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THE CRYSTAL STRUCTURE OF TRIS-μ-[(ETHOXY)(*N-p*-TOLYLIMINO)METHYL-*N*,*C*]TRIGOLD(I), [(EtO)(MeC$_6$H$_4$N=)CAu]$_3$

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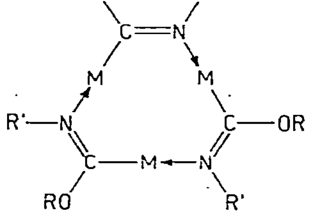
Summary

The crystal structure of the compound [(EtO)(MeC$_6$H$_4$N=)CAu]$_3$ has been determined by X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions: a 15.110(13), b 14.267(11), c 7.913(8) Å; α 87.6(1), β 108.6(1), γ 100.5(1)°; V 1589(1) Å^3. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.055$ for 2608 observed reflections. Trimeric complexes are present in which three C(OEt)=N(C$_6$H$_4$Me) groups bridge the gold atoms through the N and C atoms. The gold atoms are two coordinated in a nearly linear arrangement. The Au—Au distances (3.224, 3.288 and 3.299 Å) exclude significant metal—metal interactions. The nine-membered ring is rather irregular and puckered.

Introduction

The trimeric molecule [AuC(OMe)=NC$_6$H$_{11}$]$_3$ was described some years ago by Minghetti and Bonati [1], who suggested the structure A (R = Me and R′ =



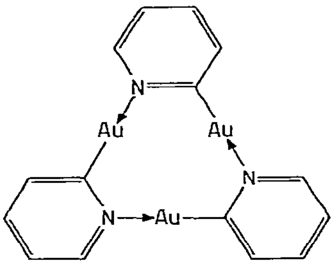
A (M = Au, Ag)

C_6H_{11}) where the gold atoms are two-coordinate and the ligand $C(OMe){=}NC_6H_{11}$ acts as a bridge between two gold atoms through the N and C atoms. Later other examples of such compounds were obtained [2] by reaction 1, where R′

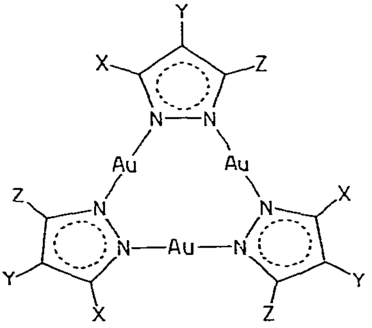
$$3(CH_3)_2SAuCl + 3\ R'N{\equiv}C + 3\ KOH + 3\ ROH \rightarrow$$
$$3(CH_3)_2S + [AuC(OR){=}NR']_3 + 3\ KCl + 3\ H_2O \qquad (1)$$

is an aliphatic, cycloaliphatic or aromatic group. In all cases these compounds were trimeric in solution and in the vapour phase (mass spectrometry) [3]. From simple geometrical considerations these trimers were suggested to be nearly planar, with gold—gold distances of ca. 3.3 Å which exclude significant metal—metal interactions, so that they constitute examples of polynuclear derivatives not containing a cluster of metal atoms.

Analogous trimeric systems were suggested for the corresponding silver derivatives [4] and also for some gold(I) derivatives of pyridines [5] (structure B) and pyrazoles [6] (structure C).



B



C

Such an arrangement seems now to be rather common for elements of Group IB (in the oxidation state +1); and so in order to check the proposed structure of this class of complexes, the crystal structure of the title compound was determined by X-ray diffraction.

Experimental

Collection of X-ray data

The compound $[(EtO)(MeC_6H_4N{=})CAu]_3$, m.p. (dec.) 181—183°C, was obtained as described in ref. [2] but with use of EtOH in place of MeOH. It was recrystallized from $CHCl_3/Et_2O$ as very thin colourless needles. It was very difficult to find a crystal having dimensions suitable for an X-ray analysis but finally a crystal with dimensions of ca. 0.05 × 0.09 × 0.20 mm was obtained and used for data collection. Preliminary cell parameters obtained by rotation and Weissenberg photographs were subsequently refined by least-squares fit to θ values of 17 reflections carefully measured on a Siemens AED single crystal diffractometer. Cell dimensions and crystal data are summarized in Table 1.

