Crystal Structures and Spectra of Two Forms of Chloro(triphenylarsine)gold(I)

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Introduction

In a continuing study on luminescent Au(I) complexes,[1,2] polycrystalline samples of chloro(triphenylarsine)gold(I), $Ph_3AsAuCl$, showed variable spectral results. These variations were traced to the existence of two crystalline forms of the complex. The two forms are obtained simultaneously, although in varying amounts, by recrystallization. They exhibit different prominent habits, needles and prisms, which allows the two types to be separated easily. We report herein the crystal structures and Raman spectra of the two forms.

Experimental Section

$Ph_3AsAuCl$ was synthesized by standard methods.[3] A 2:1 mole ratio of Ph_3As dissolved in CH_2Cl_2 was slowly added to $HAuCl_4$ dissolved in absolute ethanol. The light yellow solution was stirred for ≈1 h and then refrigerated at 5 °C for ≈4 h. The resulting crystals were removed by filtration, washed with ethanol, and recrystallized by diffusion of ether into a CH_2Cl_2 solution. Rapid recrystallization leads mainly to colorless needles, while gradual recrystallization yields predominantly colorless prisms. Crystals of the two habits were separated by hand under a microscope.

Crystals were cooled to 130 K, and data sets were collected with a Siemens P4 (needles) or a Syntex $P2_1$ (prisms) X-ray diffractometer using Mo Kα radiation. The structures were solved by Patterson and difference Fourier methods and refined by full-matrix least squares (based on *F*) using SHELXTL PLUS.[4] The absolute structures were readily determined. An absorption correction was applied.[5] Final difference maps were featureless except for small density in the region of the heavy atoms. Table 1 gives the crystal data of the two forms of $Ph_3AsAuCl$, and atomic positional parameters are presented in Table 2.

Raman spectra of the samples at 77 K were excited by the 488 nm line of an argon ion laser and recorded with a Spex Ramalab spectrometer. The Raman samples were coarsely ground to minimize polarization effects.

Results and Discussion

Both forms are orthorhombic, space group $P2_12_12_1$ with $Z = 4$. Table 3 summarizes the bond lengths and angles, except those involving the phenyl groups. All of the bond lengths and angles, including those of the phenyl groups, are normal and similar in the two forms. The torsional angles of the phenyl groups, as evident from Figure 1, differ and are 51.6(9), 39.4(9), 114.4(9)° versus 79.4(4), 44.6(4), 112.9(4)° for the needle and prism forms, respectively.

Table 1. Crystal Data for the Two Forms of $Ph_3AsAuCl$

	needles	prisms
formula	$C_{18}H_{15}AsAuCl$	$C_{18}H_{15}AsAuCl$
fw	538.6	538.6
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a/Å	10.203(4)	10.974(2)
b/Å	12.186(4)	11.919(2)
c/Å	13.228(5)	12.622(2)
V/Å^3	1644.7(10)	1650.9(4)
Z	4	4
ϱ_{calc}/g cm^{-3}	2.175	2.167
T/K	130	130
λ/Å	0.710 73	0.710 73
μ/mm^{-1}	11.08	11.05
$R(F_o)^a$	0.058	0.041
$R_w(F_o)^b$	0.054	0.043

