Crystal Structure of Tetrakis(triphenylstibine)gold(I) Bis(pentafluorophenyl)aurate(I)

Peter G. Jones

Anorganisch-Chemisches Institut der Universität, Tammannstraße 4, D-3400 Göttingen

Z. Naturforsch. **37 b**, 937–940 (1982); received March 15, 1982

Crystal Structure, Tetrahedral Gold(I)

The crystal structure of the title compound has been determined ($P\bar{3}c1$, $a = 2161.5(3)$, $c = 2859.8(4)$ pm, $Z = 6$; $R_w = 0.07$ for 2217 observed reflections). There are three independent $(Ph_3Sb)_4Au^+$ cations, each with one Au–Sb bond directed along a crystallographic threefold axis. Deviations from ideal tetrahedral coordination are small (max. 8 pm, 1°).

Introduction

The existence of tetrahedrally coordinated gold(I) in the solid state was established in 1957 by a partial X-ray structure of $[(o\text{-}C_6H_4(AsR_2)_2)_2Au]^+I^-$ (R = Et) [1]; we have since determined the complete structure of the R = Me analogue [2]. Tetrahedral coordination in cations of the form AuL_4^+ (where L is a monodentate ligand) has long been assumed, but only recently have attempts been made to confirm or disprove this in the solid state. Thus Mößbauer spectra of the species $L = Ph_3P$ [3], Ph_2MeP and Ph_3As [4] at 4 K are all singlets, which is consistent with tetrahedral geometry; yet room temperature X-ray structure determinations of $L = Ph_3P$ revealed either trigonal geometry with one very distant ligand or (in a second modification) 1:1 disorder between tetrahedral and trigonal sites (7:1 at 123 K) [5]. The X-ray structure of $L = Ph_2MeP$ was the first to establish simple tetrahedral coordination at Au(I) [6].

Related complexes with mixed ligands have also been studied. X-ray structures of two modifications of $(Ph_3P)_3AuSCN$ have shown different degrees of distortion; one has a long Au–S contact (293.1 pm) and is effectively trigonal [7], whereas the other may be described as intermediate between trigonal and tetrahedral (Au–S 279.1 pm) [8].

In view of these unexpected variations in geometry at the metal atom, we have undertaken an X-ray structural investigation of the compound $[(Ph_3Sb)_4Au]^+[(C_6F_5)_2Au]^-$ [2].

Data Collection, Structure Solution and Refinement

Colourless crystals in the form of thick plates were obtained from dichloromethane/petroleum ether. Data were collected on a Stoe four-circle diffractometer (monochromated MoKα radiation) to a maximum 2θ of 45°. The 5165 measured intensities were subjected to Lp and absorption corrections ($\mu = 5.1$ mm^{-1}, crystal size 0.25 × 0.2 × 0.06 mm). 2217 reflections with $F > 4\sigma(F)$ were used for all calculations. Laue symmetry and systematic absences were consistent with space groups $P3c1$ or $P\bar{3}c1$. Accurate cell constants were obtained *via* 2θ values of 36 reflections in the range $20° < 2\theta < 22°$.

Attempts to solve the structure in $P\bar{3}c1$ proved unsuccessful; although three gold sites (0, 0, 0; 0, y, 1/4; 1/3, 2/3, z) could be refined, these were inconsistent with the expected stoichiometry and site symmetries, and the structure could not be extended. In $P3c1$, use of direct methods led to a double image in which Au and Sb atoms could not be distinguished by peak heights. A self-consistent set of 10 atoms was extracted by inspection; it consisted of one gold atom (assumed to belong to the anion) on a general position and three $AuSb_4$ groups, each possessing crystallographic 3 symmetry. Refinement of these atoms gave $R = 0.17$. Light atom location was rendered difficult by the pseudosymmetry, the relatively small number of data, and the high thermal motion of some atoms (notably in the anion), but was achieved by the use of rigid groups (C–C 139.5, C–H 96, C–F 135.2 pm, all sp^2 angles 120°). An unsatisfying feature of the later stages of refinement ($R_w = 0.071$) was the wide range of Au–Sb bond lengths (252–272 pm). The alternative model with all coordinates changed in sign (corresponding to a change of polar axis direction) gave less variation (259–267 pm) and a marginally lower final R_w (0.070 with weighting scheme $w^{-1} = \sigma^2(F) + 0.0005\,F^2$; corresponding unweighted $R = 0.084$) and was thus preferred. Errors in bond length compo-

0340–5087/82/0800–0937/$ 01.00/0

nents in the polar axis direction (when this direction is incorrectly assigned) have been discussed as a special case of inappropriate treatment of anomalous scattering effects [9]. Final atom coordinates and derived parameters are given in the Tables.

