Complexes of Copper, Silver, and Gold with Urea Homologues. Crystal Structures of $[\{\mu^2\text{-}SeC(NH_2)_2\}Ag\{SeC(NH_2)_2\}_2]_2^{2+}2Cl^- \cdot 4DMF$ and $[Ph_3PAu\{SC(NHMe)_2\}]^+Cl^- \cdot SC(NHMe)_2$

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Coinage Metal Complexes, X-Ray, Urea Homologues

The title compounds were prepared from chloro(organophosphine)metal(I) complexes and the urea homologues $SeC(NH_2)_2$ and $SC(NHMe)_2$ in good yields. Recrystallization of $[Ph_3PAg\{SeC(NH_2)_2\}]^+Cl^-$ from DMF/CH_2Cl_2 leads in low yield to the dinuclear complex $[\{\mu^2\text{-}SeC(NH_2)_2\}Ag\{SeC(NH_2)_2\}_2]_2^{2+}2Cl^- \cdot 4DMF$. The crystal structure reveals short Ag–Ag contacts and unexpectedly acute angles at the bridging selenium atom. The crystal structure of $[Ph_3PAu\{SC(NHMe)_2\}]^+Cl^- \cdot SC(NHMe)_2$ shows short N···Cl and N···S contacts that probably correspond to hydrogen bonding.

Introduction

Little is known about the molecular structures of selenourea metal complexes, although some complexes of that type have been known for more than a hundred years (*e.g.* $[Ag(SeC(NH_2)_2]^+Cl^-$) [1]. However, thiourea and thiolate complexes of gold have attracted attention because of their potential use as anti-tumor and anti-rheumatoid drugs [2]. Some biologically active compounds, such as 2-thiouracil or 2-pyrimidinethiol, can be seen as thiourea derivatives and gold complexes of those ligands may have a potential use in medicine [3,4].

We have recently reported the synthesis and crystal structures of the (organophosphine)gold(I)-selenourea complexes $[Ph_3PAuSeC(NH_2)_2]^+Cl^-$ and $dppm[AuSeC(NH_2)_2]_2^{2+}2Cl^-$ (dppm = bis(diphenylphosphino)methane) [5]. The preparation is as follows:

$$Ph_3PAuCl + SeC(NH_2)_2 \rightarrow [Ph_3PAuSeC(NH_2)_2]^+Cl^-$$

$$dppm(AuCl)_2 + 2SeC(NH_2)_2 \rightarrow dppm[AuSeC(NH_2)_2]_2^{2+}2Cl^-$$

In order to compare the reactivity and the structural features of metal complexes with urea derivatives, we have prepared some new complexes of copper, silver and gold and determined the crystal structures of the dinuclear silver(I) complex $[\{\mu^2\text{-}SeC(NH_2)_2\}Ag\{SeC(NH_2)_2\}_2]_2^{2+}2Cl^- \cdot 4DMF$ and of the gold(I) thiourea complex $[Ph_3PAu\{SC(NHMe)_2\}]^+Cl^- \cdot SC(NHMe)_2$.

Experimental

^1H, $^{31}P\{^1H\}$ NMR spectroscopy: Bruker AC 200 (standards: $TMS_{int.}$, $H_3PO_{4ext.}$), – Elemental analyses: locally and *Lab.* Beller, Göttingen. The reactions were performed in dried and freshly distilled solvents under N_2-atmosphere.

Synthesis of the gold-selenourea complexes **1,2**

A solution of the (phosphine)chlorogold complex in 100 ml acetone (2 mmol) is added with stirring to a solution of selenourea (2 mmol) in 50 ml acetone. After 0.5 h, the white product precipitates. After separation, it is dissolved in refluxing 100 ml CH_3CN/5 ml CH_3OH and crystallizes on cooling.

$[MePh_2PAuSeC(NH_2)_2]^+Cl^-$ **(1)**

Yield: 0.89 g (80%); F.: 167 °C (dec.); ^1H NMR (CD_3OD): δ (ppm) 2.29 (d, 3H, $^2J_{H-P}$ 10.5 Hz, $-CH_3$), 7.58 (m, 4H, *o*-Ph), 7.76 (m, 6H, *m*- and *p*-Ph), no N–H group detected; ^{31}P NMR (CD_3OD): δ (ppm) 25.8 (s).

