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Dihalo(tetraphenyldithioimidodiphosphinato)gold(III) Complexes. Crystal and Molecular Structure of [$AuCl_2(SPPh_2NPPh_2S)$]

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Abstract

The reaction of $SPPh_2NHPPh_2S$ with $AuCl_3(tht)$ gives $AuCl_2(SPPh_2NPPh_2S)$, containing the deprotonated ligand. Oxidation with halogens (X = Cl, Br or I) of $[Au(SPPh_2NPPh_2S)]_2$ leads to $AuX_2(SPPh_2NPPh_2S)$. The structure of the dichloro complex has been determined by X-ray crystallography.

Introduction

A number of interesting complexes with tetraphenyldithioimidodiphosphinato, $[SPPh_2NPPh_2S]^-$, as ligand have been described [1–3], but only two gold derivatives $[Au(SPPh_2NPPh_2S)]_2$ and $Au(C_6F_5)_2(SPPh_2NPPh_2S)$ are known [4].

Here we report the preparation of $AuX_2(SPPh_2NPPh_2S)$ (X = Cl, Br or I) and the crystal structure of the dichloro derivative.

Experimental

The instrumentation employed and general experimental techniques were as described earlier [5]. The yields, melting points, C, H, N and Au analyses, conductivities and molecular weights of the novel complexes are listed in Table I.

Preparation of the Complexes

All reactions were carried out at room temperature.

$AuX_2(SPPh_2NPPh_2S)$

These complexes can be obtained in three different ways.

(a) X = Cl (I). To a solution of $AuCl_3(tht)$ (obtained by reaction of equimolar amounts of AuCl(tht) [6] and Cl_2 in dichloromethane) (0.039 g, 0.1 mmol) in 15 ml of dichloromethane was added $SPPh_2NHPPh_2S$ [7] (0.045 g, 0.1 mmol). The

TABLE I. Analytical Data of Complexes

Complex	Yield (%)	Analysis: found (calc.) (%)				Λ_M[a]	Molecular weight (Found (calc.))	Melting point (°C)
		C	H	N	Au			
I $AuCl_2(SPPh_2NPPh_2S)$	80	40.0 (40.2)	2.95 (2.8)	1.6 (1.95)	27.9 (27.49)	20	1433 (716)	152
II $AuBr_2(SPPh_2NPPh_2S)$	80	35.55 (35.8)	2.6 (2.5)	1.8 (1.75)	24.5 (24.45)	15	1590 (805)	195
III $AuI_2(SPPh_2NPPh_2S)$	80	31.65 (32.05)	2.3 (2.1)	1.2 (1.55)	22.1 (21.9)		1230 (899)	185(d)

[a] In acetone, ohm^{-1} cm^2 mol^{-1}.

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solution instantaneously turned red and was stirred for 30 min. Thereafter the solution was vacuum evaporated to *ca.* 5 ml and hexane (15 ml) was added. The red solid was filtered off.

(b) X = Cl (I), Br (II) or I (III). To a suspension of $[Au(SPPh_2NPPh_2S)]_2$ [4] (0.129 g, 0.1 mmol) in 10 ml of dichloromethane was added 2 ml of a chlorine or bromine solution in CCl_4 (0.1 M), or iodine (0.051 g, 0.2 mmol) and the mixture was stirred for 15 min. The red (**I**, **II**) or violet (**III**) solution was vacuum evaporated to *ca.* 5 ml. Slow addition of hexane (15 ml) produced crystals of complexes **I**–**III**.

(c) X = Br (II) or I (III). To a solution of complex **I** (0.071 g, 0.1 mmol) in 20 ml of acetone was added KX [X = Br (0.048 g, 0.4 mmol) or I (0.066 g, 0.4 mmol)]. The mixture was stirred for 1 h. Thereafter the solution was evaporated and the residue was treated with dichloromethane (15 ml). The excess of KX was filtered off and the solution was vacuum concentrated to *ca.* 5 ml. Addition of hexane (15 ml) precipitated the complex **II** or **III**.

