

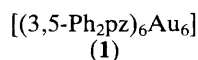
The Synthesis and Crystal Structure of a Novel Gold(I)–Pyrazolate Hexamer Containing an 18-Membered Inorganic Ring

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The reaction of ClAuPPh_3 with sodium 3,5-diphenylpyrazolate in tetrahydrofuran with added AgOCOPh yields hexakis(μ -3,5-diphenylpyrazolato- N,N')-hexagold(I) (**1**), a compound with a novel 18-membered twisted ring and a fused-edge bi-tetrahedral grouping of gold atoms, as determined crystallographically.

During exploratory studies of polynuclear complexes with the potential to yield heterovalent species¹ we have synthesized the unusual complex (**1**). Here we report the synthesis and the results of the *X*-ray structural analysis of (**1**). The chemistry of gold is receiving considerable attention, particularly as it finds applications in arthritis treatment,^{2a} electron microscopy,^{2b} and the electronics industry.³ Soluble oligomeric complexes of the type $[\text{AuL}]_n$ may prove to be valuable sources of organic-soluble gold, particularly as functionalization of the ligand *L* can direct deposition to specific sites.



The highly symmetric trinuclear complex $[\text{Au}(3,5\text{-Ph}_2\text{pz})]_3$ (pz = pyrazolate) (Figure 1), was prepared from the reaction

of ClAuPPh_3 with an equimolar amount of the sodium salt of the 3,5-disubstituted pyrazole in tetrahydrofuran (THF).⁴ When this reaction was performed using a Au:pyrazolate ratio of 0.66:1 in the presence of silver benzoate to precipitate the chloride ions, complex (**1**) was obtained, in good yield.[†]

[†] *Synthesis:* Complex (**1**): ClAuPPh_3 (40.4 mmol) was dissolved in THF (20 ml). To this solution AgOCOPh (26.2 mmol) and sodium 3,5-diphenylpyrazolate (60.7 mmol) were added. The turbid solution was stirred in ambient temperature for 18 h. The reaction was filtered and the solvent was removed *in vacuo*. The resulting white solid was readily dissolved in methylene chloride (~10 ml). Diethyl ether vapour was allowed to diffuse slowly into the methylene chloride solution. Colourless crystals, m.p. 310–314°C (decomp., colour change at ~280°C) were obtained by this procedure. Complex (**1**) is stable to air oxidation in solution as well as in the solid state.

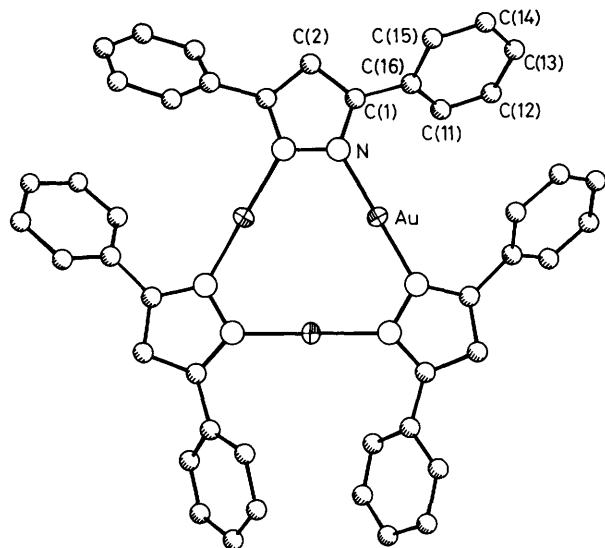


Figure 1. Drawing of $[\text{Au}(3,5\text{-Ph}_2\text{pz})]_3$ (see ref. 4). Au–N 1.978(9) Å, N–Au–N 179.6(3)°, N–N 1.377(2) Å, N–N–Au 120.2(7)°, Au ⋯ Au 3.368(1) Å. For clarity, only the Au centres are represented by their thermal ellipsoids at the 50% probability level; C and N atoms are spheres of arbitrary radii.

The crystal used for the crystallographic investigation† was grown by slow diffusion of diethyl ether into a methylene chloride solution of (1).