Analysis

Calcd	C 30.3	H 3.1	N 5.0%,
Found	C 29.3	H 3.0	N 5.1%.

$[Me_2PhPAuSeC(NH_2)_2]^+Cl^-$ **(2)**

Yield: 0.93 g (95%); F.: 183 °C dec.); ^1H NMR (d_6-DMSO): δ (ppm) 1.93 (d, 6H, $^2J_{H-P}$ 10.5 Hz,

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$-CH_3$), 7.55 (m, 2H, *o*-Ph), 7.86 (m, 3H, *m-p*-Ph), 8.48 (s, br, 2H, $-NH_2$), 8.69 (s, br, 2H, $-NH_2$); ^{31}P NMR (d_6-DMSO): δ (ppm) 11.9 (s).

Analysis

Calcd	C 21.9	H 3.1	N 5.7%,
Found	C 20.7	H 2.9	N 5.7%.

Synthesis of $[Ph_3PCuSeC(NH_2)_2]^+Cl^-$ **(3)**

A solution of 0.361 g $[Ph_3PCuCl]_4$ (0.25 mmol) in 20 ml CH_2Cl_2/40 ml acetone is added with stirring to a solution of 0.123 g $SeC(NH_2)_2$ (1 mmol) in 40 ml acetone over a period of 20 min. After stirring for 22 h at ambient temperature, the solvent is removed *in vacuo,* leaving an off-white, analytically pure product.

Yield: 0.4 g (83%); F.: 196 °C (dec.); ^1H NMR (d_6-DMSO): δ (ppm) 7.40 (m, 15H, Ph), 7.94 (s, br, 2H, $-NH_2$), 8.45 (s, br, 2H, $-NH_2$); ^{31}P NMR (d_6-DMSO): δ (ppm) −4.5 (s).

Analysis

Calcd	C 47.2	H 3.9	N 5.8%,
Found	C 47.2	H 4.0	N 5.8%.

Synthesis of $[Ph_3PAuSC(NHMe)_2]^+Cl^-$ **(4)**

A solution of 0.996 g Ph_3PAuCl (2 mmol) in 100 ml acetone is added with stirring to a solution of 0.21 g $SC(NHMe)_2$ in 50 ml acetone over a period of 20 min. After stirring for 3 h at ambient temperature the solvent is removed *in vacuo,* leaving an off-white product. A crystalline product can be obtained from CH_2Cl_2/diethyl ether.

Yield: 1.03 g (86%); F.: 143 °C (dec.); ^1H NMR ($CDCl_3$): δ (ppm) 3.06 (d, 6H, $^3J_{H-H}$ 4.5 Hz, $-CH_3$), 7.50 (m, 15H, −Ph), 7.90 (s, br, 2H, −NH); ^{31}P NMR ($CDCl_3$): δ (ppm) 34.6 (s).

Analysis

Calcd	C 42.1	H 3.9	N 4.7	S 5.4%,
Found	C 42.5	H 3.9	N 4.7	S 5.6%.

Synthesis of $[Ph_3PAgSeC(NH_2)_2]^+Cl^-$ **(5)**

A solution of 0.82 g $[Ph_3PAgCl]_4$ (0.5 mmol) in 100 ml CH_2Cl_2 is added with stirring to a solution of 0.246 g $SeC(NH_2)_2$ (2 mmol) in 50 ml acetone. A white precipitate is immeadiately formed. After stirring for 1 h at ambient temperature, the solvent is removed *in vacuo,* leaving an off-white amorphous solid. An analytically pure sample can be obtained by recrystallization from refluxing acetone/DMF.

Yield: 0.91 g (86%); F.: 181 °C (dec.); ^1H NMR (d_6-DMSO): δ (ppm) 7.45 (m, 15H, −Ph), 7.90 (s, br, 2H, $-NH_2$), 8.39 (s, br, 2H, $-NH_2$); ^{31}P NMR (d_6-DMSO) δ (ppm) 4.3 (s).

Analysis

Calcd	C 43.2	H 3.6	N 5.3%,
Found	C 43.0	H 3.5	N 5.3%.

