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MONO-, DI-, AND TETRA-AURATED DERIVATIVES OF BARBITURIC ACID, INCLUDING A NEW TYPE OF POLYNUCLEAR GOLD COMPOUND. CRYSTAL STRUCTURE OF 1,3-BIS(TRIPHENYLPHOSPHINEGOLD)-5,5-DIETHYLBARBITURIC ACID

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Summary

Reaction of barbituric acid (2,4,6-pyrimidinetrione) or its derivatives with LAuCl (L = triphenylphosphine) gave 3-LAu-5,5-diethyl-, 1,3-(L′Au)$_2$-5,5-diethyl- (L′ = L or L′ = Cy$_3$P), 1,3-dimethyl-5,5-bis(LAu)-, or 1,3,5,5-tetrakis-(LAu)barbituric acid, which were characterized as *N*-, *N*,*N*′-, *C*,*C*-, or *N*,*N*′,*C*,*C*-gold derivatives, respectively, by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. In the case of 1,3-(LM)(L″M)-5,5-diethylbarbituric acid compounds with M = gold and L″ either Cy$_3$P, Ph$_3$As, or (4-tolyl)$_3$P, or ML = ML″ = HgMe were prepared. An X-ray diffraction study of 1,3-(LAu)$_2$-5,5-Et$_2$-pyrimidin-2,4,6-trione $\cdot$ 3C$_6$H$_6$ revealed that (a) the heterocyclic ring is planar, (b) there is no inter- or intra-molecular Au $\cdots$ Au interaction, and (c) the coordination around each gold atom is approximately linear (P–Au–N 178.3(4)°), with Au–N 2.022(12) and Au–P 2.233(5) Å. The molecular parameters are compared with those for barbituric acid and other barbiturates.

Introduction

In our study of gold complexes [1] we have investigated the derivatives of several nitrogen-containing heterocycles containing a five-membered ring (e.g.: pyrazoles [2a], pyrazolones [2b], imidazoles [2c] [2d], or triazoles [2d]), a six-membered ring (pyrimidines [2e], or pyridones [2f]), or both a five- and a six-membered ring (adenine, guanine, azaguanine, theobromine, or theophylline [2f]). The species obtained included adducts (such as (imidazole)$_n$AuCl(n = 1, 1.5, or 2) [2g] [2h]) *N*-aurated azolyl derivatives (such as polymeric 1-Au-2-methylimidazole [2g] or 1-L′Au-2-i-Pr-imidazole (L′ = cyclo-hexylphosphine [21])), involving this last type of

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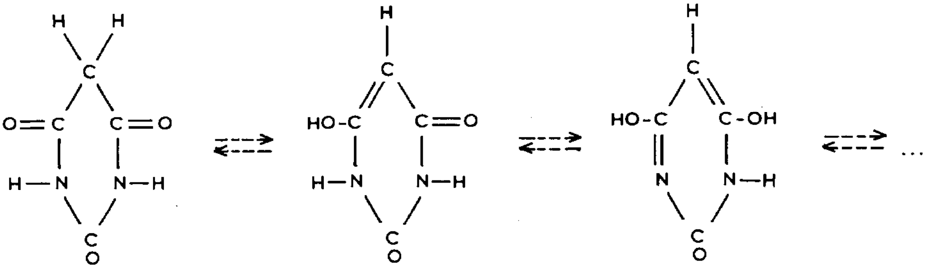
compound (e.g. 1-LAu-imidazole · imidazole, LAu(Im-*N*) · ImH [2c]) and *C*-aurated derivatives (such as 1-phenyl-3-methyl-4,4′-bis(LAu)-pyrazolone-5, where L = triphenylphosphine [2b]).

Because of the pharmaceutical interest in barbituric acid and its gold(I) derivatives [3], and in view of the possible existence of many tautomers **1a**–**1c** etc., of the acid, each of which may undergo auration, we decided to extend our investigations



(a) (b) (c)

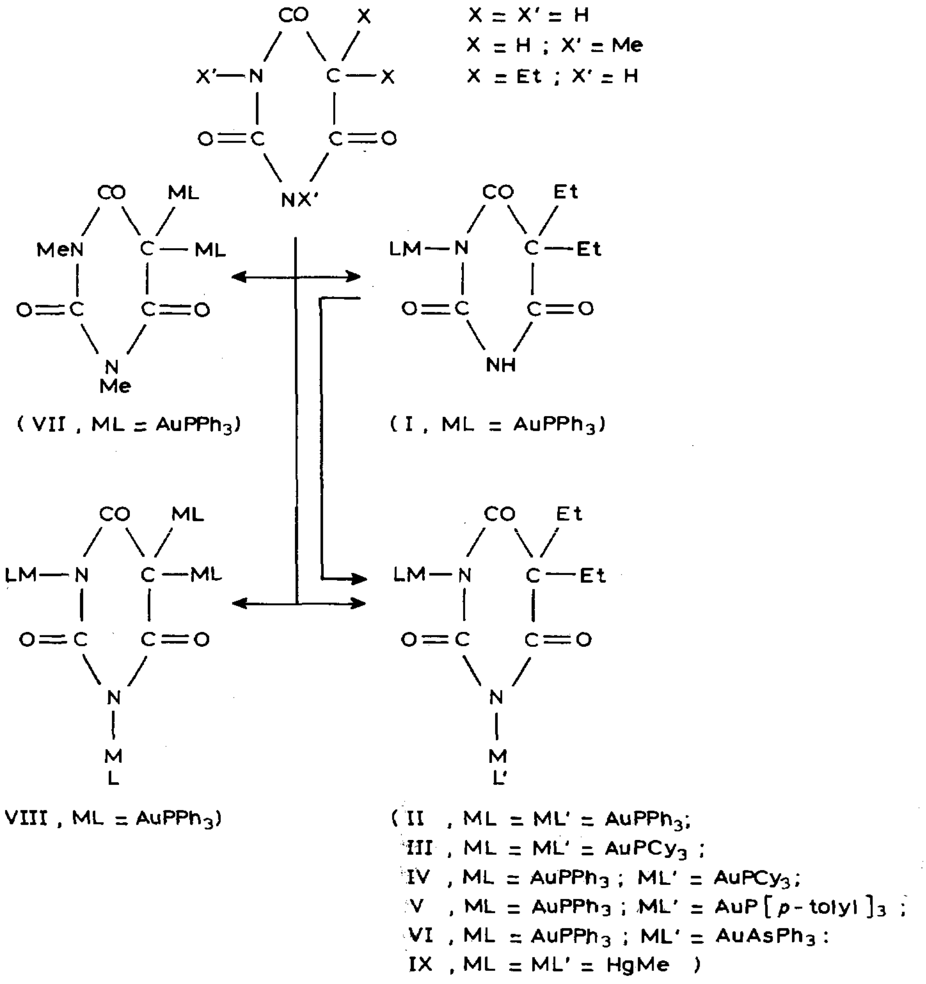
to the preparation and characterization of gold derivatives of barbituric acids, including the 5,5-diethyl derivative, commonly known as "veronal". In this paper the preparations of the mono-, di-, or tetra-aurated species are described.

