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Structural Switching in Luminescent Polynuclear Gold Imidoyl Complexes by Intramolecular Hydrogen Bonding

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Summary: A subtle interplay of covalent bond, hydrogen bond, aurophilic interactions, and steric hindrance controls the nuclearity and the luminescent properties of $[Au\{2\text{-}PyN{=}C(E)Me\}]_n$ *(E = O, NH) complexes. For E = O a molecular structure with* $n = 4$ *is formed, describing a 20-membered tetrametallacycle. For E = NH the structure formed shows a trigonal prismatic arrangement of six gold atoms formed by gold−gold interactions between two gold triangles* ($n = 3 \times 2$)*. Both complexes display luminescent properties.*

Introduction

Self-organized systems with specific properties and functions are receiving attention as potential advanced materials.[1,2] Weak forces such as hydrogen bonds and aurophilic interactions can be decisive in their formation. An interesting example is the gold imidoyl (alternative names for imidoyl ligands are iminoacyl or carbeniato) complex $[Au(MeN{=}COMe)]_3$, which displays an uncommon luminescent behavior called solvoluminescence.[3] This behavior is related to its crystalline structure, containing a stacking of trinuclear molecules where the three gold atoms of one molecule lie directly above and below neighboring molecules to form a trigonal prismatic array, with Au···Au interactions along the columns and between gold atoms of the same molecule. The extended columnar stacking reported for $[Au(MeN{=}COMe)]_3$,[3] with the trimer units eclipsing each other, is not found when the substituents in the bridging ligand are bulkier, and other variations of the gold−gold interactions for similar trinuclear complexes have been reported.[4,5]Also the formation of adducts with organic acceptors such as nitrofluorenone or with trinuclear complexes of Hg(II) has been reported.[5] On these grounds we decided to study imidoylgold compounds of the type $[Au\{2\text{-}PyN{=}C(E)Me\}]_n$ (E = O, NH) containing a 2-pyridyl group in place of the usual phenyl group. The potential of the pyridyl group to act as H-acceptor in hydrogen bonding should provide a new tool to control and modulate the molecular or supramolecular structure through the formation or not of hydrogen bonds between the nitrogen of the 2-pyridyl moiety and the E group.

Results and Discussion

The reaction of the carbene complex $[AuCl\{C(NHMe)(NHPy\text{-}2)\}]$[6] with KOH in methanol leads to the formation of $[Au(2\text{-}PyN{=}CNHMe)]_3$ (**1**) (eq 1).

$$3\,[\mathrm{AuCl\{C(NHMe)(NHPy\text{-}2)\}}] + 3\,\mathrm{KOH} \rightarrow [\mathrm{Au(2\text{-}PyN{=}CNHMe)}]_3 + 3\,\mathrm{H_2O} + 3\,\mathrm{KCl} \quad (1)$$

The X-ray molecular structure of **1** is represented in Figure 1. The structure framework is a typical triangular arrangement of gold atoms C=N bridged by imidoyl groups C(NHMe)=NPy-2. The Au···Au separation in the trimer (3.2532(9) Å) is much longer than in metallic gold,[7] but close to the highest values found between peripheral atoms in gold clusters,[8] so weak Au···Au bonding interactions within the trimetallic moiety cannot be discarded.[9]

The hydrogen atoms of the amine groups in **1** were located in a difference Fourier map and refined.[10] They are involved in N(amine)−H···N(pyridyl) intramolecular contacts. The H(8B)···N(2) distance is 1.916(8) Å, whereas the N(2)−H(8B)−N(3B) angle is 126.1(4)°. The H(8B)···N(2) distance is within the usual range for H−N moderate hydrogen bonds.[11] The ^{1}H NMR chemical shift assigned to the amine hydrogen of the imidoyl group (12.5 ppm) supports that the intramolecular hydrogen bonds with the pyridyl nitrogen found in the solid state are retained in $CDCl_3$ solution.