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $Ph_3AsAuCl$

atom	*x*	*y*	*z*	U^a
		Needle Form		
Au	8177.2(11)	9400.3(9)	7590.0(8)	20.0(3)
As	10285(3)	8788(2)	7198(2)	19.1(9)
Cl	6115(8)	9972(7)	7993(6)	32(3)
C(1)	10296(29)	7881(23)	5959(20)	18(6)
C(2)	9563(35)	8173(28)	5187(23)	31(8)
C(3)	9507(37)	7516(28)	4273(27)	38(9)
C(4)	10258(36)	6574(28)	4279(25)	35(8)
C(5)	11068(42)	6248(33)	5101(26)	49(10)
C(6)	11074(31)	6912(24)	5913(21)	20(7)
C(7)	11529(27)	9934(24)	7039(20)	22(7)
C(8)	12253(32)	10087(30)	6117(23)	33(8)
C(9)	13146(38)	10941(24)	6057(22)	32(7)
C(10)	13453(31)	11660(25)	6907(21)	28(8)
C(11)	12689(30)	11511(25)	7776(23)	32(8)
C(12)	11762(33)	10674(25)	7868(21)	33(7)
C(13)	11017(30)	7851(23)	8263(21)	17(6)
C(14)	12372(28)	7793(23)	8316(20)	13(6)
C(15)	12952(35)	7117(26)	9084(22)	32(8)
C(16)	12194(30)	6530(25)	9645(22)	25(7)
C(17)	10794(36)	6541(30)	9600(26)	35(9)
C(18)	10260(32)	7231(22)	8840(20)	19(7)
		Prism Form		
Au	7395.9(4)	8375.3(3)	9710.7(3)	22(1)
As	7466.4(11)	10040.1(9)	8743.8(8)	22(1)
Cl	7306(3)	6747(2)	10669(2)	34(1)
C(1)	6029(11)	10245(11)	7887(9)	22(3)
C(2)	5031(11)	8553(9)	8010(9)	20(3)
C(3)	3996(11)	9647(10)	7377(10)	24(3)
C(4)	3977(11)	10503(11)	6600(9)	24(3)
C(5)	4975(11)	11208(10)	6467(10)	24(3)
C(6)	5994(11)	11080(10)	7102(9)	18(3)
C(7)	7578(10)	11388(12)	9594(10)	30(3)
C(8)	6782(13)	12293(11)	9441(12)	37(4)
C(9)	6818(14)	13181(10)	10126(14)	43(5)
C(10)	7662(14)	13221(11)	10958(10)	38(4)
C(11)	8457(14)	12327(12)	11121(11)	38(4)
C(12)	8415(11)	11411(10)	10425(10)	29(4)
C(13)	8805(12)	10118(10)	7727(9)	26(4)
C(14)	9289(14)	11155(12)	7408(14)	38(5)
C(15)	10118(13)	11175(11)	6593(13)	33(4)
C(16)	10520(12)	10181(12)	6119(12)	34(4)
C(17)	10037(15)	9153(13)	6496(13)	42(5)
C(18)	9189(13)	9153(12)	7281(12)	33(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor for the Au, As, and Cl atoms of the needle form and for all atoms of the prims form. The C atoms of the needle form were refined with isotropic displacements.

Marked differences are also found in the shortest Au···Au contact, namely 6.913(1) Å for the needle form and 5.916(1) Å for the prism form. However, the strength and number of

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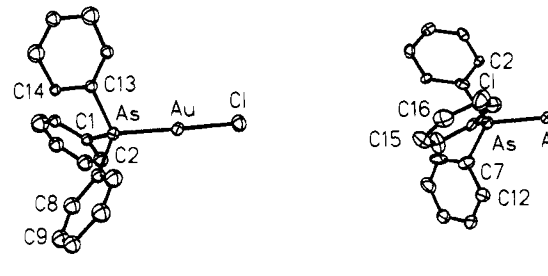
Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Two Forms of $Ph_3AsAuCl$

	needles	prisms		needles	prisms
Au··Au′[a]	6.913(1)	5.916(1)	Cl−Au−As	178.9(2)	179.3(1)
Cl−Au	2.280(8)	2.288(3)	Au−As−C	111.6(9)	112.0(4)
Au−As	2.334(3)	2.331(1)		112.2(9)	114.2(4)
As−C	1.900(28)	1.928(12)		113.9(9)	114.7(4)
	1.961(28)	1.937(13)	C−As−C	104.7(12)	104.0(5)
	1.978(27)	1.953(12)		105.6(12)	104.9(5)
				108.4(12)	106.1(5)

[a] Symmetry code: Au′ at 1.5 − *x*, 2 − *y*, 0.5 + *z*.



needles prisms

Figure 1. Computer-generated drawing of the two forms of $Ph_3AsAuCl$ showing thermal ellipsoids at the 50% probability level.