Crystal structure determination of $[\{\mu^2\text{-}SeC(NH_2)_2\}Ag\{SeC(NH_2)_2\}_2]_2^{2+}2Cl^-\cdot 4DMF$ **(6)**

Crystal data: $C_{18}H_{52}Ag_2Cl_2N_{16}O_4Se_6$, M = 1317.2, space group $P2_1/n$, a = 588.3(2), b = 2681.6(5), c = 1415.1(3) pm, β = 95.54(2)°, U = 2.2225 nm^3, Z = 2, D_x = 1.97 Mg m^{-3}, F(000) = 1272, $\lambda(MoK_\alpha)$ = 71.073 pm, μ = 6.0 mm^{-1}, T = 173 K.

Data collection and reduction: A colourless prism 0.2×0.15×0.15 mm was mounted on a glass fibre in inert oil. 4064 intensities were measured on a Siemens R3 diffractometer with an LT-2 low temperature attachment using monochromated MoKα radiation ($2\theta_{max.}$ 50°). An empirical absorption correction was applied, with transmission factors 0.38−0.65. Merging equivalents gave 3910 unique reflections (R_{int} 0.018). Cell constants were refined from setting angles of 50 reflections in the range 2θ = 20−23°.

Structure solution and refinement: The structure was solved by the heavy-atom method and refined anisotropically on F^2 to $wR(F^2)$ 0.134 and $R(F)$ 0.045. H atoms were included using a riding model. The weighting scheme was $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$, a = 0.052, b = 3.674; 221 parameters; max. Δ/σ 0.002; max. $\Delta\varrho$ 1.0×10^{-6} e pm^{-3}; S 1.03. Final atomic coordinates are given in Table I, with derived molecular dimensions in Table II [6]. The crystallographic program system used was SHELXL-93 [7].

Cystal structure determination of $[Ph_3PAu\{SC(NHMe)_2\}]^+Cl^-\cdot SC(NHMe)_2$ **(7)**

Crystal data: $C_{24}H_{31}AuClN_4PS_2$, M = 703.3, space group $P2_1/c$, a = 884.0(3), b = 2975.1(8), c = 1057.7(3) pm, β = 102.36(3)°, U = 2.7173 nm^3, Z = 4, D_x = 1.72 Mg m^{-3}, F(000) = 1384, λ(MoKα) = 71.073 pm, μ = 5.75 mm^{-1}, T = 173 K.

Data collection and reduction: As above, but with the following differences: Colourless prism 0.65×0.3×0.2 mm, 7476 intensities to $2\theta_{max.}$ 50°, 4813 unique ($R_{int.}$ 0.032), ψ-scans, transmission factors 0.74−0.90.

Structure solution and refinement: as above, but with $R(F)$ = 0.022, $wR(F^2)$ = 0.053; weighting parameters a = 0.0172, b = 3.201, extinction correc-

tion of the form $F_{corr} = F_c[1+(0.001xF_c^2\lambda^3)/\sin 2\theta]^{-0.25}$, where x refined to $7.5(8)\times10^{-4}$, 303 parameters; max. $\Delta\varrho$ 0.9×10^{-6} e pm^{-3}; S = 1.07. Final atomic coordinates are given in Table III, with derived bond lengths and angles in Table IV [6].

Table I. Atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters (pm$^2\times10^{-1}$) for **6.** U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ag	5045.9(15)	5551.2(3)	4954.2(6)	32.4(2)
Se(1)	2347(2)	6084.3(4)	3739.3(8)	33.7(3)
Se(2)	2047(2)	5022.2(4)	5944.0(7)	29.5(2)
Se(3)	8098(2)	6038.7(4)	6091.1(8)	37.0(3)
C(1)	4543(16)	6447(4)	3145(8)	33(2)
C(2)	3705(18)	5232(4)	7078(7)	30(2)
C(3)	6454(17)	6590(4)	6441(8)	36(3)
N(1)	3876(14)	6808(3)	2546(6)	43(2)
N(2)	6726(14)	6356(3)	3301(7)	48(3)
N(3)	2976(16)	5611(3)	7545(6)	43(2)
N(4)	5568(13)	4996(3)	7424(6)	37(2)
N(5)	4422(15)	6708(3)	6021(7)	49(3)
N(6)	7404(16)	6896(3)	7111(7)	52(3)
Cl	1269(4)	2820.1(10)	8088(2)	44.2(7)
C(4)	5778(30)	6792(9)	9502(13)	156(10)
C(5)	4280(48)	7616(7)	9775(12)	174(12)
C(6)	2236(27)	7037(6)	8768(11)	87(5)
N(7)	3973(17)	7153(4)	9336(7)	49(3)
O(1)	1519(15)	6659(4)	8399(7)	69(3)
C(7)	1908(28)	4458(7)	8890(11)	100(6)
C(8)	−1417(26)	4017(7)	9324(13)	106(6)
C(9)	1401(29)	4324(6)	10515(10)	76(5)
N(8)	692(18)	4280(4)	9641(7)	53(3)
O(2)	3248(18)	4514(4)	10828(7)	83(3)

