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 species[1] 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 $[AuL]_n$ may prove to be valuable sources of organic-soluble gold, particularly as functionalization of the ligand L can direct deposition to specific sites.

$[(3,5\text{-}Ph_2pz)_6Au_6]$
(**1**)

The highly symmetric trinuclear complex $[Au(3,5\text{-}Ph_2pz)]_3$ (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.

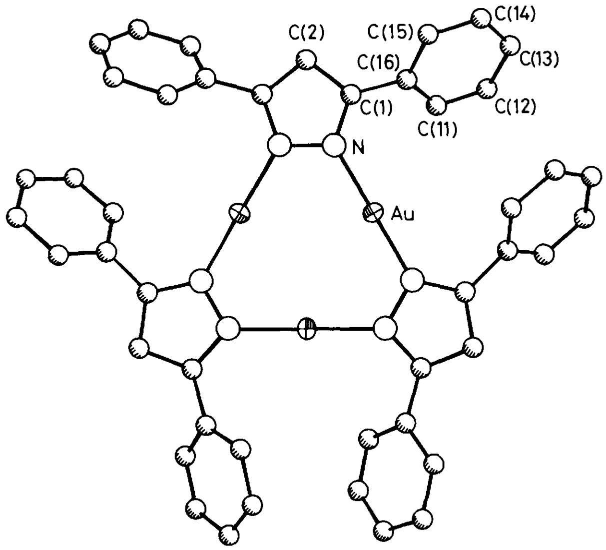

Figure 1. Drawing of [Au(3,5-Ph$_2$pz)]$_3$ (see ref. 4). Au–N 1.978(9) Å, N–Au–N 179.6(3)°, N–N 1.377(2) Å, N–N–Au 120.2(7)°, Au $\cdots$ Au 3.368(1) Å. For clarity, only the Au centres are represented by their thermal ellipsoids at the 50% probability level; C and N atoms are spheres of arbitrary radii.

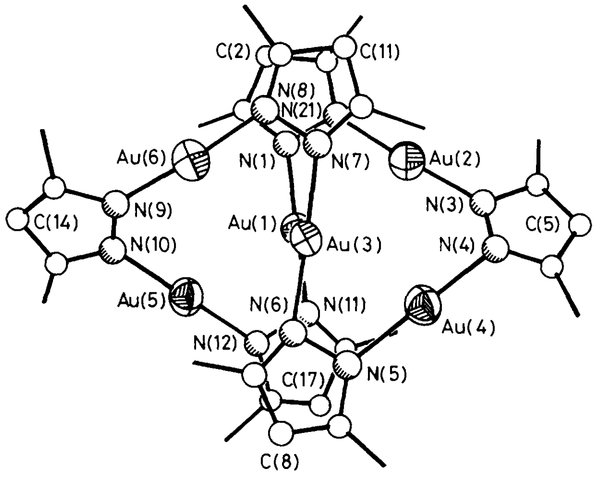

Figure 2. Drawing of (**1**); the twelve phenyl rings have been omitted and the C and N atoms are drawn as spheres of arbitrary size for clarity. The Au atoms are represented by their thermal ellipsoids at a 50% probability level. Selected angles (°): N–N–Au, range, 108.5(18)—129.8(20); N(1)–Au(1)–N(11) 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).

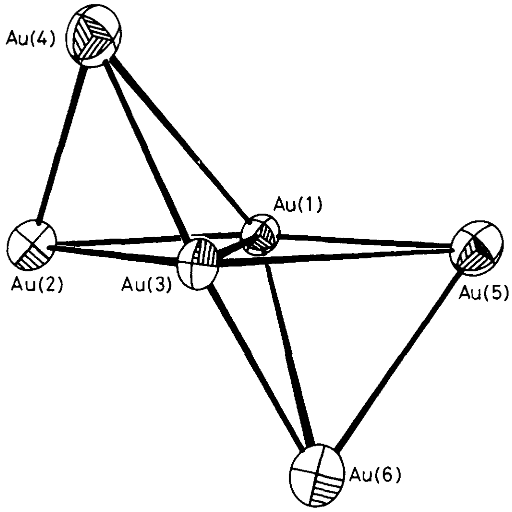

Figure 3. Drawing of the Au backbone of (**1**) showing the fused-edge bi-tetrahedral nature of the metal skeleton. All atoms are represented by their thermal ellipsoids at the 50% probability level.

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 [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 [AuL]$_n$ are the[7] pentameric [Au(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 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 [Au(3,5-Ph$_2$pz)]$_3$. Deviations from the ideal geometry of [Au(3,5-Ph$_2$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

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[‡] *Crystal data:* $C_{90}H_{66}Au_6N_{12}$, (**1**), monoclinic, space group $P2_1/n$, a = 16.048(3), b = 17.850(3), c = 29.663(5) Å, β = 92.47(1)°, U = 8489(2) Å^3, 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).

shorter than the Au · · · Au distances measured in $[Au(3,5\text{-}Ph_2pz)]_3$ 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 $Au_6(PPh_3)_4[Co(CO)_4]_2$ 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 $[AuL]_6{}^{2+}$ cluster, has been suggested[11] 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.

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