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X-ray Crystal Structure of Tris[μ-3,5-bis(trifluoromethyl)pyrazolato-N,N′]trigold(I), a Compound Containing an Inorganic Nine-membered Ring

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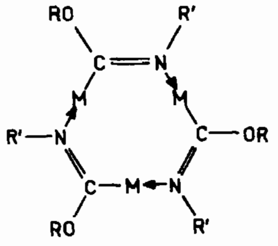
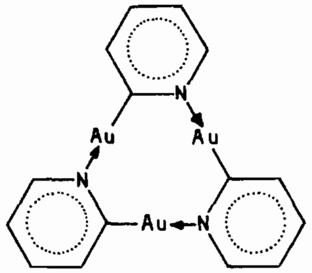
In the $\overline{Au-N-N-Au-N-N-Au-N-N}$ *non-planar ring the three linearly coordinated gold atoms are 3.344–3.355(2) Å apart, while a separation of at least 3.998(2) Å between metals belonging to different trimers rules out any intermolecular interaction, such as that found in the related* $[Au-C(OEt)=NC_6H_4Me]_3$ *compound. The unusual distances inside the planar pyrazolato rings and the very short Au–N distances (1.93(1), average) may be taken as evidence for a π-interaction between the gold atoms and the attached pyrazolato rings.*



A *I* (M = Au, R = C_2H_5, R′ = C_6H_4-*p*-CH_3)



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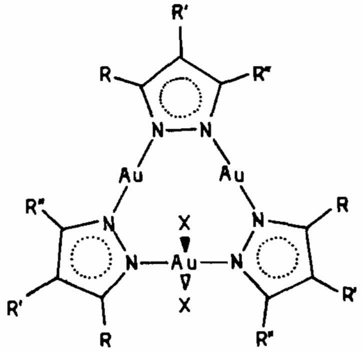

C (X is missing) or *D* (X = I)

Introduction

In the chemistry of the group IB metals linear coordination is generally not uncommon and is usual with gold(I). With coordination number two no immediate advantage is foreseen by the use of chelating moieties; nevertheless, interesting problems may arise when bidentate ligands are employed because polynuclear compounds are often obtained where the metal atoms are sufficiently far apart so as to avoid cluster formation (another characteristic of the chemistry of gold [1–3]. Nevertheless, the intermolecular distances are often such that gold–gold interactions seem to be present [4, 5].

In a series of explorative investigations on the chemistry of the group IB elements, non-cluster-like compounds were isolated for which a $M^I(\mu\text{-}L)_3$ formula was suggested. These compounds include species like *A* where L is the carbeniato anion, $-C(OR)=NR'$, and M is either gold [6] or silver [7], or *B*, where L may be an α-pyridyl, or related group [8], or *C*, where L may be a pyrazolato anion and M either gold [9, 10] or copper [11]; in addition they may include also (1-methylbenzimidazol-2-yl)gold(I)

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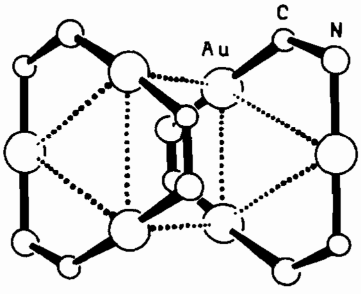
[12] and mixed-valence compounds such as $Au_3(\mu$-pyrazolato-N,N$')_3I_2$, *D* [9, 13]. We established the trinuclear nature of several of these compounds through molecular weight determination, cryoscopy, osmometry and mass-spectrometry [14]; only in the case of $[Au-C(OEt)=N(p\text{-tolyl})]_3$, *I*, is crystal structure determination available [15] which confirmed the presence of a nine-membered ring, a feature suggested to be not uncommon in this part of the periodic table [7].

The ring in the compound *I* was expected to be planar because of simple geometrical considerations. Indeed, linear *sp* hybridization of Au(I) and sp^2 hybridization of the gold-bonded nitrogen or carbon atoms require that in the $[Au-C(OR)=NR']_3$ compounds the sum of the internal angles of the ring should be $3x(180 + 120 + 120)° = 1260°$, *i.e.* the value required for a planar enneagon. Actually, the enneaatomic ring was found in the solid state to be neither regular nor planar, but rather irregular and puckered; correspondingly there was some bending of the C–Au–N groups (176.0(11), 173.0(9) and 176.1(9)°) as well as some difference in the Au···Au distances inside the ring: 3.288(1), 3.299(1) and 3.225(1) Å. Moreover the last value is comparable to the Au···Au intermolecular separations between metal atoms in a couple of trimeric molecules. The couple was found to be so arranged in the crystal as to give a characteristic Au_6 'chair', as in *E*, an arrangement which was observed also in other gold(I) derivatives, *e.g.* in the cation $[(Ph_3PAu)_3S]^+$ [4, 5].