These trinuclear units are disposed in pairs with an Au···Au separation between them of 3.2645(12) Å. Therefore, attractive aurophilic interactions between the metal centers of different trimers are also proposed. Consequently, the structure of the

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[10] To correct the systematic shortening of N−H bonds measured by X-ray diffraction, normalized H atom positions were used. An N−H distance of 1.009 Å was imposed. This value has been observed in amines by neutron diffraction: Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

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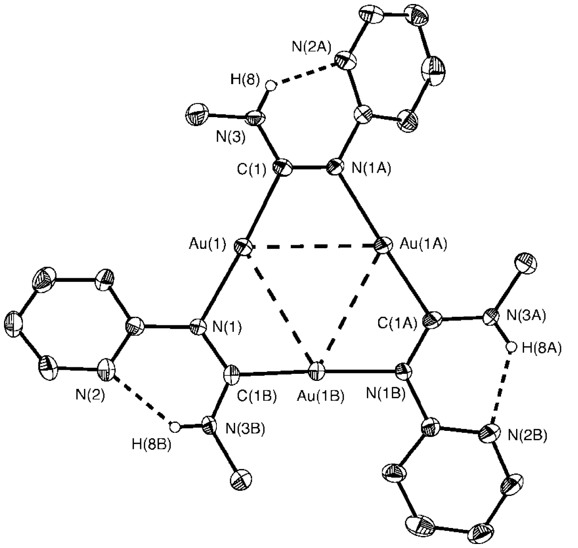

Figure 1. Molecular structure of **1** showing 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Au(1)−C(1) 2.007(8), Au(1)−N(1) 2.072(7), Au(1)−Au(1A) 3.2532(9), N(1)−C(1B) 1.334(12), H(8B)−N(2) 1.916(8), C(1)−Au(1)−N(1) 176.3(3), Au(1A)−Au(1)−Au(1B) 60.0, N(2)−H(8B)−N(3B) 126.1(4).

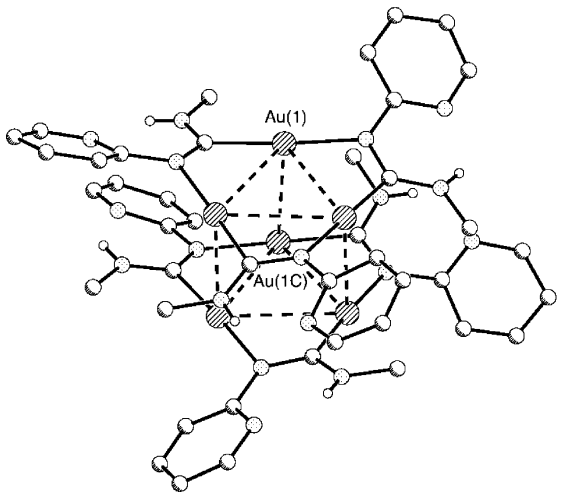

Figure 2. Pairwise association through Au⋯Au contacts (Au(1)−Au(1C) 3.2644(12) Å) in $\mathbf{1}_2$.

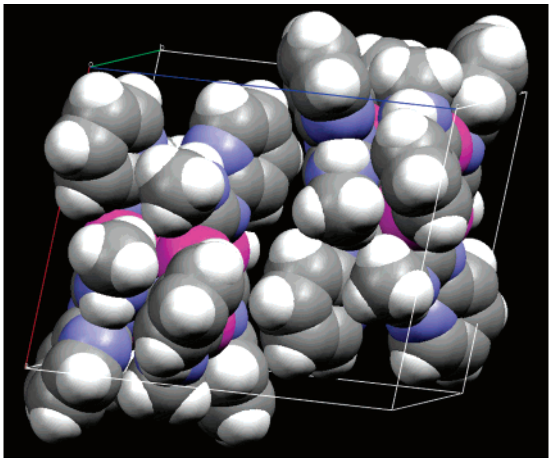

Figure 3. Space-filling view of the unit cell of **1**.

complex is better described as a dimer of trimers, $\mathbf{1}_2$. This simple pairwise association through Au⋯Au contacts, forming a trigonal prismatic array of six gold atoms (Figure 2), had not been observed before, although it is a motif forming part of the columnar arrangement found for the supramolecular structure of [Au(MeN═COEt)]$_3$ with the acceptor nitrofluorenone.[4] The three pyridyl groups of one trimer in complex $\mathbf{1}_2$ are in a staggered orientation with respect to the three groups of the other trimer, presumably to minimize steric hindrance. However, the ligands still protrude out of the prismatic top and bottom planes defined by each trimer, preventing these hexagold units from establishing additional Au⋯Au contacts to give a columnar arrangement.

