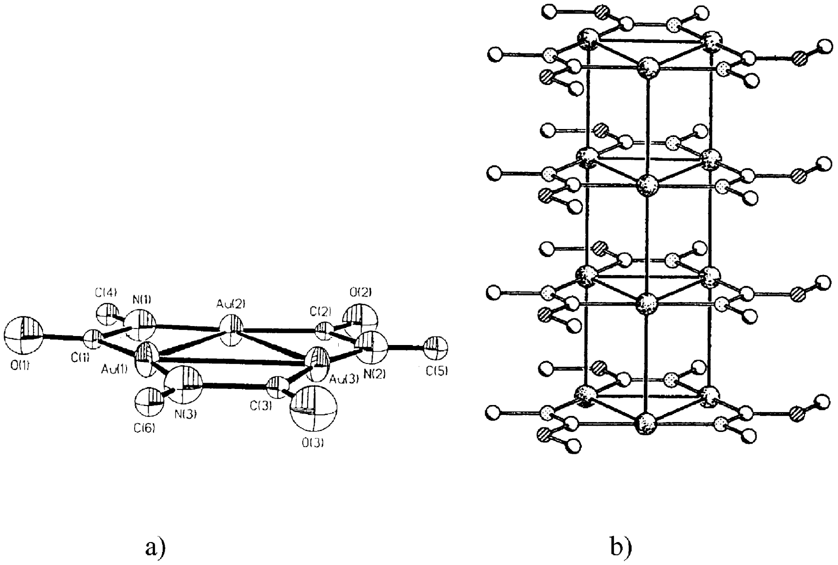


Figure 4. (a) The structure of an individual molecule of $[\mu\text{-C(OMe)}=\text{N(Me)Au}]_3$, 3. (b) A view of the more ordered columnar structure in crystalline 3.

to gold-gold intramolecular interactions: Au(1)...Au(2) 3.309(2) Å, Au(1)...Au (1′) 3.346(3) Å. The second unit possesses a similar structure. The structure of both forms, in the unit cell, show self-association through aurophilic intermolecular interactions that give two distinct

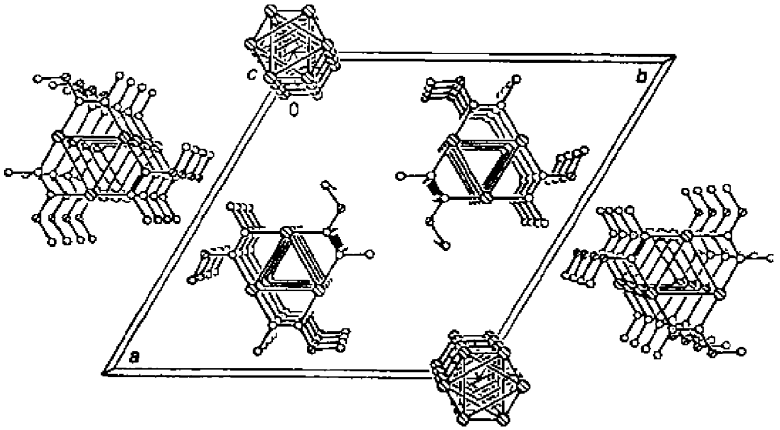


Figure 5. View down the c axis of the unit cell in 3. For clarity only the positions of the gold atoms are shown for the disordered stacks.

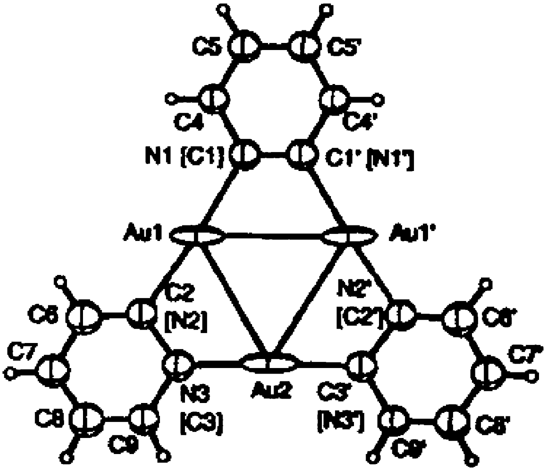


Figure 6. A drawing of the molecular structure of **1** with the carbon and nitrogen atoms disordered.

motifs, Type a and Type b (Figure 7). The intermolecular Au…Au contacts are shorter than the intramolecular Au…Au contacts and fall in the range 3.105(2)-3.143(3) Å. Both CTCs form a dimer with a chair conformation (Type a) of the gold atoms, but the pyridinate, **1**, is then further assembled (Type b) by the apical gold atoms of the chairs, to form extended stepwise chains (Figure 7). (It should be noted that Balch[12]

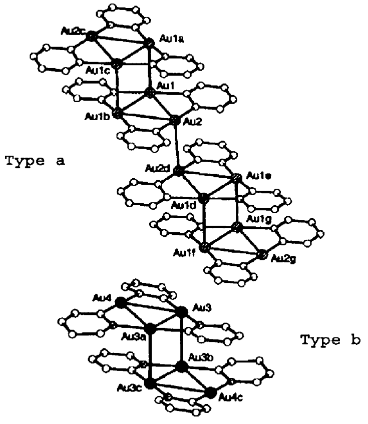


Figure 7. Self-association of [μ-N^1,C^2-pyAu]$_3$ into extended chains of type a and type b Au…Au interactions.

found that crystals of Vaughn's complex **1** produce an unusual hourglass formation of light shading in the crystals after sitting over a period of a month or more).

