

Gold(I) Complexes with Amino-acid Derivatives: The Crystal Structure of Triphenylphosphine(hippurato)gold(I)

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The reaction between Ph_3PAuCl and silver salts of *N*-substituted glycines leads to complexes Ph_3PAuX , where X is the substituted glycinate; the X-ray structure determination of the hippurato-complex confirms the presence of an Au–O bond.

Gold complexes are used in the treatment of rheumatoid arthritis¹ and also exhibit some anti-tumour activity.² However, the mechanisms of action of gold drugs are not well understood. There is evidence that gold species bind to sulphur and, to a lesser extent, nitrogen donor functions of biological molecules such as sulphur-containing proteins;³ it would therefore be expected that simple amino-acid complexes of gold could act as models for such systems. To the best of our knowledge, no such complex has been subjected to X-ray structure analysis and few have been reported.⁴ This may be attributed to several factors: (i), gold(III) species are redox active towards some amino-acids;⁵ (ii), it is difficult to find suitable solvent systems for amino-acids and gold-containing starting materials (the commonly used SOCl_2 reacts with many amino-acids⁵); (iii), even when reactions take place, *e.g.* between $(\text{OC})\text{AuCl}$ and lysine, the products are generally insoluble in all common solvents, difficult to obtain pure, and subject to decomposition within a few hours.⁶

We have shown that complexes $\text{Ph}_3\text{PAu}(\text{O}_2\text{CR})$ ($\text{R} = \text{Me}$, Ph) are stable crystalline solids.^{7,8} We therefore decided to

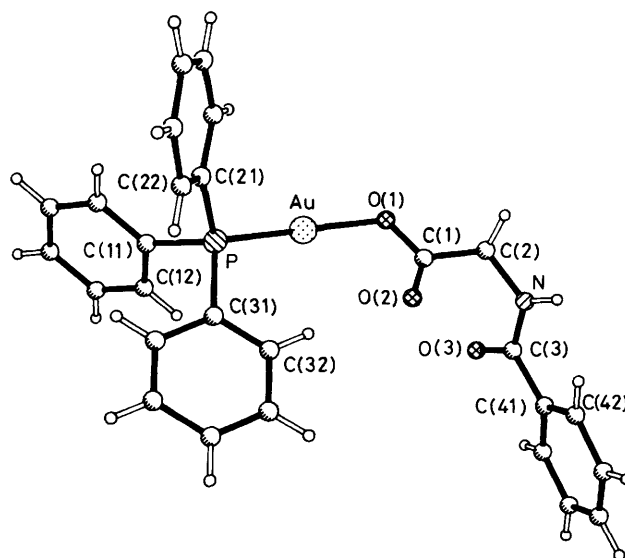


Figure 1. The molecule of the title compound in the crystal (radii arbitrary; one H atom on C(2) is eclipsed).

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depart from the received wisdom that amino-acid complexes of gold(I) must involve S or N donors, and to attempt the preparation of O-bonded complexes. We chose *N*-substituted glycines in order to increase the solubility in organic solvents and to reduce the donor properties and redox activity of the NH₂ group.

The reaction between silver salts Ag(O₂CCH₂NHC(O)R) (R = Me, Ph) and Ph₃PAuCl led to the required products Ph₃PAu(O₂CCH₂NHC(O)R). The silver salts were obtained from the sodium salts and AgNO₃ and then stirred with Ph₃PAuCl in benzene for 15 h. AgCl was filtered off and the solution evaporated to dryness under reduced pressure. The

resulting gum was recrystallized from CH₂Cl₂/petrol (R = Me) or CH₂Cl₂ alone (R = Ph). Satisfactory ¹H and ¹³C n.m.r. spectra and elemental analyses were obtained.

An X-ray structure determination of the benzoylglycinato ('hippurato') derivative confirmed the expected nature of the product (Figure 1).[‡] The co-ordination at gold is linear, with Au–P 2.212(2), Au–O 2.077(5) Å, P–Au–O 174.6(1)°. The molecules are linked by H bonding between N and the benzoyl O (N···O 3.00 Å).

Our results indicate that the possibility of gold–carboxylate interactions in biological systems should not be ignored, at least as a minor effect. We are currently attempting to extend our studies to derivatives of other amino-acids and simple peptides.

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[‡] *Crystal structure determination: Crystal data:* C₂₇H₂₃AuNO₃P, *M*_r = 637.4, orthorhombic, *Pbca*, *a* = 8.990(1), *b* = 27.050(3), *c* = 19.307(2) Å, *U* = 4695 Å³ (by refinement of 2θ values of 50 reflections in the range 20–23°), *Z* = 8, *D*_c = 1.80 Mg m^{−3}, *F*(000) = 2480, crystal size 0.35 × 0.15 × 0.1 mm (colourless prism), μ(Mo-Kα) = 6.4 mm^{−1}. *Data collection and processing:* Stoe-Siemens four-circle diffractometer, monochromated Mo-Kα radiation, 7650 profile-fitted intensities (2θ_{max} 50°), 4112 unique (*R*_{int} 0.023), 3032 with *F* > 4σ(*F*) used for all calculations (program system SHELX-76, locally modified by its author Prof. G. M. Sheldrick). Absorption correction based on ψ-scans; transmissions 0.63–0.80. *Structure analysis and refinement:* heavy-atom method, full-matrix anisotropic refinement on *F*, H atoms included using riding model. *R* 0.041, *R*_w 0.033, 298 parameters, weighting scheme *w*^{−1} = σ²(*F*) + 0.0002 *F*², *S* 1.3, max. Δ/σ 0.001, max. Δρ 0.8 e Å^{−3}. *Deposition:* Full details of the structure determination (atomic co-ordinates, temperature factors, structure factors, complete bond lengths and angles) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, FRG; any request for this material should quote a full literature citation and the deposition number CSD 53232. Atomic co-ordinates, bond lengths and angles, and thermal parameters have also been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.