E

In order to check whether the intermolecular interactions leading to the formation of the gold 'chair' are responsible for the observed distortions from the expected planar and regular enneaatomic ring, it was decided to determine the X-ray crystal structure of tris [μ-3,5-bis(trifluoromethyl)pyrazolato-N,N$'$]trigold(I), *II*. Here the presence of eighteen fluorine atoms (or of six strongly electronegative substituents) in proximity of the perimeter of the ring should minimize any intermolecular interaction; indeed, in spite of a molecular weight of 1200.21, *II* was found to be fairly volatile so that is could be sublimed at 140°/0.1 torr.

In this paper the X-ray crystal structure determination of *II* is reported, a complex with an inorganic Au–N–N–Au–N–N–Au–N–N ring, and some unusual features are discussed.

Results and Discussion

The crystal structure of the title compound consists of discrete trimeric molecules. The representation of the molecule with the numbering scheme, drawn with the program ORTEP [16], is given in Fig. 1. Since the differences among chemically equivalent interatomic distances or angles in the trimer have only relative meaning, their average values are given in Table I, whereas the individual values are listed in Table II.

The molecule exhibits no crystallographic symmetry and all atoms occupy general positions. Although a more regular structure of the trimer may result from solution studies (owing to averaging), in the solid state however the nine-membered ring is rather irregular and non-planar. The least-squares planes of molecular fragments, the displacements of atoms from them, the χ^2 values with the probability *P* that the fragments are non-planar, and the dihedral angles are given in Table III. The packing of the molecules in the crystal is determinated by Van der Waals approaches. The shortest intermolecular distances are given in Table IV.

Each Au atom is two-coordinated in a nearly linear arrangement with Au–N average distance of 1.93(1) Å and N–Au–N average angle of 178.7(7)°. A comparison of the N–N, C–N, and C–C average distances inside the five-membered ring for this and for other various pyrazole derivatives is given in Table V.

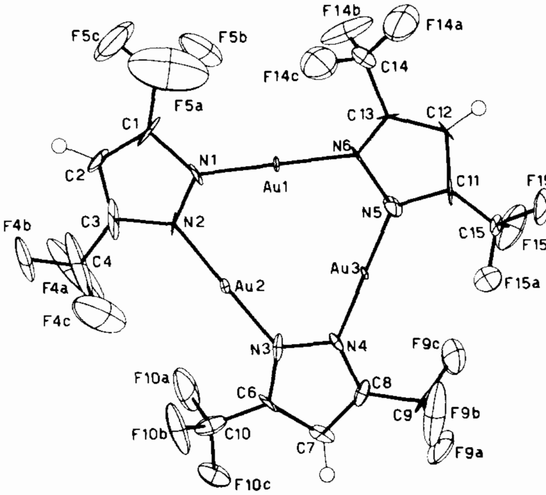


Fig. 1. ORTEP drawing of the molecular structure, with the atom labeling scheme, as viewed down *c*. The thermal ellipsoids are 50% equiprobability envelopes, the hydrogen atoms are spheres of arbitrary diameter.

TABLE I. Average Bond Distances (Å) and Angles (°) with their Standard Errors.

	N	x_m	σ_m	σ_m'
Au•••Au	3	3.348	0.003	0.001
Au–N	6	1.928	0.010	0.011
N–N	3	1.419	0.051	0.021
N–C	6	1.423	0.036	0.018
C–C	6	1.436	0.009	0.020
C–CF_3	6	1.425	0.023	0.021
C–F	18	1.350	0.011	0.012
C–H	3	0.999		
N–Au–N (endocyclic)	3	178.7	0.4	0.7
Au–N–N	6	119.9	1.6	0.8
Au–N–C	6	132.6	1.4	0.9
N–N–C	6	107.2	1.1	1.0
N–C–C	6	110.5	1.8	1.2
C–C–C	3	104.0	1.7	1.6
N–C–CF_3	6	121.1	0.9	1.3
C–C–CF_3	6	127.9	1.4	1.3
C–C–F	18	111.3	0.5	0.8
F–C–F	18	107.3	0.8	0.8
C–C–H	6	127.9		

All values were calculated with the formulae taken from ref. [17]:

$$x_m = \sum_{i=1}^{N} (x_i/\sigma_i^2) \Big/ \sum_{i=1}^{N} (1/\sigma_i^2)$$

$$\sigma_m = \left(\sum_{i=1}^{N} (x_i - x_m)^2/\sigma_i^2 \Big/ (N-1) \sum_{i=1}^{N} (1/\sigma_i^2) \right)^{1/2}$$

$$\sigma_m' = \left(\sum_{i=1}^{N} 1/\sigma_i^2 \right)^{-1/2}$$

In the structure of *II* there are three remarkable points, namely:

– the N–N, C–N and C–C average distances are longer than in all the selected pyrazoles and pyrazole derivatives listed in Table V; it might be said that the heterocyclic ring has 'expanded'.

– The Au–N average distance is significantly shorter than the Au–N σ-bonds found in the literature: 2.03(2) in i-$PrNH_2AuCl$ [27], 2.07(2) in (piperidine)AuCl [28], 2.018–2.045 in the compound *I* [15], or 2.00(2) Å in [Ph_3PAu(3,5-dimethylpyrazole-N]BF_4 [29].