The crystal packings of the gold(I) pyrazolate CTCs range from individual molecules to complex supramolecular systems. The molecular structure of **7** (Figure 8) is the first of a gold CTC containing a pyrazolate bridging ligand with a N-Au-N environment.[13] Also in this case the 9-membered ring is rather irregular and non-planar, the Au-N average distance of 1.93(1) Å, shorter than found in other CTCs, is indicative of a metal-ligand π-interaction. The two coordinate gold atoms have a nearly linear geometry with N-Au-N average angle of 178(7)°. The average Au...Au distance is 3.348(3) Å. The long intermolecular Au...Au distance of 3.998(2) Å rules out any interaction between the CTCs due to the bulky substituents on the pyrazolate rings.

A similar structure to **7** has been found for complex **6** (Figure 9),[9c] with phenyl substituents on the pyrazolate rings. The discrete CTCs in the unit of **6** are coplanar with the *c*-axis. Long Au...Au distances $\geq$7.567 Å exclude any intermolecular interaction. The complex sits on a 3_2 axis with a Au-N bond distance of 1.978(9) Å and a N-Au-N′ angle of

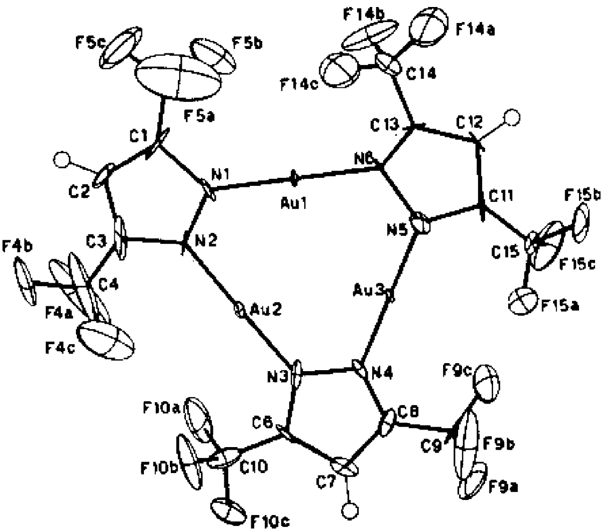


Figure 8. View down *c* axis of the molecular structure of complex [μ-N,N-3,5-$(CF_3)_2$pzAu]$_3$, **7**.

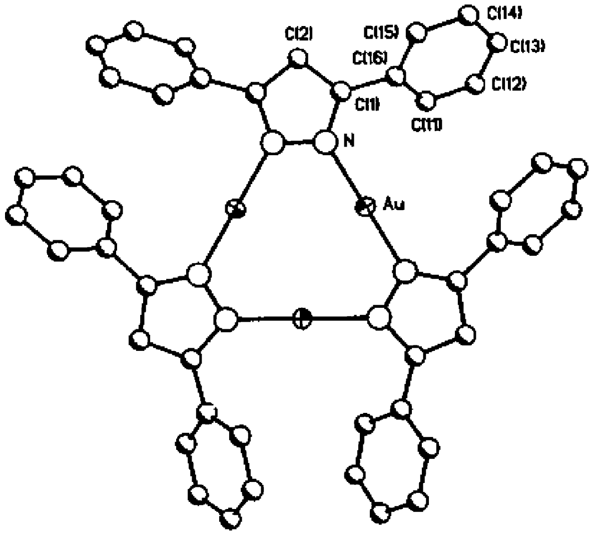


Figure 9. **A drawing of the CTC [μ-N,N-3,5-$Ph_2pzAu]_3$, 6.**

179.6(3)°. The 9-membered ring is regular and planar with Au…Au intramolecular distance of 3.368(1) Å.

Recently, gold pyrazolate CTCs have been described that produce room-temperature columnar mesophases.[9d] These complexes have long chain substituents in the 3,5 positions of the pyrazolate ring. X-ray powder diffraction measurements have demonstrated that the supramolecular columnar arrangement is present in the crystalline solids as well as in the mesomorphic phase. The X-ray crystal structure of complex **8**, which has an anisole unit on the pyrazolates, yields a unit cell that contains two independent CTCs. They are slightly different in the twist about the central metallocycle core and more markedly in the relative conformations of the phenyl substitutents (Figure 10).[14]

The molecular structure of **8** consists of slightly irregular and puckered 9-membered cycles, where N-Au-N angles range from 174.9(8) to 177.2(8)°. The N-Au bond distances range between 1.99(2) and 2.07(2) Å. In complex **8** the intramolecular Au…Au average distance is 3.3380(7) Å. The intermolecular Au…Au distance is greater than 4.252 Å with a mean stacking separation between two consecutive trimers of 4.54 Å. The crystal structure of **8** shows a columnar arrangement of the gold CTC parallel to the crystallographic *c* axis (Figure 11). The packing