Table III. Atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters (pm$^2\times10^{-1}$) for **7.** U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Au	6491.1(2)	9191.3(1)	669.9(1)	22.1(1)
P	5713.1(10)	9548.7(3)	2308.6(9)	19.8(4)
C(11)	6804(4)	10057.1(12)	2835(4)	22(2)
C(12)	6642(4)	10414.9(13)	1966(4)	28(2)
C(13)	7402(5)	10817.8(13)	2310(4)	34(2)
C(14)	8368(5)	10860.1(14)	3523(4)	35(2)
C(15)	8555(5)	10505.6(14)	4391(4)	33(2)
C(16)	7769(4)	10102.5(13)	4051(4)	26(2)
C(21)	6029(4)	9163.8(12)	3682(4)	23(2)
C(22)	4964(5)	9118.6(13)	4461(4)	30(2)
C(23)	5207(5)	8797.7(14)	5448(4)	38(2)
C(24)	6506(5)	8530.7(14)	5660(4)	36(2)
C(25)	7579(5)	8579.6(14)	4881(4)	35(2)
C(26)	7339(5)	8895.1(14)	3896(4)	32(2)
C(31)	3703(4)	9723.5(12)	2054(3)	22(2)
C(32)	3274(4)	10100.4(13)	2672(4)	28(2)
C(33)	1720(5)	10210.8(14)	2519(4)	34(2)
C(34)	608(5)	9946.4(15)	1775(4)	38(2)
C(35)	1023(5)	9573(2)	1162(4)	39(2)
C(36)	2577(4)	9463.3(13)	1284(4)	28(2)
S(1)	7569.2(12)	8823.7(3)	− 858.4(9)	28.4(6)
C(6)	8209(4)	8316.1(12)	− 122(3)	23(2)
N(1)	9354(4)	8103.4(11)	− 506(3)	31(2)
C(1)	10205(5)	8278(2)	−1420(4)	40(2)
N(2)	7568(4)	8138.1(10)	781(3)	29(2)
C(2)	8032(6)	7706.7(15)	1402(5)	45(3)
S(2)	11233.4(12)	7859.1(3)	5302.7(10)	32.9(6)
C(5)	12410(4)	7835.6(13)	4202(4)	27(2)
N(3)	12300(4)	8134.0(11)	3252(3)	30(2)
C(3)	11220(5)	8507.9(14)	3033(4)	38(2)
N(4)	13477(4)	7507.7(11)	4300(3)	28(2)
C(4)	14496(5)	7452(2)	3406(4)	41(2)
Cl	4165.3(11)	8368.2(3)	1022.0(10)	32.0(5)

Table II. Selected bond lengths [pm] and angles [°] for **6.**

Ag−Se(3)	263.9(2)	Ag−Se(1)	264.46(14)
Ag−Se(2)#1	270.64(13)	Ag−Se(2)	275.01(14)
Se(1)−C(1)	188.0(10)	Se(2)−C(2)	188.2(10)
Se(3)−C(3)	185.9(10)	C(1)−N(2)	130.5(12)
C(1)−N(1)	132.0(13)	C(2)−N(3)	130.8(12)
C(2)−N(4)	131.8(12)	C(3)−N(5)	132.1(12)
C(3)−N(6)	133.5(13)		
Se(3)−Ag−Se(1)	117.32(4)	Se(3)−Ag−Se(2)#1	98.29(5)
Se(1)−Ag−Se(2)#1	111.64(5)	Se(3)−Ag−Se(2)	112.16(5)
Se(1)−Ag−Se(2)	103.62(5)	Se(2)#1−Ag−Se(2)	114.31(4)
C(1)−Se(1)−Ag	100.1(3)	C(2)−Se(2)−Ag#1	105.7(3)
C(2)−Se(2)−Ag	88.6(3)	Ag#1−Se(2)−Ag	65.69(4)
C(3)−Se(3)−Ag	102.4(3)	N(2)−C(1)−N(1)	118.3(9)
N(2)−C(1)−Se(1)	122.3(8)	N(1)−C(1)−Se(1)	119.5(7)
N(3)−C(2)−N(4)	119.2(10)	N(3)−C(2)−Se(2)	119.7(8)
N(4)−C(2)−Se(2)	121.1(8)	N(5)−C(3)−N(6)	118.1(10)
N(5)−C(3)−Se(3)	122.8(8)	N(6)−C(3)−Se(3)	119.0(8)

