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The Crystal and Molecular Structure of the Orthorhombic Form of Thiocyanatotris(triphenylphosphine)gold(I) Monohydrate, $[(Ph_3P)_3Au(SCN)]\cdot H_2O$

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The crystal and molecular structure of the orthorhombic form of thiocyanatotris(triphenylphosphine)gold(I) monohydrate, $[(Ph_3P)_3Au(SCN)]\cdot H_2O$, has been determined. The gold is four-coordinate with an extremely long Au–S bond distance of 2.928(17) Å. The coordination number of the gold atom and the average Au–P distance were compared with other complexes of gold, $[(R_3P)_nAuX]$, where R_3P is a monodentate tertiary phosphine and X includes Cl, Br, I, SCN, CN, Me, and $SnCl_3$. The average Au–P distance depends more strongly on coordination number than on X, R, or net charge. Crystallographic data are as follows: $P2_12_12_1$ with a = 13.95(5) Å, b = 30.44(10) Å, c = 11.09(4) Å, V = 4709 Å^3, Z = 4, d_c = 1.495 g cm^{-3}. The structure was refined by least squares methods to a conventional R *factor of 8.5%, using 2030 unique Weissenberg data.*

Introduction

Linear, two-coordinate complexes of gold(I) can add ligands to form three- or four-coordinate complexes [1–7]. Several such adducts have been isolated and characterized [8–10] as part of a study of the reactions of neutral ligands, such as phosphines, with LAuX, where L is a tertiary phosphine and X is halide or thiocyanate. However, substitution reactions sometimes occur instead of addition, to give two-coordinate, ionic complexes, such as $[(Cy_3P)_2Au]SCN$, where Cy is cyclohexyl [11]. The factors that determine whether the two-coordinate substitution product or the three- or four-coordinate addition product is isolated in a particular case are not well understood.

Therefore, it was of interest that two different crystalline forms of the tris phosphine complex $(Ph_3P)_3AuSCN$ were obtained from the reaction of $[(Ph_3P)_2AuSCN]$ with excess phosphine. Most of the crystals were found to have the monoclinic structure in which the gold atom was four-coordinate with an unusually long Au–S distance [9]. However, a few crystals obtained from the same reaction mixture were orthorhombic, with systematically absent reflections corresponding to space group $P2_12_12_1$ [12]. It was of interest to see whether the coordination about the gold in this crystalline form was four or less. This work presents the structure of the orthorhombic form.

Experimental

Materials

The complex $NaAuCl_4\cdot 2H_2O$ was prepared from gold metal (99.99% pure) by following methods in the literature [13, 14]. All other materials were reagent grade and used without purification.

Preparation of $[(Ph_3P)_2AuSCN]$ [8]

This compound was unexpectedly obtained as the major product from the attempted synthesis of $Ph_3PAuSCN$ by the method of De Stefano and Burmeister [15]. To 0.40 g (1.0 mmol) of $NaAuCl_4\cdot 2H_2O$ in 10 ml ethanol were added 0.32 g (4.0 mmol) of NaSCN in 20 ml ethanol. After 10 min of stirring, NaCl was filtered off. A solution of 0.53 g (2.0 mmol) of Ph_3P in 30 ml ethanol was added to the dark red filtrate. The solution rapidly became colorless and was stirred for 15 min. Solvent was removed under reduced pressure until white crystals began to form. The product was filtered, washed first with

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ethanol, then with ether, and dried over $CaSO_4$ in a vacuum desiccator. The product was shown [8] to be thiocyanatobis(triphenylphosphine)gold(I), m.p. 183–186 °C. *Anal.*: Calcd. for $C_{37}H_{30}AuNP_2S$: C, 57.00; H, 3.88; N, 1.80%. Found: C, 57.41; H, 3.99; N, 1.78%.