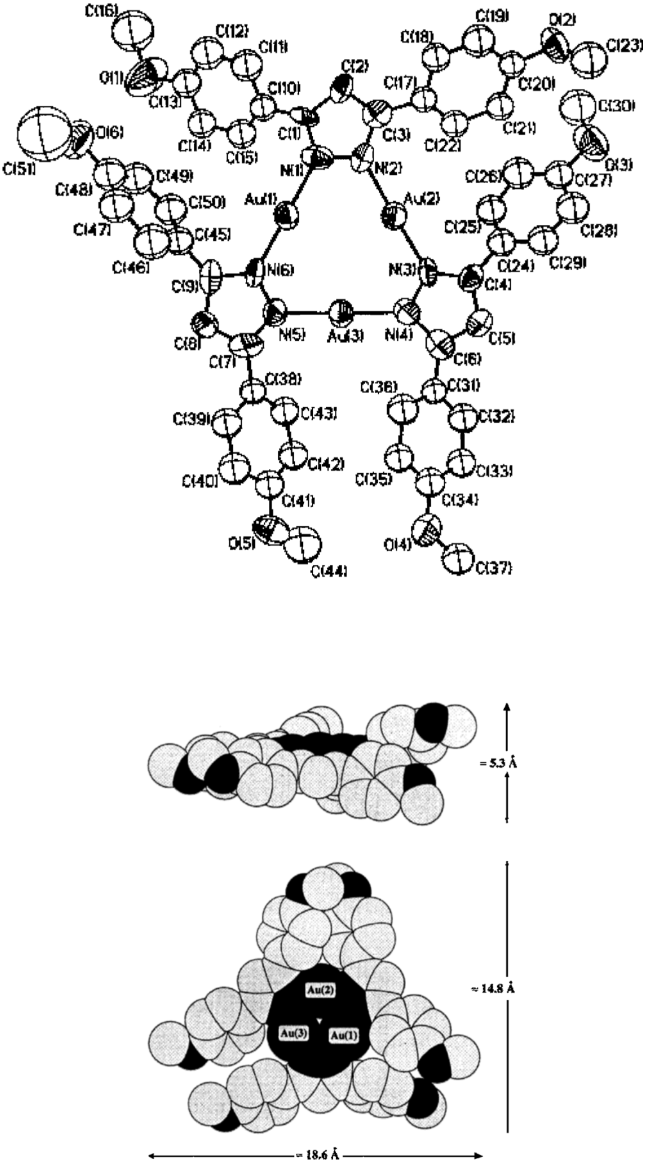


Figure 10. View of the molecular structure (top) and space filling representation (bottom) of the complex $[\mu\text{-N,N-3,5-(4'-MeOPh)}_2\text{pzAu}]_3$, **8**.

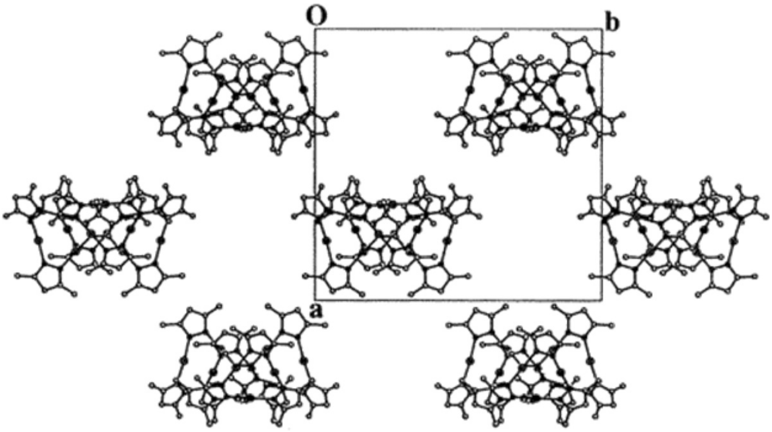


Figure 11. View of the crystal structure of complex [μ-N,N-3,5-(4′-MeOPh)$_2$pzAu]$_3$, **8** along the *c* axis showing the columnar arrangement present in the solid state. For clarity, only the C_{ipso} carbon of the methoxyphenyl substituents of the pyrazolate ligands are represented.

mode observed appears to be controlled by the van der Waals forces (i.e. no Au…Au interactions).

A more complex supramolecular architecture has been discovered for the complexes [μ-N,N-pzAu], **9** and [μ-N,N-4-MepzAu]$_3$, **10**.[15] The molecular structure of **9** consists of the usual 9-membered ring with Au-N distances and N-Au-N angles in the range of 1.992(6)-2.014(6) Å and 176.9(3)-178.9(3)°, respectively. Intramolecular aurophilic gold-gold interactions are present with Au…Au distances 3.372(1)-3.401(1) Å.

Complex **9** forms a two-dimensional network by self-assembly of the CTCs through intermolecular aurophilic interactions. Each [μ-N,N-pzAu]$_3$ forms a dimer such as those found in other CTCs, with two gold-gold interactions (Au(2)…Au(3b) and Au(2b)…Au(3), 3.313(1) Å). Moreover, each dimer interacts with four other dimers through single Au…Au contacts (Au1…Au3a, 3.160(1) Å) to form a net (Figure 12).

Figure 13 presents the intricate supramolecular network formed by complex **10**. The sixteen CTC aggregate is generated by an inversion center located at the center of the Au10-Au11-Au10a-Au11a parallelogram forming a chain of CTCs with side arms. The bond distances, the angles and the gold-gold interactions are consistent with those of **9** and other gold pyrazolate trimers.

In summary, trinuclear 9-membered rings are formed by gold(I) ions with exobidentate C,N or N,N monoanionic ligands. Except for high

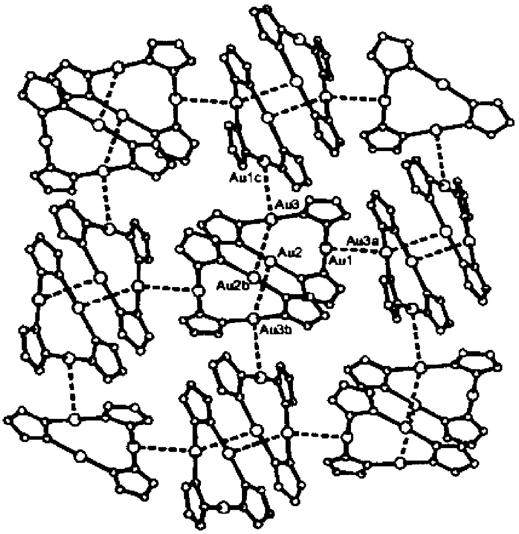


Figure 12. Two-dimensional structure of [μ-N,N-pzAu]$_3$, **9.** Intermolecular Au…Au interactions of less than 3.6 Å are shown as broken lines.

crystallographic symmetry systems, the structures are generally slightly irregular and puckered. Gold-gold intramolecular interactions are always present and the CTCs themselves exhibit a roughly D_{3h} symmetry.

