

**Data collection**

Rebuilt Philips PW1100 (Gomm, 1993) diffractometer	1076 reflections with $F^2 > 2.5\sigma(F^2)$
$\theta/2\theta$ scans	$R_{\text{int}} = 0.105$
Absorption correction: Gaussian by integration (Busing & Levy, 1957)	$\theta_{\text{max}} = 25.0^\circ$ $h = 0 \rightarrow 46$ $k = -8 \rightarrow 8$ $l = -8 \rightarrow 8$
$T_{\text{min}} = 0.813$ , $T_{\text{max}} = 0.833$	6 standard reflections
7648 measured reflections	every 50 reflections
1885 independent reflections	intensity decay: 3.8%

**Refinement**

Refinement on $F^2$	$\Delta\rho_{\text{max}} = 0.61 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.039$	$\Delta\rho_{\text{min}} = -0.73 \text{ e } \text{\AA}^{-3}$
$S = 0.95$	Extinction correction: Larson (1970)
1076 reflections	Extinction coefficient: $33.(2) \times 10^2$
108 parameters	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
H atoms not refined	
$w = 1/[\sigma^2(F^2_{\text{obs}}) + 0.001F^2_{\text{obs}} + 10]$	
$(\Delta/\sigma)_{\text{max}} < 0.001$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Cd	0	0	0	0.0322 (1)
Cl1	0.06491 (3)	-0.0134 (3)	0.0477 (2)	0.0444 (4)
Cl2	-0.00802 (4)	0.2256 (2)	0.2753 (2)	0.0387 (5)
N	0.0589 (1)	0.5290 (8)	0.0111 (7)	0.047 (2)
C1	0.0942 (1)	0.4657 (9)	-0.0422 (9)	0.058 (3)
C2	0.1206 (2)	0.5815 (9)	0.036 (1)	0.081 (3)
C3	0.1569 (1)	0.505 (2)	0.012 (1)	0.070 (2)
C4	0.1691 (2)	0.376 (1)	0.129 (2)	0.104 (5)
C5	0.2022 (3)	0.311 (1)	0.110 (2)	0.115 (5)
C6	0.2223 (2)	0.374 (1)	-0.025 (2)	0.101 (5)
C7	0.2110 (2)	0.495 (2)	-0.142 (1)	0.103 (4)
C8	0.1777 (2)	0.559 (1)	-0.128 (1)	0.083 (4)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cd—Cl1	2.548 (1)	Cd—Cl2	2.650 (1)
Cd—Cl2'	2.645 (1)		
Cl2'—Cd—Cl1	90.00 (5)	Cl2—Cd—Cl2'	89.73 (4)
Cl2—Cd—Cl1	92.03 (5)	Cd—Cl2—Cd'	162.36 (6)

Symmetry codes: (i)  $x, y, z - \frac{1}{2}, \frac{1}{2}, z$ ; (ii)  $x, \frac{1}{2} + y, \frac{1}{2} - z$ .Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

<i>D</i> — <i>H</i> ... <i>A</i>	<i>H</i> ... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> — <i>H</i> ... <i>A</i>
N—H6...Cl2'	2.30	3.241 (5)	166
N—H7...Cl1 <sup>ii</sup>	2.60	3.421 (5)	143
N—H8...Cl1 <sup>iii</sup>	2.34	3.273 (4)	165

Symmetry codes: (i)  $-x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (ii)  $x, 1 + y, z$ ; (iii)  $x, \frac{1}{2} + y, \frac{1}{2} - z$ .Table 4. Statistics of  $F^2$  values

	All	$3\sigma \leq F^2$	$5\sigma \leq F^2$	$10\sigma \leq F^2$	$20\sigma \leq F^2$
<i>F</i> -lat. ref.	566	548	526	421	223
non- <i>F</i> ref.	1319	406	204	78	17
non- <i>F</i> (%)	70.0	42.6	27.9	15.6	7.1
All ref.	1885	954	730	499	240

Notes: *F* reflections: *ggg, uuu*; non-*F* reflections: *ggu, gug, guu, ugg, ugu, uug*.

Data collection: local software (Gomm, 1993). Cell refinement: local software. Data reduction: local software. Program(s) used to solve structure: *CRYSTAN* (Burzlaff & Rothammel, 1988). Program(s) used to refine structure: *CRYSTAN* (Spengler & Zimmermann, 1996). Molecular graphics: *CRYSTAN*. Software used to prepare material for publication: *CRYSTAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1289). Services for accessing these data are described at the back of the journal.