Preparation of $(Ph_3P)_3AuSCN \cdot H_2O$

To a solution of triphenylphosphine (3.15 g, 12 mmol) in 40 ml benzene was added 0.8 g (1.0 mmol) of $(Ph_3P)_2AuSCN$. The resultant suspension was refluxed until a clear solution was obtained. The hot solution was filtered and left to crystallize. After 48 hr the first crop was filtered and air-dried. This crop contained two crystalline forms. The major yield was in the form of monoclinic crystals, whose structure has already been reported, [8] m.p. 155–158 °C. *Anal.*: Calcd. for $C_{55}H_{46}AuNP_3SO$: C, 63.40; H, 4.35; N, 1.34; P, 8.92%. Found: C, 63.44; H, 4.63; N, 1.25; P, 8.65%.

There were also a few needle-shaped, orthorhombic crystals, in insufficient quantity to characterize except by X-ray diffraction. These were separated manually from the rest of the crop with the aid of a microscope.

X-ray Crystallography. Data Collection

A small needle-like crystal was chosen and mounted with its *c*-axis parallel to that of a standard goniometer head. Weissenberg and Precession photographs showed systematic extinctions characteristic of space group $P2_12_12_1$. The latter photographs were used to determine the lattice parameters. Crystal data for $[(P(C_6H_5)_3)_3AuSCN] \cdot H_2O$, $AuC_{55}H_{47}NP_3SO$, are as follows: orthorhombic, a = 13.95(5) Å, b = 30.44(10) Å, c = 11.09(4) Å, V = 4709 Å^3, Z = 4, mol wt. = 1059.9, d_c = 1.495 g cm^{-3}, F(000) μ(Cu K$_\alpha$) = 1732, μ(Cu K$_\alpha$) = 67.6 cm^{-1}; space group $P2_12_12_1$.

Intensity data were collected for 5881 reflections having indices ±*h*, ±*k*, +*l* on levels $l = 0$ to 7 using a Weissenberg camera with Ni-filtered Cu radiation. Intensities were estimated visually, using a calibrated film strip. After data reduction, averaging of equivalent reflections gave 2032 unique data.

TABLE I. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 × 10^3).