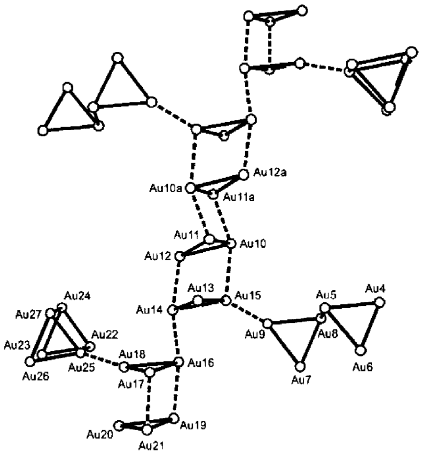


Figure 13. View of the self-association of sixteen trimers in [μ-N,N-4-MepzAu]$_3$, **10.** C, N atoms are omitted for clarity. Intramolecular Au…Au contacts are shown as solid lines, intermolecular Au…Au interactions of less than 3.6 Å are shown as broken lines.

Crystal structures show individual isolated complexes, dimers, supramolecular columnar packing or more complex supramolecular aggregates. Bulky substituents on the ligands can cause the formation of tetranuclear cyclic gold(I) complexes.[9c,17]

1.2. Reactivity

Gold CTCs undergo oxidative-addition reactions of halogens at the metal centers.[18] There is evidence that electronic more than steric factors may influence the reactivities of the gold atoms in these compounds. In fact, except for complex **3**, only one metal center appears to be oxidized to give mixed-valence Au_2^I/Au^{III} metallocycles. Surprisingly, aqua regia also fails to give complexes beyond the Au_2^I/Au^{III} oxidation state for the pyrazolates. Thus an unusual stability of the $d^{10}d^{10}d^8$ configuration for the gold CTCs is observed. The electronic communication between the gold atoms may be the origin of this effect. The oxidation of the first gold atom may improve the π-acceptor ability of the two ligands coordinated to it so that they decrease sufficient electron density from the remaining two Au^I atoms and prevent their oxidation. However, this hypothesis is not supported by crystallographic data. No changes in the gold-ligand bond lengths are observed. When complex **6** is reacted with aqua regia halogenation at the 4-position of the pyrazolate rings occurs causing the formation of $[\mu\text{-N,N-3,5-Ph}_2\text{-4-Cl-pzAu}]_3Cl_2$, Figure 14, and ultimately $[\mu\text{-N,N-3,5-Ph}_2\text{-4-Cl-pzAu}]_3Cl_6$. The crystal structure of this complex shows that there is no statistically significant difference between the Au^I-N and the Au^{III}-N bond lengths, which range from 1.98(3) to 2.05(2) Å[18c], just as it had been seen in the structure of $[\mu\text{-N,N-3,5-Ph}_2\text{pzAu}]_3Cl_2$.[18c] Complex **3** seems to be unique in the family of the gold CTCs and, in fact, it is the only CTC of gold(I) that gives the stepwise addition of halogens, resulting in the formation of either mixed-valent or completely oxidized trinuclear gold complexes, Scheme 5. The X-ray structures of these derivatives were recently reported,[18g] many years later after their synthesis.[18a] Figure 15 is the ORTEP drawings of these chlorinated TR(carb)s.

These crystallographic results for the iodine oxidized **3** confirm the structures originally proposed.[18a] All the structures retain the frame of the starting complex **3**. The variation in the intramolecular Au...Au separation is small. However, there is a trend toward increased Au...Au distance as more iodine is added to the complex. Nevertheless the

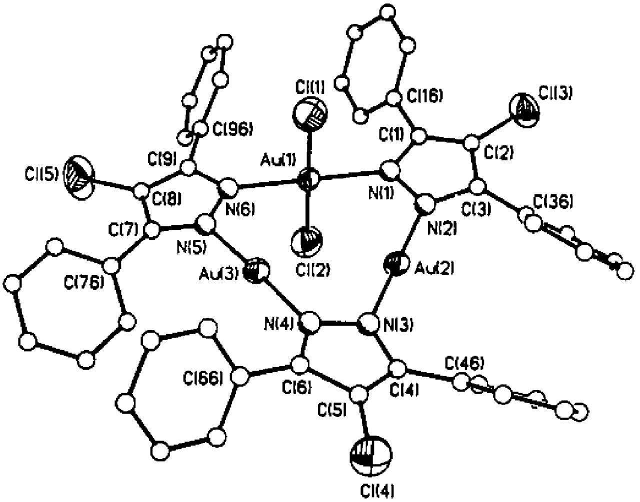
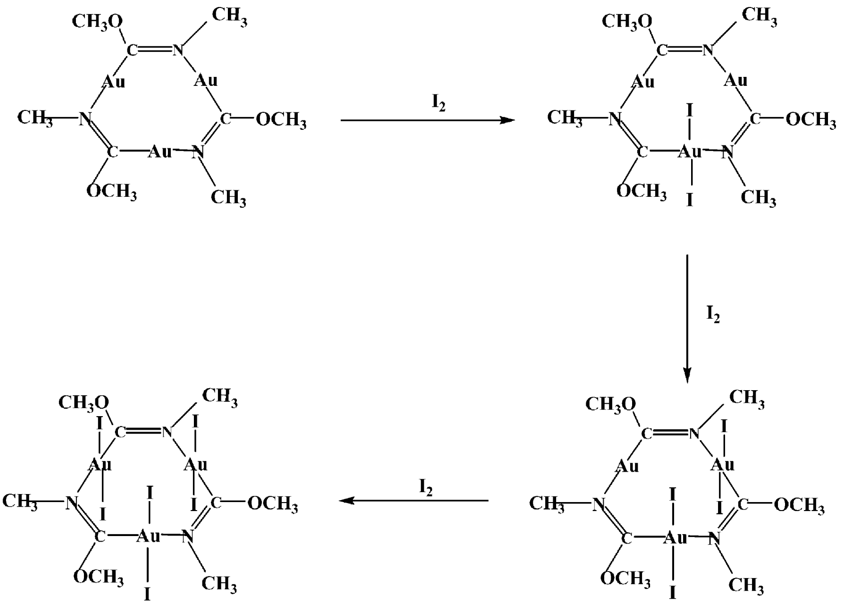


Figure 14. A view of the molecular structure of complex [μ-N,N-3,5-Ph_2-4-Cl-pzAu]$_3Cl_2$. Carbon and nitrogen atoms are of arbitrary radii for clarity.