In effect, in an isolated trimer **1** the participation of the pyridyl nitrogen in hydrogen-bonding formation should produce a planar molecule, where the best hydrogen-bonding interaction should be reached. However, the structure found shows that in the dimer of trimers $\mathbf{1}_2$ the pyridyl rings are tilted as the blades of a propeller, making an angle of 29.9° with the plane defined by the three gold atoms. Also the H−N−Me fragment is tilted with the Me toward and H away from the space defined by the two planes containing the two gold triangles.

This way the Me group is accommodated in the space created by the tilting of the pyridyl groups. The two trimers in a pair have the same helicity, resulting in a chiral C_3 symmetry for the hexanuclear complex $\mathbf{1}_2$. The prismatic arrangement of six gold atoms produces a complex that presents "concave" bases at both extremes of the prism. This moderate perturbation from planarity suffices to hinder a columnar infinite stacking of trimers, while it helps to stabilize the pairwise interaction over other less efficient packing arrangements. The unit cell (Figure 3) contains two $\mathbf{1}_2$ pairs with opposite helicity, making the crystal racemic.

The perturbation from trimer planarity in the paired molecules is reached at the expense of a weakening of the N(amine)−H⋯N(pyridyl) interactions (their possible best value should be reached in a planar arrangement) and must be compensated by the formation of strong enough Au⋯Au interactions. This gives an indication of the approximate range of strength of these aurophilic interactions.

To check whether the pyridyl N atoms would compete with the imidoyl nitrogen for the metal coordination site, giving rise to a different structure, we decided to use as starting materials a gold carbene [AuCl{C(OMe)(NHPy-2)}][6] in which, after imidoyl formation, there is no hydrogen left for intramolecular hydrogen bonding with the pyridyl nitrogen. In this case the reaction (eq 2) afforded a tetranuclear compound [Au(2-PyN═COMe)]$_4$ (**2**), where the pyridyl N atoms are coordinated to gold and the imidoyl nitrogen atoms are not involved in metal coordination.

$$4\,[\mathrm{AuCl\{C(OMe)(NHPy\text{-}2)\}}] + 4\,\mathrm{KOH} \rightarrow [\mathrm{Au(2\text{-}PyN{=}COMe)}]_4 + 4\,\mathrm{H_2O} + 4\,\mathrm{KCl} \quad (2)$$

Complex **2** is poorly soluble in common organic solvents and could not be characterized by NMR, but, fortunately, crystals suitable for X-ray diffraction were isolated. The perspective view of **2**·0.5CH$_2$Cl$_2$ is given in Figure 4. There are four two-coordinated gold atoms per molecule, involved in the formation of a 20-membered tetrametallacycle.

The molecule is centrosymmetric with only half the macrocycle as the asymmetric unit. The gold atoms show a linear coordination (C(16)−Au(1)−N(2), 173.9(3) Å; C(26)−Au(2)−N(1), 177.0(3) Å), and the Au−C and Au−N distances are in the usual range for Au$^{\mathrm{I}}$ compounds.[3−5]

As shown in Figure 4, the bridging ligand C(OMe)═NPy-2 is now coordinated to the gold atom through the pyridyl