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**Dimethylammonium Trichloropalladate**

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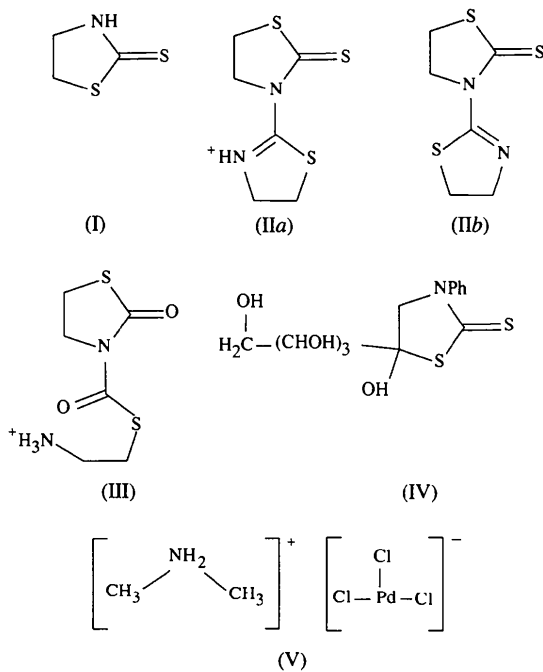
(Received 26 March 1996; accepted 6 March 1997)

**Abstract**

The title compound,  $[\text{NH}_2(\text{CH}_3)_2][\text{PdCl}_3]$ , was produced as a minor product of the reaction involving 1,3-thiazolidine-2-thione and  $\text{K}_2\text{PdCl}_4$  in aqueous HCl. The structure contains  $[\text{NH}_2(\text{CH}_3)_2]^+$  cations and  $[\text{PdCl}_3]^-$  anions. The anion consists of  $\text{Pd}^{\text{II}}$  atoms bonded to a combination of bridging and terminal  $\text{Cl}^-$  ions in the form of an infinite chain of general formula  $[\text{Pd}(\mu\text{-Cl})(\text{Cl})_2]_2$ . Each  $\text{Pd}^{\text{II}}$  atom is bonded in a four-coordinate square-planar configuration. The cations are hydrogen bonded to the  $[\text{PdCl}_3]^-$  chain.

### Comment

Heterocyclic thioamides, including 1,3-thiazoline-2-thione (tztH) and thiazolidine-2-thione (tzdtH), react with  $K_2PdCl_4$  in weakly acidic media producing mostly  $[Pd(RSH)_4]Cl_2$  species. The complexed cations have square-planar geometry and monodentate thione S-coordinating ligands, in addition to ionic chlorides (tzdtH: Kubiak & Głowiak, 1982; tztH: Raper, Britton & Clegg, 1990). In the case of the reaction with tzdtH, (I) (Kubiak & Głowiak, 1982), however, small quantities of the title compound, (V), were also obtained.



The structure consists of  $[NH_2(CH_3)_2]^+$  cations and centrosymmetric  $[PdCl_3]^-$  anions (Fig. 1). These are assembled into parallel chains (Fig. 2) by means of pairs of weak  $N-H \cdots Cl$  bonds involving cationic H atoms and terminal anionic Cl atoms [ $N \cdots Cl_2(1-x, -y, -z)$  3.366 (1),  $N-H_4$  0.96 (4),  $H_4 \cdots Cl_2$  2.551 (4) Å and  $N-H_4 \cdots Cl_2$  142 (3)°].

The trichloropalladate(II) anions contain both terminal and bridging Cl atoms [ $\{Pd(Cl_{br})(Cl_t)_2\}_n$ ] that are involved in the formation of an unusual infinite polymeric chain. The  $Pd^{II}$  atoms have four-coordinate centrosymmetric square-planar geometry formed from two terminal [ $Pd-Cl_t$  2.306 (1) Å] and two bridging [ $Pd-Cl_{br}$  2.311 (1) Å] Cl atoms. The two  $Pd^{II}$  atoms [ $Pd \cdots Pd$  3.571 (1) Å] are symmetrically bridged with a bridging angle  $Pd-Cl-Pd(-x, y, \frac{1}{2}-z)$  of 101.20 (4)°. The dihedral angle between the two adjacent coordination planes is 81.5°.