Scheme 5

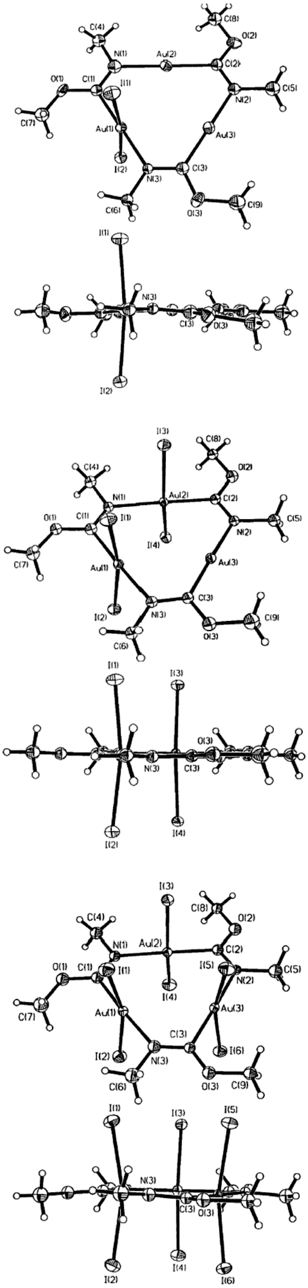


Figure 15. Two views of the mixed-valence or completely oxidized complexes [μ-C(OMe) = N(Me)Au]$_3$I$_n$(n = 2–6).

C-Au-N angles vary little from 180°. The Au-I distances fall in a range of 2.614(6)-2.633(7) Å. As a consequence of the repulsive intramolecular I-I contacts, the I-Au-I angles deviate significantly from linearity. They become smaller and smaller with increased numbers of iodide atoms bonded to the gold centers. The structure of $[\mu\text{-C(OMe)}=\text{N(Me)Au}]_3 I_6 \bullet CH_2Cl_2$ shows the formation of columns with short intermolecular I- - -I interactions ranging from 3.636(2) to 3.716(2) Å, 0.3–0.5 Å (Figure 16). The interaction between terminal iodide ligands appears, to have a directional component.

Oxidative-addition of iodine also was investigated for complex **5**. This substrate behaves similarly to most of the CTCs since it adds iodine at only one gold center to yield $[\mu\text{-N}^1,\text{C}^2\text{-bzimAu}]_3I_2$. Figure 17 shows its structure.[19] It consists of discrete trinuclear complexes with the gold atoms bridged by three l-benzylimidazolate groups. The coordination about Au(2) and Au(3) is nearly linear, while Au(1) has nearly a square planar arrangement. The Au-C, Au-N, and Au-I bond lengths are similar to those found in the analogous carbeniate derivatives. The I-Au-I angle is more linear than that found in the carbeniate CTC (175.8(1)° vs. 172.61(6)°). A different behavior of complex 5 was observed when it was reacted with other reagents capable of oxidative-addition such as alkyl or acyl halides. In these cases the products were characterized by X-ray crystal structure[18d,18f] or by ^{197}Au Mössbauer investigation.[19] Moreover, an oxidation was observed when complex **5** reacted with Me_3SiI (Au^I/Au_2^{III}) or $SOCl_2$ (Au_3^{III}).[18d,k,19]

SUPRAMOLECULAR ENTITIES OF TRINUCLEAR GOLD(I) COMPLEXES SANDWICHING SMALL ORGANIC ACIDS

Extended linear chain inorganic compounds have special chemical and physical properties.[20,21] This has lead to new developments in fields such as supramolecular chemistry, acid-base chemistry, luminescent materials, and various optoelectronic applications. Among the recent examples are the developments of a vapochromic light emitting diode from linear chain Pt(II)/Pd(II) complexes,[22] a luminescent switch consisting of an Au(I) dithiocarbamate complex that possesses a luminescent linear chain from only in the presence of vapors of organic solvents,[23] mixed-metal Tl/Au compounds that exhibit different colors and emissions when different organic solvents are introduced or removed,[24] and the discovery of the new phenomenon, solvoluminescence,[25] in the CTC of Au(I) in which

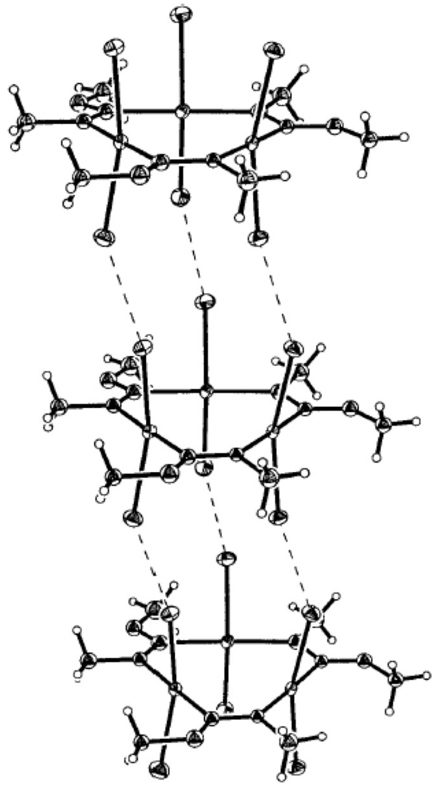


Figure 16. Columns formation through I- - -I contacts present in the molecular packing of the complex [μ-C(OMe)=N(Me)Au]$_3$I$_6$.

an extended chain structure is responsible for storage of light energy and its release as a long-lived orange phosphorescence upon contact with solvent.