Results and discussion

The reactions carried out on barbituric acid and on its derivatives are illustrated in the Scheme 1.

They were carried out in methanol containing sodium methoxide, or in the heterogeneous phase by use of a standard phase transfer procedure [2c]. The compounds obtained are air-, moisture- and light-stable colourless solids, soluble in organic solvents which are often clathrated in the crystal, as shown by analytical and spectral data (Tables 1–5), as well as by the X-ray crystal structure carried out on IIc.

When the 5-position bears two alkyl groups an **a**-type tautomer has to be considered; it was possible to replace the hydrogen of both NH groups of this form by R_3PAu moieties, affording compound II (R = phenyl), for which an X-ray crystal structure is reported here, or III (R = cyclo-hexyl). It is noteworthy that metal replacement at one N–H bond seems to be quicker than at the second, and thus it was possible to isolate also a monoaurated product, I. Since this compound still contains a free N–H bond, it was treated with another (ligand)gold(I) moiety to give a product in which the two nitrogen atoms bore different substituents: along with triphenylphosphinegold(I) we introduced either tri-cyclo-hexylphosphine-, tri-*p*-tolylphosphine- or triphenylarsine-gold(I), to give compounds IV, V, and VI, respectively. An attempt was made to obtain a barbiturate-containing gold and another metal, but the desired species was not obtained from I with MeHgCl; instead one species containing two atoms of gold, II was isolated together with a second containing two atoms of mercury, IX; the identity of the latter was confirmed by its independent preparation from methylchloromercury(II) and 5,5-diethylbarbituric acid.



(VII, ML = AuPPh$_3$)

(I, ML = AuPPh$_3$)

VIII, ML = AuPPh$_3$)

(II, ML = ML' = AuPPh$_3$;
III, ML = ML' = AuPCy$_3$;
IV, ML = AuPPh$_3$; ML' = AuPCy$_3$;
V, ML = AuPPh$_3$; ML' = AuP[p-tolyl]$_3$;
VI, ML = AuPPh$_3$; ML' = AuAsPh$_3$:
IX, ML = ML' = HgMe)

SCHEME 1

When the two ring nitrogens are alkylated, tautomers of type **a** and **b**, (but not **c**) are possible. The compound VII, obtained upon auration, was derived from the tautomer **a**, i.e. two (triphenylphosphine)gold(I) moieties had replaced the two hydrogens in the 5 position: the phosphorus nuclei are equivalent, since the ^{31}P(^{1}H) NMR spectrum shows only a sharp singlet at 37.27 ppm.

Finally, when unsubstituted barbituric acid was used all the four hydrogen atoms were replaced by four (Ph$_3$P)Au groups, yielding VIII, which, like the other compounds, was characterized by its carbonyl absorptions in the infrared (Table 4). In principle this per-aurated molecule could be derived from any of the possible tautomers, **a**, **b**, **c**, etc., but the structure shown in Scheme 1 is supported by the following evidence:

(i) The proton NMR spectrum suggests the presence of only two types of P-coupled aromatic rings.

(ii) The ^{31}P(^{1}H) NMR spectrum shows only two singlets; one of these lies nearly at the same position (33.0 ppm) as that for I or II (32.16 or 32.84 ppm respectively).

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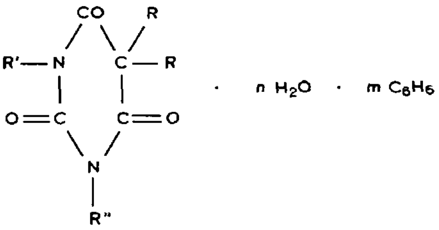
TABLE 1

ELUCIDATION OF COMPOUNDS I–IX



Compound	R	R′	R″	*n*	*m*
I	Et	$AuPPh_3$	H	0	0
IIa	Et	$AuPPh_3$	$AuPPh_3$	0	0
IIb	Et	$AuPPh_3$	$AuPPh_3$	0.5	0
IIc	Et	$AuPPh_3$	$AuPPh_3$	0	3
III	Et	$AuPCy_3$	$AuPCy_3$	0	0
IV	Et	$AuPPh_3$	$AuPCy_3$	0	0
V	Et	$AuPPh_3$	AuP(*p*-tolyl)$_3$	0.5	0
VI	Et	$AuPPh_3$	$AuAsPh_3$	0.5	0
VII	$AuPPh_3$	Me	Me	0	0
VIII	$AuPPh_3$	$AuPPh_3$	$AuPPh_3$	1	0
IX	Et	HgMe	HgMe	0	0

TABLE 2

ANALYTICAL AND OTHER DATA

Compound	Method [a]	Yield (%)	M.p. (°C)	Analyses (Found (calcd.)(%))			Reaction conditions	
				C	H	N	*T* (°C)	Time (h)
I	A	80	245–247	48.79 (48.61)	4.12 (4.08)	3.88 (4.36)	40	4
IIa	A	68	> 280 (dec.)	47.79 (48.01)	3.90 (3.66)	2.54 (2.54)	40	16
IIb	B	89	> 280 (dec.)	47.37 (47.62)	3.64 (3.72)	2.58 (2.52)	r.t.	12
IIc	B		> 280 (dec.)	55.36 (55.78)	4.42 (4.38)	2.07 (2.10)	r.t.	12
III	B	69	> 280	46.33 (46.48)	7.01 (6.74)	2.39 (2.46)	r.t.	12
IV	B	78	182–184	47.98 (47.23)	5.18 (5.22)	2.73 (2.50)	40	8
V	B	67	245–247	49.65 (49.01)	4.25 (4.11)	2.28 (2.43)	40	8
VI	B	82	> 250 (dec.)	45.52 (45.81)	3.52 (3.58)	2.45 (2.43)	40	4
VII	B	82	242–245	46.54 (47.03)	3.43 (3.38)	2.56 (2.61)	40	6
VIII [b]	B	70	240–242	46.12 (46.12)	3.09 (3.16)	1.51 (1.41)	40	6
IX	[c]	79	158–160	19.72 (19.58)	2.61 (2.63)	4.86 (4.57)	40	12

[a] Methods A and B are described in the experimental part. [b] Additional data: Found % (calcd.) Au, 39.40 (39.80); O, 3.28 (3.23); P, 6.23 (6.26). [c] See text.