	x	*y*	*z*	*U*
Au	4651(1)	6215(1)	1893(2)	62(1)*
P(1)	2996(7)	6032(4)	1678(11)	65(7)*
P(2)	5116(8)	6951(4)	1466(10)	66(8)*
P(3)	5832(8)	5664(4)	1431(10)	59(9)*
S	4439(10)	6220(6)	4520(12)	116(9)*
C	5597(29)	6126(12)	4928(34)	58(12)
N	6407(36)	6093(15)	5285(46)	146(18)
C(111)	2177(19)	6183(11)	2944(25)	58(11)
C(112)	2330(19)	6616(11)	3309(25)	98(16)
C(113)	1735(19)	6806(11)	4177(25)	143(22)
C(114)	988(19)	6562(11)	4680(25)	106(19)
C(115)	836(19)	6129(11)	4315(25)	97(16)
C(116)	1430(19)	5940(11)	3447(25)	109(18)
C(121)	2738(18)	5457(10)	1567(24)	88(16)
C(122)	2100(18)	5269(10)	748(24)	58(13)
C(123)	2034(18)	4813(10)	656(24)	67(14)
C(124)	2606(18)	4545(10)	1382(24)	67(15)
C(125)	3244(18)	4734(10)	2201(24)	78(14)
C(126)	3310(18)	5190(10)	2293(24)	72(14)
C(131)	2433(22)	6250(10)	305(20)	89(15)
C(132)	1457(22)	6349(10)	244(20)	97(16)
C(133)	1048(22)	6474(10)	−851(20)	81(16)
C(134)	1615(22)	6500(10)	−1885(20)	100(16)
C(135)	2590(22)	6402(10)	−1824(20)	66(13)
C(136)	2999(22)	6277(10)	−729(20)	41(10)
C(211)	6240(17)	7100(9)	2112(31)	87(14)
C(212)	6913(17)	7375(9)	1569(31)	73(14)
C(213)	7743(17)	7493(9)	2192(31)	84(15)
C(214)	7899(17)	7336(9)	3357(31)	94(16)
C(215)	7226(17)	7061(9)	3900(31)	104(16)
C(216)	6396(17)	6943(9)	3277(31)	121(19)
C(221)	5210(22)	7054(9)	−166(19)	70(14)
C(222)	5292(22)	6694(9)	−939(19)	61(12)
C(223)	5386(22)	6760(9)	−2178(19)	96(15)
C(224)	5399(22)	7186(9)	−2644(19)	92(15)
C(225)	5318(22)	7546(9)	−1871(19)	79(13)
C(226)	5223(22)	7479(9)	−632(19)	63(13)
C(231)	4285(21)	7389(8)	1898(30)	99(16)
C(232)	4517(21)	7655(8)	2881(30)	66(12)
C(233)	3896(21)	7989(8)	3237(30)	100(16)
C(234)	3043(21)	8059(8)	2609(30)	68(13)
C(235)	2811(21)	7794(8)	1626(30)	103(18)
C(236)	3432(21)	7459(8)	1270(30)	110(18)
C(311)	7087(18)	5825(11)	1583(31)	99(17)
C(312)	7744(18)	5582(11)	2259(31)	82(15)
C(313)	8683(18)	5733(11)	2390(31)	95(16)
C(314)	8965(18)	6125(11)	1845(31)	98(14)
C(315)	8308(18)	6367(11)	1169(31)	92(17)
C(316)	7368(18)	6217(11)	1038(31)	85(13)
C(321)	5841(19)	5135(8)	2188(32)	68(15)
C(322)	5708(19)	5153(8)	3433(32)	95(18)
C(323)	5710(19)	4767(9)	4110(32)	118(19)
C(324)	5844(19)	4363(9)	3542(32)	120(21)
C(325)	5977(19)	4345(9)	2296(32)	98(17)
C(326)	5976(19)	4731(9)	1619(32)	130(21)
C(331)	5712(24)	5505(10)	−138(23)	76(15)
C(332)	4794(24)	5370(10)	−472(23)	84(15)
C(333)	4571(24)	5309(10)	−1687(23)	75(13)
C(334)	5266(24)	5384(10)	−2567(23)	106(17)
C(335)	6184(24)	5519(10)	−2234(23)	99(17)
C(336)	6407(24)	5580(10)	−1019(23)	71(13)
O**	1685(43)	1140(23)	63(67)	106(35)

*U_{eq} is 1/3 of the trace of the orthogonalized U matrix.
**The occupancy of the O site is 0.45(6).

TABLE II. Bond Distances (Å) and Angles (Deg.)

Au–P(1)	2.387(13)[a]	Au–P(2)	2.381(15)
Au–P(3)	2.407(14)	Au–S	2.928(17)
P(1)–C(111)	1.867(26)	P(1)–C(121)	1.791(30)
P(1)–C(131)	1.837(25)	P(2)–C(211)	1.782(24)
P(2)–C(221)	1.841(25)	P(2)–C(231)	1.831(24)
P(3)–C(311)	1.825(25)	P(3)–C(321)	1.815(36)
P(3)–C(331)	1.813(28)	S–C	1.701(42)
C–N	1.203(47)	N···O	2.69(6)
P(1)–Au–P(2)	117.6(4)	P(1)–Au–P(3)	118.6(4)
P(2)–Au–P(3)	115.3(4)	S–C–N	174.0(4.0)
S–Au–P(1)	90.2(4)	Au–S–C	99.7(1.4)
S–Au–P(2)	102.8(4)	S–Au–P(3)	106.5(4)

[a] esd values in parentheses include errors in cell constants.

TABLE III. Comparison of Bond Distances (Å) and Angles (Deg.) in $[L_3AuX]$ Complexes, L = Ph_3P.

