Some Piperidine Derivatives of Gold(I): Crystal and Molecular Structure of Chloro(piperidine)gold(I)

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The preparation and isolation of (I) [Au(pip)Cl], (II) $[AuCl(pip)_2]$, and (III) $[Au(pip)_2][PF_6]$ (where pip = piperidine) are described. The *X*-ray structure of (I) is reported; it consists of linear [(pip)AuCl] molecules arranged in tetramers, the gold atoms forming a loose square cluster. The structure was determined by the heavy-atom method from 1089 unique reflections measured by diffractomer and refined by least-squares techniques to *R* 0.064. Crystals are tetragonal, $a = 12.474(20)$, $c = 9.694(10)$ Å, $Z = 8$.

GOLD(I) forms many complexes of the form [LAuCl] (*e.g.* L = phosphines,[1] isocyanides,[2,3] carbenes,[3] olefins,[4] CO,[5] pyridine [6]) and many of these may be made by the action of L on $[AuCl(Me_2S)]$.[3,6] However, no such compounds where L is an aliphatic amine have been reported, gold(I) being a typical class B metal. Here we report the first such compound, [AuCl(pip)] (pip = piperidine), and its crystal structure.

Gold(I) also forms complexes $[AuClL_2]$ [*e.g.* L = etu (ethylenethiourea),[7] PPh_3, or PEt_3 [8]] about which there has been much discussion regarding the co-ordination number. $[AuCl(PPh_3)_2]$ has been shown [9] to be three-co-ordinate, but this is the only such compound to have been investigated by *X*-ray techniques. We have prepared $[AuCl(pip)_2]$ (again the first such compound with L = amine), but it has so far proved impossible to obtain crystals of the compound.

We also report the first bis(amine)gold(I) cation, in the compound $[Au(pip)_2][PF_6]$.

EXPERIMENTAL

*Preparation of Complexes.—Chlorobis(piperidine)*gold(I), (II). Chloro(dimethyl sulphide)gold(I) (0.55 g, 1.87 mmol) was dissolved in an excess of piperidine (2.5 ml), and almost immediately gave a white precipitate. After cooling (refrigerator), the filtered product was washed with diethyl ether and dried *in vacuo* (0.65 g, 1.61 mmol, 86%) (Found: C, 29.4; H, 5.45; N, 7.00. $C_{10}H_{22}AuClN_2$ requires C, 29.82; H, 5.51; N, 6.96%). The compound gradually darkens on exposure to air but can be stored at −20 °C in a desiccator. It is soluble in dichloromethane and chloroform, but solutions decompose rapidly, metallic gold being precipitated. This instability makes structural investigation difficult, but the ^{197}Au Mössbauer spectrum [10] indicates linear two-co-ordination of gold.

Chloro(piperidine)gold(I), (I). In an attempt to obtain crystals of (II), a layer of light petroleum (b.p. 40—60 °C) was carefully run onto a solution of the compound in dichloromethane. Despite the precipitation of metallic gold, a few small colourless crystals were obtained after 12 h. These darkened rapidly in air, and slowly in sealed tubes. The yield was too small to permit analysis, but crystallographic investigation revealed the nature of the compound (see later).

Bis(piperidine)gold(I) *hexafluorophosphate*, (III). Chlorobis(piperidine)gold(I) (0.25 g, 0.62 mmol) was dissolved in dry chloroform (20 ml) and a solution of $Ag[PF_6]$ (0.187 g, 0.71 mmol) in dichloromethane was added. After filtration, diethyl ether (15 ml) was added, and the solution placed in a refrigerator for 7 h. The product formed as very pale brown crystals, which were washed with diethyl ether and dried *in vacuo* (0.27 g, 0.53 mmol, 85%) (Found: C, 23.60; H, 4.25; N, 5.05. $C_{10}H_{22}AuF_6N_2P$ requires C, 23.45; H, 4.33; N, 5.47%). (III) darkens rapidly in air, but can be stored in a desiccator at −20 °C.

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[1] F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1937, 1828.

[2] A. Sacco and M. Frenzi, *Gazzetta*, 1956, **86**, 195.

[3] F. Bonati and G. Minghetti, *Gazzetta*, 1973, **103**, 373.

[4] R. Hüttel and H. Reinheimer, *Chem. Ber.*, 1966, **99**, 2778.

[5] D. B. Dell'Amico and F. Calderazzo, *Gazzetta*, 1973, **103**, 1099.

[6] P. C. Ray and D. S. Sen, *J. Indian Chem. Soc.*, 1930, **7**, 67.

[7] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1928, 143.

[8] C. Kowala and J. M. Swan, *Austral. J. Chem.*, 1966, **19**, 547.

[9] N. C. Baenziger, K. M. Dittemore, and J. R. Doyle, *Inorg. Chem.*, 1974, **13**, 803.

[10] G. C. H. Jones, P. G. Jones, A. G. Maddock, M. J. Mays, P. A. Vergnano, and A. F. Williams, *J.C.S. Dalton*, submitted for publication.