TABLE 3. ^{1}H AND ^{31}P MAGNETIC RESONANCE DATA[a]

Compound	Aryl protons	Other protons	^{31}P NMR
I	7.37–7.8 m (15)	0.88 t (6) $J = 7.3$; 2.02 q (4) $J = 7.4$ 8.34 s (1) [b]	32.16 s
IIa	7.37–7.8 m (30)	0.90 t (6) $J = 7.4$; 2.03 q (4) $J = 7$	
IIb	7.37–7.8 m (30)	0.90 t (6) $J = 7.4$; 2.03 q (4) $J = 7$; 1.80 s (1) [b]	32.84 s
IIc	7.37–7.8 m (48)	0.90 t (6) $J = 7.4$; 2.03 q (4) $J = 7$;	
III		0.87 t (6) $J = 4.5$; 0.90–2.7 m (70)	
IV	7.37–7.8 m (15)	0.87 t (6); 1.06–2.4 m (37)	
V	7.10–7.80 m (27)	0.88 t (6) $J = 7.4$; 1.68 s (1) [b]; 2.02 q (4) $J = 7$; 2.38 s (9)	
VI	7.37–7.80 m (30)	0.90 t (6) $J = 7$; 1.75 s (1) [b]; 2.05 q (4) $J = 7.3$	
VII	7.0–7.90 m (30)	3.35 s (6)	37.27 s
VIII	7.0–8.0 m (60)	2.52 s (2) [b]	33.01 s; 37.02 s
IX		0.8 t (6) $J = 7.4$; 1.06 s (6); 2.02 q (4) $J = 7.4$	

[a] NMR spectra were recorded in a Varian or Bruker instrument operating at 90 or 80 MHz for ^{1}H or ^{31}P, respectively. Solvent was always $CDCl_3$ and reference Me_4Si or external 85% H_3PO_4; s, singlet; q, quadruplet; m, multiplet. Coupling constants in Hz. [b] This signal disappears on deuteration.

TABLE 4. SELECTED INFRARED DATA[a]

Compound	3600–2500 cm^{-1} region	1700–1500 cm^{-1} region
I	2500–3300br	1720s; 1675s; 1628s; 1585w; 1570w
IIa		1675w; 1625m; 1595s; 1582m; 1560w
IIb	2500–3600br,w	1672w; 1620m; 1600s; 1582m; 1555w
IIc [b]		1672w; 1620m; 1600s; 1582m; 1555w
III		1670w; 1607s; 1590s; 1555m
IV		1670w; 1608s; 1600s; 1555m
V	2500–3600br,w	1670w; 1620s; 1595s; 1552m
VI	2500–3600br,w	1672w; 1615s; 1595s; 1542m
VII		1668s; 1610s; 1600s; 1581m; 1570m; 1529w
VIII	2500–3600br,w	1635w; 1595m; 1572m; 1535s,br
IX		1638s; 1585s; 1550m

[a] Recorded as Nujol mulls in the NaCl region on a Perkin–Elmer 297 instrument. [b] A strong band at 680 cm^{-1} is observed due to clathrated benzene.

TABLE 5. ^{13}C NUCLEAR MAGNETIC RESONANCE DATA[a]

Compound	Barbituric nucleus [b]				Alkyl group	Phenyl
	C(2)	C(4)	C(5)	C(6)		
Ia	n.o.	n.o.	56.56	n.o.	9.41; 31.50	127.08; 129.63 $J = 11.7$; 132.23; 134.82 $J = 13.7$
IIb	165.18	182.7	60.69	182.7	11.71; 34.42	129.90 $J = 19.0$; 130.60 $J = 11.7$; 133.0; 135.80 $J = 14.0$
VII	156.10	176.43 [c]	n.o.	176.43 [c]		130.37; 130.41 $J = 11.6$; 132.59; 135.72 $J = 14.3$
VIII	n.o.	n.o.	n.o.	n.o.	29.78 (N-Me)	128.23–134.84 m

[a] NMR data were recorded on a Varian FT-80A spectrometer operating at 20 MHz in $CDCl_3$ solution (DMSO) for Ia). [b] Sometimes the C=O signals could not be detected because the solubility was not enough or because long accumulation times could not be used owing to decomposition of the sample. [c] Tentative assignment; the signal was very weak.

The other is at 37.0 ppm, close to that for VII (37.27 ppm), for which only a bis-*C*,*C*-gold structure is possible. In addition 1-phenyl-3-methyl-4,4-bis-(LAu)pyrazolone-5 has its $^{31}P\{^{1}H\}$ signal at 35.58 ppm [2b].

Crystal structure of IIc

The X-ray crystal structure of compound IIc consists of discrete monomeric molecules with no Au $\cdots$ Au interactions, the lowest values for this separation being 5.725(1) Å. An ORTEP [4] representation of the molecule, with the numbering scheme, is shown in Fig. 1: there is a C_2 symmetry axis passing through the atoms C(3), C(6) and O(8). The bond distances and angles are given in Table 6. The packing of the molecule in the crystal (Fig. 2) allows for three clathrated molecules of benzene; since these show only Van der Waals contacts with the complex molecules, a benzenoid π-molecular complex (cf. ref. 5) is ruled out. Clathrated molecules are rather common in complexes containing the Ph_3PAu moiety. The shortest intermolecular approaches between the molecule x, y, z and the equivalent ones, viz x, $y-1$, z; $x+1/2$, $y+1/2$, z; $x+1/2$, $-y+1/2$, $z+1/2$; $-x$, $y+1$, $-z+1/2$; $-x+1/2$, $y+1/2$, $-z+1/2$, are normal Van der Waals contacts.