Crystal data

$C_{72}H_{60}Sb_4Au^+C_{12}F_{10}Au^-$. Trigonal, space group $P3c1$, $a = 2161.5(3)$, $c = 2859.8(4)$ pm, $U = 11.57$ nm^3, $Z = 6$, $\varrho_{calc.} = 1.84$ Mg m^{-3}.

Discussion

The crystal structure shows three independent $(Ph_3Sb)_4Au^+$ cations, each with one Au–Sb bond

Table I. Atom coordinates ($\times 10^4$) and temperature factors (pm$^2 \times 10^{-1}$).

	x/a	y/b	z/c	U
Au(1)	3333	6667	5000	
Sb(11)	3333	6667	4067(5)	
Sb(12)	4017(3)	7988(3)	5313(3)	
Au(2)	10000	10000	6377(2)	
Sb(21)	10000	10000	7281(5)	
Sb(22)	9231(3)	8661(3)	6065(3)	
Au(3)	6667	3333	5760(4)	
Sb(31)	6667	3333	4834(3)	
Sb(32)	5406(2)	3072(2)	6051(3)	
Au(4)	10708(2)	7416(2)	8215(3)	
C(11)	2272(27)	6203(21)	3721(14)	84(25)
C(12)	1753(27)	6365(21)	3866(14)	70(21)
C(13)	1065(27)	5992(21)	3680(14)	54(19)
C(14)	896(27)	5457(21)	3349(14)	205(49)
C(15)	1415(27)	5296(21)	3203(14)	135(37)
C(16)	2103(27)	5669(21)	3389(14)	132(37)
C(21)	3615(23)	8674(22)	5096(15)	39(18)
C(22)	3571(23)	8787(22)	4619(15)	135(37)
C(23)	3219(23)	9145(22)	4469(15)	70(25)
C(24)	2911(23)	9389(22)	4795(15)	93(26)
C(25)	2955(23)	9276(22)	5272(15)	92(25)
C(26)	3306(23)	8919(22)	5422(15)	85(22)
C(31)	4000(26)	8052(26)	6030(21)	92(26)
C(32)	3415(26)	7807(26)	6330(21)	138(37)
C(33)	3518(26)	7869(26)	6813(21)	121(31)
C(34)	4208(26)	8175(26)	6996(21)	46(18)
C(35)	4793(26)	8419(26)	6697(21)	255(64)
C(36)	4689(26)	8358(26)	6214(21)	159(40)
C(41)	5114(28)	8639(20)	5097(16)	161(43)
C(42)	5513(28)	8298(20)	5044(16)	58(20)
C(43)	6203(28)	8671(20)	4861(16)	113(32)
C(44)	6494(28)	9385(20)	4730(16)	126(35)
C(45)	6095(28)	9726(20)	4783(16)	141(40)
C(46)	5405(28)	9353(20)	4966(16)	131(36)
C(51)	10987(21)	10437(21)	7612(14)	31(15)
C(52)	11242(21)	11026(21)	7910(14)	47(19)
C(53)	11928(21)	11327(21)	8096(14)	87(27)
C(54)	12361(21)	11038(21)	7986(14)	44(19)
C(55)	12106(21)	10449(21)	7689(14)	80(25)
C(56)	11420(21)	10148(21)	7502(14)	37(18)
C(61)	9579(19)	7929(18)	6268(14)	95(29)

Table I (continued).