To the authors' knowledge, no similar bridging complexes of Pd and Pt have been described. The remarkable feature of this polymeric chain is the almost

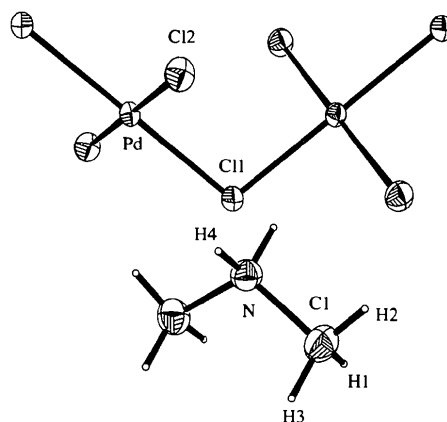


Fig. 1. The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

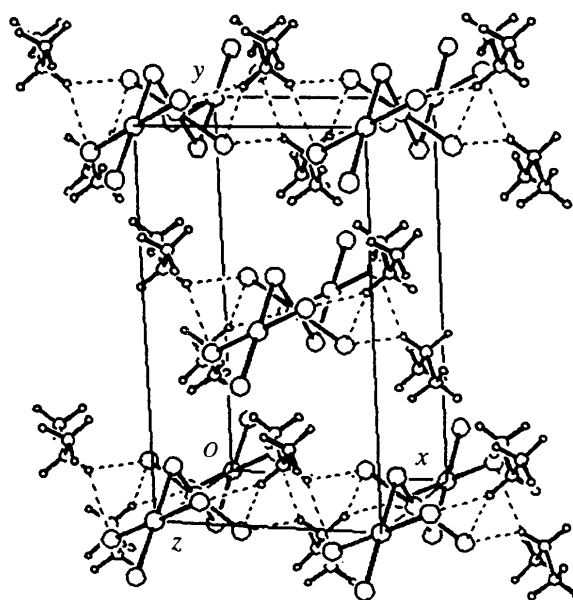


Fig. 2. The packing arrangement in the crystal.

rectangular symmetry of the  $PdCl_4$  moiety and obtuse  $Pd-Cl-Pd$  angle. For comparison, in  $[\{PdCl(Cl_{br})L\}_2]$  compounds, the  $Pd-Cl_{br}$  and  $Pd-Cl_t$  bond lengths differ significantly, and the  $Pd-Cl-Pd$  angles are more acute, leading to a shortening of the  $Pd \cdots Pd$  contacts (Ang, Cai, Kwik & Rheingold, 1990).

The dimensions of the cations are unexceptional and similar to other reported values (Wilson, McKee, Penfold & Wilkins, 1984). Furthermore, the cation results from the oxidative degradation of (I). Previous work has shown that (I), in common with other organothiones and thiols (Sheldon & Rocha, 1981), is susceptible to oxidation. One oxidation product, 2-(2-thioxo-1,3-thiazolidin-3-yl)-4,5-dihydro-1,3-thiazole [tzdtzS, (IIa)], is obtained

as a protonated species both individually (Raper, Kubiak & Głowiak, 1996) and in  $[\text{Zn}(\text{tzdtS})\text{Cl}_3(\text{H}_2\text{O})]$  (Kubiak & Głowiak, 1986). The alternative *S,N*-chelating isomer, (IIb), occurs in the polymeric halogen-bridged complex  $[\text{Cu}(\text{tzdtS})\text{Cl}_2]_n$  (Ainscough *et al.*, 1985). Reaction of (I) with  $\text{ZnCl}_2/\text{H}_2\text{O}_2$  produced the (2-oxo-1,3-thiazolidin-3-yl)carbonylthioethylammonium ion, (III) (Kubiak, Głowiak & Raper, 1995), a product which involves oxidation of both exocyclic thione ( $=\text{C}=\text{S}$ ) and endocyclic ( $=\text{C}-\text{N}$ ) bonds. In addition, the thioetheral  $=\text{C}-\text{S}-$  bonds of the 3-benzyl-5-hydroxy-5-(1,2,3,4-tetrahydroxy-*n*-butyl) derivative, (IV), have been shown to undergo intramolecular rearrangement in the presence of  $\text{Cu}^{\text{II}}$ , leading to the production of a dithiocarbamic acid derivative with its anion subsequently coordinated to the metal (Basson & du Preez, 1974). Production of  $[\text{NH}_2(\text{CH}_3)_2]^+$ , the most extensively degraded product of (I) so far isolated, is intriguing. Previous proposals for the oxidative degradation of heterocyclic thiones have involved the production and recombination of thyl and other free radicals, together with thione-S abstraction as organic sulfate (Raper, 1994). However, the reaction processes involved in the production of the  $[\text{NH}_2(\text{CH}_3)_2]^+$  cation also probably involve metal catalyzed fission of both the endocyclic  $\text{C}-\text{N}$  and  $\text{C}-\text{S}$  bonds of (I).