The coordination around the gold atom is approximately linear (P–Au–N 178.3(4)°). The Au–N and the Au–P distances, 2.022(12) or 2.233(5) Å, respec-

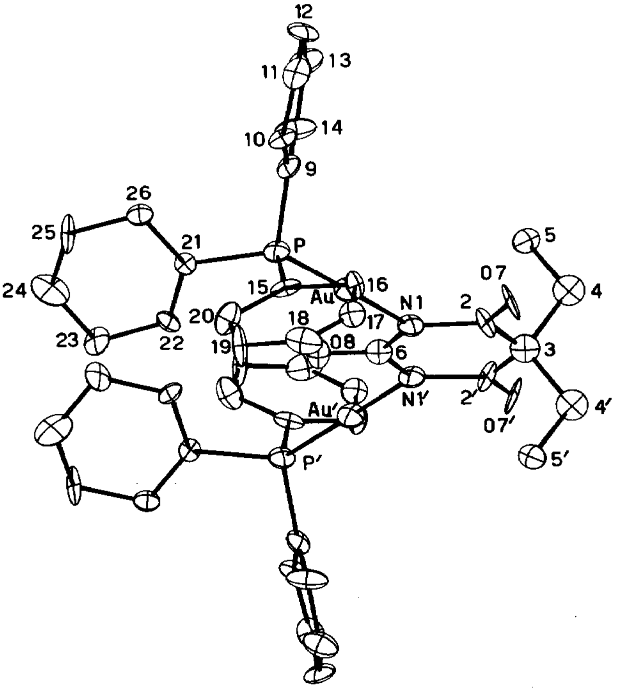


Fig. 1. ORTEP plot and numbering scheme of atoms viewed down the *a* axis. Thermal ellipsoids enclose 20% of the electron density. Carbon atoms are indicated only by numbers. Hydrogen atoms are omitted for clarity.

TABLE 6

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) (with e.s.d.'s in parentheses)

In the coordination sphere			
Au–P	2.233(5)	P–Au–N(1)	178.3(4)
Au–N(1)	2.02(1)		
In the barbital ligand			
N(1)–C(2)	1.45(3)	N(1)–C(2)–C(3)	118(2)
N(1)–C(6)	1.38(2)	N(1)–C(2)–O(7)	118(2)
C(2)–C(3)	1.49(3)	C(3)–C(2)–O(7)	124(2)
C(2)–O(7)	1.22(3)	C(2)–C(3)–C(2′)	119(2)
C(3)–C(4)	1.57(3)	C(2)–C(3)–C(4)	108(1)
C(4)–C(5)	1.51(3)	C(4)–C(3)–C(4′)	106(2)
C(6)–O(8)	1.18(4)	C(3)–C(4)–C(5)	110(2)
Au–N(1)–C(2)	124(1)	N(1)–C(6)–N(1′)	126(3)
Au–N(1)–C(6)	117(2)	N(1)–C(6)–O(8)	117(1)
C(2)–N(1)–C(6)	119(2)		
In the phosphine ligand			
P–C(9)	1.77(1)	C(15)–P–C(21)	100.6(8)
C(9)–C(10)	1.42(2)	P–C(9)–C(10)	119(1)
C(10)–C(11)	1.37(2)	P–C(9)–C(14)	120(1)
C(11)–C(12)	1.42(3)	C(10)–C(9)–C(14)	121(1)
C(12)–C(13)	1.42(3)	C(9)–C(10)–C(11)	118(1)
C(13)–C(14)	1.40(2)	C(10)–C(11)–C(12)	122(1)
C(14)–C(9)	1.34(2)	C(11)–C(12)–C(13)	117(1)
P–C(15)	1.80(2)	C(12)–C(13)–C(14)	119(2)
C(15)–C(16)	1.39(2)	C(13)–C(14)–C(9)	122(1)
C(16)–C(17)	1.36(3)	P–C(15)–C(16)	116(1)
C(17)–C(18)	1.40(4)	P–C(15)–C(20)	122(1)
C(18)–C(19)	1.37(4)	C(16)–C(15)–C(20)	122(2)
C(19)–C(20)	1.42(3)	C(15)–C(16)–C(17)	123(2)
C(20)–C(15)	1.41(3)	C(16)–C(17)–C(18)	115(2)
P–C(21)	1.82(2)	C(17)–C(18)–C(19)	125(2)
C(21)–C(22)	1.38(2)	C(18)–C(19)–C(20)	119(2)
C(22)–C(23)	1.45(3)	C(19)–C(20)–C(15)	116(2)
C(23)–C(24)	1.39(3)	P–C(21)–C(22)	117(1)
C(24)–C(25)	1.39(3)	P–C(21)–C(26)	122(1)
C(25)–C(26)	1.40(3)	C(22)–C(21)–C(26)	119(2)
C(26)–C(21)	1.38(2)	C(21)–C(22)–C(23)	118(2)
Au–P–C(9)	110.3(6)	C(22)–C(23)–C(24)	116(2)
Au–P–C(15)	114.6(6)	C(23)–C(24)–C(25)	119(2)
Au–P–C(21)	114.5(5)	C(24)–C(25)–C(26)	121(2)
C(9)–P–C(15)	108.6(7)	C(25)–C(26)–C(21)	119(2)
C(9)–P–C(21)	107.6(7)		
In the clathrated benzene [a]			
C(27)–C(28)	1.39(4)	C(32)–C(27)–C(28)	119(2)
C(28)–C(29)	1.36(5)	C(27)–C(28)–C(29)	121(3)
C(29)–C(30)	1.38(5)	C(28)–C(29)–C(30)	117(3)
C(30)–C(31)	1.35(4)	C(29)–C(30)–C(31)	119(3)
C(31)–C(32)	1.36(4)	C(30)–C(31)–C(32)	119(3)
C(32)–C(27)	1.35(4)	C(31)–C(32)–C(27)	120(2)
C(33)–C(34)	1.35(3)	C(34)–C(33)–C(35′)	123(2)
C(33)–C(35′)	1.37(3)	C(33)–C(34)–C(35)	119(2)
C(34)–C(35)	1.40(4)	C(34)–C(35)–C(33′)	117(2)

[a] In one benzene the atoms C(33′) and C(35′) are equivalent positions with coordinates: $1/2-x$, $1/2-y$, $1-z$.