	x/a	y/b	z/c	U
C(62)	9776(19)	7945(18)	6734(14)	21(15)
C(63)	10000(19)	7476(18)	6890(14)	87(27)
C(64)	10026(19)	6992(18)	6580(14)	61(19)
C(65)	9829(19)	6976(18)	6113(14)	94(24)
C(66)	9605(19)	7445(18)	5958(14)	89(24)
C(71)	8158(22)	8144(22)	6245(16)	16(13)
C(72)	7922(22)	7428(22)	6346(16)	92(28)
C(73)	7216(22)	6976(22)	6482(16)	70(24)
C(74)	6746(22)	7239(22)	6517(16)	95(28)
C(75)	6982(22)	7955(22)	6417(16)	114(31)
C(76)	7688(22)	8407(22)	6280(16)	215(55)
C(81)	9132(21)	8553(25)	5327(22)	60(23)
C(82)	9767(21)	8706(25)	5104(22)	140(36)
C(83)	9781(21)	8637(25)	4620(22)	275(70)
C(84)	9160(21)	8416(25)	4359(22)	241(58)
C(85)	8525(21)	8264(25)	4582(22)	63(21)
C(86)	8511(21)	8332(25)	5066(22)	54(19)
C(91)	7695(26)	3855(25)	4484(15)	69(18)
C(92)	7940(26)	4399(25)	4152(15)	92(25)
C(93)	8643(26)	4718(25)	3993(15)	136(34)
C(94)	9101(26)	4492(25)	4166(15)	97(23)
C(95)	8856(26)	3947(25)	4498(15)	96(26)
C(96)	8153(26)	3628(25)	4657(15)	56(19)
C(101)	4917(25)	2463(25)	6668(17)	61(16)
C(102)	4225(25)	2320(25)	6766(17)	128(32)
C(103)	3887(25)	1966(25)	7178(17)	178(39)
C(104)	4240(25)	1756(25)	7492(17)	117(29)
C(105)	4932(25)	1898(25)	7394(17)	139(33)
C(106)	5270(25)	2252(25)	6983(17)	111(28)
C(111)	5382(21)	4022(25)	6129(12)	58(19)
C(112)	5628(21)	5302(25)	6240(12)	82(23)
C(113)	5625(21)	5165(25)	5824(12)	79(22)
C(114)	5377(21)	5302(25)	6240(12)	82(23)
C(115)	5131(21)	4800(25)	6600(12)	105(26)
C(116)	5134(21)	4160(25)	6545(12)	79(22)
C(121)	4500(23)	2442(19)	5571(13)	43(20)
C(122)	4075(23)	1703(19)	5614(13)	92(24)
C(123)	3563(23)	1312(19)	5274(13)	85(23)
C(124)	3477(23)	1662(19)	4892(13)	86(23)
C(125)	3902(23)	2401(19)	4848(13)	150(37)
C(126)	4413(23)	2791(19)	5188(13)	90(24)
C(131)	11693(13)	8345(15)	8197(11)	111(19)
C(132)	11821(13)	8878(15)	8521(11)	90(31)
C(133)	12474(13)	9515(15)	8522(11)	275(74)
C(134)	13000(13)	9619(15)	8198(11)	106(25)
C(135)	12873(13)	9087(15)	7874(11)	83(27)
C(136)	12220(13)	8449(15)	7873(11)	100(32)
F(132)	11311(13)	8777(15)	8835(11)	218(31)
F(133)	12597(13)	10031(15)	8836(11)	200(27)
F(134)	13633(13)	10237(15)	8198(11)	212(22)
F(135)	13383(13)	9188(15)	7559(11)	211(30)
F(136)	12096(13)	7933(15)	7558(11)	137(19)
C(141)	9713(11)	6480(13)	8260(9)	70(20)
C(142)	9561(11)	5931(13)	7943(9)	89(25)
C(143)	8886(11)	5322(13)	7938(9)	133(32)
C(144)	8361(11)	5261(13)	8249(9)	158(35)
C(145)	8512(11)	5809(13)	8565(9)	163(37)
C(146)	9188(11)	6419(13)	8571(9)	121(32)
F(142)	10070(11)	5991(13)	7642(9)	172(22)
F(143)	8739(11)	4790(13)	7631(9)	178(22)
F(144)	7706(11)	4670(13)	8243(9)	170(20)
F(145)	8003(11)	5750(13)	8867(9)	156(19)
F(146)	9334(11)	6950(13)	8878(9)	140(18)

Table I (continued).

Anisotropic temperature factors ($pm^2 \times 10^{-1}$).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	60(3)	U_{11}	80(5)	0	0	$U_{11}/2$
Sb(11)	91(5)	U_{11}	40(7)	0	0	$U_{11}/2$
Sb(12)	82(5)	64(5)	84(5)	−9(4)	−7(4)	29(4)
Au(2)	53(2)	U_{11}	27(3)	0	0	$U_{11}/2$
Sb(21)	52(4)	U_{11}	65(9)	0	0	$U_{11}/2$
Sb(22)	54(4)	63(4)	64(4)	−9(3)	−8(3)	28(3)
Au(3)	44(1)	U_{11}	86(4)	0	0	$U_{11}/2$
Sb(31)	62(3)	U_{11}	71(6)	0	0	$U_{11}/2$
Sb(32)	47(3)	51(3)	78(3)	9(3)	11(3)	26(3)
Au(4)	140(4)	111(4)	88(2)	0(4)	−16(4)	73(2)

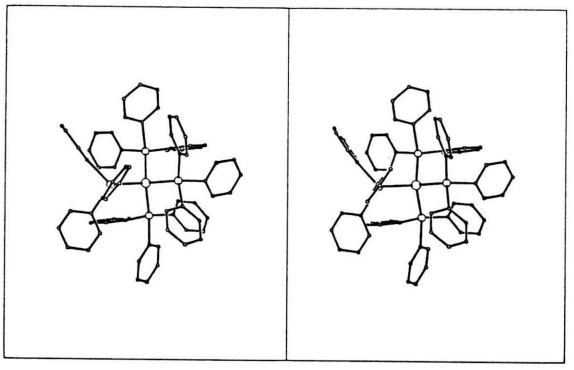

Fig. 1. Stereo plot of the $(Ph_3Sb)_4Au^+$ cation involving Au(1).