	$[L_3AuSCN]\cdot H_2O^a$ (orthorhombic)	$[L_3AuSCN]\cdot H_2O^b$ (monoclinic)	$[L_3AuCl]^c$
Au–P (ave)	2.392	2.399	2.410
P–Au–P (ave)	117.2	117.6	117.4
Au–X	2.938(17)	2.791(3)	2.710(2)
X–Au–P(1)	90.2(4)	91.8(1)	92.0(1)
X–Au–P(2)	102.8(4)	98.1(1)	98.3(1)
X–Au–P(3)	106.5(4)	106.6(1)	107.7(1)
Au–S–C	99.7(1.4)	105.2(4)	
S–C–N	174.0(4.0)	175.4(1.1)	
S–C	1.701(42)	1.577(15)	
C–N	1.203(47)	1.199(20)	
N•••O	2.69(6)	2.85(2)	
Au–P_3 plane	0.41(1)	0.38(1)	0.39(1)
Au–P–C (ave)	115.3	115.2	115.0
C–P–C (ave)	103.1	103.2	103.4

[a] This work. [b] Data taken from ref. 8. [c] Data taken from ref. 10.

Structure Solution and Refinement

Solution of the structure was begun via heavy-atom methods, using SHELX76 [16], and it refined to $R = 0.16$ for a model consistent with a nearly trigonal-planar $[(Ph_3P)_2AuSCN]$ and a distant Ph_3P of solvation. This model was unsatisfactory, however, since only one of the ligands on the gold atom could be unmistakably identified as Ph_3P. At this point SHELXTL [16] was used to calculate a series of sharpened difference Fourier syntheses. The use of rigid phenyl groups and these syntheses improved the resolution in the c-direction sufficiently to show that the orthorhombic structure is in fact a second modification of four-coordinate $[(Ph_3P)_3AuSCN]$. This structure then refined to $R = 0.085$ and $R\Omega = \Sigma\omega^{1/2}\Delta/\Sigma\omega^{1/2}|F_o| = 0.081$, for a model in which the Au, S, and P atoms were anisotropic, and the rigid phenyl groups were retained. Anisotropic U_{33} values were constrained to be the average of U_{11} and U_{22}, to avoid correlation and singular matrix problems. Neutral atom scattering factors were used except for Au^+. The weight used for each unique reflection was the number of non-zero equivalent reflections measured. The highest peak in the difference Fourier synthesis was now 1.9 e Å^{-3}, at an intermolecular location. When this peak was included as a fully-occupied oxygen site it gave a temperature factor U of 0.34(3) Å^2.

Since this is 50% higher than the value of 0.23(7) Å^2 found for the monoclinic modification, it seemed possible that the Fourier peak, in the orthorhombic form was spurious and that the orthorhombic form was anhydrous. When both occupancy and temperature factors for the oxygen atom were allowed to

TABLE IV. Au–P Bond Distances (Å) in Gold(I) Complexes with Monodentate Tertiary Phosphine Ligands.