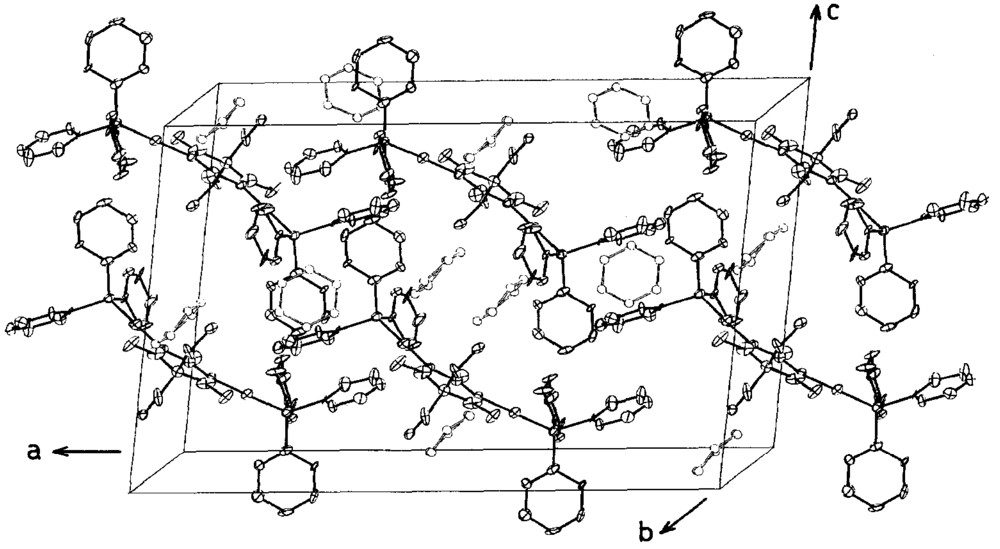


Fig. 2. Packing in the unit cell viewed along the *b* axis.

tively, are in line with values for other compounds containing a P–Au^I–N linkage, e.g.: 2.019(5) and 2.255(2) Å in 1-(tri-cyclo-hexylphosphinegold)-2-iso-propylimidazole [2i], respectively.

In the phosphine ligands the P–C distances and the C–P–C or Au–P–C angles are in the range reported for other gold(I) phosphine complexes (e.g. [2i,2j]). However, it should be noted that of the three Au–P–C angles that involve C(9), Au–P–C(9) is smaller than the other two: 110.3(6)° compared with 114.5(5) and 116.5(5)°; correspondingly of the C–P–C angles those involving C(9), C(9)–P–C(21) and C(9)–P–C(15), are quite similar to one another, viz. 107.6(7) and 108.6(7)°, while the remaining one, C(15)–P–C(21) is appreciably smaller, viz. 100.6(8)°.

Comparison between the values of the bond distances and of the bond angles in our compound and those reported for barbituric acid and some of its organic or inorganic derivatives can be made by use of published data [6] reproduced in Table 7. It can be seen that of the compounds listed IIc has the largest N(1)–C(6)–N(1′) angle, 126.3(2.7)°, the smallest C(6)–N(1)–C(2) or C(6)–N(1′)–C(2′) angle, 119.1(1.8)°, the longest N(1)–C(2) (or N(1′)–C(2′)) bond distance, 1.45(2) Å, and the second largest C(2)–C(3)–C(2′) angle, 119.2° (the largest being 119.9° for ammonium barbiturate), while the remaining angles and distances are not significantly outside the range of the literature values.

Although the e.s.d. values for our data must be kept in mind, the presence of four unusual parameters is unlikely to be coincidental, and a tentative explanation is offered below. This can be checked against crystal structures determined for other compounds of this type in the future.

Repulsion between gold and oxygen atoms may be one cause of the observed anomalies. The Van der Waals radii of gold and oxygen are 1.70 and 1.50 Å, respectively [7], and although their sum corresponds exactly with the separation between Au and O(7) (or Au′ and O(7′)), 3.215(13), it is larger than the separation between Au and O(8) (or Au′ and O(8)), 2.927(6). The maximization of the Au · · · O distances in IIc gives rise to some of the highest or lowest molecular parameters observed for barbituric acid or its derivatives, namely:

(i) Both C(6)–N(1)–C(2) and C(6)–N(1′)–C(2′) become small (119.1(1.8)°), thus increasing all the Au · · · O separations.

(ii) The two gold atoms lie slightly (±0.0722(7) Å) out of the best plane passing through the heterocycle (and including C(2), C(6), O(8)) thus increasing Au · · · O(8) and Au′ · · · O(8′).

(iii) Similarly the two oxygen atoms O(7) and O(7′) are slightly out of this best plane (±0.06(1)), so increasing Au · · · O(7) and Au′ · · · O(7′).

(iv) Both N(1)–C(2) and N(1′)–C(2′) distances are increased, thus allowing Au · · · O(7) and Au′ · · · O(7′) to reach the observed value.

As a consequence of the narrowing of the C(6)–N(1)–C(2) and of C(6)–N(1′)–C(2′) and of the planarity of the barbiturate ring, the other angles inside the ring are increased: this happens with N(1)–C(6)–N(1′), 126.3(2.7)°, and with C(2)–C(3)–C(2′), 119.5(2.2)°, a remarkably large value for a carbon atom bearing four substituents.

Steric hindrance due to the presence of the two bulky phosphine ligands is unlikely to be cause of the observed features because of the observed separation between the two different PPh_3. Crystal packing forces may be important, but cannot be assessed: they were evident in the case of calcium barbiturate, in which three of the four independent molecules are not planar [6b].

Conclusion

Our results show that auration can be achieved at either NH or activated CH_2 groups or simultaneously at both, affording mono-, di-, or tetra-aurated compounds which are stable, and soluble in organic solvents. They include the per-aurated biomolecule VIII which is one of the rapidly expanding number of polynuclear gold compounds but which is a new type. It is not one of the various types of coordination oligomers or polymers (e.g.: $[(Cy\text{-}N{=})(MeO)CAu]_3$ [8a], $(MeCS_2Au)_4$ [8b], $[KAu_9Te_7]^{4-}$ [8c], $[Au_{12}S_8]^{4-}$ [8d], or species used as drugs [8e] which are formulated as Au_nQ_n or $[Au_nQ_{n+1}]^-$ where Q is thiomalate and n may be six) nor it is a cluster [9], because no gold is directly connected with any of the other metal atoms. Furthermore, it cannot be classed together with other types of polynuclear compounds, such as $[(LAu)_3O]^+$ [10] or $[(LAu)_4N]^+$ [11], which contain only identical LAu–X bonds.