## Experimental

Red-brown prisms with well developed faces were obtained by slow evaporation of an aqueous solution.

### Crystal data

$(\text{C}_2\text{H}_8\text{N})[\text{PdCl}_3]$

$M_r = 258.84$

Monoclinic

$C2/c$

$a = 7.802(2) \text{ \AA}$

$b = 13.221(3) \text{ \AA}$

$c = 7.1420(10) \text{ \AA}$

$\beta = 91.24(3)^\circ$

$V = 736.5(3) \text{ \AA}^3$

$Z = 4$

$D_x = 2.334 \text{ Mg m}^{-3}$

$D_m = 2.30 \text{ Mg m}^{-3}$

$D_m$  measured by flotation in  $\text{C}_2\text{H}_4\text{Br}_2/\text{CHBr}_3$

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 3-30^\circ$

$\mu = 3.498 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Prism

$0.12 \times 0.10 \times 0.08 \text{ mm}$

Red-brown

### Data collection

Syntex  $P2_1$  diffractometer

$\theta/2\theta$  scans

Absorption correction: none

1119 measured reflections

1066 independent reflections

908 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\text{max}} = 30.06^\circ$

$h = 0 \rightarrow 10$

$k = 0 \rightarrow 17$

$l = -10 \rightarrow 10$

2 standard reflections

every 100 reflections

intensity decay: 2%

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.067$

$S = 1.192$

1066 reflections

52 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.4125P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.012$

$\Delta\rho_{\text{max}} = 1.18 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.36 \text{ e \AA}^{-3}$

Extinction correction:

$SHELXL93$  (Sheldrick, 1993)

Extinction coefficient:

0.0046 (6)

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Pd	0	0	0	0.02568 (12)
Cl1	0	0.11093 (8)	1/4	0.0353 (2)
Cl2	0.24957 (10)	-0.07267 (6)	0.11471 (11)	0.0399 (2)
C1	0.5803 (5)	0.1884 (3)	0.4001 (6)	0.0463 (8)
N	1/2	0.1264 (3)	1/4	0.0376 (8)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Pd—Cl2	2.306 (1)	Cl—N	1.478 (4)
Pd—Cl1	2.311 (1)		
Cl2—Pd—Cl1	90.23 (3)	Cl—N—C1 <sup>ii</sup>	112.6 (4)
Pd—Cl1—Pd <sup>i</sup>	101.20 (4)		
Cl2 <sup>iii</sup> —Pd—Cl1—Pd <sup>i</sup>	122.41 (3)		

Symmetry codes: (i)  $-x, y, \frac{1}{2} - z$ ; (ii)  $1 - x, y, \frac{1}{2} - z$ ; (iii)  $-x, -y, -z$ .

The unit-cell parameters and space group were found initially from oscillation and Weissenberg photographs. The structure was solved in the centrosymmetric space group  $C2/c$ . All heavy-atom positions were found using direct methods. The Pd, Cl1 and N atoms are in special positions. The H atoms were found from difference maps and their parameters were refined without restriction. The data were not corrected for absorption because of a rather low value of  $\mu r$ . The residual electron density on the final difference map was between 1.18 and  $-1.36 \text{ e \AA}^{-3}$ , and the highest peaks were found around the Pd atom.

Data collection: *XTLIXTLE* (Syntex, 1976). Cell refinement: *XTLIXTLE*. Data reduction: *XTLIXTLE*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

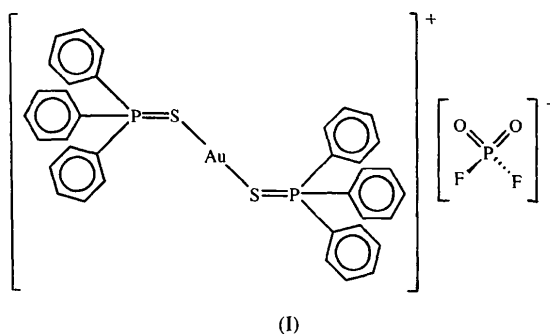
Supplementary data for this paper are available from the IUCR electronic archives (Reference: MU1264). Services for accessing these data are described at the back of the journal.