	Au–P Bond Distance (Å)	Ref.
Two-coordinate Complexes		
$[(Cl_3P)AuCl]$	2.19 (not refined)	22
$[(PhO)_3PAuCl]$	2.192(5)	21
$[Ph_2PCHCHPPh_2(AuCl)_2]$	2.233(9)[a]	23
$[(Ph_3P)AuCl]$	2.235(3)	24
$[(Ph_3PAu)_2Cl][ClO_4]\cdot CH_2Cl_2$	2.235(5)[a]	25
$[Ph_2PCH_2PPH_2(AuCl)_2]$	2.238(5)	26
$[(Ph_3P)Au(Ph_4Cp)]$	2.239(3)	27
$[(Ph_3PAu)_3O][BF_4]$	2.26(1)[a]	28
$[(Ph_3PAu)_3S][PF_6]$	2.269(12)[a]	29
$[(Ph_3P)AuCN]$	2.27(1)	30
$[(Ph_3P)AuMe]$	2.279(8)	31
$[(Ph_3P)_2Au][TCNQ]$	2.286(3)[a]	32
$[(Cy_3P)_2Au][SCN]$	2.306(15)[a]	11
$[(Ph_3P)_2Au][PF_6]$	2.312(4)[a]	33
$[(Ph_2MeP)_2Au][PF_6]$	2.316(4)[a]	34
$[(Cy_3P)_2Au][PF_6]$	2.325(1)[a]	35
Three-coordinate Complexes		
$[(PhMe_2P)_2Au(SnCl_3)]$	2.314(6)[a]	20
$[(Ph_3P)_2AuCl]\cdot \frac{1}{2}C_6H_6$	2.331(11)[a]	2
$[(Ph_3P)_2AuI]$	2.34	36
$[(Ph_3P)_2AuSCN]$	2.348(2)[a]	8
$[(Ph_3P)_3Au][B_9H_{12}S]$	2.373(24)[a]	37
$[(Ph_3P)_3Au][BPh_4]$	2.384(19)[a]	38
$[(Ph_3P)_3Au][BPh_4]\cdot Ph_3P\cdot CHCl_3$	2.402(9)[a]	39
Four-coordinate Complexes		
$[(Ph_3P)_3AuSCN]\cdot H_2O$ (orthorhombic)	2.392(14)[a]	This work
$[(Ph_3P)_3AuSCN]\cdot H_2O$ (monoclinic)	2.399(15)[a]	9
$[(Ph_3P)_3AuCl]$	2.410(19)[a]	10
$[(Ph_2MeP)_4Au][PF_6]$	2.449(1)	18
$[(Ph_3P)_4Au][BPh_4]\cdot EtOH$	2.447(14)[a] trigonal site	39
$[(Ph_3P)_4Au][BPh_4]\cdot EtOH$	2.606(6)[a] tetrahedral site	39

[a] Estimated sample standard deviation calculated from the various Au–P bond distances.

vary, however, the final model converged to an occupancy of 0.45(6) and a very acceptable U value of 0.11(4) Å^2.

The other enantiomorph obtained by changing the signs of the atomic coordinates was discarded, since it resulted in an increase of *R* to 0.098 and a greater spread of Au–P and P–C bond distances. Final atomic coordinates are given in Table I, and bond lengths and angles in Table II. A listing of observed and calculated structure factor amplitudes for this refinement is available as supplementary material.

Discussion

The orthorhombic modification of the $[(Ph_3P)_3AuSCN]$ molecule is shown in Fig. 1. The coordina-

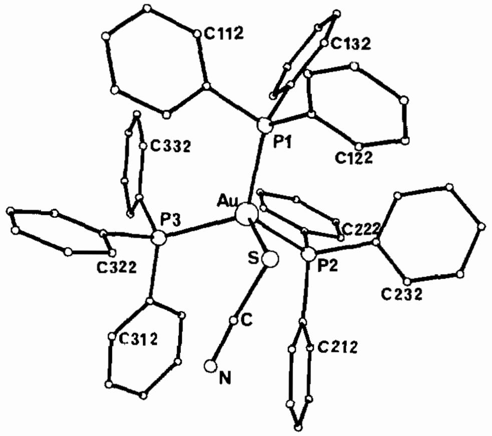

Fig. 1. The $[(Ph_3P)_3AuSCN]$ molecule. For clarity only the ortho position is labeled for each phenyl ring.