A total of 4966 independent reflections with $\theta \leqslant 24°$ were measured at room temperature on the same diffractometer, using the ω—2θ scan technique and

TABLE 1

CRYSTAL DATA FOR THE COMPOUND $[(EtO)(MeC_6H_4N{=})CAu]_3$

a 15.110(13) Å	Triclinic
b 14.267(11) Å	Space group: $P\bar{1}$
c 7.913(8) Å	Mo-K_α radiation
α 87.6(1)°	μ 133.4 cm^{-1}
β 108.6(1)°	$Z = 2$
γ 100.5(1)°	d_{calc} 2.25 g cm^{-3}
V 1589(1) $Å^3$	

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$)

	x/a (σ)	y/b (σ)	z/c (σ)
Au(1)	—795(1)	5065(1)	2118(2)
Au(2)	1416(1)	5436(1)	2107(2)
Au(3)	573(1)	3456(1)	3611(2)
O(1)	—1150(12)	2287(14)	3962(27)
O(2)	—648(12)	7125(13)	1360(25)
O(3)	3086(13)	4511(14)	2614(29)
N(1)	—1364(15)	3728(15)	2677(38)
N(2)	714(15)	6543(15)	1697(29)
N(3)	1949(13)	3726(13)	3610(27)
C(11)	—767(17)	3112(18)	3526(29)
C(21)	—553(18)	1615(16)	4708(42)
C(31)	—1210(23)	689(17)	4930(51)
C(12)	—196(19)	6343(19)	1759(32)
C(22)	—1621(18)	6970(20)	1395(44)
C(32)	—1882(23)	7961(21)	1334(49)
C(13)	2174(17)	4428(17)	2796(30)
C(23)	3396(24)	5366(23)	1712(48)
C(33)	4301(25)	5270(35)	1335(68)
C(101)	—5324(16)	2615(25)	2241(49)
C(102)	3117(20)	10035(18)	995(44)
C(103)	4218(25)	834(23)	6652(50)
C(41)	—2384(9)	3458(12)	2524(24)
C(51)	—2793(9)	4030(12)	3340(24)
C(61)	—3745(9)	3771(12)	3236(24)
C(71)	—4288(9)	2941(12)	2315(24)
C(81)	—3880(9)	2369(12)	1499(24)
C(91)	—2928(9)	2627(12)	1604(24)
C(42)	1227(11)	7471(10)	1532(23)
C(52)	2159(11)	7650(10)	2683(23)
C(62)	2760(11)	8499(10)	2564(23)
C(72)	2430(11)	9169(10)	1294(23)
C(82)	1499(11)	8990(10)	143(23)
C(92)	898(11)	8141(10)	262(23)
C(43)	2554(12)	2994(12)	4392(25)
C(53)	2221(12)	2055(12)	3764(25)
C(63)	2751(12)	1347(12)	4500(25)
C(73)	3614(12)	1579(12)	5862(25)
C(83)	3946(12)	2519(12)	6489(25)
C(93)	3416(12)	3226(12)	5754(25)

Zr-filtered Mo-K_α radiation. 2608 reflections were used in the structure analysis as their intensities were greater than twice their standard deviations. The intensity data were corrected for Lorentz and polarization factors, but no absorption correction was applied because of the low value of μR. The absolute scale and the mean temperature factor were determined by the Wilson's method.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods. The refinement was carried out by full-matrix least squares using the SHELX system of programs [7] with anisotropic thermal parameters for the non-tolyl atoms. The tolyl groups were refined as a rigid body and with isotropic thermal parameters. The

TABLE 3

THERMAL PARAMETERS ($\times 10^4$) IN THE FORM: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12})]$