– The enneaatomic ring is non-planar, as in the compound *I*.

The 'expansion' of the heterocyclic ring is not due to the peculiar type of pyrazole used. Indeed, our distances are also longer than those relating to another 3,5-bis(trifluoromethyl)pyrazolate, *trans*-($Ph_3P)_2$(OC)Ir(pz″-N), in which the plane of the heterocycle makes an angle of 85.8° with the coordination plane around the iridium atom [18]. Only in the case of [(ON))Ni(μ-pz′-N,N′)]$_2$ [26] does the nitrogen–nitrogen distance (1.457(4)) lie outside the usual range of values (1.33–1.39 Å) and for this compound, an example of trigonal planar Ni(O), back-donation through a p_π–d_π interaction between the pyrazolyl π-system and filled orbitals on nickel was proposed to account for the observed lengthening of the N–N bond. In the nearly planar nickel complex both the Ni$(NN)_2$Ni and the pyrazolato rings are slightly but significantly non-planar. On the other hand, in our compound the pyrazolato rings are planar, the aromatic character then being maintained; therefore the Au-ligand π interaction is not limited to the nitrogen atoms but is able to reach all the

TABLE II. Interatomic Distances (Å) and Bond Angles (°) with e.s.d. s in Parentheses.

Au(1)•••Au(2)	3.355(2)
Au(1)•••Au(3)	3.344(2)
Au(2)•••Au(3)	3.346(2)
Au(1)–N(1)	1.93(3)
Au(1)–N(6)	1.95(3)
Au(2)–N(2)	1.96(3)
Au(2)–N(3)	1.93(3)
Au(3)–N(4)	1.91(3)
Au(3)–N(5)	1.89(3)
N(1)–Au(1)–N(6)	179(1)
N(2)–Au(2)–N(3)	178(1)
N(4)–Au(3)–N(5)	180(1)
Au(1)–N(1)–N(2)	124(2)
Au(1)–N(1)–C(1)	128(2)
Au(1)–N(6)–N(5)	114(2)
Au(1)–N(6)–C(13)	138(2)
Au(2)–N(2)–N(1)	118(2)
Au(2)–N(2)–C(3)	132(3)
Au(2)–N(3)–N(4)	121(2)
C(7)–H(7)	1.02
C(9)–F(9a)	1.38(4)
C(9)–F(9b)	1.38(5)
C(9)–F(9c)	1.37(5)
C(10)–F(10a)	1.35(5)
C(10)–F(10b)	1.34(5)
C(10)–F(10c)	1.27(4)
C(6)–N(3)–N(4)	109(2)
N(3)–N(4)–C(8)	105(3)
N(4)–C(8)–C(7)	115(3)
C(8)–C(7)–C(6)	102(3)
C(7)–C(6)–N(3)	109(3)
N(3)–C(6)–C(10)	123(3)
C(7)–C(6)–C(10)	127(3)
C(6)–C(7)–H(7)	126
C(8)–C(7)–H(7)	133
N(4)–C(8)–C(9)	119(3)
C(7)–C(8)–C(9)	126(3)
C(8)–C(9)–F(9a)	111(3)

(continued overleaf)