Complex (1) contains an 18-membered $[\text{Au-N-N}]_6$ ring, unprecedented in transition metal–pyrazole or gold chemistry. Typical metal–pyrazolate complexes are dimeric or trimeric.⁵ To the best of our knowledge only one other hexanuclear gold(I) complex has been reported,⁶ excluding cluster molecules. The largest Au^{I} oligomers of the form $[\text{AuL}]_n$ are the⁷ pentameric $[\text{Au}(\text{mesityl})]_5$ and the hexamer mentioned.

The Au–pz ring of (1) forms a two-blade propeller-like body (D_2 symmetry) about the Au(1)–Au(3) axis with a pitch defined by the 72.9° dihedral angle between§ the pz(5) and pz(14) pyrazolate rings (Figure 2). Some important angles and distances for (1) are listed in the caption to Figure 2. The pairs of pyrazolates linked by Au(1) [pz(8), pz(11)] and Au(3) [pz(2), pz(17)] are in a *trans*-arrangement to each other with respect to the N–Au–N axes. All other Au-linked pyrazolate pairs have a *cis*-relationship. The dihedral angles formed by any two Au-linked pyrazolates range between 34.4 and 44.2°. The pyrazolate rings pz(2) and pz(11) are parallel and ~3.50 Å apart. The same is true for the pyrazolate rings pz(7) and pz(8). The co-ordination around gold shows small deviations

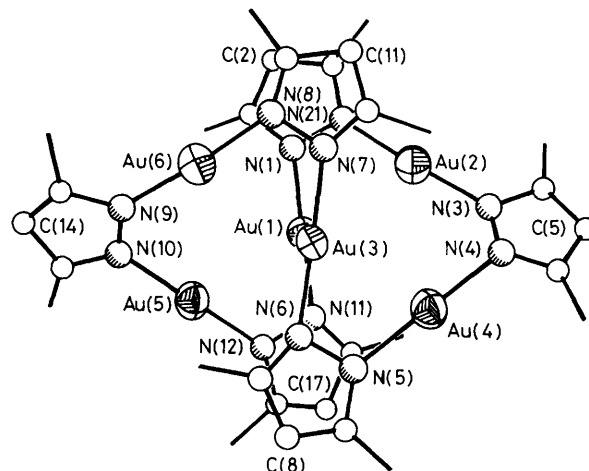


Figure 2. Drawing of (1); the twelve phenyl rings have been omitted and the C and N atoms are drawn as spheres of arbitrary size for clarity. The Au atoms are represented by their thermal ellipsoids at a 50% probability level. Selected angles (°): N–N–Au, range, 108.5(18)–129.8(20); N(1)–Au(1)–N(11) 174.7(11); N(2)–Au(2)–N(3) 175.6(11); N(6)–Au(3)–N(7) 176.7(10); N(4)–Au(4)–N(5) 178.9(11); N(10)–Au(5)–N(12) 179.3(09); N(8)–Au(6)–N(9) 176.0(09). Selected distances (Å): Au–N, range 2.00(3)–2.16(3); N–N, range 1.28–1.44(4); Au(1)–Au(2) 3.128(2); Au(1)–Au(3) 3.495(1); Au(1)–Au(4) 4.141(1); Au(1)–Au(5) 3.121(2); Au(1)–Au(6) 3.864(1); Au(2)–Au(3) 3.925(1); Au(2)–Au(4) 3.678(1); Au(2)–Au(5) 6.010(1); Au(2)–Au(6) 5.181(1); Au(3)–Au(4) 3.085(2); Au(3)–Au(5) 4.079(1); Au(3)–Au(6) 3.149(2); Au(4)–Au(5) 5.619(1); Au(4)–Au(6) 5.998(1); Au(5)–Au(6) 3.631(1).