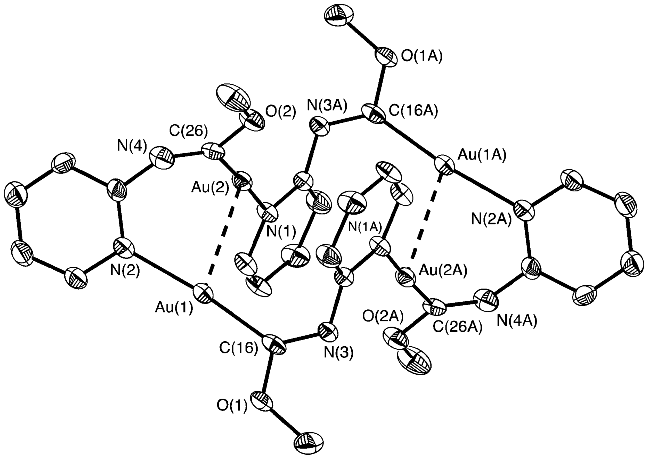

Figure 4. Molecular structure of $\mathbf{2}\cdot 0.5CH_2Cl_2$ showing 30% thermal ellipsoids (CH_2Cl_2 molecule has been omitted for clarity). Selected bond lengths (Å) and angles (deg): Au(1)−C(16) 1.998(9), Au(1)−N(2) 2.083(7), Au(1)−Au(2) 3.0854(13), Au(2)/Au(2A) 4.373(8), Au(1)/Au(2A) 5.082(8), Au(2)−C(26) 1.999(8), Au(2)−N(1) 2.078(6), N(3)−C(16) 1.273(9), N(4)−C(26) 1.296(10), C(16)−Au(1)−N(2) 173.9(3), C(26)−Au(2)−N(1) 177.0(3).

Table 1. Luminescence Data of Complexes 1 and 2

	medium (T/K)	excitation λ/nm	emission λ/nm
1	solid (298)	411	523
	CH_2Cl_2 (298)	342	536
	CH_2Cl_2 (77)	352	460
2	solid (298)	436	558

nitrogen. The Au(1)⋯Au(2) separation in the tetramer (3.0854(3) Å) is in the range of attractive aurophilic interactions proposed in the literature.[9] On the contrary, the Au(1)/Au(2A) and Au(2)/Au(2A) distances (5.082(8) and 4.373(8) Å, respectively) reveal no interaction.

Complexes **1** and **2** display intense luminescence (Table 1). All the emission spectra are very similar in the solid state and in solution and show one broad emission band with the maximum in the range 460−558 nm. The lifetimes in the solid state for **1** and **2** have been measured,[12] affording 84 and 79 μs, respectively.

These long lifetime values support a phosphorescence nature of the emission band that can be attributed to the presence of gold−gold interactions, as reported for similar trinuclear gold complexes.[13] Moreover, since the Au⋯Au interactions are intramolecular, they should survive in solution and produce similar luminescent behavior in solution, as observed. It is worth noting that compound **2** (which presents a shorter Au⋯Au separation (3.08 Å) than compound **1** (3.25 Å)) displays luminescent emission at lower energy, revealing a direct relationship between the luminescence wavelength and the crystallographic Au⋯Au ground-state distances, in concordance with observations on other Au^I complexes.[14]

In summary, these complexes illustrate how replacing a phenyl group for a pyridyl group opens new perspectives to classical systems. This synthetically small variation offers the opportunity to easily influence the resulting polynuclear systems with a complex interplay of different bond types (coordination bond, Au⋯Au bond, and hydrogen bond), by controlling the possibility of formation of the latter. Other interesting cases are being explored in our lab.

Table 2. Crystal Data and Structure Refinement for 1 and $\mathbf{2}\cdot 0.5CH_2Cl_2$

	1	$\mathbf{2}\cdot 0.5CH_2Cl_2$
empirical formula	$C_{21}H_{24}Au_3N_9$	$C_{14.5}H_{15}Au_2ClN_4O_2$
fw	993.39	706.69
temperature (K)	298(2)	293(2)
wavelength (Å)	0.71073	0.71073
cryst syst	trigonal	triclinic
space group	$P\bar{3}1c$	$P\bar{1}$
a (Å)	14.209(3)	8.675(5)
b (Å)	14.209(3)	10.097(6)
c (Å)	15.720(5)	11.709(7)
α (deg)	90	70.158(10)
β (deg)	90	70.274(10)
γ (deg)	120	74.736(11)
V (Å^3)	2748.5(12)	895.2(9)
Z	4	2
D_{calc} (g cm^{-3})	2.401	2.622
absorp coeff (mm^{-1})	15.999	16.532
F(000)	1800	642
cryst size (mm)	0.28 × 0.12 × 0.12	0.27 × 0.05 × 0.03
θ range for data collection	1.65 to 23.25°	2.18 to 23.30°
no. of reflns collected	12 818	4200
no. of indep reflns	1332	2560
absorp corr	SADABS	SADABS
max. and min. transmn factor	1.000000 and 0.565420	1.000000 and 0.490978
no. of data/restraints/ params	1332/0/105	2560/0/225
goodness-of-fit on F^2	1.002	1.013
R_1 [$I > 2\sigma(I)$]	0.0305	0.0257
wR_2 (all data)	0.1085	0.0680