Symmetry transformations used to generate equivalent atoms:
#1 $-x+1, -y+1, -z+1$.

Table IV. Selected bond lengths [pm] and angles [°] for **7**.

Au–P	226.23(10)	Au–S(1)	231.89(11)
P–C(31)	181.5(4)	P–C(11)	181.6(4)
P–C(21)	182.4(4)	S(1)–C(6)	173.7(4)
C(6)–N(2)	132.2(5)	C(6)–N(1)	132.9(5)
N(1)–C(1)	144.2(5)	N(2)–C(2)	146.0(5)
S(2)–C(5)	172.1(4)	C(5)–N(3)	132.9(5)
C(5)–N(4)	134.5(5)	N(3)–C(3)	145.2(5)
N(4)–C(4)	144.9(5)		
P–Au–S(1)	173.45(4)	C(31)–P–C(11)	104.2(2)
C(31)–P–C(21)	106.0(2)	C(11)–P–C(21)	107.4(2)
C(31)–P–Au	118.00(13)	C(11)–P–Au	113.44(12)
C(21)–P–Au	107.17(12)	C(6)–S(1)–Au	103.93(12)
N(2)–C(6)–N(1)	120.2(4)	N(2)–C(6)–S(1)	121.6(3)
N(1)–C(6)–S(1)	118.2(3)	C(6)–N(1)–C(1)	125.1(4)
C(6)–N(2)–C(2)	123.7(3)	N(3)–C(5)–N(4)	118.7(3)
N(3)–C(5)–S(2)	121.8(3)	N(4)–C(5)–S(2)	119.5(3)
C(5)–N(3)–C(3)	124.9(3)	C(5)–N(4)–C(4)	123.8(3)

Discussion

Complexes of copper, silver and gold with urea homologues can easily be prepared from the appropriate chloro(organophosphine)metal(I) complexes according to the following equation:

$$R^1{}_3PMCl + XC(NR^2R^3)_2 \rightarrow [R^1{}_3PMXC(NR^2R^3)_2]^+Cl^-;$$

with R^1 = Ph; R^2 = H; R^3 = H, Me; X = S, Se; M = Cu, Ag, Au.

The resulting ionic complexes are air-stable, but in case of selenourea somewhat sensitive to moisture because of hydrolysis of the ligand. The complexes $[Ph_3PMSeC(NH_2)_2]^+Cl^-$ (M = Cu, Ag) are soluble in dimethylformamide and dimethylsulfoxide. In protic solvents decomposition and the formation of elemental selenium is observed. An attempt to recrystallize $[Ph_3PAgSeC(NH_2)_2]^+Cl^-$ from DMF/diethyl ether led to the unexpected phospine-free complex $[\{\mu^2\text{-}SeC(NH_2)_2\}Ag\{SeC(NH_2)_2\}_2]_2^{2+}2Cl^-$ (**6**) in low yield. As a by-product in this reaction Ph_3PSe can be detected by NMR techniques. The binuclear silver complex is probably a reaction intermediate in the redox reaction of AgCl with $SeC(NH_2)_2$, which leads to the formation of $[(H_2N)_2CSeSeC(NH_2)_2]^{2+}$ [8].