TABLE II *(continued)*

Au(2)–N(3)–C(6)	131(2)	C(8)–C(9)–F(9b)	111(3)
Au(3)–N(4)–N(3)	120(2)	C(8)–C(9)–F(9c)	112(3)
Au(3)–N(4)–C(8)	134(2)	F(9a)–C(9)–F(9b)	106(3)
Au(3)–N(5)–N(6)	124(2)	F(9a)–C(9)–F(9c)	103(3)
Au(3)–N(5)–C(11)	133(2)	F(9b)–C(9)–F(9c)	113(3)
N(1)–N(2)	1.33(4)	C(6)–C(10)–F(10a)	108(3)
N(1)–C(1)	1.51(4)	C(6)–C(10)–F(10b)	111(3)
C(1)–C(2)	1.40(5)	C(6)–C(10)–F(10c)	110(3)
C(2)–C(3)	1.43(6)	F(10a)–C(10)–F(10b)	110(3)
C(3)–N(2)	1.41(5)	F(10a)–C(10)–F(10c)	110(3)
C(1)–C(5)	1.36(5)	F(10b)–C(10)–F(10c)	108(4)
C(3)–C(4)	1.42(6)	N(5)–N(6)	1.50(3)
C(2)–H(2)	0.97	N(5)–C(11)	1.49(4)
C(4)–F(4a)	1.35(7)	C(11)–C(12)	1.46(4)
C(4)–F(4b)	1.37(6)	C(12)–C(13)	1.42(5)
C(4)–F(4c)	1.34(6)	C(13)–N(6)	1.26(5)
C(5)–F(5a)	1.47(6)	C(11)–C(15)	1.38(5)
C(5)–F(5b)	1.34(6)	C(13)–C(14)	1.50(5)
C(5)–F(5c)	1.29(5)	C(12)–H(12)	1.00
C(1)–N(1)–N(2)	108(3)	C(14)–F(14a)	1.38(6)
N(1)–N(2)–C(3)	110(3)	C(14)–F(14b)	1.26(5)
N(2)–C(3)–C(2)	108(3)	C(14)–F(14c)	1.38(6)
C(3)–C(2)–C(1)	107(3)	C(15)–F(15a)	1.37(4)
C(2)–C(1)–N(1)	106(3)	C(15)–F(15b)	1.35(4)
N(1)–C(1)–C(5)	124(3)	C(15)–F(15c)	1.35(4)
C(2)–C(1)–C(5)	130(3)	C(11)–N(5)–N(6)	103(2)
C(1)–C(2)–H(2)	127	N(5)–N(6)–C(13)	109(2)
C(3)–C(2)–H(2)	125	N(6)–C(13)–C(12)	117(3)
N(2)–C(3)–C(4)	121(4)	C(13)–C(12)–C(11)	103(3)
C(2)–C(3)–C(4)	130(4)	C(12)–C(11)–N(5)	108(3)
C(3)–C(4)–F(4a)	111(5)	N(5)–C(11)–C(15)	119(3)
C(3)–C(4)–F(4b)	109(4)	C(12)–C(11)–C(15)	132(3)
C(3)–C(4)–F(4c)	110(4)	C(11)–C(12)–H(12)	125
F(4a)–C(4)–F(4b)	109(5)	C(13)–C(12)–H(12)	131
F(4a)–C(4)–F(4c)	111(5)	N(6)–C(13)–C(14)	120(3)
F(4b)–C(4)–F(4c)	106(4)	C(12)–C(13)–C(14)	123(3)
C(1)–C(5)–F(5a)	107(4)	C(13)–C(14)–F(14a)	113(3)
C(1)–C(5)–F(5b)	115(3)	C(13)–C(14)–F(14b)	114(4)
C(1)–C(5)–F(5c)	114(4)	C(13)–C(14)–F(14c)	109(3)
F(5a)–C(5)–F(5b)	107(4)	F(14a)–C(14)–F(14b)	109(4)
F(5a)–C(5)–F(5c)	111(4)	F(14a)–C(14)–F(14c)	102(4)
F(5b)–C(5)–F(5c)	102(3)	F(14b)–C(14)–F(14c)	110(4)
N(3)–N(4)	1.40(4)	C(11)–C(15)–F(15a)	113(3)
N(3)–C(6)	1.44(4)	C(11)–C(15)–F(15b)	110(3)
C(6)–C(7)	1.46(5)	C(11)–C(15)–F(15c)	114(3)
C(7)–C(8)	1.44(5)	F(15a)–C(15)–F(15b)	103(3)
C(8)–N(4)	1.40(4)	F(15a)–C(15)–F(15c)	109(3)
C(6)–C(10)	1.48(6)	F(15b)–C(15)–F(15c)	108(3)
C(8)–C(9)	1.43(5)		

heterocyclic moiety. As a consequence not only the N–N distances but also the C–N and C–C bonds are affected so as to reach the average values reported here. Obviously, such an interaction is not possible for the iridium complex where the coordination plane and the azolato ring are nearly perpendicular.

Such a gold–azolato π-interaction might be the cause of the short Au–N distances. Indeed, an interaction between gold *5d* or—perhaps [30]—*6p* orbitals and a π^* vacant orbital belonging to the pyrazolato ring allows back-bonding to take place; as a consequence there is a short Au–N bond, a lengthening of the N–N bond and a change of the electron density on the pyrazolato ring.

An additional reason for the very short Au–N bond may be a small *trans*-influence of the 3,5-bis(trifluoromethyl)pyrazolato ligand. On the basis of the X-ray crystal structure of $[Ph_3PAuL]BF_4$

TABLE III. Planarity of Molecular Fragments.

Plane	Equation[a], χ^2, P	Atoms	Displacements (Å)
I	$0.2570X' - 0.3022Y' - 0.9179Z' + 1.3976 = 0$	Au(1)*	0.0005(13)
		Au(2)*	−0.0003(14)
	$\chi^2 = 37.60$ (n = 6)	Au(3)*	−0.0002(13)
	$P > 99.0\%$	N(1)*	0.008(30)
		N(2)*	−0.109(31)
		N(3)*	0.078(26)
		N(4)*	0.080(30)
		N(5)*	−0.063(28)
		N(6)*	−0.052(26)
II	$0.2568X' - 0.3021Y' - 0.9180Z' + 1.3997 = 0$	Au(1)*	0
		Au(2)*	0
		Au(3)*	0
		N(1)	0.007(30)
		N(2)	−0.110(31)
		N(3)	0.078(26)
		N(4)	0.081(30)
		N(5)	−0.063(28)
		N(6)	−0.053(26)
III	$0.2016X' - 0.2133Y' - 0.9560Z' + 1.4708 = 0$	N(1)*	−0.011(30)
		N(2)*	0.018(32)
	$\chi^2 = 1.02$ (n = 2)	C(1)*	0.003(36)
	$P = 39.1\%$	C(2)*	0.010(37)
		C(3)*	−0.030(44)
		C(4)	−0.046(47)
		C(5)	0.134(43)
		Au(1)	−0.162(1)
		Au(2)	0.206(1)
		H(2)	−0.009
IV	$0.2960X' - 0.3077Y' - 0.9042Z' + 0.9804 = 0$	N(3)*	−0.001(26)
		N(4)*	−0.005(30)
	$\chi^2 = 0.41$ (n = 2)	C(6)*	0.010(38)
	$P = 18.5\%$	C(7)*	−0.013(36)
		C(8)*	0.017(41)
		C(9)	−0.010(40)
		C(10)	−0.108(37)
		Au(2)	−0.005(1)
		Au(3)	−0.022(1)
		H(7)	−0.051
V	$0.2378X' - 0.3583Y' - 0.9028Z' + 1.9201 = 0$	N(5)*	0.015(28)
		N(6)*	−0.011(26)
	$\chi^2 = 0.97$ (n = 2)	C(11)*	−0.020(34)
	$P = 37.6\%$	C(12)*	0.009(32)
		C(13)*	0.009(41)
		C(14)	0.121(43)
		C(15)	0.138(36)
		Au(1)	−0.078(1)
		Au(3)	0.017(1)
		H(12)	0.021