Table 4. Summary of the Raman Spectra for the Two Forms of $Ph_3AsAuCl$ at 77 K

$Ph_3AsAuCl$			Ph_3As	
prisms	needles	lit.[a]	lit.[b]	assgnt[a−c]
73 mw	76 vw		77 s	lattice and torsion modes
81 w	81 vw			
95 m	94 w	94 s	93 s	
	106 m	104 vs	104 s	
108 m, b				
	113 mw		117 m	
122 s		121 m		
151 s				
173 m	174 s	171 s		Au−As
191 m	188 s	188 s	188−199 m	ν_x X-sens
201 w	204 m	203 m		As−Ph bend
221 s	220 m	217 m		As−Ph bend
243 m	244 s	242 s	235−245 m	ν_u X-sens
250 m	250 m	249 s	249 w	
259 mw	260 mw	259 w	252 w	
322 w	322 w	324 sh		$Au-{}^{37}Cl$
330 m,b	330 s	327 s		$Au-{}^{35}Cl$
616 vw	616 w		618 w	ν_s α(C−C−C)
672 m	674 m		667 m	ν_r X-sens
677 w, sh	676 w, sh		669 sh	ν_r X-sens
996 m, sh	998 vs		1000 s	ν_p ring
1000 s	1000 s, sh		1003 vs	ν_p ring
1024 m	1024 m, b		1024−1026 m	ν_b β(C−H)
1087 w	1090 w		1076−1084 w	ν_q X-sens
1156 w	1162 w		1155−1158 w	ν_c β(C−H)
	1185 w			
1575 w	1576 w		1572−1574 w	ν_l ν(C−C)
1581 m	1582 m		1580−1584 m	ν_k ν(C−C)

[a] Reference 10. [b] Reference 11. [c] "X-sens" indicates that the mode is sensitive to the substituent on the phenyl ring.

possible Cl··H interactions as well as Au··H agostic interactions are similar in the two forms. A comparison with the structures of analogous phosphorus,[6] bromide,[7,8] and iodide[9] compounds reveals that the needle form is common to the group and that these structures are isomorphous, whereas the prism structure is new. Figure 2 depicts the molecular packing of the needle form, which may be compared to the packing of the prism form in Figure 3. The most striking difference occurs in the nearly parallel alignment of the As−Au−Cl line with the *bc* plane in the prism form (2.2(4)°); no such alignment exists in the needle form (22.7(4)°).

The Raman spectra of the two forms at 77 K are summarized in Table 4. As expected from the structural data, spectral differences occur mainly at low frequency in the regions of the torsional and lattice modes. The most prominent are two strong bands in the spectrum of the prisms at 122 and 151 cm^{-1} that are absent in the spectrum of the needles. Table 4 includes the Raman shifts previously reported for $Ph_3AsAuCl$ at ≈100 K by Jones and Powell[10] and for the free ligand, Ph_3As, at ≈80 K by Clark *et al.*[11] A comparison of the data shows that the modes above 600 cm^{-1}, which are associated with the phenyl moieties, are not significantly changed in the spectrum of the complex. The comparison also suggests that the earlier data of Jones and Powell involved mainly the needle form of $Ph_3AsAuCl$.

Other spectral measurements also show small differences between the two forms. As reported elsewhere,[1] both forms of $Ph_3AsAuCl$ are luminescent at room temperature, showing an intense, structured system with an origin peak at ≈455 nm. A very similar emission has been reported for Ph_3PAuCl.[12] The decays of the 455 nm band at room temperature are exponential