	$U_{11}(\sigma)$	$U_{22}(\sigma)$	$U_{33}(\sigma)$	$U_{23}(\sigma)$	$U_{13}(\sigma)$	$U_{12}(\sigma)$
Au(1)	38(1)	47(1)	63(1)	6(1)	16(1)	3(1)
Au(2)	42(1)	45(1)	63(1)	7(1)	20(1)	9(1)
Au(3)	34(1)	52(1)	65(1)	10(1)	17(1)	6(1)
O(1)	35(10)	68(13)	87(16)	13(12)	19(10)	—1(9)
O(2)	53(12)	61(13)	70(14)	3(10)	32(10)	6(9)
O(3)	54(12)	65(13)	102(17)	14(12)	39(12)	3(10)
N(1)	29(12)	38(13)	139(24)	—5(14)	20(14)	—7(10)
N(2)	50(14)	43(13)	51(14)	—12(11)	12(11)	8(10)
N(3)	42(12)	31(11)	55(14)	20(11)	28(10)	7(9)
C(11)	43(15)	57(17)	19(14)	15(12)	10(11)	—10(13)
C(21)	56(18)	28(13)	100(24)	19(15)	25(17)	7(12)
C(31)	112(27)	37(16)	135(33)	9(18)	67(25)	10(16)
C(12)	52(18)	59(17)	31(15)	—32(13)	13(13)	6(13)
C(22)	29(16)	119(28)	90(26)	5(21)	29(16)	16(16)
C(32)	72(23)	85(25)	115(29)	8(21)	39(21)	44(19)
C(13)	44(16)	45(15)	24(14)	—5(12)	14(12)	2(11)
C(23)	143(35)	82(24)	100(28)	31(21)	84(27)	7(23)
C(33)	97(28)	174(47)	189(49)	35(38)	77(32)	45(30)
C(101)	98(12)					
C(102)	79(10)					
C(103)	108(13)					
C(41)	45(7)					
C(51)	53(7)					
C(61)	56(8)					
C(71)	66(8)					
C(81)	69(9)					
C(91)	57(7)					
C(42)	42(6)					
C(52)	54(7)					
C(62)	63(8)					
C(72)	62(8)					
C(82)	60(8)					
C(92)	63(8)					
C(43)	58(8)					
C(53)	72(9)					
C(63)	65(8)					
C(73)	64(8)					
C(83)	73(9)					
C(93)	66(9)					

final R was 0.055 for the observed reflections only. The atomic scattering factors (corrected for the anomalous dispersion of gold) were taken from ref. 8. Unit weights were used in the first stages of the refinement, then a weighting factor $w^{-1} = \sigma^2(F_0) + 0.002F_0^2$ was introduced. The atomic fractional coordinates and thermal parameters are listed in Tables 2 and 3.

A list of observed and calculated structure factors is available from the authors on request.

All the calculations were performed on the CYBER 76 computer of Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna) with financial support from the University of Parma.

Discussion and results

The structure of the compound is represented in Fig. 1. It consists of discrete trimeric molecules formed by three $C(OEt)=N(C_6H_4Me)$ groups bridging the gold atoms through the N and C atoms. Bond distances and angles in the trimer are given in Table 4. The gold atoms are two coordinated in a nearly linear arrangement with Au—C distances of 1.935(28), 1.953(25) and 1.975(26) Å, Au—N distances of 2.018(22), 2.037(23) and 2.045(21) Å and C—Au—N angles of 173.1(9), 176.0(11) and 176.1(9)°. Little and often only poorly accurate information on Au^I—C and Au^I—N σ-bonds is contained in the literature. An Au—C distance of 1.94(2) Å formed to an acetylenic carbon was found in $[(C_3H_7NH_2)Au(C{\equiv}CPh)]$ [9], and distances of 2.05(6) and 2.10 Å formed to

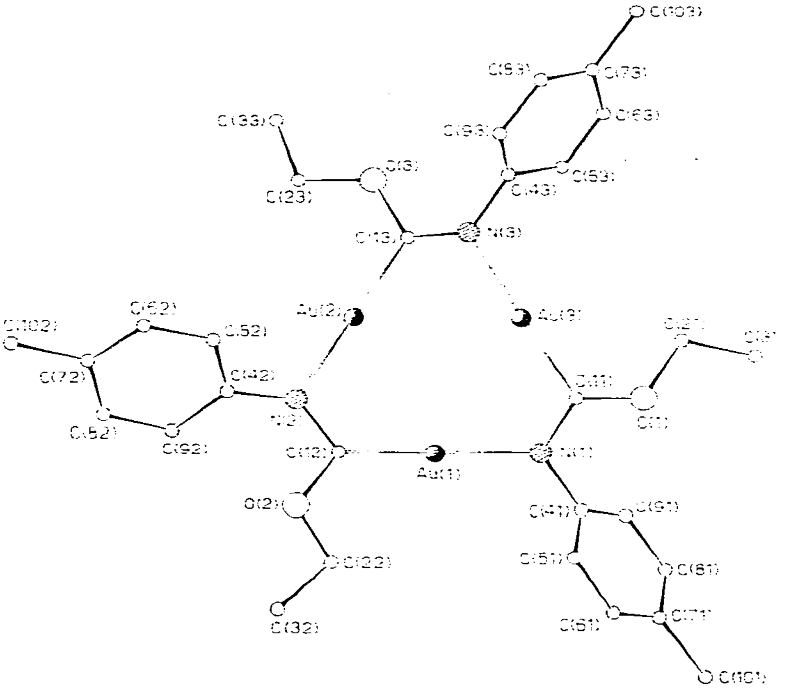


Fig. 1. View of the structure of the compound $[(EtO)(MeC_6H_4N=)CAu]_3$.