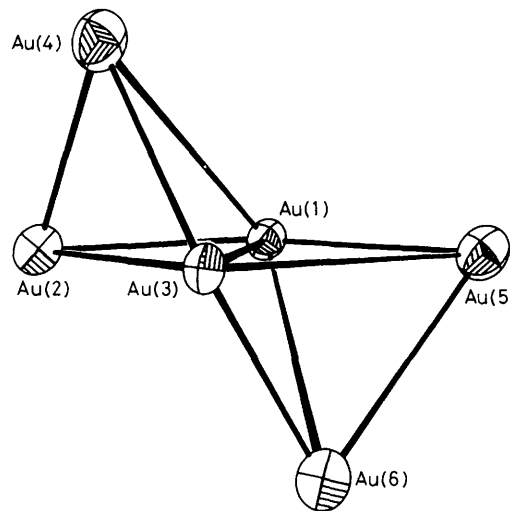


Figure 3. Drawing of the Au backbone of (1) showing the fused-edge bi-tetrahedral nature of the metal skeleton. All atoms are represented by their thermal ellipsoids at the 50% probability level.

† *Crystal data:* $\text{C}_{90}\text{H}_{66}\text{Au}_6\text{N}_{12}$, (1), monoclinic, space group $P2_1/n$, $a = 16.048(3)$, $b = 17.850(3)$, $c = 29.663(5)$ Å, $\beta = 92.47(1)^\circ$, $U = 8489(2)$ Å³, $Z = 4$, $D_c = 1.96$ g cm^{−3}, 12 385 reflexions measured, 11 885 unique reflexions, 6052 unique reflexions with $I > 3.0 \sigma(I)$; $R = 0.0776$, $R_w = 0.0834$. All gold, nitrogen, and carbon atoms except those of the phenyl groups were refined anisotropically. All calculations were performed using Nicolet SHELXTL crystallographic programs. Data for (1) were collected at ambient temperature with graphite-monochromated Mo- K_α radiation. All data were corrected for Lorentz, decay, polarization, and absorption effects. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ pz(5) identifies the (μ -3,5-diphenylpyrazolato) ring (metal coordinated) by using the crystallographic numbering scheme of the carbon in the 4 position of the ring (Figure 2).

from linearity; the largest distortion observed is on Au(1), 174.7(11)°. All gold–nitrogen bonds are considerably longer than the 1.978(9) Å bonds of $[\text{Au}(3,5\text{-Ph}_2\text{pz})]_3$. Deviations from the ideal geometry of $[\text{Au}(3,5\text{-Ph}_2\text{pz})]_3$ are also observed in all the pyrazolate ligands. The N–N bonds of the ‘blade-tip’ pyrazolates, pz(5) and pz(14), are greatly shortened, 1.30(4) and 1.28(4) Å respectively, while the N(1)–N(2) bond, 1.44(4) Å, is the longest one. The distances of Au(1) and Au(3) from their two closest neighbours, 3.085(2)–3.149(2) Å, are

shorter than the Au...Au distances measured in $[\text{Au}(3,5\text{-Ph}_2\text{pz})_3]$ and are within the range of a non-bonding metal-metal interaction for gold(I).⁸ It should be noted that a bonding interaction between two gold(I) centres separated by 3.176(1) Å has been reported for a Ru_3Au_2 -cluster molecule.⁹ The six gold atoms of (1) form a fused-edge bi-tetrahedron where the Au(1)–Au(3) edge is shared by the tetrahedra Au(1)–Au(2)–Au(3)–Au(4) and Au(1)–Au(3)–Au(5)–Au(6) (Figure 3). In this respect there is a striking resemblance in the topologies of (1) and $\text{Au}_6(\text{PPh}_3)_4[\text{Co}(\text{CO})_4]_2$ reported by Van der Velden *et al.*,¹⁰ even though the Au–Au interactions of the latter are clearly bonding. Furthermore, a double bond, Au=Au, along the common edge of this bitetrahedral $[\text{AuL}]_6^{2+}$ cluster, has been suggested¹¹ based on electronic considerations. In (1) the relative orientation of the d_z^2 orbitals of Au(1) and Au(3) are such that the potential for Au–Au bond formation exists *via* oxidative-addition. In view of the current interest in d^{10} metal centre interactions,¹² the investigation of the chemical behaviour of (1) promises to be rewarding.

The financial support of the Welch Foundation, The National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Texas A&M Center for Mineral Resources is gratefully acknowledged.

Received, 19th November 1986; Com. 1652

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