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Supramolecular Assembly of Trimeric Gold(I) Pyrazolates through Aurophilic Attractions

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The supramolecular architecture of trinuclear gold(I) pyrazolato aggregates is held together by intermolecular aurophilic attractions, sterically governed by the substituents on the pyrazole rings. A two-dimensional network of [Au(μ-pz)]$_3$ complexes, **1** (pz = pyrazolato anion, $C_3H_3N_2^-$), and a large intricate aggregate of 16 [Au(μ-4-Me-pz)]$_3$ complexes in **2** have been determined crystallographically. Under UV irradiation at ambient temperature, solid samples of **1** and **2** luminesce with λ_{max} = 626 and 631 cm^{-1}, respectively, attributed to intermolecular Au···Au aurophilic contacts.

Attractive interactions between closed-shell Au(I) centers—aurophilic attractions[1]—are responsible for the formation of aggregates in the solid-state structures of several mono- and oligonuclear gold complexes.[2] Furthermore, the preorganization of mononuclear units through aurophilic interactions in solution has been shown to exert a templating effect on the course of subsequent oligomerization reactions.[3] Additional interest in supramolecular structures of Au(I) complexes is derived from the recognition that short d^{10}–d^{10} contacts are responsible for the luminescent properties of such materials.[4] Spectacular solvoluminescence has been reported by Balch et al. to be emitted from trimeric gold carbene complexes with trigonal prismatic columnar structure.[5] Recently, some trimeric gold(I)–pyrazolates with long alkyl side arms have been shown to organize into hexagonal columnar mesophases, or form micrometer-scale luminescent superhelical fibers, whose detailed three-dimensional structures remain unknown.[6]

We report herein the synthesis, crystallization, and X-ray structural characterization of two gold–pyrazolato trimers, [Au(μ-pz)]$_3$ (**1**) and [Au(μ-4-Me-pz)]$_3$ (**2**), as well as the crystal structure of [Au(μ-3-Me-5-Ph-pz)]$_3$ (**3**) (pz = pyrazolato anion, $C_3H_3N_2^-$) (Scheme 1). Intermolecular aurophilic attractions of 3.160(1)–3.569(2) Å support the supramolecular architectures of the luminescent complexes **1** and **2**, while only intramolecular Au···Au contacts of 3.314(1)–3.338(1) Å are present in the structure of nonluminescent **3**.

Several attempts at the synthesis of **1** resulted initially in intractable solids. Single crystals of **1** appropriate for X-ray study can be prepared as follows: Au(tht)Cl (0.1 mmol, 32 mg) and pyrazole (0.2 mmol, 13.6 mg) are dissolved in 4 mL of MeOH–THF (1:1) (tht = tetrahydrothiophene). Into the resulting clear solution, Et_3N vapors are allowed to slowly diffuse in a closed system. Colorless tiny needles appear within 10 min, and the crystallization is allowed to proceed for approximately 1 month, resulting finally in some well-shaped prismatic crystals of **1** in 65% yield.[7] Comparison of X-ray powder diffraction patterns obtained from the intractable bulk precipitate or the initially formed colorless needles with patterns calculated from the single-crystal diffraction data reveal that all three materials are identical.[8]

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(7) Decomposition before melting, ca. 160 °C. Anal. Calcd for $C_9H_9Au_3N_6$, [Au(μ-pz)]$_3$ (**1**): C, 13.63; H, 1.14; N, 10.60. Found: C, 13.35; H, 1.21; N, 10.42. Crystal data: Siemens SMART CCD diffractometer, monoclinic, space group $P2_1/c$, a = 8.336(1) Å, b = 14.383(1) Å, c = 11.056(1) Å, β = 106.887(2)°, V = 1268.4(2) Å^3, Z = 4, ρ_{calcd} = 4.148 g cm^{-3}, μ(Mo Kα) = 34.604 mm^{-1}. Least-squares refinement based on 1654 reflections with $I > 2\sigma(I)$ and 164 parameters led to convergence, with final R1 = 0.0216, wR2 = 0.0489, and GOF = 1.037.

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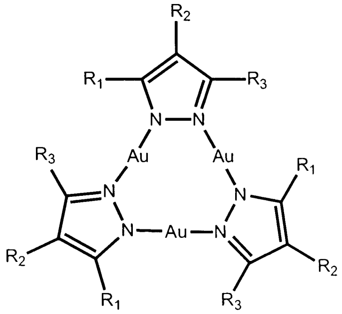
Scheme 1