The trinuclear compounds **4** and **5** are colorless and do not form extended-chain structures like **3**. However, they can produce brightly colored complexes by sandwiching naked Tl$^+$ and Ag$^+$ ions to form linear chain complexes with fascinating luminescence properties such as a luminescence thermochromism.[26] Recent results have demonstrated that the electron-rich trinuclear Au(I) complexes can interact with neutral electron-acceptor entities such as C_6F_6, TCNQ, or $Hg_3(\mu\text{-}C_6F_4)_3$ to produce infinite linear chain complexes.[27,28] Balch and co-workers also demonstrated that trinuclear Au(I) compounds with alkyl-substituted carbeniate bridging ligands can interact with the large organic acceptors

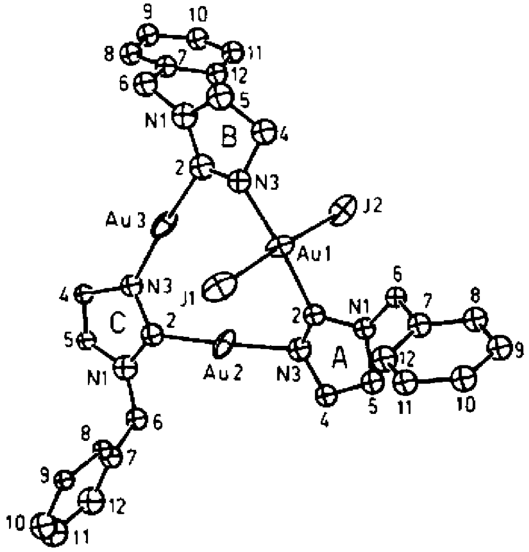


Figure 17. A view of the mixed-valence complex [μ-N^1,C^2-bzimAu$]_3I_2$.

nitro-9-fluorenones.[26] DFT calculations clearly show that the donor regions in the trinuclear Au(I) compounds are located at the center of the 9-membered ring and that they extend to regions in space above and below the ring plane.[27] A pi-acid pi-base complex with a columnar structure forms when a small tetracyano-substituted organic acceptor reacts with **5**. Previously attempted for the reactions with cyano-substituted organic acceptors lead to the rupture of the trinuclear Au(I) unit and formation of mononuclear cations.[29]

The crystal structure of [TR(bzim)$]_2$·TCNQ is shown in Figure 18. The TCNQ molecule is sandwiched between two units of **5**, in a face-to-face manner so that it is best represented by the formula (π-**5**) (μ-TCNQ)(π-**5**). The cyanide groups are clearly not coordinated to the gold atoms. The distance between the centroid of TCNQ to the centroid of the Au_3 unit is 3.964 Å. The packing of 5·TCNQ shows a stacked linear-chain structure with a repeat pattern of …(Au_3)(Au_3)(μ-TCNQ) (Au_3)(Au_3)(μ-TCNQ) an ABBABB repeat. The complex 5·TCNQ contains two very short intermolecular Au…Au distances of 3.152 Å (identical for the two aurophilic bonds). The intermolecular Au…Au distance is even shorter than the intramolecular distances in the starting compound, which are 3.475, 3.471, and 3.534 Å. The adjacent Au_3 units

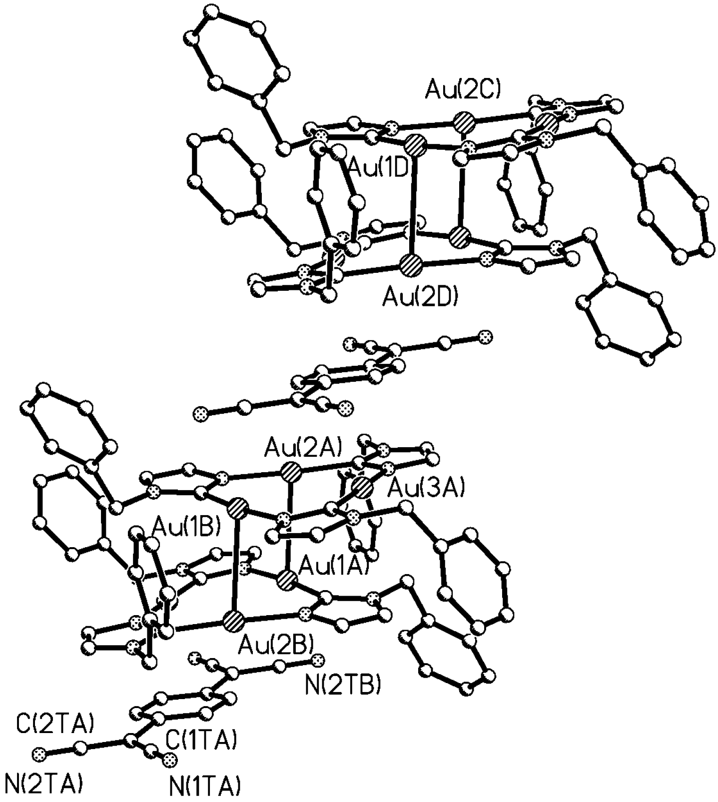


Figure 18. The stacked acid-base complex formed from TCNQ and a TR(bzim), 5.

in 5·TCNQ form a chair-type structure rather than the face-to-face (nearly eclipsed) pattern reported in Balch's studies of the nitro-9-fluorenones adducts with the trinuclear Au(I) alkyl-substituted carbeniate complexes.