Dihedral angles (°)

I/III	173.6	I/IV	177.6	I/V	176.5
III/IV	171.8	III/V	170.9	IV/V	175.6

[a] Transformation matrix from triclinic X, Y, Z to orthogonal X', Y', Z' coordinates: $\begin{pmatrix} \sin\gamma & 0 & -\sin\alpha\cos\beta^* \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\sin\beta^* \end{pmatrix}$

*These atoms were included in the calculation of the plane.

TABLE IV. Shortest Intermolecular Approaches (Å).

Au(1)···Au(3)	(i) 3.998(2)	C(8)···F(14c)	(i) 3.15(6)
Au(2)···Au(3)	(ii) 4.042(2)	F(4a)···F(15c)	(ii) 2.65(6)
C(1)···F(15a)	(i) 3.06(4)	F(5a)···F(9b)	(i) 2.43(5)
C(3)···F(9c)	(ii) 3.08(6)		

Symmetry code
(i) $2-x$ $2-y$ $1-z$ (ii) $2-x$ $2-y$ $-z$

[29] and of the $^1J(^{195}Pt-^{31}P)$ NMR coupling constants of several $\{Ph_2P(CH_2)_2PPh_2\}Pt(pz\text{-}N)_2$ compounds or $[Ph_2P(CH_2)_nPPh_2PtL_2]^{2+}$ cations ($n = 2, 3, 4$) [31], it has been already pointed out that when L is 3,5-dimethylpyrazole these heterocycles have a weak *trans*-influence, comparable to that of the chloride group. It is therefore not untenable that the wide variation of the Au–N distances, from 2.07 to 1.93 Å, might reflect *trans*-influence, and that in this hypothesis the 3,5-bis(trifluoromethyl)pyrazolato ligand might be the weakest between the nitrogen ligands compared [27, 28, 15, 29] owing to its peculiar substituents. A similar conclusion is reached upon consideration of the X-ray crystal structure of *trans*-$(Ph_3P)_2(OC)Ir(pz''\text{-}N)$ [18].

In order to appreciate the importance of *trans*-influence in the chemistry of gold(I), it is pointed out that a span of 0.27 Å is covered by the Au–C distances in the series LAuCN: from 2.12 when L = CN, through 2.01 (L = MeNC) down to 1.85(4) Å when L = PPh_3 [32, 33].

The average intramolecular Au···Au distance, 3.348(3) Å, indicates a weak metal–metal interaction. Indeed, although longer than the separation found in gold clusters (2.84–3.2 Å) [5] or in $[Au\text{–}C(OEt){=}NC_6H_4Me]_3$ (3.225–3.229 Å) [15], it is comparable with the value recorded for ClAu(CO) (3.38 Å) [34] and is still shorter than the intermolecular interaction (3.40 Å) in $(AuS_2CNPr_2)_2$ [35]. Amongst the pyrazolato derivatives of the group IB elements a related, more complex molecule, namely $[Cu_3(OH)(Pz)_3(HPz)_2(NO_3)_2]\cdot H_2O$, was recently shown [36] to contain *inter alia* a nine-membered ring formed by three copper(II) atoms and by three bridging pyrazolato ligands. Although smaller, the copper atoms have intratrimer separations (3.3247(7)–3.3652(7) Å) in the same range as gold atoms in our compound *II*;

TABLE V. Comparison of the Distances inside Pyrazole Rings.

