

Table 3. Comparison of Au—P and Au—S bond lengths (Å) in some Au^I complexes

Compound (L = Ph ₃ P)	Au—P	Au—S
[L ₂ AuSCN]	2.348 (2)*	2.468 (4)
[L ₃ AuSCN]·H ₂ O	2.399 (15)*	2.791 (4)
[L ₃ Au][BPh ₄]·L·CHCl ₃	2.402 (9)*	(Au—P in non-bonded L is 3.95 Å)
[L ₄ Au][BPh ₄]·EtOH, disordered structure	2.447 (14)*	(Trigonal site)
[(MePh ₂ P) ₃ Au][PF ₆]	2.606 (6)*	(Tetrahedral site)
	2.449 (1)	

* Average bond lengths are given, together with the sample standard deviation.

Sheldrick, 1981). [L₄Au][BPh₄] has been studied in powder form (Malatesta, Naldini, Simonetta & Cariati, 1966), and more recently has been crystallized as a variety of solvates. None of these (Jones, 1980b, 1982) show the sought-after regular tetrahedral geometry: the chloroform solvate contains a trigonal-planar cation with three short Au—P bonds (average 2.402 Å), and a very remote (3.95 Å) Ph₃P ligand, while the ethanol and acetonitrile analogs are disordered between tetrahedral and trigonal components. The ethanol analog has average Au—P bond lengths of 2.447 Å (trigonal component) and 2.606 Å (tetrahedral component).

The only monodentate four-coordinate Au^I complex which shows nearly regular tetrahedral geometry in the solid state is [Au(Ph₂Me)₄][PF₆] (Elder, Zeiher, Onady & Whittle, 1981). Here the Au atom occupies a site of 4 symmetry and the coordination about the Au is close to ideal tetrahedral, with Au—P 2.449 (1) Å and P—Au—P angles of 105.24 (4) and 118.32 (4)°. The Au—P bonds in [L₃AuSCN]·H₂O are thus longer than those of [L₂AuSCN], the same in length as those of

[L₃Au][BPh₄]·L·CHCl₃, shorter than those found for [(Ph₂MeP)₄Au][PF₆], and much shorter than those found for either site in [L₄Au][BPh₄]·EtOH. As can be seen from Table 3, there is clearly some correlation of both Au—P and Au—S bond lengths with degree of steric crowding about the Au atom.

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Structure of the 1:1 Complex of Mercury(II) Trifluoroacetate with 2,2'-Bipyridyl*

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Abstract. [Hg(C₂F₃O₂)₂]₂(C₁₀H₈N₂)₂·C₂₈H₁₆F₁₂Hg₂N₄·O₈, triclinic, *P*1, *a* = 12.59 (1), *b* = 16.07 (2), *c* = 9.73 (1) Å, α = 109.1 (1), β = 113.9 (1), γ = 73.4 (1)°, *U* = 1673.78 Å³, *F*(000) = 1087.96, *Z* = 2, *D*_x = 2.309, *D*_m = 2.318 Mg m⁻³. The structure, determined from 2496 observed diffractometer-

measured intensities (*R* = 0.057), shows two independent Hg each coordinated to one 2,2'-bipyridyl: Hg(1)—N = 2.24 (2), 2.36 (2) Å; Hg(2)—N = 2.30 (2), 2.28 (2) Å. Each Hg is also coordinated to two trifluoroacetate groups: Hg(1)—O = 2.21 (1), 2.53 (2), 2.58 (2), 2.81 (2), 2.88 (2) Å; Hg(2)—O = 2.23 (1), 2.35 (2), 2.78 (3), 2.82 (2) Å.

* Recommended IUPAC name: catena-poly {[2,2'-bipyridyl](trifluoroacetato-*O,O'*)mercury}-μ-(trifluoroacetato-*O,O'*:*O'*)-[2,2'-bipyridyl](trifluoroacetato-*O,O'*)mercury}-μ-(trifluoroacetato-*O*:*O'*).

Introduction. It has been shown (Halfpenny, Small & Thorpe, 1978; Halfpenny & Small, 1980, 1981) that

pyridine is effective in displacing the O atoms of trifluoroacetate groups from sites of close coordination to Hg in mercury(II) trifluoroacetate and its derivatives. More rigid and bulky nitrogen donor ligands such as 2,2'-bipyridyl, which are less able to

satisfy the preferred near-linear coordination of Hg, may be less effective in this respect. The structure of the title compound was determined in order to investigate this point.

