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Gold(I) complexes with amino acid derivatives: preparation and crystal structure of triphenylphosphine-(*N*-benzoyl-L-alaninato)gold(I)

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Abstract

The title compound was synthesized from Ph_3PAuCl and the silver salt of the amino acid derivative. Its X-ray structure reveals the presence of two independent molecules, each with approximately linear coordination at gold. The amino acid backbones display different conformations, one being extended and the other similar to that of the hippurato derivative.

Introduction

Despite the importance of gold in bioinorganic chemistry [1], little is known about gold complexes with amino acids or their derivatives. We have published a short series of papers on the preparation and structure of gold(I) complexes with various non-biological oxoanions [2] and have successfully extended these studies to *N*-acetylglycinato and *N*-benzoylglycinato (hippurato) complexes [3]. Here we report the preparation and crystal structure of triphenylphosphine-(*N*-benzoyl-L-alaninato)gold(I).

Experimental

Preparation of $[Ph_3PAu\{OC(O)CH(CH_3)NHC(O)Ph\}]$

To a solution of 148 mg (0.3 mmol) Ph_3PAuCl in 40 ml dichloromethane/benzene (1:1) was added 100 mg (0.33 mmol) silver *N*-benzoyl-L-alaninate. After stirring overnight, silver chloride was filtered off and the solvent removed *in vacuo*. The residue was crystallized from dichloromethane/light petroleum/di-isopropylether (*c*. 1:2:1) in the form of colourless plates. The product is air-stable but darkens slowly on exposure to light. Yield 120 mg (61.5%), m.p. 162–166 °C(d). *Anal.* Found: C, 51.1; H, 4.0; N, 2.1; Au, 30.0. Calc. for $C_{28}H_{25}AuNO_3P$ (651.44): C, 51.6; H, 3.9; N, 2.1; Au, 30.2%. ^1H NMR: δ 1.61 (d, 3H, CH_3, $J=6.0$ Hz), 4.70 (apparent quintet, 1H, CH, line separation 6.7 Hz), 7.4–7.6 (m, 20H, Ph), 7.85 (poorly resolved, NH).

X-ray structure determination

Most of the crystals proved to be twinned, but eventually a single crystal fragment was cut from a larger plate.

Crystal data

Tetragonal, space group $P4_32_12$, $a=14.3431(16)$, $c=49.909(10)$ Å, $U=10268$ Å^3, $Z=16$, $D_X=1.686$ Mg m^{-3}, λ(Mo Kα)$=0.71069$ Å, $\mu=5.8$ mm^{-1}, $F(000)=5088$, $T=18$ °C.

Data collection and reduction

A plate fragment *c*. 0.4×0.3×0.02 mm was mounted in a glass capillary. Measurements were made on a Stoe-Siemens four-circle diffractometer using monochromated Mo Kα radiation. Despite the long *c* axis, the reflections were narrow and could be resolved using ω-scans. A total of 13 528 intensities, including a full set of Friedel opposites, was registered in profile-fitting mode [4] in the 2θ range 7–50°. Absorption corrections, based on ψ-scans and a crystal lamina with faces ±001, gave transmission factors

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0.37–0.87. Cell constants were refined from ± ω values of 66 reflections in the 2θ range 20–23°. Averaging equivalents gave 8736 unique reflections (R_{int} 0.038), of which 5564 with $F > 4\sigma(F)$ were used for all calculations (program system SHELXS/XLS, modified by its author G. M. Sheldrick).

Structure solution and refinement

The structure was solved by hand interpretation of the Patterson function to locate the two independent Au atoms, followed by appropriate refinement and difference syntheses. The weak data precluded a full anisotropic refinement; only Au and P atoms were refined anisotropically, phenyl groups with idealized geometry and other H atoms using a riding model. The absolute configuration (and thus the space group) were determined by an η refinement; η was negative in the space group first assumed ($P4_12_12$), then +0.98(3) for the correct configuration. The final R value was 0.087, with R_w 0.062, for 197 parameters; S 1.63, weighting scheme $w^{-1} =$