In the case of mercury (II) derivatives, permetallated heterocyclic molecules such as 2,3,4,5-tetra(acetatomercury)furan are described in the old literature [12]. Our results thus once again [2b] reveal an analogy between the organic chemistry of gold and that of one of its neighbours, in that polymetallation, typical of mercury(II), also occurs with gold(I).

Experimental

Elemental analyses were performed in our microanalytical laboratory or by Mr. A. Canu (University of Sassari). The starting (tertiary phosphine)chlorogold(I) compounds were prepared by a standard method [2c]. Evaporation was always carried out under reduced pressure.

TABLE 7

COMPARISON OF STRUCTURAL DATA (bond distances (Å) and angles (°)) [a]

Ref and name	C(6)–N(1)–C(2)	N(1)–C(2)–C(3)	C(2)–C(3)–C(2′)	N(1)–C(6)–N(1′)	N(1)–C(2)–O(7)
[6a]	126.7(2)	116.8(2)	113.5(2)	119.0(2)	
	121.6(2)	122.1(2)			
[6b]	124.6(6)	118.0(6)	111.9(6)	120.6(6)	120.8(6)
	120.4(6)	122.8(6)			120.9(6)
	123.8(6)	117.8(6)	113.1(6)	122.4(6)	119.7(6)
	120.6(6)	122.3(6)			119.7(6)
	124.1(6)	116.9(6)	112.8(6)	122.6(6)	121.0(6)
	119.7(6)	122.3(6)			119.3(6)
	124.1(6)	118.0(6)	112.7(6)	121.2(6)	120.5(6)
	119.6(6)	123.7(6)			120.5(6)
[6c]	125.2(8)	117.0(8)	119.9(8)	115.1(8)	117.6(8)
	125.7(8)	117.1(8)			117.6(8)
[6d]	125.8(3)	118.6(3)	113.7(3)	117.5(3)	120.3(3)
	124.9(3)	118.4(3)			119.6(4)
[6e]	121.6(2)	118.3(2)	116.7(2)	117.6(2)	119.0(2)
	125.7(2)	115.4(2)			119.2(2)
[6f]	124.9(6)	117.3(6)	111.2(7)	116.4(7)	120.9(6)
[6g]	122.3(6)	118.7(6)	113.3(6)	117.6(6)	120.8(6)
	127.2(6)	116.5(6)			120.8(6)
[6h]	123.7(2)	117.6(3)	117.3(2)	119.4(2)	121.5(3)
[6i]	127.6(3)	117.5(3)	114.0(3)	116.3(3)	120.1(3)
	123.8(3)	120.6(3)			119.3(3)
[6j]	122.6(3)	118.6(3)	113.3(3)	121.4(3)	119.9(3)
	121.2(3)	122.4(3)			119.1(3)
[6k]	127.4(2)	117.1(2)	114.3(2)	115.9(2)	120.4(3)
	126.1(2)	118.8(2)			119.6(3)
[6l]	125.5(4)	116.7(4)	112.4(4)	121.3(4)	121.1(4)
	119.2(4)	123.8(4)			118.9(4)
[6m]	126.8(3)	118.7(2)	113.7(2)	115.1(3)	120.1(2)
	126.3(2)	118.4(2)	114.1(2)	116.4(2)	119.8(2)
	126.4(2)	118.2(2)			119.7(2)
min.	119.2	115.4	111.2	115.1	117.6
av.	124.0	118.9	114.0	118.6	120.0
max.	127.6	123.8	119.9	122.6	121.5
IIc	119.1(18)	118.1(18)	119.5(22)	126.3(27)	118.0(19)

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[a] The numbering of atoms is the same as used in compound IIc; when the ring has no symmetry axis passing through C(3), C(6) and O(8), two sets of values are given for each independent species found in the crystal: in each set, the lower line, when present, refers to the corresponding primed atoms. Only the authors' values are reported, as no attempt has been carried out to calculate the missing data. The letters in the square brackets correspond to the compounds below: [a] bis(hydrogen-5,5-diethylbarbiturato)bis(imidazole)zinc(II); the corresponding bond lengths and angles in the cobalt and zinc complexes are said to be very similar [6a]; [b] calcium hydrogenbarbiturate trihydrate (the second set of values refers to the planar barbiturate anion); [c] ammonium hydrogenbarbiturate; [d] 2,4-diamino-5-(3,4,5-trimethoxybenzyl)pyrimidine 5,5-diethylbarbituric acid (1/1); [e] bis[ethylenediamine-(barbiturato)palladium(II)*N*,*C*] tetrahydrate; [f] molecular complex between 5-phenyl-5-ethylbarbituric acid and theophylline (1/2); [g] 1-cyclo-hexyl-5,5-diallylbarbituric acid; [h] 1,3-bis(cyclo-hexyl)-5,5-diallylbarbituric acid; [i] 1-methyl-5,5-diethylbarbituric acid; [j] sodium hydrogen-1-methyl-5,5-diethylbarbiturate; [k] 5-ethyl-5-(3,3-dimethylbutyl)-barbituric acid; [l] sodium hydrogen-5,5-diethylbarbiturate; [m] 5,5-diethylbarbituric acid. The first line refers to form II, monoclinic, the other lines to form I, trigonal.