Compound[a]	Distances (Å)			Reference
	N–N	C–N	C–C	
$Au_3(\mu\text{-}pz'')_3$	1.42(5)[b]	1.42(4)[b]	1.44(2)[b]	This work
trans-$(Ph_3P)_2(OC)Ir(pz''\text{-}N)$	1.360(7)	1.340(8) 1.347(8)	1.377(9) 1.384(9)	[18]
pyrazole	1.344(2)	1.335(3) 1.323(8)	1.369(10) 1.361(11)	[19]
1-(*o*-$NO_2C_6H_4$)-3-Me-5-t-Bu-pyrazole	1.372(3)	1.374(4) 1.324(4)	1.390(4) 1.371(4)	[20]
$[(pz'\text{-}N)HB(\mu\text{-}pz'\text{-}N,N']_2$[c]	1.386(8)	1.343(9) 1.349(10)	1.368(12) 1.368(11)	[21]
The same,[d]	1.364(8)	1.357(11) 1.364(8)	1.320(10) 1.389(12)	[21]
$P(Pz\text{-}N)_3$	1.374(6)	1.303(8) 1.333(5)	1.331(8) 1.372(10)	[22]
$[(ON)_2Fe(\mu\text{-}pz'\text{-}N,N')]_2$	1.381(2)	1.347(2) 1.351(2)	1.377(3) 1.382(3)	[23]
$(C_5H_5)_3UPz$	1.318(10)	1.350(12) 1.358(13)	1.340(16) 1.347(16)	[24]
e	1.393(4)	1.329(5) 1.338(5)	1.363(9) 1.402(8)	[25]
$[(ON)Ni(\mu\text{-}pz'\text{-}N,N')]_2$	1.457(4)	1.338(4) 1.344(4)	1.368(6) 1.370(6)	[26]

[a] Pz indicates the pyrazolato anion, $C_3H_3N_2^-$; pz′ indicates the 3,5-dimethylpyrazolato and pz″ the 3,5-bis(trifluoromethyl)-pyrazolato anion, resp. [b] Averaged values. [c] Values for the bridging pyrazolato ligands. [d] Values for the terminal pyrazolato ligands. [e] [Dimethyl(3,5-dimethylpyrazol-1-yl)(ethanolamino)gallato(N(2),O,N(3))] = (η^3-cycloheptatrienyl)dicarbonylmolybdenum.

and, being in a d^9 configuration, their interaction is put into evidence thanks to relatively strong magnetic coupling (intratrimer).

The Au•••Au distance between trimers is not smaller than 3.998(2) Å, so that it excludes any metal–metal interaction (already observed in the compound *I* [15] and in several other gold compounds [5]). It is then likely that some of the irregularities and the puckering of the enneaatomic ring in the case of *I* are consequences of solid-state gold–gold interactions, which result in the formation of an Au_6 chair. In addition, such interactions—which are common in the crystalline compounds of gold(I) [5, 15]—must be rather weak, since they are not found when bulky substituents are present as in the case of the compound *II*, which appears to have a less irregular and puckered enneaatomic ring than the compound *I*.

Experimental

The title compound was obtained as described in ref. [10], and recrystallized from MeOH/toluene as colourless neeedles.

Data Collection

A prismatic crystal having approximate dimensions 0.58 × 0.13 × 0.14 mm was used for data collection.

Accurate unit-cell dimensions were obtained by least-squares procedure of 2ϑ values for 25 reflections measured on a single-crystal Philips PW 1100 computer controlled diffractometer with graphite-monochromated MoKα radiation at the Centro di Studio per la Cristallografia Strutturale del C.N.R., Pavia, Italy.

The intensities of 3853 independent reflections were collected at room temperature within the angular range $2 \leqslant \vartheta \leqslant 24°$, using the $\omega/2\vartheta$ scan technique with a constant speed of $0.120° \ s^{-1}$ in ω. Three standard reflections, monitored every 240 min, revealed an evident decomposition of the specimen with formation of small gold particles: for this reason the structure refinement could not be accurate.

The intensities were corrected for Lorentz and polarization effects, and for absorption [37]. The structure factors were put on an absolute scale [38] and an overall isotropic thermal factor was obtained thereby. 2360 reflections having $I \geqslant 3\sigma(I)$ were considered observed and used in the structure analysis.

Crystal Data

$C_{15}H_3N_6F_{18}Au_3$, F.W. 1200.21, triclinic, *a* 11.904(3), *b* 12.171(4), *c* 9.346(1) Å, α 98.63(1), β 81.94(1), γ 113.47(2)°; *V* 1223.1 Å^3; $Z = 2$, *Dc* 3.26 g cm^{-3}; $F(000) = 1068$, λ(Mo-Kα) 0.7107 Å, μ(Mo-$K\alpha$) 187.13 cm^{-1}.

The statistical distribution of the normalized structure factors indicates the centric space group $P\bar{1}$.

Structure Determination and Refinement

The structure was solved by Patterson and Fourier methods. The positional and isotropic thermal parameters of the three unique gold atoms, derived from the Patterson map, were refined in three cycles of least-squares refinement to *R* 0.178. All the remaining non-hydrogen atoms were located from a three-dimensional difference Fourier map, phased on the Au atoms. Three cycles of least-squares refinement, including scale factor and individual isotropic thermal parameters for Au, N, C, F atoms, reduced the *R* index to 0.141. After several anisotropic refinement cycles the *R* index dropped to 0.078.

The three hydrogen atoms were located from a final difference Fourier map and included in the subsequent least-squares refinement in fixed positions with the same isotropic thermal parameters as the atom to which they were attached. The final *R* was 0.066 for the observed reflections.