Crystal Structure Determination of Complex I

Brown tabular crystals were obtained by liquid diffusion of n-hexane into a solution of **I** in dichloromethane.

Crystal data

$C_{24}H_{20}AuCl_2NP_2S_2$, $M = 716.4$, monoclinic, space group $P2_1/n$, $a = 11.869(3)$, $b = 14.512(3)$, $c = 15.152(3)$ Å, $\beta = 98.26(2)°$, $U = 2582.7$ Å^3, $Z = 4$, $D_x = 1.84$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 6.1$ mm^{-1}, $F(000) = 1384$.

Data collection and processing

Stoe-Siemens four-circle diffractometer, monochromated Mo Kα radiation, profile-fitting mode. 5169 unique intensities ($2\theta_{max}$ 53°), 3895 with $F > 4\sigma(F)$ used for all calculations. Absorption correction based on ψ-scans; transmissions 0.46–0.99 for crystal size 0.4 × 0.25 × 0.1 mm. Cell constants refined from 2θ values of 38 reflections in the range 20°–24°.

Structure solution and refinement

Heavy atom method; anisotropic refinement on F to R 0.036, R_w 0.034. H atoms included using riding model and fixed isotropic temperature factors. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0002F^2$. 289 parameters; max. Δ/σ 0.01; max. $\Delta\rho$ 0.9 e Å^{-3}; $S = 1.5$. Program system SHELX-76, locally modified by its author. Final atomic coordinates and derived molecular dimensions are presented in Tables II and III.

TABLE II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Complex I

	x	*y*	*z*	*U*(eq)[a]
Au	6510.6(2)	5796.1(1)	5364.1(2)	39(1)
S(1)	7040(1)	6919(1)	4421(1)	47(1)
S(2)	5772(1)	6711(1)	6384(1)	49(1)
Cl(1)	7192(2)	4759(1)	4414(1)	66(1)
Cl(2)	6027(2)	4609(1)	6257(1)	68(1)
P(1)	7710(1)	7982(1)	5223(1)	39(1)
P(2)	5682(1)	8055(1)	5952(1)	39(1)
N	6850(4)	8499(3)	5773(3)	47(2)
C(11)	8927(5)	7586(4)	5973(4)	45(2)
C(12)	9042(6)	7835(5)	6866(4)	64(3)
C(13)	9995(7)	7568(6)	7433(5)	85(3)
C(14)	10833(8)	7089(6)	7136(6)	88(3)
C(15)	10752(8)	6861(6)	6254(7)	98(4)
C(16)	9784(7)	7098(5)	5660(6)	75(3)
C(21)	8225(5)	8777(4)	4473(4)	45(2)
C(22)	8689(6)	8488(5)	3724(5)	67(3)
C(23)	9143(8)	9127(6)	3200(6)	86(3)
C(24)	9143(7)	10040(6)	3397(6)	82(3)
C(25)	8693(7)	10331(5)	4126(6)	74(3)
C(26)	8229(6)	9704(5)	4657(4)	54(2)
C(31)	4562(5)	8187(4)	5026(4)	42(2)
C(32)	4636(7)	8894(5)	4421(5)	63(3)
C(33)	3735(8)	9048(5)	3744(5)	81(3)
C(34)	2781(8)	8514(6)	3680(6)	86(3)
C(35)	2711(7)	7818(6)	4251(6)	82(3)
C(36)	3614(6)	7637(5)	4945(5)	61(2)
C(41)	5250(5)	8607(4)	6911(4)	43(2)
C(42)	6046(6)	8800(5)	7636(5)	63(3)
C(43)	5732(7)	9203(5)	8393(5)	65(3)
C(44)	4627(7)	9392(5)	8433(5)	69(3)
C(45)	3819(7)	9188(6)	7739(6)	85(3)
C(46)	4132(7)	8792(6)	6960(5)	72(3)