The dication of $[\{\mu^2\text{-}SeC(NH_2)_2\}Ag\{SeC(NH_2)_2\}_2]_2^{2+}2Cl^-$ is shown in Fig. 1. The silver atoms are bridged by two selenourea groups; the resulting parallelogram shows a short Ag–Ag contact of 298.3 pm (cf. metallic silver 286 pm). The corresponding Ag–Se–Ag angle is 65.7(1)° and reflects the influence of the Ag–Ag contact on the coordination at selenium. Polar interactions for Ag^+ cations or relativistic effects in the valence shell of Ag(I) have been invoked to explain such interactions [9–11]. Comparable contacts can be observed in the anionic polyselenide-silver complexes $[Ag(Se_4)]_4^{4-}$ [Ag–Ag: 291.7(3), 317.8(1) pm] and $[Ag(Se_5)]_n^{n-}$ [Ag–Ag: 299.1(1)–319.3(1) pm] [12] and in the silver(I)-sulfur complexes silver(I)cyclohexanethiolate $(AgSC_6H_{11})_{12}$ [291.1(5); 310.6(5) pm] [13] and dipropylthiocarbamate-silver(I) $[(n\text{-}C_3H_7)_2NCS_2Ag]_6$ [290.5(5), 296.5(5) pm] [14]. The coordination at silver is distorted tetrahedral with

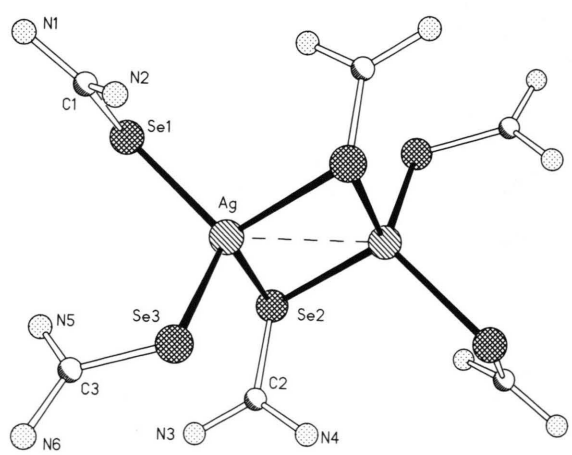

Fig. 1. The dicationic dinuclear silver complex of **6**; radii are arbitrary; H atoms are omitted. Only the asymmetric unit is numbered.

angles from 98.29(5)° [Se(3)−Ag−Se(2#); #:1-*x*, 1-*y*, 1-*z*] to 117.32(4)° [Se(1)−Ag−Se(3)] and the significantly different Ag−Se bond lengths of 263.9(2), 264.5(2) pm [Ag−Se(3), Ag−Se(1); terminal selenoureas] and 270.6(2), 275.0(2) pm [Ag−Se(2)#, Ag−Se(2); bridging selenoureas]. Only a few crystal structures of silver-selenium complexes have been determined; the Ag−Se bond lengths lie in the range 254−305 pm. Representative examples are $(Ph_3P)_2Ag(\mu\text{-}Se)_2W(\mu\text{-}Se)_2AgPPh_3 \cdot CH_2Cl_2$ [Ag−Se 254.0, 255.1(4) pm, trigonal Ag; 263.3, 264.0(4) pm, tetrahedral Ag] [15] and the above-mentioned polyselenide-silver anions with Ag−Se bond lengths in the range 255.2(1) to 275.6(1) pm [12].

The cell contents of $[\{\mu^2\text{-}SeC(NH_2)_2\}Ag\{SeC(NH_2)_2\}_2]_2^{2+}2Cl^- \cdot 4DMF$ are shown in Fig. 2. Hydrogen bonds are observed, (i) between the amino groups of the terminal selenoureas and the chloride ions [N(1)−Cl[1], Cl[2]; N(2)−Cl[1]; N(5), N(6)−Cl[3]; [1]:1-*x*, 1-*y*, 1-*z*; [2]:-x, 1-y, 1-z; [3]:0.5-x, 0.5+y, 1.5-z] with corresponding N···Cl distances of 323 to 328 pm, (ii) between the O atoms of the DMF molecules and one of the amino groups in the selenoureas [N(4)−O(2)[4], N(6)−O(1)[5]; [4]:1-*x*, 1-*y*, 2-*z*; [5]:1+*x*, *y*, *z*] with corresponding N···O distances of 283 and 296 pm and (iii) between one of the amino groups of each selenourea and the neighbouring selenourea seleniums [N(2)−Se(2)[1], N(3)−Se(3)[6], N(4)−Se(1)[1] and N(5)−Se(1); [6]:-1+*x*, *y*, *z*] with N···Se distances of 356 to 390 pm. The corresponding N−H−X angles are compatible with hydrogen bonding but the H atoms were not refined freely.