1: $R_1 = R_2 = R_3 = H$

2: $R_1 = R_3 = H$; $R_2 = CH_3$

3: $R_1 = CH_3$; $R_2 = H$; $R_3 = C_6H_5$

Complex **1** consists of a nine-membered ring of D_{3h} symmetry, common to gold−pyrazolates as well as the structurally similar gold−imidazolate-*C*,*N*, carbene, and pyridinate-*C*,*N*.[5,9] The Au−N distances of **1** fall in the range 1.992(6)−2.014(6) Å, while the N−Au−N angles are 176.9(3)−178.9(3)°. The intramolecular Au···Au distances are approximately equal in length, falling in the 3.372(1)−3.401(1) Å range, similar to the distances found in related cyclic trinuclear gold(I) complexes.[6a,b,10] The most interesting feature of this X-ray study is the two-dimensional sheets, formed by assembling $[Au(\mu\text{-pz})]_3$ trimers through intermolecular aurophilic interactions (Figure 1). Each triangular complex forms two types of Au···Au contacts with adjacent molecules: pairwise contacts involving interactions between Au2···Au3b and Au2b···Au3 of 3.313(1) Å, and an additional single, much shorter, Au1···Au3a contact of 3.160(1) Å. The pair of trimers linked by the first type of Au···Au contact are parallel to each other, with their six Au atoms defining a hexagon in chair conformation. In contrast, the trimer of the adjacent pair, across the shorter Au···Au contact, is nearly perpendicular with a dihedral angle of 83.4° (between the two Au_3 planes), as commonly observed between the coordination axes of mononuclear Au complexes exhibiting aurophilic attraction. It should be noted that the corresponding group-11 pyrazolates, $[M(\mu\text{-pz})]_n$, are known to be a one-dimensional polymeric chain in the case of M = Cu, and polymeric or trimeric complexes for M = Ag.[11]

For the preparation of $[Au(\mu\text{-4-Me-pz})]_3$, **2**, Au(tht)Cl (0.1 mmol, 32 mg) and 4-methylpyrazole (0.2 mmol, 16.4 mg) are dissolved in 3 mL of THF. To the resulting clear solution is added 0.1 mmol of Et_3N. After the mixture is stirred for 24 h, MeOH is added to dissolve the Et_3NHCl and tht reaction products, as well as to crash out the gold complex. The resulting white powder is slightly soluble in CH_2Cl_2 or benzene. X-ray quality crystals of **2**, in 78% overall yield, are obtained by slow evaporation of a CH_2Cl_2/hexane solution of this complex.[12]

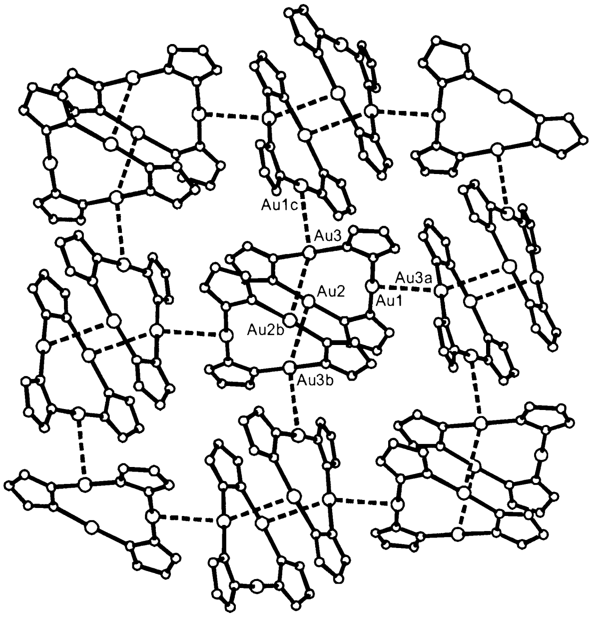


Figure 1. Two-dimensional structure of $[Au(\mu\text{-pz})]_3$. Only intermolecular Au···Au interactions of less than 3.6 Å are shown as broken lines. Symmetry codes: (a) $x, -y + {}^3/_2, z + {}^1/_2$; (b) $-x + 2, -y + 1, -z$; (c) $x, -y + {}^3/_2, z - {}^1/_2$.

X-ray analysis confirms the trimeric nature of **2**. Remarkably, 15 crystallographically independent $[Au(\mu\text{-4-Me-pz})]_3$ molecules exist in an asymmetric unit. All gold atoms adopt two-coordinate linear geometry with the Au−N bond lengths in the range 1.91(2)−2.08(2) Å and the N−Au−N angles 172.6(11)−179.7(10)°, while the intramolecular Au···Au distances range from 3.314(2) to 3.426(2) Å, all consistent with the corresponding parameters of **1**. With an intermolecular Au···Au distance of 3.6 Å considered as the upper threshold of aurophilic contact,[13] five gold trimers exist as independent units, and two more as a dimer of trimers, while the remaining eight trimers, along with their symmetry-related counterparts, constitute a 16-membered aggregate of trimers. In the dimer of trimers, the two, almost eclipsed, Au_3 units form a slightly twisted, trigonal prismatic, Au_6 array. The dihedral angle between the two Au_3 faces of the prism is 6.3°, and the intermolecular Au···Au distances—prism edges—are 3.318(2) Å (Au33−Au34), 3.600(2) Å (Au31−Au36) and 3.707(2) Å (Au32−Au35). The 16 trimer

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(8) (a) The powder diffractograms were recorded on a Siemens D 5000 X-ray diffractometer equipped with Cu Kα radiation. (b) Generating the XRPD pattern from single-crystal data: XPOW, SHELXTL 5.1, Bruke AXS, Madison, WI 1997. (c) An unidentified minor impurity is seen in the pattern of the bulk product.