TABLE 1. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³)

	x	y	z	U_{eq}[a]
Au(1)	4334.5(5)	4066.9(6)	8868.4(1)	58(1)
P(1)	4953(3)	4184(3)	9275(1)	48(2)
O(11)	3734(9)	4002(8)	8492(2)	68(4)
O(12)	2322(8)	3818(7)	8662(2)	56(3)
O(13)	1537(9)	3929(8)	7720(3)	73(4)
N(1)	1530(9)	3963(8)	8168(3)	51(4)
C(1A)	2839(13)	3951(12)	8469(4)	50(5)
C(1B)	2552(12)	4096(13)	8193(3)	54(5)
C(1C)	2831(13)	5027(13)	8085(4)	77(7)
C(1D)	1119(13)	3844(12)	7924(4)	52(5)
C(12)	−328(10)	3613(9)	7682(3)	87(7)
C(13)	−1240	3285	7656	124(10)
C(14)	−1708	2933	7879	99(8)
C(15)	−1266	2909	8128	100(8)
C(16)	−354	3237	8153	92(8)
C(11)	114	3589	7930	57(5)
C(22)	6773(10)	3872(7)	9441(2)	74(7)
C(23)	7713	4109	9466	96(7)
C(24)	8060	4893	9334	81(7)
C(25)	7468	5441	9178	74(7)
C(26)	6529	5205	9154	65(6)
C(21)	6181	4420	9285	54(5)
C(32)	4921(7)	5598(9)	9662(2)	69(6)
C(33)	4476	6298	9807	75(7)
C(34)	3551	6526	9751	77(6)
C(35)	3071	6055	9549	99(8)
C(36)	3517	5355	9404	76(7)
C(31)	4442	5126	9460	44(5)
C(42)	4802(7)	2286(9)	9328(2)	52(5)
C(43)	4651	1452	9464	66(6)
C(44)	4445	1464	9738	70(6)
C(45)	4389	2311	9874	79(7)
C(46)	4540	3146	9737	63(6)
C(41)	4746	3133	9464	45(5)
Au(2)	6603.5(5)	772.0(6)	8987.2(2)	57(1)
P(2)	7914(3)	602(4)	9215(1)	53(2)
O(21)	5444(9)	1115(9)	8761(3)	71(4)
O(22)	4752(10)	−142(11)	8884(3)	101(5)
O(23)	4575(9)	413(9)	8072(3)	80(4)
N(2)	3659(9)	54(10)	8431(3)	51(4)
C(2A)	4785(14)	573(16)	8759(4)	71(6)
C(2B)	3965(11)	884(12)	8574(3)	51(5)
C(2C)	3174(14)	1282(13)	8738(4)	82(7)
C(2D)	4053(13)	−168(13)	8187(4)	58(5)
C(52)	8845(9)	−904(9)	9434(2)	79(7)
C(53)	9220	−1802	9433	93(7)
C(54)	9130	−2362	9206	78(6)
C(55)	8664	−2025	8980	70(6)
C(56)	8288	−1128	8982	71(6)
C(51)	8379	−568	9209	50(5)
C(62)	6937(8)	601(8)	9687(2)	68(6)
C(63)	6813	757	9961	80(6)
C(64)	7500	1218	10108	72(7)
C(65)	8311	1523	9981	89(7)
C(66)	8436	1367	9707	78(7)
C(61)	7749	906	9560	47(5)
C(72)	8603(7)	2257(9)	9014(3)	80(7)
C(73)	9288	2841	8908	79(6)
C(74)	10195	2510	8873	82(7)
C(75)	10416	1596	8945	84(7)
C(76)	9731	1013	9051	64(6)
C(71)	8824	1344	9086	49(5)
C(82)	4457(7)	−1406(8)	7878(2)	67(6)
C(83)	4278	−2261	7755	71(6)
C(84)	3500	−2783	7831	82(7)
C(85)	2902	−2450	8029	63(6)
C(86)	3081	−1595	8152	50(5)
C(81)	3859	−1073	8077	58(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 2. Bond lengths (Å)

Au(1)–P(1)	2.223(5)	Au(1)–O(11)	2.070(12)
P(1)–C(21)	1.794(14)	P(1)–C(31)	1.792(13)
P(1)–C(41)	1.802(12)	O(11)–C(1A)	1.292(22)
O(12)–C(1A)	1.233(22)	O(13)–C(1D)	1.186(23)
N(1)–C(1B)	1.483(22)	N(1)–C(1D)	1.366(24)
C(1A)–C(1B)	1.452(25)	C(1B)–C(1C)	1.495(26)
C(1D)–C(11)	1.487(23)	Au(2)–P(2)	2.210(5)
Au(2)–O(21)	2.069(13)	P(2)–C(51)	1.805(13)
P(2)–C(61)	1.793(13)	P(2)–C(71)	1.804(12)
O(21)–C(2A)	1.224(25)	O(22)–C(2A)	1.203(27)
O(23)–C(2D)	1.260(23)	N(2)–C(2B)	1.455(22)
N(2)–C(2D)	1.380(23)	C(2A)–C(2B)	1.560(27)
C(2B)–C(2C)	1.511(26)	C(2D)–C(81)	1.437(22)