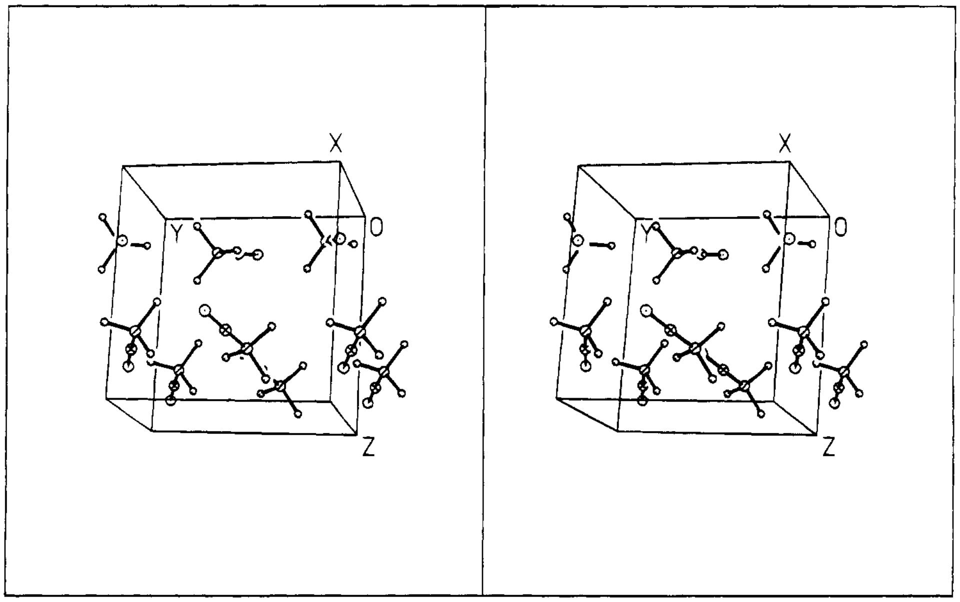


Figure 2. Molecular packing of the needle form of $Ph_3AsAuCl$. Only the *ipso* carbons of the phenyl rings are shown.

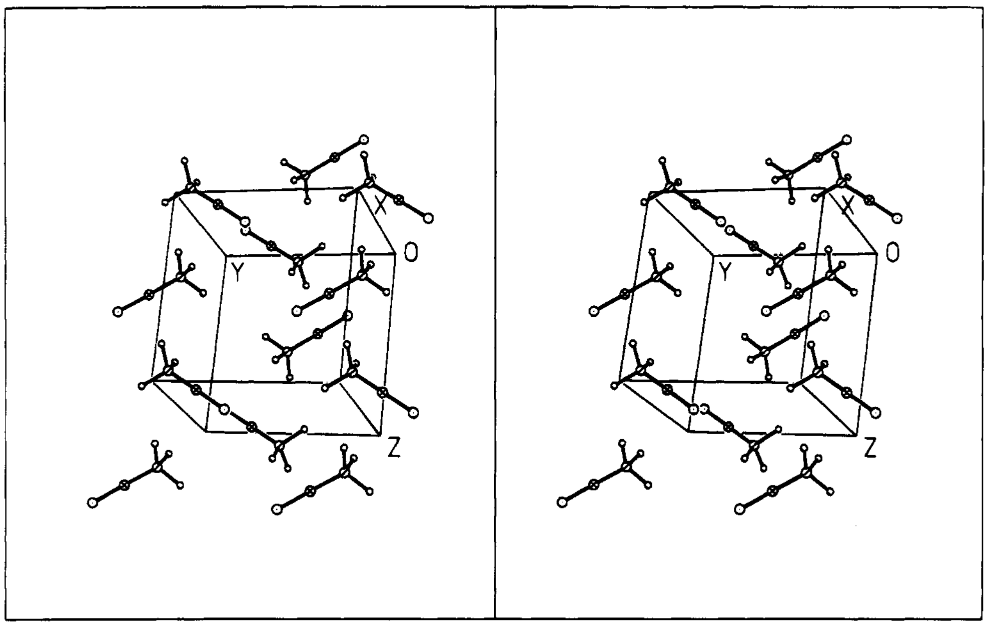


Figure 3. Molecular packing of the prism form of $Ph_3AsAuCl$. Only the *ipso* carbons of the phenyl rings are shown.

with lifetimes of 30 and 15 ms for the needle and prism forms, respectively. The prism form shows an additional, very weak emission with origin at ≈345 nm, which appears in the spectrum of the needle form only at low temperatures.

Summary

Two structures are found for crystals of $Ph_3AsAuCl$ that differ mainly in the intramolecular orientations of the phenyl groups and in the intermolecular packing. A cursory investigation of multiple crystals of $Ph_3AsAuBr$ and Ph_3PAuX ($X = Cl, Br$), prepared also by recrystallization from CH_2Cl_2/ether, showed only one structure for each compound. However, other metal complexes are known for which multiple structures are obtained.[13] The two forms of $Ph_3AsAuCl$ yield similar Raman and luminescence spectra, although some differences are apparent. In the Raman spectra, the differences occur in the low-frequency modes ($\leq 200\ cm^{-1}$), as might be expected. The luminescences[1] show differences in the lifetimes of the 455 nm band and in the overall spectra, with a second emission system that originates at 345 nm contributing weakly in the prism form. The lifetime difference may reflect a difference in either the radiationless or the radiative contribution. Both are potentially sensitive to the structural details.

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Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, H atom coordinates, and crystal refinement data for both forms of chloro(triphenylarsine)gold(I) (10 pages). Ordering information is given on any current masthead page.

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