TABLE 4

BOND DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s

Au(1)—N(1)	2.037(23)	C(21)—C(31)	1.541(40)
Au(1)—C(12)	1.935(28)	C(12)—O(2)	1.386(34)
Au(2)—N(2)	2.018(22)	O(2)—C(22)	1.455(35)
Au(2)—C(13)	1.953(25)	C(22)—C(32)	1.530(43)
Au(3)—N(3)	2.045(21)	C(13)—O(3)	1.414(33)
Au(3)—C(11)	1.975(26)	O(3)—C(23)	1.466(41)
N(1)—C(11)	1.375(35)	C(23)—C(33)	1.520(56)
N(2)—C(12)	1.369(38)	N(1)—C(41)	1.486(28)
N(3)—C(13)	1.223(31)	N(2)—C(42)	1.431(27)
C(11)—O(1)	1.300(33)	N(3)—C(43)	1.497(27)
O(1)—C(21)	1.418(33)		
N(1)—Au(1)—C(12)	176.0(11)	N(2)—C(12)—O(2)	112.6(23)
N(2)—Au(2)—C(13)	173.1(9)	C(12)—N(2)—C(42)	125.7(21)
N(3)—Au(3)—C(11)	176.1(9)	Au(2)—N(2)—C(42)	117.9(15)
Au(1)—N(1)—C(11)	119.1(18)	Au(2)—C(13)—O(3)	122.7(17)
Au(2)—N(2)—C(12)	116.1(18)	N(3)—C(13)—O(3)	114.3(22)
Au(3)—N(3)—C(13)	116.3(18)	C(13)—N(3)—C(43)	125.4(21)
Au(1)—C(12)—N(2)	122.1(20)	Au(3)—N(3)—C(43)	117.8(13)
Au(2)—C(13)—N(3)	122.5(20)	C(11)—O(1)—C(21)	118.2(21)
Au(3)—C(11)—N(1)	117.2(19)	O(1)—C(21)—C(31)	106.4(23)
Au(3)—C(11)—O(1)	124.4(19)	C(12)—O(2)—C(22)	115.9(21)
N(1)—C(11)—O(1)	117.5(23)	O(2)—C(22)—C(32)	105.9(24)
C(11)—N(1)—C(41)	118.0(21)	C(13)—O(3)—C(23)	115.8(22)
Au(1)—N(1)—C(41)	121.9(15)	O(3)—C(23)—C(33)	109.4(30)
Au(1)—C(12)—O(2)	125.1(20)		

ethylenic carbons were found in the structures of [Ph$_3$PAuC(CF$_3$)=C(CF$_3$)AuPPh$_3$] [10] and [Me$_3$PAuMe$_2$C(CF$_3$)C=C(CF$_3$)AuPMe$_3$] [11] respectively, of 2.01(5) and 1.98(5) Å in [AuCN(CNCH$_3$)] [12], of 2.07(2) Å in [PPh$_3$AuC$_6$F$_5$] [13], and of 2.09(3) and 2.10(3) Å in [Et$_2$P(CH$_2$AuCH$_2$)]$_2$ [14]. In some cases d_π—p_π interactions in these Au—C bonds could not be excluded.

For the Au—N distances values of 2.03(2) Å were found in [(C$_3$H$_7$NH$_2$)Au(C≡CPh) [9], of 2.068(18) Å in the structure of [AuCl(pip)] (pip = piperidine) [15], of 2.166 and 2.406 Å in [(bipy)AuPPh$_3$]PF$_6$ (bipy = bipyridine) [16], but in this last case the Au is trigonally coordinated.

In the trimer the Au···Au distances (Au(1)···Au(2) 3.288(1), Au(1)···Au(3) 3.299(1) and Au(2)···Au(3) 3.224(1) Å) are much longer than in metallic gold, 2.884 Å [17], but close to the highest values found between peripheral atoms in some gold clusters (in the range 2.84—3.19 Å [18—20]), so weak metal—metal bonding interactions can not be excluded. Shorter Au$^{\rm I}$—Au$^{\rm I}$ distances were found in the dimeric complexes [Et$_2$P(CH$_2$AuCH$_2$)]$_2$, 3.023 Å [14], and Au$_4$Cl$_8$, 3.095 Å [21].