Stable crystals of the title compound were obtained by recrystallization from an equimolar solution of mercury(II) trifluoroacetate and 2,2'-bipyridyl in dichloromethane; they were prisms, elongated parallel to *c*, showing the forms {001}, {010}, and {100}. Crystal data were obtained from zero-layer Weissenberg photographs about all three axes, taken with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

Intensity data were obtained with the STOE Stadi-2 automatic two-circle diffractometer using a crystal $0.19 \times 0.15 \times 0.70 \text{ mm}$ for the layers $l = 0-9$ (Mo K α radiation, $\lambda = 0.7107 \text{ \AA}$). 3068 unique intensities were measured; after elimination of those for which $I <$

Table 1. Final atomic parameters ($\times 10^3$, Hg $\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> _{eq}
Hg(1)	4029 (1)	2492 (1)	6525 (1)	63 (1)*
Hg(2)	2971 (1)	3340 (1)	1357 (1)	80 (1)*
C(5)	555 (2)	64 (1)	695 (2)	47 (5)
N(1)	459 (1)	118 (1)	717 (2)	45 (4)
C(1)	390 (2)	94 (1)	772 (3)	64 (7)
C(2)	423 (2)	10 (2)	807 (3)	75 (7)
C(3)	522 (2)	-46 (2)	782 (3)	71 (7)
C(4)	593 (2)	-21 (1)	724 (3)	61 (6)
C(6)	623 (2)	96 (1)	633 (2)	46 (5)
C(7)	731 (2)	51 (2)	618 (3)	67 (7)
C(8)	790 (2)	84 (2)	560 (3)	84 (8)
C(9)	740 (2)	163 (2)	518 (3)	69 (7)
C(10)	629 (2)	207 (1)	534 (3)	61 (6)
N(2)	574 (1)	172 (1)	591 (2)	51 (5)
C(15)	102 (2)	499 (1)	197 (2)	49 (6)
N(3)	140 (1)	417 (1)	214 (2)	55 (5)
C(11)	82 (2)	379 (2)	265 (3)	70 (7)
C(12)	-22 (2)	429 (2)	300 (3)	80 (8)
C(13)	-63 (2)	515 (2)	281 (3)	71 (7)
C(14)	-1 (2)	551 (1)	226 (3)	55 (6)
C(16)	172 (2)	532 (1)	143 (2)	49 (6)
C(17)	150 (2)	623 (2)	144 (3)	67 (7)
C(18)	220 (2)	651 (2)	91 (3)	79 (8)
C(19)	309 (2)	586 (2)	37 (3)	75 (7)
C(20)	326 (2)	495 (1)	39 (3)	63 (7)
N(4)	255 (1)	473 (1)	93 (2)	53 (5)
C(21)	163 (3)	189 (2)	-22 (5)	116 (11)
C(22)	102 (4)	108 (3)	-76 (5)	121 (12)
C(23)	378 (2)	411 (1)	574 (3)	54 (6)
C(24)	356 (2)	511 (2)	586 (3)	61 (6)
C(25)	525 (2)	261 (1)	82 (2)	50 (6)
C(26)	652 (2)	215 (2)	106 (3)	62 (6)
C(27)	166 (2)	223 (2)	521 (4)	83 (8)
C(28)	35 (3)	207 (2)	450 (4)	98 (10)
O(1)	251 (2)	192 (2)	78 (3)	136 (8)
O(2)	112 (3)	249 (2)	-83 (4)	198 (13)
O(3)	391 (1)	357 (1)	460 (2)	75 (5)
O(4)	380 (1)	396 (1)	695 (2)	69 (4)
O(5)	482 (1)	260 (2)	177 (2)	60 (4)
O(6)	474 (1)	302 (1)	-22 (2)	72 (5)
O(7)	228 (2)	185 (1)	440 (3)	115 (7)
O(8)	189 (2)	270 (1)	643 (3)	120 (7)
F(1)	121 (3)	58 (2)	-203 (4)	225 (25)*
F(2)	154 (3)	53 (2)	8 (4)	250 (26)*
F(3)	-4 (2)	123 (2)	-102 (4)	270 (28)*
F(4)	429 (1)	553 (1)	711 (2)	111 (11)*
F(5)	246 (1)	548 (1)	586 (2)	119 (12)*
F(6)	365 (1)	526 (1)	469 (2)	114 (11)*
F(7)	686 (1)	210 (1)	-10 (2)	120 (12)*
F(8)	721 (1)	255 (1)	227 (2)	116 (11)*
F(9)	662 (1)	131 (1)	100 (2)	128 (12)*
F(10)	29 (2)	131 (1)	459 (5)	278 (28)*
F(11)	-38 (1)	265 (1)	501 (3)	187 (17)*
F(12)	-6 (2)	200 (2)	309 (3)	243 (26)*

* U_{eq} from $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table 2. Bond lengths (\AA) and selected bond angles ($^\circ$)