C(3)–C(2)–O(7)	N(1)–C(6)–O(8)	N(1)–C(2)	N(1)–C(6)	C(2)–C(3)	C(2)–O(7)	C(6)–O(8)
		1.349(3)	1.390(3)	1.511(4)	1.215(3)	1.213(3)
		1.350(3)	1.357(3)	1.525(4)	1.224(3)	
121.1(6)	116.6(6)	1.340(5)	1.407(5)	1.542(5)	1.229(5)	1.228(5)
116.3(6)	122.7(6)	1.333(5)	1.345(5)	1.506(5)	1.247(5)	
122.5(6)	118.1(6)	1.355(5)	1.381(5)	1.520(5)	1.219(5)	1.248(5)
117.9(6)	119.5(6)	1.343(5)	1.323(5)	1.510(5)	1.240(5)	
122.1(6)	119.0(6)	1.352(5)	1.376(5)	1.512(5)	1.222(5)	1.251(5)
118.4(6)	118.4(6)	1.349(5)	1.326(5)	1.517(5)	1.238(5)	
121.5(6)	116.0(6)	1.343(5)	1.405(5)	1.517(5)	1.223(5)	1.235(5)
115.8(6)	122.8(6)	1.332(5)	1.340(5)	1.495(5)	1.254(5)	
125.3(8)	123.6(8)	1.398(11)	1.370(11)	1.416(11)	1.253(10)	1.234(10)
122.7(8)	121.3(8)	1.395(11)	1.357(11)	1.412(11)	1.227(11)	
121.1(4)	122.1(3)	1.364(5)	1.360(5)	1.522(5)	1.214(5)	1.218(5)
122.0(4)	120.4(3)	1.371(5)	1.379(5)	1.513(6)	1.211(5)	
122.5(2)	122.6(2)	1.367(4)	1.372(4)	1.467(4)	1.243(3)	1.223(3)
125.3(2)	119.8(2)	1.371(4)	1.383(4)	1.451(4)	1.235(3)	
121.7(6)	121.8(8)	1.361(8)	1.384(11)	1.516(11)	1.212(8)	1.207(12)
122.7(6)	122.3(6)	1.388(6)	1.384(5)	1.528(6)	1.213(5)	1.218(6)
120.3(6)	120.2(6)	1.375(6)	1.372(5)	1.513(6)	1.200(5)	
120.9(3)	120.3(2)	1.394(4)	1.387(3)	1.503(4)	1.201(5)	1.217(5)
122.4(3)	121.4(3)	1.363(3)	1.392(3)	1.508(3)	1.211(3)	1.206(3)
120.1(3)	122.3(3)	1.360(3)	1.369(3)	1.509(3)	1.221(3)	
121.5(3)	116.3(3)	1.362(2)	1.417(2)	1.509(2)	1.225(2)	1.240(2)
118.4(3)	122.3(3)	1.342(2)	1.339(2)	1.524(2)	1.233(2)	
122.5(3)	122.2(3)	1.380(3)	1.361(3)	1.513(4)	1.197(4)	1.213(4)
121.6(2)	121.8(3)	1.355(3)	1.376(3)	1.517(4)	1.208(4)	
122.2(4)	117.4(4)	1.339(2)	1.396(2)	1.520(2)	1.216(2)	1.238(2)
117.2(4)	121.3(4)	1.348(2)	1.343(2)	1.527(2)	1.245(2)	
121.2(2)	122.4(3)	1.366(3)	1.379(3)	1.514(3)	1.219(3)	1.196(4)
121.8(2)	122.0(2)	1.370(2)	1.368(2)	1.523(3)	1.211(3)	1.211(2)
122.2(2)	121.6(2)	1.381(2)	1.378(3)	1.514(3)	1.210(2)	
115.8	116.0	1.332	1.323	1.412	1.197	1.196
121.0	120.6	1.361	1.371	1.506	1.223	1.223
125.3	123.6	1.398	1.417	1.542	1.254	1.251
123.8(19)	116.9(14)	1.450(20)	1.380(20)	1.490(30)	1.220(30)	1.180(40)

Method A

A dichloromethane solution (20 ml) of (triphenylphosphine)chlorogold(I) (738 mg, 1.49 mmol) and 5,5-diethylbarbituric acid (250 mg, 1.37 mmol) was added to an ice-cold suspension of tetra-n-butylammonium hydrogen sulphate (461 mg, 1.36 mmol) in 2*N* aqueous sodium hydroxide (17 ml). After 4 h stirring at 40°C, the organic layer was separated, washed with water till neutral, dried over sodium sulphate, and evaporated to dryness. The residue was recrystallized from dichloromethane/hexane to yield the analytical sample of I. The same compound I was obtained when the monosodium salt of "veronal" (150 mg, 0.727 mmol), (triphenylphosphine)chlorogold(I) (360 mg, 0.727 mmol), and methanol (15 ml), were kept for

23 h at 40°C, and the residue after evaporation was recrystallized from dichloromethane/hexane.

Method B

To a methanol solution (25 ml) of 5,5-diethylbarbituric acid was added 200 mg (1.08 mmol) sodium methoxide (from 50 mg sodium, 2.17 mmol) in methanol (5 ml) followed by (triphenylphosphine)chlorogold(I) (1.123 g, 2.28 mmol). After 12 h stirring at room temperature the precipitate was filtered and recrystallized from dichloromethane/hexane, to give the analytical sample of IIb. A sample of IIb was recrystallized from benzene/hexane to give IIc, which was used for the X-ray diffraction study. Compounds III, VI, or VII were prepared similarly, using "veronal" and $(Cy_3P)AuCl$, or I and $(Ph_3As)AuCl$, or *N,N'*-dimethylbarbituric acid and $(Ph_3P)AuCl$, respectively. Compounds IV or V were obtained from I and the corresponding $(R_3P)AuCl$; the filtered solution was evaporated to dryness, and the residue was recrystallized from dichloromethane/hexane. Compound VIII was prepared in the same way as II but from barbituric acid (150 mg, 1.17 mmol) and $(Ph_3P)AuCl$ (2.316 g, 4.68 mmol); the product mixture was evaporated to dryness, the residue was extracted with dichloromethane, the extract was evaporated and the residue repeatedly crystallized from dichloromethane/hexane.

1,3-Bis(methylmercury)-5,5-diethylbarbituric acid (IX)

A mixture of 5,5-diethylbarbituric acid (100 mg, 0.543 mmol), sodium methoxide (1.08 mmol), methylchloromercury(II) (0.273 mg, 1.08 mmol), and methanol (30 ml) was heated 15 h at 40°C. The residue left after evaporation was extracted with diethyl ether and the extract was evaporated to leave a residue which was recrystallized from dichloromethane to give IX.

Attempt to obtain a heterobimetallic derivative

To a methanol solution (25 ml) of compound I (250 mg, 0.389 mmol) were added sodium methoxide (0.389 mmol) and methylchloromercury(II) (107 mg, 0.428 mmol). After 15 h stirring at 40°C the mercury-free precipitate (60 mg) was filtered off and identified as IIa from its infrared spectrum and analytical data. The mother liquor was evaporated to dryness; the remaining mixture was extracted with diethyl ether and the extract was evaporated to leave compound IX (30 mg), which was identified from its m.p. (158–160°C) and infrared spectrum.