Though the three Au—C and Au—N distances are very close, the nine-membered ring is rather irregular: in fact one C—N distance is much shorter than the other two, 1.223(31) for N(3)—C(13), 1.375(35) and 1.369(38) Å for N(1)—C(11) and N(2)—C(12), respectively. Moreover the ring is not planar, but puckered. By considering the plane passing through the three Au atoms (the equations of the main planes in the molecule and deviations of relevant atoms from them are given in Table 5),

TABLE 5

EQUATIONS OF LEAST SQUARES PLANES ARE IN THE FORM: $AX + BY + CZ = D$ (X, Y and Z are orthogonal coordinates in Å, obtained from fractional ones by applying the matrix: $\|a \sin \gamma, 0, -c \sin \alpha \cos \beta^{*}/a \cos \gamma, b, c \cos \alpha/0, 0, c \sin \alpha \sin \beta^{*}\|$. Deviations (Å) of relevant atoms from the planes are in square brackets).

		A	*B*	*C*	*D*
I	Au(1), Au(2), Au(3)	−0.0120	−0.3990	−0.9169	−4.4340
	[C(11) 0.13, C(12) −0.42, C(13) 0.16, N(1) 0.32, N(2) −0.41, N(3) −0.03, O(1) 0.26), O(2) −0.63, O(3) 0.32, C(41) 0.49, C(42) −0.77, C(43) −0.10]				
II	N(1), C(11), O(1), C(41)	0.1330	−0.4074	−0.9035	−4.5654
	[N(1) 0.04, C(11) −0.04, O(1) 0.01, C(41) −0.01, Au(1) −0.16, Au(3) 0.12]				
III	N(2), C(12), O(2), C(42)	0.0353	−0.1738	−0.9841	−2.8703
	[N(2) 0.04, C(12) −0.04, O(2) 0.02, C(42) −0.01, Au(1) −0.06, Au(2) 0.08]				
IV	N(3), C(13), O(3), C(43)	−0.1309	−0.4995	−0.8564	−5.0275
	[N(3) 0, C(13) 0, O(3) 0, C(43) 0, Au(2) −0.25, Au(3) 0.27]				
V	N(1), C(11), Au(1), Au(3)	0.0991	−0.3371	−0.9362	−4.1896
	[N(1) 0.09, C(11) −0.09, Au(1) 0, Au(3) 0, O(1) −0.11, C(41) 0.09]				
VI	N(2), C(12), Au(1), Au(2)	−0.0065	−0.1669	−0.9860	−2.8089
	[N(2) 0.01, C(12) −0.01, Au(1) 0, Au(2) 0, O(2) 0.08, C(42) −0.06]				
VII	N(3), C(13), Au(2), Au(3)	−0.0461	−0.3803	−0.9237	−4.3593
	[N(3) −0.10, C(13) 0.10, Au(2) 0, Au(3) 0, O(3) 0.21, C(43) −0.22]				

C(11), C(12), C(13), N(1), N(2) and N(3) deviate from this plane of 0.13, −0.42, 0.16, 0.32, −0.41 and −0.03 Å respectively. Also the three C(4)—N—C(1)—O and Au—N—C—Au moieties are not equal: C(43)—N(3)—C(13)—O(3) is perfectly planar, whereas C(41)—N(1)—C(11)—O(1) and C(42)—N(2)—C(12)—O(2) are not completely planar; the Au(1)—N(2)—C(12)—Au(2) moiety is perfectly planar, whereas the other two are sensibly not planar.

The slightly bent C—Au—N groups and the puckering of the ring could be due to metal—metal bonding interactions within and between the trimers, even if in the present structure these interactions are rather weak. The Au···Au distances within the trimers are mentioned above; only a short Au···Au contact of 3.244(1) Å is observed between the trimers; it involves Au(1) and Au(2^{I}) (I indicates the atom in the equivalent position $-x$, $1-y$, $-z$) and through this interaction the trimers are joined in pairs. The other shortest distance Au···Au in this structure, 3.950(2) Å, between Au(1) and Au(3^{II}) (II indicates the atom in the equivalent position $-x$, $1-y$, $1-z$) excludes other metal—metal interactions. The distance of 3.244 Å between the trimers, much shorter than two Van der Waals radii, is comparable with those observed between $\mathrm{Au^{I}}$ atoms of different complexes in [$(C_3H_7NH_2)$Au(C≡CPh)], 3.274 Å [9], in [AuCl(Cl_3P)], 3.14 Å [22], and in [AuCl(pip)], 3.30 Å [15]. In these compounds also the short contacts were ascribed to weak metal—metal interactions, though the nature of these interactions has not been defined.

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