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(12) Decomposition before melting, ca. 135 °C. Anal. Calcd for $C_{188}H_{250}Au_{45}Cl_2N_{90}O_3$, $\{[Au(\mu\text{-4-Me-pz})]_3\}_{15}\cdot CH_2Cl_2\cdot C_6H_{14}\cdot CH_3OH\cdot 2H_2O$ (**2**): C, 17.68; H, 1.96; N, 9.88. Found: C, 17.64; H, 2.02; N, 9.73. ^1H NMR (ppm, $C_6D_6 + CDCl_3$): 1.80 (s, 3H, Me), 7.01 (s, 2H, 3,5-pz). Crystal data: Siemens SMART CCD diffractometer, triclinic, space group $P\bar{1}$, $a = 14.913(2)$ Å, $b = 30.853(5)$ Å, $c = 31.336(5)$ Å, $\alpha = 115.722(3)°$, $\beta = 93.680(3)°$, $\gamma = 95.332(3)°$, $V = 12846(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.297$ g cm^{-3}, μ(Mo Kα) = 25.659 mm^{-1}. Least-squares refinement based on 21205 reflections with $I > 2\sigma(I)$ and 1996 parameters (only Au and N atoms refined anisotropically) led to convergence, with final R1 = 0.0545, wR2 = 0.1300, and GOF = 1.032.

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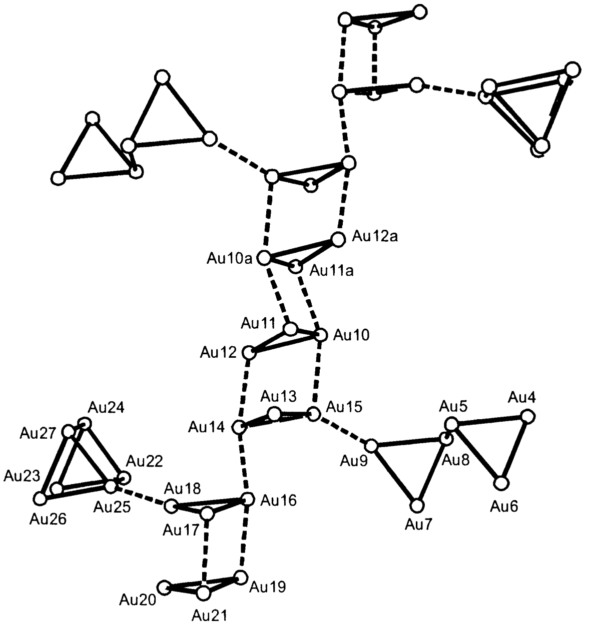

Figure 2. The aggregation of 16 trimers in [Au(μ-4-Me-pz)]$_3$. C and N atoms are omitted for clarity. Intramolecular Au···Au contacts are shown as solid lines. Only intermolecular Au···Au interaction of less than 3.6 Å are shown as broken lines. Intermolecular Au···Au distances (Å): Au5−Au8 3.176(2), Au9−Au15 3.293(2), Au10−Au15 3.569(2), Au11−Au13 3.736(2), Au12−Au14 3.357(2), Au10−Au11a 3.277(2), Au11−Au10a 3.277(2), Au14−Au16 3.204(2), Au16−Au19 3.466(2), Au17−Au21 3.380(2), Au18−Au20 3.638(2), Au18−Au25 3.316(1), Au22−Au25 3.468(2), Au23−Au26 3.623(2), Au24−Au27 3.315(2). Dihedral angles (deg): Δ-Au(10,11,12) and Δ-Au(13,14,15) 6.0, Δ-Au(16,17,18) and Δ-Au(19,20,21) 3.5, Δ-Au(22,23,24) and Δ-Au(25,26,27) 5.1, (Δ-Au(7,8,9) and Δ-Au(13,14,15) 89.4; Δ-Au(16,17,18) and Δ-Au(25,26,27) 110.7, (Δ-Au(4,5,6) and Δ-Au(7,8,9) 16.0, Δ-Au(13,14,15) and Δ-Au(16,17,18) 13.3. Symmetry code: (a) $-x + 1, -y + 2, -z + 1$.