tion about the gold is four-fold. The gold–phosphine geometry is considerably distorted from trigonal planar, with the gold atom 0.41(1) Å out of the least-squares plane through the P atoms. The Au–S and Au–P bond lengths are rather long. The Au–S is 2.928(17) Å, while the Au–P values are 2.381(11), 2.387(10), and 2.407(11) Å, to give an average value for Au–P of 2.392 Å. The geometry about the gold atom differs only slightly from that of the monoclinic modification of the same compound, [8] or from that of the analogous chloro complex, [10] as indicated in Table III. More significant differences are found in the coordination of the thiocyanato group and in the distance of the water molecule from the thiocyanato nitrogen. In both modifications the location of the oxygen site is the same, a hole near the N of SCN group. However, the N–O distance is 2.69(6) Å for the orthorhombic form and 2.85(2) Å for the monoclinic form. Other bond lengths showing significant variation are Au–S, which is 2.928(17) Å for the orthorhombic form and 2.79(3) Å for the monoclinic form, and S–C, which is 1.701(42) Å for the orthorhombic form and 1.577(15) Å for the monoclinic form. The oxygen site is only about half occupied in the orthorhombic form, but it is not at all clear that this is responsible for the existence of both modifications of the complex with their different space groups and Au–S bond lengths.

Detailed crystal structure data are available for only a few other four-coordinate Au(I) complexes. Table IV includes all the known four-coordinate Au(I) phosphine complexes which have monodentate tertiary phosphine ligands. Complexes with chelating ligands and cluster compounds are omitted. An extensive review of gold compounds has recently appeared [1]. The cation in the arsine complex $[Au(pdma)_2]$ $[(C_6F_5)_2Au]$ (pdma = *o*-phenylenebis(dimethylarsine)) displays four-fold geometry, with As–Au–As angles of 87(1) and 122(1)° within and between the bidentate chelate groups, respectively [17]. The phosphine complex closest to regular tetrahedral geometry is $[(Ph_2MeP)_4Au]$ $[PF_6]$, for which the P–Au–P angles are 105.24(4) and 118.32(4)° [18]. Ideal tetrahedral geometry is achieved by a stibine complex, $[(Ph_3Sb)_4Au]$-$[(C_6F_5)_2Au]$, in which the largest deviation from ideal tetrahedral angles in the cation is 1° [19].

When listed in order of increasing Au–P bond lengths as in Table IV, the complexes are also found to be ordered according to their coordination numbers or by the number of phosphine ligands that are present. There seems to be a much stronger correlation of Au–P bond lengths with coordination number and with steric crowding about the Au atom than with the electronegativity of the non-phosphine ligands. Thus, for L = Ph_3P, the bond lengths increase considerably from [LAuCl] to $[L_2AuCl]$ to $[L_3AuCl]$, or from $[(LAu)_3S]^+$ to $[L_2AuSCN]$ to $[L_3AuSCN]$, or from $[(Ph_2MeP)_2$-$Au]^+$ to $[(Ph_2MeP)_4Au]^+$. However, they remain relatively constant for [LAuCl], [LAuCN], and $[(LAu)_3S]^+$, or for $[L_2AuCl]$, $[L_2AuSCN]$ and $[L_2$-$AuI]$, or for $[L_3AuCl]$ and $[L_3AuSCN]$, or for $[(Ph_2MeP)_4Au]^+$ and the trigonal site in $[L_4Au]^+$. It is evident that the net charge on the complex has little effect on the Au–P bond length.

Individual variations for a given coordination number do exist. The first of the three-coordinate complexes in Table IV, $[(Me_2PhP)_2Au(SnCl_3)]$, has a Au–P bond length which is shorter than that of the longest two-coordinate complexes, but that is due to a severe distortion in that complex towards linear, two-fold coordination [20]. On the other hand, the bond length in $[(PhO)_3PAuCl]$ is unusually short, a fact which has been attributed to the effect of the electronegative substituents at the phosphorus atom on its lone-pair orbital, which is used to form the σ bond to the gold atom [21]. If such individual factors are taken into account, then Table IV may have some predictive value in the preparation of new three- and four-coordinate Au(I) complexes. However, there is as yet no clear explanation as to why $[(Ph_3P)_2AuSCN]$, $[(Ph_3P)_2AuCl]$, and $[(Ph_3P)_2AuI]$ are three-coordinate while $[(Cy_3P)_2Au]SCN$ is two-coordinate. The cyclohexyl group should not produce such a large amount of steric crowding about the gold, compared to the phenyl group.

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