The cation of $[Ph_3PAuSC(NHMe)_2]^+Cl^- \cdot SC(NHMe)_2$ (**7**) is shown in Fig. 3. The coordination at gold is linear, as in most gold(I) complexes [P−Au−S 173.5(1)°], with an Au−S bond length of 231.9(1) pm. Comparable Au−S bond lengths can be observed in the

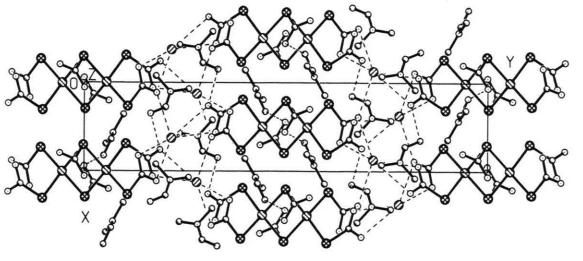

Fig. 2. Packing diagram of **6** projected along the *z*-axis; dashed lines indicate probable hydrogen bonds.

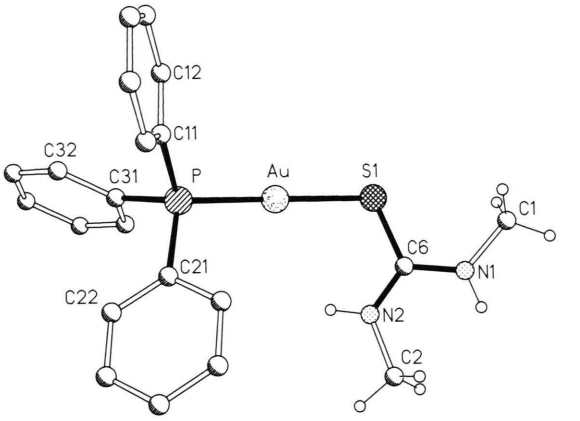

Fig. 3. The cation of compound **7** in the crystal; radii are arbitrary; H atoms are omitted.

thiourea-type gold(I) complexes $Ph_3PAu(2\text{-}TU)$ (2-TU=4-Hydroxypyrimidinethiolate(2)) with Au−S 229.6(2) pm [7], $Ph_3PAu(2\text{-}pymS)$ (2-pymS = pyrimidinethiolate(2)) with Au−S 231.0(3) pm [8] and $[(etu)_2Au]^+Cl^- \cdot H_2O$ (etu = ethylenethiourea) with Au−S 227.9(8) pm [16]. The thiourea group is planar (mean deviation: 1.8 pm) with tetrahedral angles at sulfur [C(6)−S−Au: 103.9(1)°] and a C−S bond length of 173.7(4) pm. The cell contents of **7** are shown in Fig. 4. Short non-bonding N···Cl and N···S contacts indicate hydrogen bonding, (i) between the amino groups of the thioureas and the chloride [N(2)−Cl, N(3)−Cl[1], N(4)−Cl[2]; [1]:1+*x*, *y*, *z*; [2]:1+*x*, 1.5-*y*, 0.5+*z*] with corresponding N···Cl distances of 315 to 323 pm

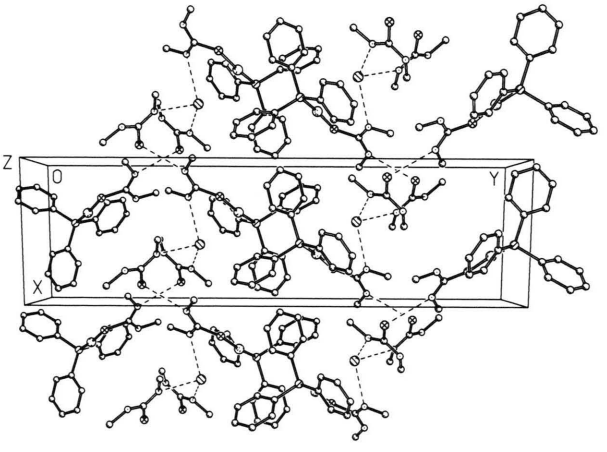

Fig. 4. Packing diagram of **7** viewed parallel to the *z*-axis; dashed lines indicate probable hydrogen bonds.

and (ii) between one amino group of the complexed thiourea and the sulfur atom of the thiourea solvate [N(1)–S(2)[3] 333 pm; [3]: x, 1.5-y, $-0.5+z$]. Additionally, a short Au···Cl contact of 327 pm is observed.

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