aggregate is generated by an inversion center located at the center of the Au10−Au11−Au10a−Au11a parallelogram forming a chain of eight trimers with four side arms (Figure 2). Four types of relative orientation between pairs of neighboring Au$_3$ trimers (Δ-Au$_3$) are seen: trigonal prism (Δ-Au(10,11,12) and Δ-Au(13,14,15); Δ-Au(16,17,18) and Δ-Au(19,20,21); Δ-Au(22,23,24) and Δ-Au(25,26,27)), two-blade propeller (Δ-Au(7,8,9) and Δ-Au(13,14,15); Δ-Au(16,17,18) and Δ-Au(25,26,27)), chair (Δ-Au(10,11,12) and Δ-Au(10a,11a,12a)), and offset (Δ-Au(4,5,6) and Δ-Au(7,8,9); Δ-Au(13,14,15) and Δ-Au(16,17,18)). In the crystal of **2**, each trimer, whether independent or part of an aggregate, is placed in a nearly parallel orientation relative to one or more neighboring trimers by Au···Au attractions and/or $\pi-\pi$ interactions.

All four types of (Δ-Au$_3$)−(Δ-Au$_3$) orientations seen in **2** are expected to be inhibited by the presence of bulky substituents at the 3- and 5-positions of pyrazoles.[10] Consistent with this, no intermolecular Au···Au contact is present in the crystal structure of the 3-Me-5-Ph-substituted complex **3**,[14] which is otherwise analogous to those of **1** and **2**; C_{3h} symmetry, intramolecular Au···Au distances of 3.314(1)−3.338(1) Å, Au−N 2.00(1)−2.05(1) Å, N−Au−N 176.0(7)−178.6(6)°.

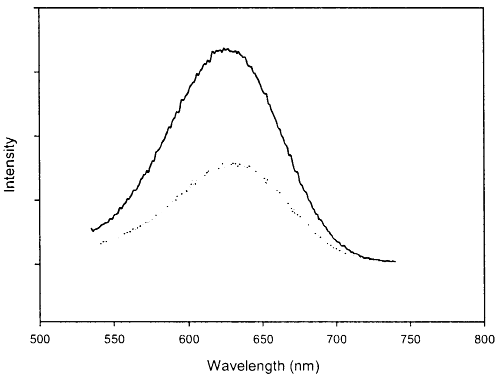

Figure 3. Luminescence spectra of solid samples of **1** (solid line) and **2** (broken line) at 25 °C, excitation at 230 nm.

Under 230 nm UV irradiation at ambient temperature, solid samples of **1** and **2** emit red luminescence with maxima at 626 and 631 nm, respectively (Figure 3). On the other hand, **3** does not luminesce under the same conditions. This implies that the luminescence of **1** and **2** arises from the intermolecular aurophilic interactions. In contrast, the luminescence of tetrameric [Au(μ-3,5-^{t}Bu$_2$-pz)]$_4$ with intramolecular Au···Au contacts of 3.118(1)−3.189(1) Å and no intermolecular interactions has been attributed to the former.[15] It appears that not only short Au−Au contacts but also a perpendicular orientation of the Au···Au relative to the N−Au−N axes is necessary for the observation of luminescence. While the 6s−6s component of the Au−Au interaction is only dependent on the Au−Au distance, the strongly directional 5d6p−5d6p component is affected by the relative orientation of the Au-coordination axes.

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Supporting Information Available: ORTEP drawings of **1**−**3** and an X-ray crystallographic file (CIF) for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) (a) Minghetti, G.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1979**, *18*, 658−663. (b) Only one of the two possible isomers of **3** is isolated as a CH$_2$Cl$_2$-soluble product of the reaction of Au(tht)Cl, 3-Me-5-Ph-pzH, and NEt$_3$ in THF; yield 35%, mp 201−203 °C (with decomposition). ^{1}H NMR (ppm, C$_6$D$_6$ + CDCl$_3$): 1.98 (s, 3H, Me), 6.33 (s, 1H, 4-pz), 7.20 (m, 3H, Ph), 8.04 (m, 2H, Ph). Crystal data for [Au(μ-3-Me-5-Ph-pz)]$_3$·THF (**3**): Siemens SMART CCD diffractometer, orthorhombic, space group $Pna2_1$, a = 7.415(1) Å, b = 15.985(3) Å, c = 26.476(4) Å, V = 3138.4(9) Å^3, Z = 4, ρ_{calcd} = 2.401 g cm^{-3}, μ(Mo Kα) = 14.028 mm^{-1}. Least-squares refinement based on 3421 reflections with $I > 2\sigma(I)$ and 376 parameters led to convergence, with a final R1 = 0.0384, wR2 = 0.0990, and GOF = 1.041.

(15) Yang, G.; Raptis, R. G. *Inorg. Chim. Acta*, in press.