Experimental Section

All reactions were carried out under N_2 except when stated otherwise. Solvents were distilled using standard methods. Combustion CHN analyses were made on a Perkin-Elmer 2400 CHN microanalyzer. IR spectra were recorded on a Perkin-Elmer FT 1720 X spectrophotometer. Luminescent data were recorded with a Perkin-Elmer LS-55 luminescence spectrometer. ^1H NMR (300.16 MHz) spectra were recorded on Bruker ARX 300 and AC 300 instruments. Chemical shifts are reported in ppm from $SiMe_4$ (^1H) with positive shifts downfield, and J values are given in Hz.

[Au(2-PyN═CNHMe)]$_3$ (1). Potassium hydroxide (0.3 mmol, 325 μL of a 0.923 M solution in methanol) was added to a suspension of 0.110 mg of [AuCl{C(NHMe)(NHPy-2)}] (0.3 mmol) in chloroform (15 mL). The complex dissolved instantaneously, and KCl precipitated. After 15 min stirring at room temperature, the yellow solution was filtered through kieselguhr and poured into water (15 mL). The organic layer was washed with water (2 × 5 mL) and dried over $MgSO_4$. The solution was concentrated to 5 mL, and diethyl ether was added dropwise. Colorless crystals appeared that were decanted, washed with diethyl ether (3 × 5 mL), and vacuum-dried, yielding 0.029 g (29%). ^1H NMR ($CDCl_3$, 298 K) δ_H: 12.53 (br, NHCH$_3$, 1H), 8.13 (m, NC_5H_4N, 1H), 8.06 (d, J 8.2, NC_5H_4N, 1H), 7.54 (m, NC_5H_4N, 1H), 6.86 (m, NC_5H_4N, 1H), 3.27 (d, J 3.7, NHCH_3, 3H). Anal. Calcd for $C_{21}H_{24}N_9Au_3$: C, 25.39; H, 2.44; N, 12.69. Found: C, 25.08; H, 2.31; N, 12.28.

[Au(2-PyN═COMe)]$_4$ (2). Potassium hydroxide (0.342 mmol, 2 mL of a 0.163 M solution in methanol) was added to a suspension of 0.063 mg of [AuCl{C(OMe)(NHPy-2)}] (0.171 mmol) in dichloromethane (15 mL), whereupon the complex dissolved instantaneously. After 15 min stirring at room temperature, the pale yellow solution was filtered through kieselguhr and poured into water (10 mL). The organic layer was washed with water (2 × 5

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mL) and dried over $MgSO_4$. The solution was concentrated to 5 mL, and *n*-hexane was added slowly. Colorless crystals appeared, which were decanted, washed with *n*-hexane (3 × 5 mL), and vacuum-dried, yielding 0.023 g of **2**·$0.5CH_2Cl_2$ (38%). Anal. Calcd for $C_{29}H_{30}Au_4Cl_2N_8O_4$: C, 24.64; H, 2.14; N, 7.93. Found: C, 24.42; H, 1.98; N, 7.56.

Experimental Procedure for X-ray Crystallography. Suitable single crystals were mounted in glass fibers, and diffraction measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å).[15] Intensities were integrated from several series of exposures, each exposure covering 0.3° in ω, the total data set being a hemisphere.[16] Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[17] The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 2).[18] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms, except H(8) in compound **1**, were taken into account at calculated positions, and their positional parameters were refined. H(8) in compound **1** was located in a difference Fourier map and refined. Complex neutral-atom scattering factors were used.[19] Compound **2** crystallized with a dichloromethane molecule near an inversion center, which was refined as a rigid group with an occupancy of 50%. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications with the following deposition numbers: CCDC-286301 and CCDC-286302 for complexes **1** and **2**·$0.5CH_2Cl_2$, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: (int) + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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