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The structure of such a complex, (I), with the triphenylphosphine sulfide ligand is reported here.



Structure solution was complicated by disorder of the anion. It was thought that the  $PF_6^-$  salt had been prepared, since a literature procedure (Jones, Maddock, Mays, Muir & Williams, 1977; Jones & Williams, 1977) and a reagent from a bottle labelled silver hexafluorophosphate (Aldrich Chemical Company) had been used. The crystallographic analysis and spectroscopic data (including IR,  $^{31}P$  and  $^{19}F$  NMR), however, suggested that hydrolysis had taken place and that the anion was actually  $PO_2F_2^-$ . The presence of the  $PO_2F_2^-$  ion instead of the expected  $PF_6^-$  has been reported several times before (Bruce *et al.*, 1988; Hirsch, Wilson & Moore, 1996; Kitagawa, Kawata, Nozaka & Munakata, 1993; Reger, Huff & Lebioda, 1991; Weidlein, 1968; White, Thompson & Maitlis, 1977) and it has been demonstrated that  $PF_6^-$  is readily hydrolyzed to  $PO_2F_2^-$  in the presence of a metal ion (Clark & Jones, 1970; Il'in, Maizel', Shcherbakova, Vol'f & Buslaev, 1982). A fairly satisfactory refinement was possible with an anion disorder comprised of three distorted tetrahedra.

The molecular cation is shown in Fig. 1. The ligating atoms form the expected almost linear arrangement around the Au atoms, with the Au atom on a crystallographic twofold axis and an S—Au—S angle of  $172.40(12)^\circ$ . The  $7.60(12)^\circ$  deviation from  $180^\circ$  is not caused by gold–gold interactions as there are no Au···Au distances less than  $7.4 \text{ \AA}$ . It may be caused by intramolecular  $\pi$ – $\pi$  interactions between phenyl rings (see below). The Au—S distance [ $2.277(2) \text{ \AA}$ ] is close to that observed for  $Ph_3PSAuCl$  [ $2.256(1) \text{ \AA}$ ] (Husain & Schlemper, 1987);  $2.264(2) \text{ \AA}$  (Jones & Bembenek, 1992)] and other bond lengths and angles are similar. The Au—S—P angle [ $103.27(12)^\circ$ ] is smaller, by about  $3^\circ$ , than the corresponding angle in  $Ph_3PSAuCl$  [ $106.35(6)^\circ$ ] (Husain & Schlemper, 1987);  $105.9(1)^\circ$  (Jones & Bembenek, 1992)], and the difference between the largest and smallest S—P—C angles is reduced from  $10.7^\circ$  in  $Ph_3PSAuCl$  to  $6.5^\circ$  in  $Au(PPh_3)_2$ . The P—S···S—P torsion angle is  $74.9(2)^\circ$ , relatively close to the  $90^\circ$  needed to maximize Au—S  $\pi$ -bonding. The three phenyl groups do not form a propeller conformation. Two of the phenyl rings are arranged so that

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## Bis(triphenylphosphine sulfide-S)gold(I) Difluorophosphate(V)

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### Abstract

The cation of the title compound,  $[Au(C_{18}H_{15}PS)_2]-(PO_2F_2)$ , lies with the Au atom on a twofold axis, with Au—S  $2.277(2) \text{ \AA}$  and S—Au—S  $172.40(12)^\circ$ . The deviation from linearity is not caused by Au···Au interactions. It may be caused by intramolecular  $\pi$ – $\pi$  interactions between phenyl rings. Bond lengths and angles are normal.

### Comment

Although a number of gold–thiol complexes have been used as drugs for the treatment of rheumatoid arthritis for more than sixty years (Sadler & Sue, 1994), some of the drugs are surprisingly poorly characterized and have resisted all crystallization attempts. The gold drug myochrysin, gold sodium thiomalate, for example, has been shown to be a mixture of at least five components, none of which have yet been conclusively characterized. During attempts to prepare and characterize gold–thiol complexes which may serve as models to the drug compounds, several 1:2 complexes have been isolated.

† Deceased.