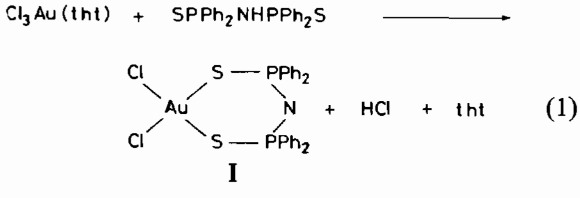
[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III. Selected Bond Lengths (Å) and Angles (°) for Complex I

Au–S(1)	2.314(2)	Au–S(2)	2.303(2)
Au–Cl(1)	2.307(2)	Au–Cl(2)	2.314(2)
S(1)–P(1)	2.052(2)	S(2)–P(2)	2.055(2)
P(1)–N	1.594(5)	P(1)–C(11)	1.798(6)
P(1)–C(21)	1.789(6)	P(2)–N	1.587(5)
P(2)–C(31)	1.800(6)	P(2)–C(41)	1.798(6)
S(2)–Au–S(1)	99.9(1)	Cl(1)–Au–S(1)	85.6(1)
Cl(1)–Au–S(2)	174.5(1)	Cl(2)–Au–S(1)	176.6(1)
Cl(2)–Au–S(2)	83.5(1)	Cl(2)–Au–Cl(1)	91.0(1)
P(1)–S(1)–Au	106.2(1)	P(2)–S(2)–Au	109.9(1)
N–P(1)–S(1)	116.1(2)	C(11)–P(1)–S(1)	110.0(2)
C(11)–P(1)–N	109.7(3)	C(21)–P(1)–S(1)	104.3(2)
C(21)–P(1)–N	109.3(3)	C(21)–P(1)–C(11)	106.9(3)
N–P(2)–S(2)	115.7(2)	C(31)–P(2)–S(2)	110.3(2)
C(31)–P(2)–N	112.9(3)	C(41)–P(2)–S(2)	100.0(2)
C(41)–P(2)–N	108.4(3)	C(41)–P(2)–C(31)	108.6(3)
P(2)–N–P(1)	122.6(3)		

Results and Discussion

Bis(diphenylphosphine)amine disulfide ($SPPh_2NHPPh_2S$) is acidic [8] and so can be easily deprotonated [1–4]. Thus, this ligand reacts with $AuCl_3$(tht) (tht = tetrahydrothiophen) by displacement not only of tht but chloride, leading to the neutral complex **I** (eqn. (1)).

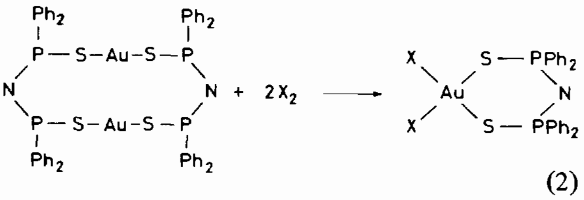


(1)

I

When an excess of the disulfide (1:2 molar ratio) is used, a reduction to gold(I) and formation of $[Au(SPPh_2NPPh_2S)]_2$ [4] is observed. The same dinuclear derivative is obtained from the reaction of complex I and $SPPh_2NHPPh_2S$.

Addition of halogen (Cl_2, Br_2 or I_2) to dichloromethane suspensions of the dinuclear gold(I) derivative (2:1 molar ratio) leads to the corresponding dihalogold(III) complexes.



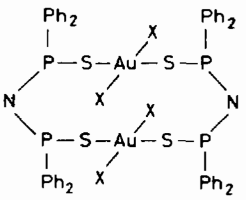
(2)

X = Cl(I), Br(II), I(III)

When halogen is used in a 1:1 molar ratio no formation of gold(II) derivatives is observed but a mixture of the complexes I, II or III and the starting product is obtained.

The dibromo and diiodo derivatives are also synthesised by the reaction between complex I and KX (65% and 60% yield, respectively for II and III).