The shortened intermolecular Au-Au distances in 5·TCNQ may be associated with charge-transfer from the electron-rich Au center to the known electron acceptor TCNQ. A partial oxidation of the Au(I) atoms leads to the shortening of Au-Au distances. In the limit of complete oxidation of Au(II), a gold-gold single bond forms with $[TCNQ]^-$. Unfortunately the presence of $[TCNQ]^-$ impurity in the crystals may be the cause of the dark color of this TCNQ complex of **5**, which itself is colorless while TCNQ is light orange. Thin crystals and films, however, are dark green as are solutions. It remains possible that charge transfer is the cause of these colors, with adduct formation remaining intact in solution.

The crystal structure of [TR(carb)]·C_6F_6 shows a columnar stack consisting of alternating C_6F_6 and **4** molecules (Figure 19). The C_6F_6 molecule is sandwiched between two units of 4 in a face-to-face manner so that a molecule of 4·C_6F_6 is best represented by the formula $(\pi\text{-}4)_{0.5}(\mu\text{-}C_6F_6)(\pi\text{-}4)_{0.5}$. The distance between the centroid of C_6F_6 to the centroid of the Au_3 unit is 3.565 Å. The packing of 4·C_6F_6 shows a stacked linear-chain structure with a repeat pattern of $\ldots(Au_3)(\mu\text{-}C_6F_6)(Au_3)(\mu\text{-}C_6F_6)\ldots$, an ABAB pattern. The crystal structure of 4 by itself shows a dimeric structure with intermolecular Au-Au bonds. Therefore, the C_6F_6 Lewis acid disrupts the intermolecular aurophilic bonding in **4** with the resulting linear chain adduct stabilized by pi acid-base interactions. These pi-acid, pi-base results with gold CTCs are similar to but opposite from the interactions reported by Gabbaï and co-workers, between the Lewis acid $Hg_3(\mu\text{-}C_6F_4)_3$ and benzene, in which benzene acts as a Lewis base coordinating in a μ-6 manner to six Hg centers, three from each side.[30,31] The two Au_3 units interacting with hexaflurobenzene in 4·C_6F_6 are eclipsed with respect to each other (nearly D_{3h}) whereas the two Hg_3 units in $Hg_3(\mu\text{-}C_6F_4)_3$·benzene are nearly staggered (D_{3d}).

The trinuclear cyclic Au^1 compounds [Au(μ-C^2,N^3-bzim)]$_3$ (bzim=1-benzylimidazolate), **5**, and [μ-C(OEt) = N(C_6H_4p-Me)Au]$_3$ 4, have been shown to interact with metal cations such as Ag^I and Tl^I to form "sandwich"

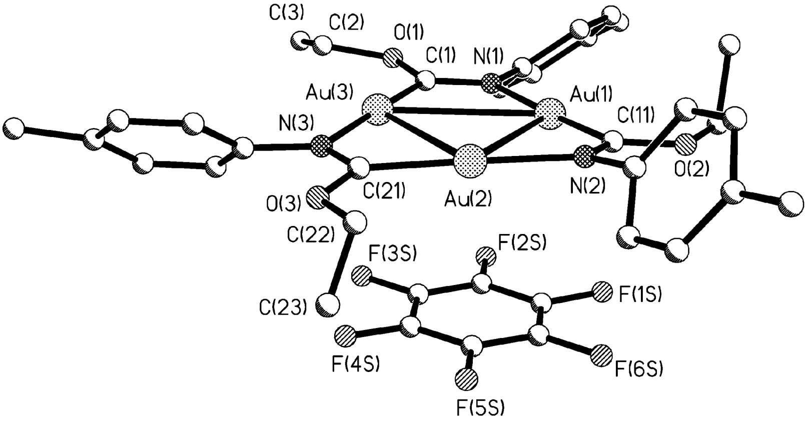


Figure 19. The stacked acid-base complex formed from C_6F_6 and a TR(carb), 4.

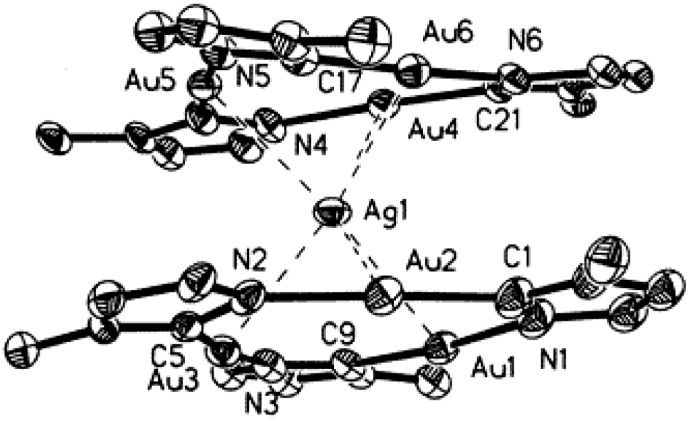


Figure 20. The acid-base complex formed from Ag^+ and a **5**.

complexes in which six Au^I atoms from two trinuclear gold molecules bond to the Ag^I or Tl^I (Figures 20–22).[26] These sandwich units stack to form linear chains with intermolecular aurophilic Au^I-Au^I bonding between four of the six Au^I atoms in adjacent units. With no cations present, the trinuclear Au^I