At all stages of the analysis the observed reflections were given unit weights, since the use of weights $\sigma^{-2}(|F_o|)$ led to the same results but also to some non-positive definite thermal factors.

Scattering factors for neutral atoms were taken from standard tables [39] and those for hydrogen atoms from ref. [40]. Anomalous dispersion effects were included in the scattering factors for Au.

The positional and thermal parameters are given in Tables VI and VII. A list of structure factors can be obtained from one of the authors, (B. Bovio) on request.

TABLE VI. Final Coordinates (with e.s.d.s in Parentheses).

Atom	*x*	*y*	*z*
Au(1)	1.1995(1)	1.0752(1)	0.3234(1)
Au(2)	1.0215(1)	1.1772(1)	0.1789(1)
Au(3)	0.9126(1)	0.8910(1)	0.2545(1)
N(1)	1.2565(24)	1.2391(21)	0.2762(32)
N(2)	1.1858(23)	1.2858(20)	0.2309(35)
C(1)	1.3823(28)	1.3379(31)	0.2922(39)
C(2)	1.3741(27)	1.4418(28)	0.2559(40)
C(3)	1.2505(42)	1.4102(29)	0.2229(48)
C(4)	1.1942(42)	1.4818(34)	0.1808(51)
C(5)	1.4817(27)	1.3194(31)	0.3206(48)
F(4a)	1.2005(64)	1.4770(49)	0.0344(54)
F(4b)	1.2522(34)	1.5989(20)	0.2363(49)
F(4c)	1.0779(37)	1.4478(43)	0.2397(48)
F(5a)	1.4691(46)	1.3083(55)	0.4776(41)
F(5b)	1.4937(31)	1.2193(30)	0.2506(45)
F(5c)	1.5860(24)	1.4022(29)	0.2819(57)
H(2)	1.4383	1.5224	0.2578
N(3)	0.8587(23)	1.0668(19)	0.1326(28)
N(4)	0.8135(23)	0.9467(21)	0.1643(33)

(continued overleaf)

TABLE VI *(continued)*

Atom	*x*	*y*	*z*
C(6)	0.7661(28)	1.0849(28)	0.0656(42)
C(7)	0.6572(29)	0.9732(30)	0.0564(39)
C(8)	0.6962(30)	0.8931(28)	0.1156(46)
C(9)	0.6234(27)	0.7691(26)	0.1352(45)
C(10)	0.7780(28)	1.2038(34)	0.0300(40)
F(9a)	0.5230(22)	0.7256(21)	0.0553(40)
F(9b)	0.5763(37)	0.7554(21)	0.2784(34)
F(9c)	0.6849(25)	0.6954(20)	0.0812(44)
F(10a)	0.8766(28)	1.2443(21)	−0.0668(31)
F(10b)	0.7927(32)	1.2832(19)	0.1495(29)
F(10c)	0.6827(24)	1.1946(24)	−0.0242(41)
H(7)	0.5771	0.9622	0.0176
N(5)	1.0109(23)	0.8355(21)	0.3421(30)
N(6)	1.1411(21)	0.9113(19)	0.3756(29)
C(11)	0.9870(31)	0.7196(24)	0.3997(37)
C(12)	1.0999(26)	0.7290(24)	0.4542(34)
C(13)	1.1824(25)	0.8485(29)	0.4323(46)
C(14)	1.3144(35)	0.8976(32)	0.4640(47)
C(15)	0.8784(27)	0.6227(25)	0.3730(40)
F(14a)	1.3407(29)	0.8229(30)	0.5396(54)
F(14b)	1.3897(21)	0.9211(32)	0.3522(36)
F(14c)	1.3370(26)	0.9999(25)	0.5615(39)
F(15a)	0.7767(18)	0.6477(19)	0.4247(30)
F(15b)	0.8661(22)	0.5319(18)	0.4495(34)
F(15c)	0.8704(24)	0.5790(21)	0.2322(26)
H(12)	1.1110	0.6633	0.4965