Crystal and Molecular Structure of [AuCl(pip)], (I)

Crystal Data.—$C_5H_{11}AuClN$, Tetragonal, $a = 12.474(20)$, $c = 9.694(10)$ Å, $U = 1\,508.4$ Å^3, $D_m = 2.75$ g cm^{-3}, $Z = 8$, $D_c = 2.796$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 190.3 cm^{-1}. Space group $P\bar{4}2_1c$ from systematic absences: $h00$ (h odd) and hhl (l odd).

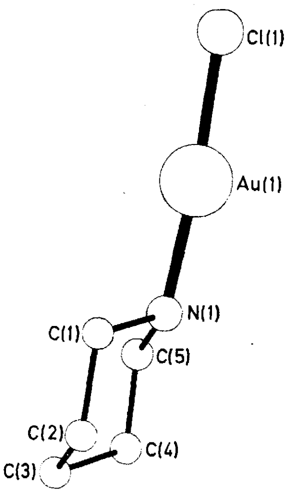

FIGURE 1 The molecule of [AuCl(pip)] (H atoms omitted for clarity)

Colourless crystals were obtained as already described.

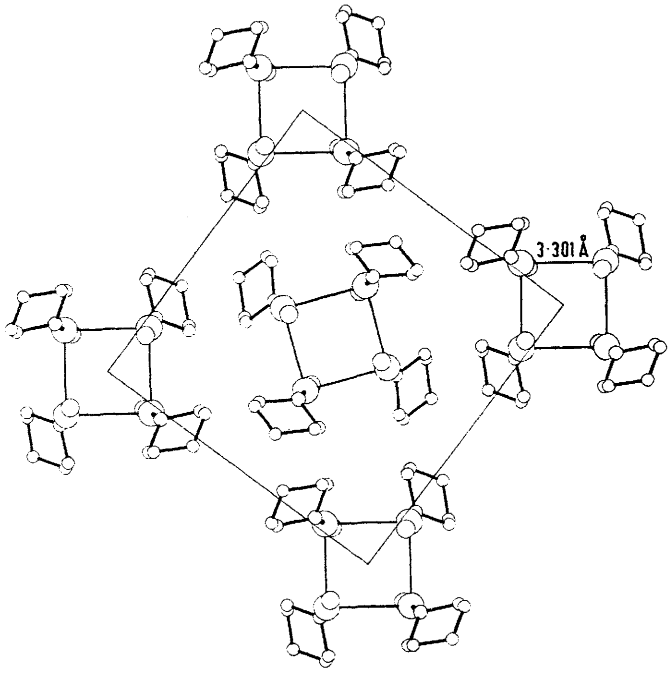

FIGURE 2 The structure in projection down z (H atoms omitted for clarity)

Intensities were determined by use of a Syntex $P2_1$ four-circle diffractometer with Mo-K_α radiation, and a crystal (in a sealed tube) of dimensions *ca.* 0.1 × 0.12 × 0.15 mm. Cell dimensions were obtained from a least-squares fit of 15 strong reflexions. Lorentz polararization and numerical absorption corrections were made. 1967 Reflexions were measured; averaging equivalent reflexions gave 1 089 unique reflexions with $F > 4\sigma(F)$.

The Au atom was located from a Patterson synthesis, and the light atoms (excluding hydrogen) were located by electron-density difference syntheses. C–H distances were fixed at 1.08, N–H at 0.98 Å, and H–C–H angles at 109.5°. The hydrogen-atom temperature factors were constrained equal.

TABLE 1

Atom co-ordinates (× 10^4) and temperature factors (Å^2 × 10^3)

	x/a	y/b	z/c	U
Au(1)	9 773(1)	8 171(1)	5 295(1)	*
Cl(1)	9 737(6)	8 428(6)	7 598(6)	*
N(1)	9 801(16)	7 822(15)	3 209(16)	30(5)
H(6)	9 941	8 511	2 757	36(19)
C(1)	10 694(20)	6 996(21)	2 897(26)	43(7)
H(11)	11 455	7 291	3 271	36(19)
H(12)	10 509	6 244	3 395	36(19)
C(2)	10 747(21)	6 831(25)	1 311(28)	53(8)
H(21)	11 318	6 203	1 090	36(19)
H(22)	11 011	7 570	840	36(19)
C(3)	9 709(19)	6 533(18)	717(23)	41(7)
H(31)	9 779	6 494	−393	36(19)
H(32)	9 471	5 758	1 109	36(19)
C(4)	8 856(19)	7 374(19)	1 112(23)	31(6)
H(41)	8 092	7 127	697	36(19)
H(42)	9 081	8 136	671	36(19)
C(5)	8 754(18)	7 498(21)	2 586(25)	35(6)
H(51)	8 161	8 105	2 805	36(19)
H(52)	8 503	6 744	3 031	36(19)

* Anisotropic temperature factors (Å^2 × 10^3). The temperature exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	35(1)	39(1)	32(1)	−1(1)	−1(1)	−1(1)
Cl(1)	51(4)	60(5)	36(3)	−5(3)	2(3)	−1(4)

TABLE 2

Bond lengths (Å)

Au(1)–Cl(1)	2.256(8)	Au(1)–N(1)	2.068(18)
Au(1)–Au(1^{II})	3.301(5)	N(1)–C(1)	1.548(34)
N(1)–C(5)	1.495(31)	C(1)–C(2)	1.552(39)
C(2)–C(3)	1.465(36)	C(3)–C(4)	1.543(35)
C(4)–C(5)	1.443(34)		

For symmetry transformation, see text.