X-ray analysis

A prismatic crystal of the compound IIc having approximate dimensions $0.38 \times 0.54 \times 0.72$ mm was used for data collection. Accurate lattice parameters were determined from a least-squares refinement of 2ϑ values for 25 reflections centered on a single-crystal Philips PW1100 computer controlled diffractometer with graphite-monochromated Mo-K_α radiation at the Centro di Studio per la Cristallografia Strutturale del C.N.R., Pavia, (Italy). Three-dimensional intensity data were collected at room temperature using the $\omega/2\vartheta$ scan technique (with a constant speed of 0.120° s^{-1} in ω) within the angular range $2 \leqslant \vartheta \leqslant 25°$. Three standard reflections monitored every 240 min showed only small random variations. The intensity data were corrected for Lorentz and polarization factors; an empirical absorption correction [13] with minimum and maximum absorption factors of

1.0007 and 1.8694 was applied. An approximate absolute scale and a mean thermal factor of 3.93 Å^2 were determined by Wilson's method [14]. Of the 4825 independent reflections measured, 2963 reflections with $I \geqslant 3\sigma(I)$ were considered as observed and used in the structure analysis.

Crystal data. $C_{44}H_{40}N_2O_3P_2Au_2 \cdot 3C_6H_6$; FW 1307.03; a 25.882(4); b 12.5175(4); c 17.062(2) Å; β 97.47(1)°. V 5481(1) Å^3; $Z = 4$; D_c 1.58 g cm^{-3}; $F(000) = 2624$; λ(Mo-K_α) 0.7107 Å; μ(Mo-K_α) 56.3 cm^{-1}.

Systematic absences $h0l$, $l \neq 2n$ and hkl, $h + k \neq 2n$; space group $C2/c$, from the statistical distribution of the normalized structure factors ($\langle E \rangle = 0.744$, $\langle E^2 - 1 \rangle = 1.089$, $\langle E^3 \rangle = 1.754$, $\langle E^4 \rangle = 3.64$) which agrees with a centric space group.

TABLE 8

FINAL COORDINATES
(with e.s.d.'s in parentheses)

Atom	*x*	*y*	*z*
Au	0.09955(3)	0.01466(6)	0.34532(4)
N(1)	0.0435(4)	0.1103(12)	0.2895(6)
C(2)	0.0453(9)	0.2260(17)	0.2916(11)
C(3)	0.0	0.2861(22)	0.2500
C(4)	−0.0219(8)	0.3614(22)	0.3117(13)
C(5)	−0.0511(9)	0.2967(21)	0.3667(15)
C(6)	0.0	0.0603(27)	0.2500
O(7)	0.0851(5)	0.2685(10)	0.3233(7)
O(8)	0.0	−0.0343(22)	0.2500
P	0.1599(2)	−0.0951(4)	0.4062(3)
C(9)	0.1674(6)	−0.0730(12)	0.5095(8)
C(10)	0.2176(6)	−0.0810(17)	0.5531(8)
C(11)	0.2230(6)	−0.0563(15)	0.6322(10)
C(12)	0.1794(8)	−0.0445(17)	0.6735(8)
C(13)	0.1293(7)	−0.0415(19)	0.6279(10)
C(14)	0.1251(5)	−0.0599(18)	0.5462(9)
C(15)	0.2228(6)	−0.0853(15)	0.3727(7)
C(16)	0.2460(6)	0.0151(14)	0.3788(8)
C(17)	0.2938(9)	0.0344(21)	0.3568(9)
C(18)	0.3183(8)	−0.0549(26)	0.3287(11)
C(19)	0.2972(8)	−0.1557(17)	0.3205(13)
C(20)	0.2469(8)	−0.1740(18)	0.3423(11)
C(21)	0.1460(5)	−0.2367(14)	0.3896(8)
C(22)	0.1204(10)	−0.2652(18)	0.3169(11)
C(23)	0.1189(6)	−0.3774(18)	0.2951(11)
C(24)	0.1187(8)	−0.4490(23)	0.3571(15)
C(25)	0.1414(7)	−0.4179(14)	0.4321(13)
C(26)	0.1502(8)	−0.3098(17)	0.4504(9)
C(27)	0.4552(10)	0.1220(21)	0.4418(18)
C(28)	0.4893(11)	0.1511(25)	0.3893(19)
C(29)	0.5011(13)	0.2554(28)	0.3786(13)
C(30)	0.4704(11)	0.3300(28)	0.4100(16)
C(31)	0.4466(17)	0.3032(25)	0.4735(13)
C(32)	0.4348(8)	0.1989(21)	0.4842(11)
C(33)	0.2020(6)	0.2625(18)	0.4605(11)
C(34)	0.2431(11)	0.3012(22)	0.4276(13)
C(35)	0.2935(9)	0.2827(21)	0.4657(14)

Structure determination and refinement

The structure was solved by Patterson and Fourier methods. The position of the gold atom was derived from a three-dimensional Patterson map and refined to $R = 0.243$ in three cycles of full-matrix least-squares refinement. A difference Fourier synthesis phased on the Au atom revealed the positions of all the non-hydrogen atoms of the complex molecule. The full-matrix least-squares refinement of the positional and initially isotropic and then anisotropic thermal parameters reduced R to 0.128. The positions of the C atoms of the clathrated benzene molecules were found on a subsequent difference Fourier map. Further refinement cycles, including scale factor and individual anisotropic thermal parameters gave R 0.087. Hydrogen atoms were located from a difference Fourier map and included in the subsequent refinement with the same isotropic thermal parameters as their bonded atoms. Refinement was terminated at R 0.073 (R_w 0.067) when the largest shift/error ratio was 0.68. A final difference Fourier map showed maximum and minimum $\Delta\rho$ values 0.81 and -0.73 e Å^{-3}. In the early stages of the structure analysis the observed reflections were given unit weights, in the last cycles a weight $w = 1/\sigma^2(|F_o|)$ was used. The atomic scattering factors for the non-hydrogen atoms were taken from ref. 15 and those for hydrogen atoms from ref. 16. Anomalous dispersion effects were included in the scattering factors. The final positional parameters for non-hydrogen atoms are listed in Table 8. Lists of hydrogen atom positions, thermal parameters and structure factors can be obtained from one of the authors (B. Bovio) on request.

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