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TABLE VII. Thermal Parameters, with e.s.d.'s in Parentheses.[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au(1)	0.0023(1)	0.0004(1)	0.0096(2)	0.0001(1)	−0.0018(1)	0.0010(1)
Au(2)	0.0023(1)	0.0010(1)	0.0095(2)	0.0005(1)	−0.0011(1)	0.0013(1)
Au(3)	0.0020(1)	0.0007(1)	0.0094(2)	0.0005(1)	−0.0019(1)	0.0014(1)
N(1)	0.0059(25)	0.0015(19)	0.0132(46)	0.0021(18)	−0.0051(27)	0.0006(23)
N(2)	0.0037(22)	0.0005(18)	0.0169(52)	−0.0010(16)	−0.0013(27)	0.0022(24)
C(1)	0.0036(27)	0.0061(32)	0.0111(51)	−0.0043(24)	−0.0056(29)	0.0056(32)
C(2)	0.0024(25)	0.0047(28)	0.0115(54)	−0.0019(21)	−0.0015(29)	0.0055(32)
C(3)	0.0147(52)	0.0018(27)	0.0154(69)	0.0005(30)	−0.0038(46)	0.0049(34)
C(4)	0.0507(170)	0.0058(43)	0.0137(86)	0.0130(72)	−0.0190(102)	−0.0015(48)
C(5)	0.0007(23)	0.0043(28)	0.0193(70)	−0.0013(21)	−0.0009(31)	−0.0019(34)
F(4a)	0.0624(130)	0.0261(76)	0.0239(97)	0.0355(92)	−0.0252(88)	−0.0060(67)
F(4b)	0.0228(47)	0.0027(18)	0.0556(100)	0.0058(24)	−0.0099(54)	0.0003(32)
F(4c)	0.0207(47)	0.0264(65)	0.0312(72)	0.0180(47)	0.0036(47)	0.0062(54)
F(5a)	0.0327(69)	0.0601(102)	0.0174(62)	0.0310(73)	−0.0067(51)	0.0082(61)
F(5b)	0.0173(38)	0.0155(37)	0.0384(82)	0.0134(33)	−0.0027(43)	−0.0015(43)
F(5c)	0.0072(25)	0.0188(35)	0.0737(129)	−0.0061(25)	−0.0114(46)	0.0242(57)
N(3)	0.0058(24)	0.0010(19)	0.0056(38)	−0.0004(17)	−0.0002(24)	0.0010(21)
N(4)	0.0042(22)	0.0022(20)	0.0133(47)	0.0019(18)	−0.0015(25)	0.0029(24)
C(6)	0.0049(28)	0.0039(27)	0.0136(59)	0.0037(24)	0.0017(32)	0.0048(32)
C(7)	0.0052(29)	0.0062(30)	0.0097(51)	0.0035(25)	−0.0031(30)	0.0034(31)
C(8)	0.0048(29)	0.0018(26)	0.0173(67)	−0.0009(22)	−0.0043(35)	−0.0019(32)
C(9)	0.0023(25)	0.0018(24)	0.0157(64)	−0.0019(20)	−0.0017(32)	−0.0004(31)
C(10)	0.0031(27)	0.0095(39)	0.0069(50)	0.0016(26)	−0.0022(29)	0.0004(36)
F(9a)	0.0088(24)	0.0079(23)	0.0449(75)	−0.0035(19)	−0.0163(36)	0.0084(33)
F(9b)	0.0294(54)	0.0049(21)	0.0160(48)	−0.0022(26)	0.0083(40)	0.0007(25)
F(9c)	0.0110(28)	0.0046(20)	0.0440(84)	0.0029(20)	−0.0001(38)	−0.0014(31)

(continued on facing page)

TABLE VII *(continued)*

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
F(10a)	0.0187(37)	0.0072(21)	0.0196(48)	0.0067(24)	0.0042(33)	0.0076(26)
F(10b)	0.0270(46)	0.0046(19)	0.0136(41)	0.0086(25)	0.0028(33)	−0.0002(22)
F(10c)	0.0103(27)	0.0105(27)	0.0437(80)	0.0057(22)	−0.0105(37)	0.0079(36)
N(5)	0.0056(24)	0.0030(21)	0.0100(41)	0.0019(19)	−0.0052(25)	0.0004(23)
N(6)	0.0037(20)	0.0010(17)	0.0093(39)	0.0015(16)	−0.0023(22)	0.0008(20)
C(11)	0.0076(32)	0.0003(21)	0.0087(48)	0.0006(21)	0.0032(31)	0.0012(24)
C(12)	0.0049(26)	0.0019(22)	0.0073(43)	0.0028(20)	−0.0006(26)	0.0008(25)
C(13)	0.0005(22)	0.0044(28)	0.0204(70)	0.0010(21)	−0.0022(31)	−0.0003(35)
C(14)	0.0066(33)	0.0054(33)	0.0133(66)	0.0040(29)	−0.0021(40)	0.0020(37)
C(15)	0.0038(27)	0.0020(24)	0.0126(56)	−0.0007(21)	−0.0035(30)	0.0048(30)
F(14a)	0.0121(32)	0.0142(35)	0.0631(112)	−0.0002(28)	−0.0170(50)	0.0170(52)
F(14b)	0.0034(20)	0.0246(48)	0.0221(57)	0.0019(24)	−0.0029(28)	0.0001(40)
F(14c)	0.0120(29)	0.0113(29)	0.0322(68)	0.0044(24)	−0.0122(37)	−0.0053(35)
F(15a)	0.0054(19)	0.0075(20)	0.0217(47)	0.0022(16)	0.0010(23)	0.0037(24)
F(15b)	0.0108(25)	0.0040(18)	0.0343(59)	−0.0018(17)	−0.0085(31)	0.0096(26)
F(15c)	0.0129(28)	0.0089(23)	0.0108(36)	−0.0035(20)	−0.0057(26)	−0.0012(22)

Atom	B (Å^2)	Atom	B (Å^2)	Atom	B (Å^2)
H(2)	2.71	H(7)	2.52	H(12)	1.64

[a] The anisotropic parameters are in the form: exp $-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

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