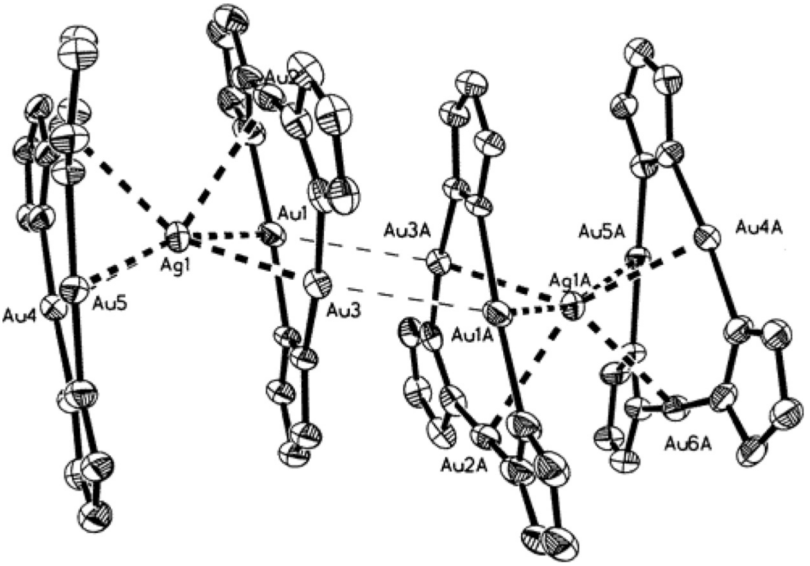


Figure 21. The stacked acid-base complex formed from Ag^+ and a **5**, TR(bzim).

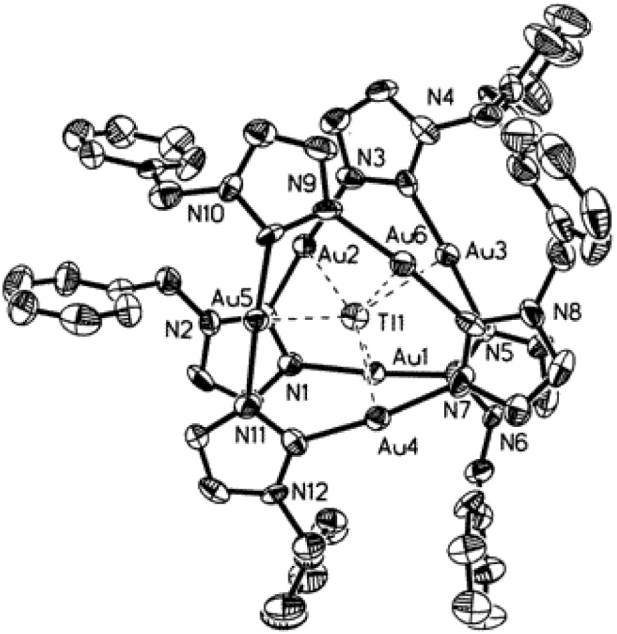


Figure 22. The acid-base complex formed from Tl^+ and TR(bzim).

complexes of this type generally do not stack with the exception of $[Au(\mu\text{-}C(OMe){=}NCH_3)]_3$,[7a, 11] while 4 exists as a dimer.

Since the trinuclear Au^I compounds interact with cations in a similar manner to the cation-π interactions studied by Dougherty,[32] and since Hawthorne[33] has demonstrated that polynuclear mercury complexes form crown compounds with anions and various organic and aromatic organometallic substrates, it seemed plausible that acid-base stacking might occur between the trinuclear Hg^{II} complex $[Hg(\mu\text{-}C,C\text{-}C_6F_4)]_3$ and the trinuclear Au^I complexes. Upon reaction of **5** with the trinuclear Hg^{II} complex, a stack of the gold and mercury CTCs formed with a $[Au_3Hg_3Au_3]_n$ repeat pattern (ABBABBA). The intermolecular Au- - -Au distances between the four aurophilically bonded Au^I atoms (ca. 3.3–3.5 Å) are typical of distances found in other Au^I complexes having such bonding (Figures 23). The Hg^{II} atoms interact with the Au^I atoms in adjacent rings with Hg···Au distances as short as 3.27 and 3.24 Å in **4** and **5**, respectively. Gabbai et al. suggests that benzene in the 1:1 π-stacked complex with $[Hg_3(C_6F_4)_3]$ shows each C-C bond in benzene interacting with a different Hg(II) center.[30,31]

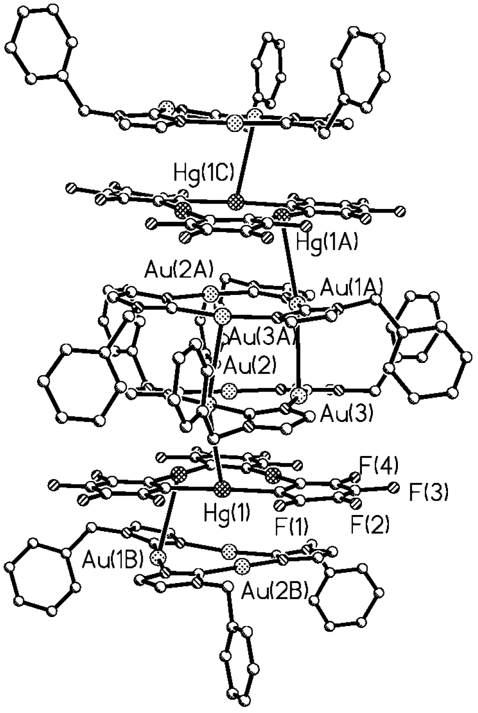


Figure 23. The stacked product of a acid-base reaction between $[Hg(C_6F_4)]_3$ and TR(bzim).

Crystals of these mixed-metal compounds are luminescent at both ambient and cryogenic temperatures. The emission intensity is very strong with the Hg-Au interactions. The spectrum shows vibronic structure with an average spacing of $\sim(1.4 \pm 0.2) \times 10^3\,cm^{-1}$, corresponding to a progression in the $\nu_{C=N}$ vibrational mode of the carbeniate ligand as determined from the infrared spectrum ($\sim 1500\,cm^{-1}$). This vibronic pattern indicates that the emission has a strong C-N ligand character. The supramolecular chains formed are stabilized by electrostatic interactions between the Hg_3 and Au_3 units, and by aurophilic bonding between adjacent Au_3 units. The properties of these stacked compounds appear promising for optoelectronic applications.

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