directed along a crystallographic threefold axis. The tendency of gold(I) to form one long and three short bonds in ostensibly four-coordinate complexes [5, 7, 8] is not followed here; each $AuSb_4$ unit possesses non-crystallographic $\bar{4}$ symmetry to a good approximation (see Table II). Au(2) shows the greatest deviation from this ideal geometry, with Au(2)–Sb(21) (along the threefold axis) 8 pm shorter than the three Au(2)–Sb(22) bonds. The largest deviation from ideal tetrahedral angles is 1°. The Au–Sb bond lengths are comparable with Au–P in the room temperature tetrahedral component of $(Ph_3P)_4Au^+$ [5]; it has been suggested [6] that these very long bonds result from steric effects of the bulky Ph_3P ligands. This would imply that the Au–M bond length in $(Ph_3M)_4Au^+$ would be largely independent of M, which seems to be confirmed by the current structure. However, the analogous zerovalent palladium complex $(Ph_3P)_4Pd$ [10] can accommodate Pd–P bonds of 242.7, 245.8 pm.

The high thermal motion and consequent inaccurate dimensions of the anion preclude useful comparison with a previously published $Au(C_6F_5)_2^-$ anion [2].

Calculations were performed at the Gesellschaft für wissenschaftliche Datenverarbeitung, Göttingen, with programs written by Prof. G. M. Sheldrick. I thank Prof. R. Usón, University of Zaragoza, for a gift of the title compound, and the Fonds der chemischen Industrie for financial support.

Table II. Unique bond lengths and angles at gold (pm, deg.).

Au(1) –Sb(11)	266.9(14)	Au(1) –Sb(12)	263.0(7)
Au(2) –Sb(21)	258.5(12)	Au(2) –Sb(22)	266.9(7)
Au(3) –Sb(31)	264.8(12)	Au(3) –Sb(32)	262.7(6)
Au(4) –C(131)	207.2(24)	Au(4) –C(141)	209.5(21)
Sb(11)–Au(1)–Sb(12)	109.9(3)	Sb(12)–Au(1)–Sb(12a)	109.0(3)
Sb(21)–Au(2)–Sb(22)	109.5(3)	Sb(22)–Au(2)–Sb(22b)	109.4(3)
Sb(31)–Au(3)–Sb(32)	108.5(3)	Sb(32)–Au(3)–Sb(32c)	110.4(3)
C(131)–Au(4)–C(141)	177.9(11)		

Symmetry operators: (a) $1-y, 1+x-y, z$; (b) $2-y, 1+x-y, z$; (c) $1-y, x-y, z$.

Au–Sb bond lengths calculated with an inappropriate polar axis direction (see text) (esd's as above):

Au(1)–Sb(11)	253.3	Au(1)–Sb(12)	266.8
Au(2)–Sb(21)	272.2	Au(2)–Sb(22)	263.9
Au(3)–Sb(31)	252.5	Au(3)–Sb(32)	266.8

[1] W. Cochran, F. A. Hart, and F. G. Mann, J. Chem. Soc. **1957,** 2816.
[2] R. Usón, A. Laguna, J. Vicente, J. Garcia, P. G. Jones, and G. M. Sheldrick, J. Chem. Soc., Dalton Trans. **1981,** 655.
[3] R. V. Parish and J. D. Rush, Chem. Phys. Lett. **63,** 37 (1979).
[4] R. V. Parish, O. Parry, and C. A. McAuliffe, J. Chem. Soc., Dalton Trans. **1981,** 2098.
[5] P. G. Jones, J. Chem. Soc., Chem. Commun. **1980,** 1031.
[6] R. C. Elder, E. H. Kelle Zieher, M. Onady, and R. R. Whittle, J. Chem. Soc., Chem. Commun. **1981,** 900.
[7] J. A. Muir, M. M. Muir, S. Arias, P. G. Jones, and G. M. Sheldrick, Acta Crystallogr., submitted for publication.
[8] J. A. Muir, M. M. Muir, S. Arias, C. F. Campana, and S. K. Dwight, Acta Crystallogr., in press.
[9] D. W. J. Cruickshank and W. S. McDonald, Acta Crystallogr. **23,** 9 (1967).
[10] V. G. Adrianov, I. S. Akhrem, N. M. Chistovalova, and Y. T. Struchkov, Zh. Strukt. Khim. (Engl.) **17,** 135 (1976).