Complexes I–III are red (I), dark red (II) or violet (III) solids, stable to air and moisture at room temperature. They are soluble in acetone, dichloromethane and chloroform and insoluble in diethyl ether and hexane. Complexes I and II are moderately conducting in acetone, although the measured molar conductivities (Table I) are lower than expected for 1/1 electrolytes. Complex III rapidly decomposes in acetone and gives pale yellow solutions which behave as 1/1 electrolytes (Λ_M, 82 ohm^{-1} cm^2 mol^{-1}). Their molecular weights in chloroform solutions (isopiestic method) are higher than expected for a mononuclear derivative (Table I). Complexes I and II are probably dimeric in solution and III probably exists as a mixture of the mono- and dinuclear derivatives. The ^{31}P NMR spectra (^1H decoupled, in $CDCl_3$) consist of a singlet at 36.9 (I), 36.6 (II) or 36.5 (III) ppm. The IR spectra of Nujol suspensions show a band at 560(s) cm^{-1} due to the vibration ν(P–S), and the *cis* disposition of the two chlorine in I is confirmed by the presence of two bands at 330(m) and 315(m) cm^{-1} due to ν(Au–Cl) [9]. A band at 225(m, br) cm^{-1} in II is assigned to ν(Au–Br).



The X-ray structure analysis of I confirms that it is monomeric in the solid state (Fig. 1). The coordination geometry at gold is, as expected, square planar to a good approximation; the planarity is almost exact (mean deviation of five atoms 0.006 Å), but there are some deviations from ideal angles (notably S2–Au–S1 99.9° in the chelate ring).

Surprisingly few Au(III) complexes with sulphur ligands have been studied crystallographically; this may be attributed to the tendency of sulphur compounds to reduce gold(III). We are aware of no other structure determination of a gold(III) complex with two sulphur and two chlorine ligands*. However, the bond lengths at gold can be regarded as broadly normal; the Au–S bond lengths of 2.303, 2.314(2) Å are comparable with the range 2.29–2.32 Å observed in dithiolate complexes [10], and the Au–Cl bond lengths of 2.307, 2.314(2) Å are appreciably longer than the *ca.* 2.28 Å usually observed *trans* to N or Cl ligands [10].

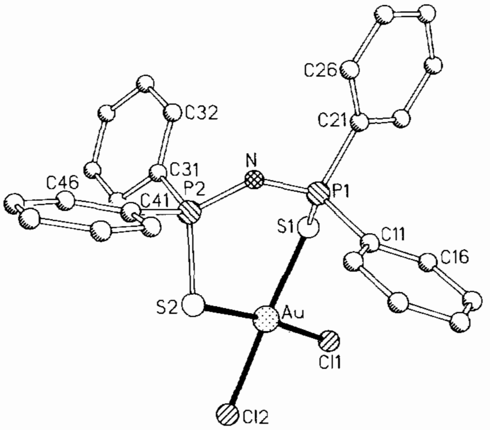


Fig. 1. The molecule of complex I in the crystal, showing the atom numbering scheme. Radii are arbitrary; H atoms have been omitted for clarity.

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*See 'Note Added in Proof', p. 236.

The extent of delocalisation in the ligand is difficult to establish. The chelate ring is not planar (torsion angles about the ring bonds are: Au–S1, 40°; Au–S2, 8°; S1–P1, –65°; S2–P2, –58°; P1–N, 19°; P2–N, 47°). The P–N bond lengths of 1.594, 1.587(5) Å lie in a range usually associated with multiple bonding character [11], whereas the P–S bond lengths of 2.052, 2.055(2) Å correspond to slightly short single bonds [11]. A simplified description of the ligand would then postulate the resonance form $^{-}S{-}P\phi_2{=}N{-}P^{+}\phi_2{-}S^{-}$ together with the corresponding form with single and double bonds reversed at N.

Supplementary Material

Additional crystallographic data (complete bond lengths and angles, H atom coordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, F.R.G. Any request for this material should quote a full literature citation and the reference number CSD 53154.

Acknowledgements

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Note Added in Proof

Since the submission of this manuscript, the structure of an AuS_2Cl_2 system has been published [12].

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