TABLE 3

Bond angles (°)

Cl(1)–Au(1)–N(1)	176.0(5)
N(1)–Au(1) · · · Au(1^{II})	86.9(6)
N(1)–Au(1) · · · Au(1^{IV})	90.2(6)
N(1)–C(1)–C(2)	108.2(21)
C(2)–C(3)–C(4)	109.8(21)
N(1)–C(5)–C(4)	110.6(20)
Cl(1)–Au(1) · · · Au(1^{II})	95.8(3)
Cl(1)–Au(1) · · · Au(1^{IV})	92.8(3)
Au(1^{II}) · · · Au(1) · · · Au(1^{IV})	88.3(1)
Au(1)–N(1)–C(1)	110.1(14)
Au(1)–N(1)–C(5)	115.9(15)
C(1)–N(1)–C(5)	111.7(19)
C(1)–C(2)–C(3)	112.7(22)
C(3)–C(4)–C(5)	112.3(20)

For symmetry transformations, see text.

The final R' [$= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|$] was 0.051, with a corresponding R of 0.064; the weighting scheme was $w = 1/[\sigma^2(F) + 0.000350\ F^2]$ which gave a mean $w\Delta^2$ varying only slightly with sin θ or $|F_o|$. Complex neutral-atom scattering factors were used. Results are given in Tables 1—4.*

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* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21838 (8 pp., 1 microfiche). See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

DISCUSSION

The molecules of (I) (Figure 1) are approximately linear (N–Au–Cl 176.0°) as would be expected for gold(I). The Au atoms are arranged in groups of four (Figure 2), forming almost square clusters with $Au^{I} \cdots Au^{II}$ 3.30 Å and $Au^{II} \cdots Au^{I} \cdots Au^{IV}$ 88.3°. The atoms forming the square are Au^{I} at x,y,z, Au^{II} at $2-y,x,1-z$, Au^{III} at $2-x,2-y,z$, and Au^{IV} at $y,2-x,1-z$. The square plane is $z = 1/2$ and deviations from it are ±0.29 Å for alternate Au atoms. The clusters lie in the planes $z = n/2$ (n integral).

The Au $\cdots$ Au distance is longer than that in metallic gold (2.88 Å) and much longer than that in $[Au(C_3H_7)_2(NCS)_2]_2$, in which there is a gold(I) $\cdots$ gold(I) bond of 2.76 Å.[11] It is, however, significantly shorter than two van der Waals radii. Similar distances have been observed between gold(I) in $[(C_3H_7NH_2)Au(C{\equiv}CPh)]$ (3.274 Å) [12] and in $[AuCl(Cl_3P)]$ (3.14 Å).[13] In both these cases the linear molecules are stacked to form Au chains; [(pip)AuCl] is the first compound in which an Au_4 square has been located.

It has been suggested [11] that these short contacts are due to the ease of packing linear molecules to form Au chains, rather than to any bonding interaction. The structure of $[AuCl(Ph_3P)]$,[14] with a bulky ligand and no short Au $\cdots$ Au contacts, agrees with this hypothesis. However, the cluster $[\{(p\text{-}MeC_6H_4)_3P\}_6Au_6]^{2+}$ has Au $\cdots$ Au distances of up to 3.1 Å,[15] and so bonding interactions in [Cl(pip)Au] cannot be ruled out.

We thank the S.R.C. for providing the diffractometer, and for financial support (to J. J. G. and P. G. J.). Calculations were performed on the Cambridge University IBM 370/165 computer with programs written by G. M. S., and the Figures were drawn with the program PLUTO written by Dr. W. D. S. Motherwell.

[6/394 *Received*, 26*th February*, 1976]

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[11] R. Hesse and P. Jennische, *Acta Chem. Scand.*, 1972, **26**, 3855.

[12] P. W. R. Corfield and H. M. M. Shearer, *Acta Cryst.*, 1967, **23**, 156.

[13] G. J. Arai, *Rec. Trav. chim.*, 1962, **81**, 307.

[14] N. C. Baenziger, W. E. Bennett, and D. M. Soboroff, *Acta Cryst.*, 1976, **B22**, 962.

[15] P. Bellon, M. Manassero, and M. Sansoni, *J.C.S. Dalton*, 1973, 2423.