TABLE 3. Bond angles (°C)

P(1)–Au(1)–O(11)	177.9(4)	Au(1)–P(1)–C(21)	115.5(4)
Au(1)–P(1)–C(31)	111.3(4)	C(21)–P(1)–C(31)	104.2(5)
Au(1)–P(1)–C(41)	110.4(4)	C(21)–P(1)–C(41)	107.8(5)
C(31)–P(1)–C(41)	107.2(6)	Au(1)–O(11)–C(1A)	119.8(11)
C(1B)–N(1)–C(1D)	121.2(14)	O(11)–C(1A)–O(12)	122.5(16)
O(11)–C(1A)–C(1B)	111.0(15)	O(12)–C(1A)–C(1B)	126.5(17)
N(1)–C(1B)–C(1A)	109.9(14)	N(1)–C(1B)–C(1C)	110.5(14)
C(1A)–C(1B)–C(1C)	113.1(15)	O(13)–C(1D)–N(1)	122.3(17)
O(13)–C(1D)–C(11)	122.3(17)	N(1)–C(1D)–C(11)	115.4(15)
C(1D)–C(11)–C(12)	114.5(9)	C(1D)–C(11)–C(16)	125.1(9)
P(1)–C(21)–C(22)	120.4(4)	P(1)–C(21)–C(26)	119.3(4)
P(1)–C(31)–C(32)	122.3(4)	P(1)–C(31)–C(36)	117.6(4)
P(1)–C(41)–C(42)	117.7(4)	P(1)–C(41)–C(46)	122.3(4)
P(2)–Au(2)–O(21)	172.0(4)	Au(2)–P(2)–C(51)	114.0(4)
Au(2)–P(2)–C(61)	110.8(4)	C(51)–P(2)–C(61)	107.0(6)
Au(2)–P(2)–C(71)	111.4(4)	C(51)–P(2)–C(71)	105.9(6)
C(61)–P(2)–C(71)	107.3(6)	Au(2)–O(21)–C(2A)	118.4(13)
C(2B)–N(2)–C(2D)	119.8(14)	O(21)–C(2A)–O(22)	124.6(20)
O(21)–C(2A)–C(2B)	114.0(18)	O(22)–C(2A)–C(2B)	121.5(18)
N(2)–C(2B)–C(2A)	106.4(14)	N(2)–C(2B)–C(2C)	110.3(14)
C(2A)–C(2B)–C(2C)	110.8(15)	O(23)–C(2D)–N(2)	119.5(16)
O(23)–C(2D)–C(81)	122.6(16)	N(2)–C(2D)–C(81)	117.9(15)
P(2)–C(51)–C(52)	118.9(4)	P(2)–C(51)–C(56)	121.1(4)
P(2)–C(61)–C(62)	118.0(4)	P(2)–C(61)–C(66)	121.8(4)
P(2)–C(71)–C(72)	118.7(4)	P(2)–C(71)–C(76)	121.2(4)
C(2D)–C(81)–C(82)	117.5(9)	C(2D)–C(81)–C(86)	122.4(9)

$\sigma^2(F)+0.00025F^2$; max. Δ/σ 0.001, max. $\Delta\rho$ 2 e Å^{-3}. Final atomic coordinates are given in Table 1, with derived bond lengths and angles in Tables 2 and 3.

Discussion

There are two independent molecules of the title compound in the asymmetric unit (Fig. 1). The coordination geometry at gold is, as expected, linear (177.9(4), 172.0(4)°). The Au–O bond lengths of 2.070(12) and 2.069(13) Å are in good agreement with values of 2.063–2.077(5–6) Å for the hippurate, acetate and sulfate complexes of Ph$_3$PAu; in the benzoate complex the bond is shorter (2.033 Å). The Au–P bond in molecule 2 is short (2.210(5) Å), as expected *trans* to a weak oxygen ligand, but somewhat longer in molecule 1 (2.223(5) Å), although the difference is barely significant; for the other carboxylate complexes the Au–P bond lengths lie in the narrow range 2.207–2.216 Å [2, 3].