Hg(1)-N(1)	2.24 (2)	C(23)-O(3)	1.20 (2)
Hg(1)-N(2)	2.36 (2)	C(23)-O(4)	1.26 (2)
Hg(1)-O(3)	2.88 (2)	C(23)-C(24)	1.53 (3)
Hg(1)-O(4)	2.21 (1)	C(24)-F(4)	1.29 (3)
Hg(1)-O(7)	2.53 (2)	C(24)-F(5)	1.33 (3)
Hg(1)-O(8)	2.58 (2)	C(24)-F(6)	1.30 (3)
Hg(1)-O(6')	2.81 (2)	C(21)-O(1)	1.15 (4)
Hg(2)-O(1)	2.35 (2)	C(21)-O(2)	1.18 (4)
Hg(2)-O(2)	2.78 (3)	C(21)-C(22)	1.53 (5)
Hg(2)-O(3)	2.82 (2)	C(22)-F(1)	1.30 (4)
Hg(2)-O(5)	2.23 (1)	C(22)-F(2)	1.26 (4)
Hg(2)-N(3)	2.30 (2)	C(22)-F(3)	1.22 (4)
Hg(2)-N(4)	2.28 (2)	C(25)-O(5)	1.25 (2)
N(2)-C(10)	1.36 (3)	C(25)-O(6)	1.23 (2)
C(10)-C(9)	1.42 (3)	C(25)-C(26)	1.51 (3)
C(9)-C(8)	1.37 (3)	C(26)-F(7)	1.34 (3)
C(8)-C(7)	1.37 (3)	C(26)-F(8)	1.25 (3)
C(7)-C(6)	1.39 (3)	C(26)-F(9)	1.30 (3)
C(6)-N(2)	1.31 (2)	N(4)-C(16)	1.33 (2)
C(6)-C(5)	1.49 (3)	N(4)-C(20)	1.38 (3)
C(5)-N(1)	1.32 (2)	C(16)-C(15)	1.47 (3)
N(1)-C(1)	1.38 (3)	C(16)-C(17)	1.40 (3)
C(1)-C(2)	1.41 (3)	C(17)-C(18)	1.41 (3)
C(2)-C(3)	1.37 (3)	C(18)-C(19)	1.43 (3)
C(3)-C(4)	1.42 (3)	C(19)-C(20)	1.41 (3)
C(4)-C(5)	1.40 (3)	C(15)-N(3)	1.32 (2)
C(27)-O(7)	1.23 (3)	N(3)-C(11)	1.38 (3)
C(27)-O(8)	1.16 (3)	C(11)-C(12)	1.43 (3)
C(27)-C(28)	1.57 (4)	C(12)-C(13)	1.37 (3)
C(28)-F(10)	1.28 (4)	C(13)-C(14)	1.43 (3)
C(28)-F(11)	1.24 (3)	C(14)-C(15)	1.41 (3)
C(28)-F(12)	1.24 (4)		
O(3)-Hg(1)-O(4)	49.3 (5)	O(1)-Hg(2)-O(2)	45.9 (9)
O(4)-Hg(1)-O(7)	113.1 (6)	O(2)-Hg(2)-N(3)	78.0 (8)
O(7)-Hg(1)-O(8)	50.0 (7)	O(2)-Hg(2)-N(4)	105.7 (9)
N(2)-Hg(1)-O(8)	155.6 (7)	N(3)-Hg(2)-N(4)	71.3 (6)
N(1)-Hg(1)-O(4)	156.1 (6)	N(4)-Hg(2)-O(1)	151.6 (8)
O(6')-Hg(1)-N(1)	77.6 (5)	N(4)-Hg(2)-O(5)	117.6 (6)
N(1)-Hg(1)-N(2)	71.3 (6)	O(5)-Hg(2)-O(1)	84.2 (7)
N(2)-Hg(1)-O(3)	82.1 (5)	O(3)-Hg(2)-N(3)	76.6 (6)
Hg(1)-N(2)-C(6)	85.7 (7)	O(1)-Hg(2)-O(3)	96.1 (7)
Hg(1)-N(1)-C(5)	118.8 (13)	O(2)-Hg(2)-O(3)	129.8 (8)
N(1)-C(5)-C(6)	117.9 (18)	O(1)-C(21)-O(2)	122.3 (43)
N(2)-C(6)-C(5)	115.7 (18)	O(5)-C(25)-O(6)	125.2 (21)
O(7)-C(27)-O(8)	129.4 (31)	Hg(2)-N(4)-C(16)	116.6 (14)
O(3)-C(23)-O(4)	127.8 (22)	Hg(2)-N(3)-C(15)	117.7 (14)
Hg(1)-O(3)-Hg(2)	131.1 (6)	N(3)-C(15)-C(16)	115.7 (18)
		N(4)-C(16)-C(15)	117.7 (18)

(') = *x, y, z*.