The amino acid backbone of molecule 1 is in an extended conformation, with torsion angles about C1a–C1b 176, C1b–N1 −165, N1–C1d 172, C1d–C11 171°; the corresponding values in molecule 2 are 137, −90, 169, −161°, and molecule 2 thus shows a conformation similar to that of the hippurato derivative (166, −70, 167, 167° [3]).

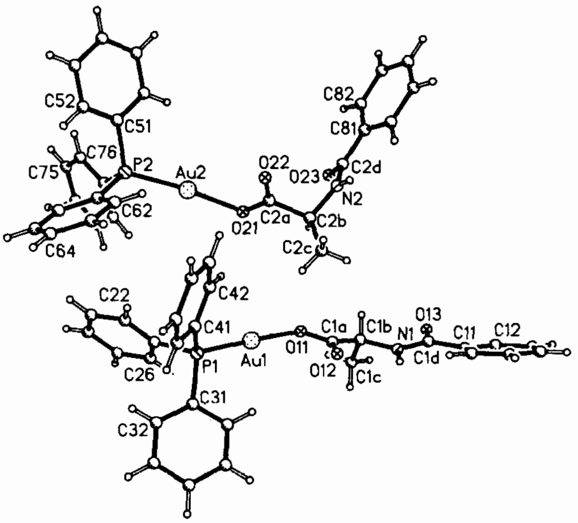

Fig. 1. The two independent molecules of the title compound in the crystal, showing the atom numbering scheme. Radii are arbitrary.

The molecules are linked by hydrogen bonds between the N–H and carboxylate C=O groups (Fig. 2; N2· · ·O12 3.04, O22· · ·N1 3.17 Å, second atoms at $0.5-x$, $-0.5+y$, $1.75-z$) into layers perpendicular to the long *c* axis. This contrasts with the hippurato complex, in which the molecules are linked into

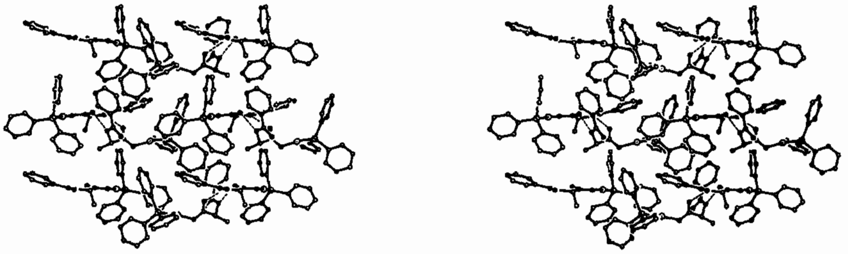

Fig. 2. Stereographic packing diagram of part of the layer structure of the title compound, viewed perpendicular to the long *c* axis. Hydrogen bonds are indicated by dashed lines. H atoms omitted for clarity.

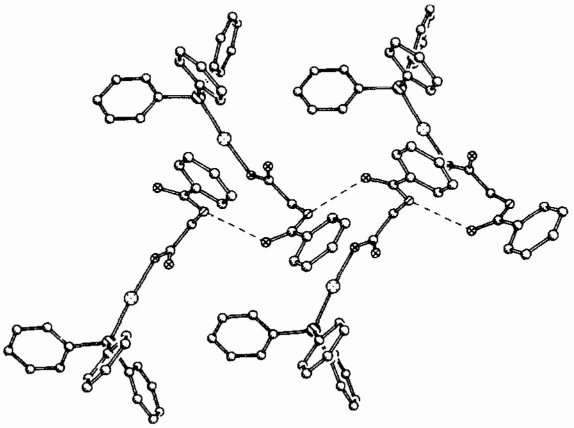

Fig. 3. The extended structure of the hippurato derivative [3], showing the hydrogen bonds that link the molecules into chains.

chains by H bonds between the N–H and benzoyl C–O groups [3] (N· · ·O 3.00 Å; Fig. 3).

Supplementary material

Further details of the crystal structure determination (H atom coordinates, temperature factors, structure factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, F.R.G. Any request for this material should quote a full literature citation and the reference number CSD 54978.

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