$3\sigma(I)$, 2496 remained. Apart from a preliminary data reduction, absorption corrections ($\mu = 8.92 \text{ mm}^{-1}$) and all other calculations were made with the *SHELX* suite of programs (Sheldrick, 1976).

Hg-atom coordinates were obtained from the Patterson map and used to phase ($F_o - F_c$) maps which gave the remaining (non-H) atomic positions. Anisotropic U_{ij} for Hg and also, in later cycles, for F, were used in full-matrix least-squares refinement of atomic coordinates with unit weights. At a later stage, individual scale factors for the intensity-data-collection layers were included in the refinement. The refinement was terminated when $R = 0.057$ and the shifts were less than 0.10 e.s.d. Atomic scattering factors for Hg (including anomalous scattering) were taken from Cromer & Mann (1968) and Cromer & Liberman (1970); those for other atoms were from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates and temperature factors (U_{eq} and U) are given in Table 1.* Bond distances and selected bond angles are given in Table 2.

Discussion. The asymmetric unit (Fig. 1) contains two independent mercury(II) trifluoroacetate–2,2'-bipyridyl units. The overall coordination of the two Hg atoms is different, Hg(1) being seven- and Hg(2) six-coordinate (Table 2). Each 2,2'-bipyridyl ligand is bound to an Hg atom in a bidentate manner, the bond distances falling within the range expected for Hg–N bonds. The 'bite' angles of the two 2,2'-bipyridyl ligands are identical [$71.3(6)^\circ$]; both 2,2'-bipyridyl groups are twisted about the bond joining the two rings [torsion angle $\text{N}(1)\text{--C}(5)\text{--C}(6)\text{--N}(2) = 6.6(18)^\circ$, $\text{N}(3)\text{--C}(15)\text{--C}(16)\text{--N}(4) = 10.4(18)^\circ$]. Both Hg atoms remain closely coordinated to O atoms of the trifluoroacetate groups. In the case of Hg(1) there is one short (covalent) distance to O(4) [$2.21(1) \text{ \AA}$] and two longer contacts to O(7) and O(8) of the other trifluoroacetate group [$2.53(2)$ and $2.58(2) \text{ \AA}$ respectively]; these latter Hg–O distances are longer than covalent bonds and are near to the value of 2.53 \AA estimated for the ionic Hg–O distance (Halfpenny & Small, 1978). Hg(2) makes covalent contact with O(1) and O(5) [$2.35(2)$ and $2.23(1) \text{ \AA}$ respectively].

The two molecular units, one centred on Hg(1) and the other on Hg(2), are joined *via* O(3) which bridges the Hg atoms. A further weak link, Hg(1)–O(6') [$2.81(2) \text{ \AA}$] joins structural units related by the translation c [$(') = x, y, 1 + z$]. It can be seen (Fig. 1, Table 2) that the 2,2'-bipyridyl ligand has displaced some Hg–O covalent contacts and that there is now no approximately linear coordination at Hg.

The large U_{ij} values of the F atoms indicate some disorder of the CF_3 groups within the trifluoroacetates. This feature has been noted in all other mercury(II) trifluoroacetate derivatives examined (e.g. Halfpenny & Small, 1982). The atoms O(1), O(2), C(21) and C(22) also have large U_{ij} values. This may indicate that the whole of one trifluoroacetate group [$\text{C}(21)\text{C}(22)\text{O}(1)\text{O}(2)\text{F}(1)\text{F}(2)\text{F}(3)$] is disordered to some extent, although there is no obvious reason why this group should be more disordered than any of the others. O(7) and O(8) of another trifluoroacetate group may also be slightly disordered.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36788 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

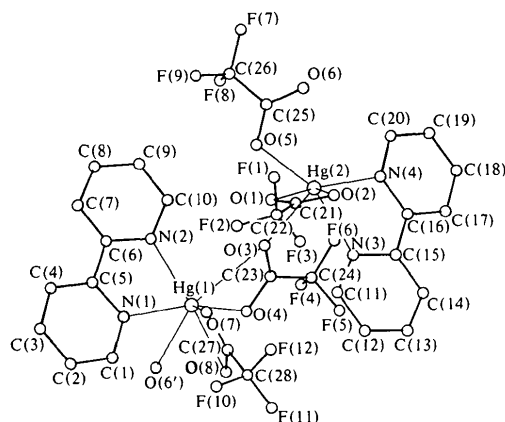


Fig. 1. View of one unit of structure of the 1:1 complex of mercury(II) trifluoroacetate with 2,2'-bipyridyl.

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