Table 4. *Important planes in the molecule and atomic deviations* (Å) *from them*

Atoms marked with an asterisk were not included in the least-squares calculation.

(*a*) Plane C(1), C(2), B(4), B(7), B(8); $\chi^2 = 11\cdot2$

$$0\cdot6769x + 0\cdot7191y - 0\cdot1574z - 4\cdot0162 = 0$$

C(1)	−0·001 (5)	B(7)	−0·011 (6)
C(2)	0·008 (5)	B(8)	0·010 (5)
B(4)	−0·007 (6)	Fe*	−1·531 (6)

(*b*) Plane C(1′), C(2′), B(4′), B(7′), B(8′); $\chi^2 = 1\cdot8$

$$0\cdot2576x + 0\cdot8443y - 0\cdot4699z - 0\cdot6298 = 0$$

C(1′)	−0·003 (5)	B(7′)	−0·004 (5)
C(2′)	0·005 (5)	B(8′)	0·002 (6)
B(4′)	0·001 (6)	Fe*	1·531 (6)

(*c*) Plane B(5), B(6), B(9), B(11), B(12); $\chi^2 = 5\cdot04$

$$0\cdot6652x + 0\cdot7257y - 0\cdot1756z - 5\cdot4990 = 0$$

B(5)	−0·007 (7)	B(11)	−0·008 (6)
B(6)	0·009 (7)	B(12)	0·004 (6)
B(9)	0·002 (6)	B(10)*	0·920 (6)

(*d*) Plane B(5′), B(6′), B(9′), B(11′), B(12′); $\chi^2 = 0\cdot35$

$$0\cdot2722x + 0\cdot8454y - 0\cdot4595z + 0\cdot8336 = 0$$

B(5′)	−0·000 (6)	B(11′)	0·002 (6)
B(6′)	−0·001 (7)	B(12′)	−0·002 (6)
B(9′)	0·002 (6)	B(10′)*	−0·949 (6)

(*e*) Plane Fe, O, B(8), B(8′); $\chi^2 = 132\cdot31$

$$0\cdot4294x - 0\cdot5437y - 0\cdot7211z + 2\cdot7238 = 0$$

Fe	−0·018 (1)	C(1)*	0·786 (6)
O	−0·030 (4)	C(2)*	−0·783 (6)
B(8)	0·024 (5)	C(1′)*	−0·842 (6)
B(8′)	0·024 (5)	C(2′)*	0·736 (6)
C*	0·699 (6)		

Angles between planes (°): (*a*)–(*b*) 31·2 (5); (*c*)–(*d*) 28·9 (4); (*a*)–(*e*) 89·2 (1·4); (*b*)–(*e*) 90·5 (1·3).

nomenclature of Janoušek, Plešek, Heřmánek, Baše, Todd & Wright (1981), as having the *e* 1–2′ conformation for both ligands.

The packing of the molecules within the unit cell is shown in Fig. 2.

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Acta Cryst. (1982). B**38**, 2031–2034

Structure of Tetrakis(1,3-thiazolidine-2-thione)palladium(II) Dichloride–1,3-Thiazolidine-2-thione (1:2)

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Abstract. $[Pd(C_3H_5NS_2)_4]Cl_2.2(C_3H_5NS_2)$, M_r = 892·6, triclinic, space group $P\bar{1}$, a = 11·075 (3), b = 9·363 (3), c = 8·531 (3) Å, α = 102·78 (2), β = 85·50 (2), γ = 94·87 (2)°, U = 858 Å^3, Z = 1, D_c = 1·73, D_m = 1·74 (1) Mg m^{-3}, μ(Mo $K\alpha$) = 1·41 mm^{-1}. The structure was refined to R = 0·046 for 2013 counter reflections. It consists of discrete $[Pd(C_3H_5NS_2)_4]^{2+}$ cations, Cl^- anions and uncoordinated $C_3H_5NS_2$ solvent molecules, linked by a network of NH···Cl hydrogen bonds. All four ligands are S-bonded to the metal with Pd–S bonds of 2·322 (2) and 2·327 (2) Å, to give a square-planar PdS_4 unit with

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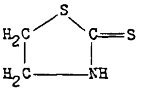
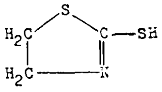
a S—Pd—S angle of 92·7 (1)°. The bond lengths indicate that the 2-mercaptothiazoline ligand exists mainly in the thione form as thiazolidine-2-thione.

Introduction. 2-Mercaptothiazoline (ttz) is a potentially ambidentate ligand with either the exocyclic S or heterocyclic N atom available for coordination. A ligand molecule may exist, when free, as two tautomeric forms (I) (thiazolidine-2-thione) and (II) (2-thiazoline-2-thiol) in a thione–thiol equilibrium.



(I)



(II)

Spectroscopic studies of Pd^{II} and Pt^{II} interactions with ttz (De Filippo, Devillanova, Trogu, Verani, Preti & Viglino, 1973; Dehand & Jordanov, 1976) have suggested that the complexes formed at low pH are N-bonded species.

This conclusion, however, did not seem very convincing and because of the possible biological importance of such systems (Dehand & Jordanov, 1976) we have reinvestigated the Pd^{II} complexes with ttz crystallized from acidic solution.

The title compound crystallizes as yellow prisms from an aqueous solution of K_2PdCl_4 and ttz in the presence of a small excess of HCl. The presence of the Cl^- ions in the crystals has been demonstrated by means of an X-ray microanalyser.

Preliminary Weissenberg photographs showed the crystal to be triclinic. All measurements for a crystal 0·15 × 0·15 × 0·20 mm were made on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The cell parameters were determined by least squares from the setting angles of 15 reflections. The intensities were measured by the θ–2θ scan technique. After each group of 15 reflections the intensity of a standard was measured; no significant change was observed. The data were corrected for Lorentz and polarization effects only. Of the 3502 reflections with $2\theta \leq 55°$, 2013 had $F > 6\sigma(F)$ and were used in subsequent calculations. The centrosymmetric space group $P\bar{1}$ was assumed. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares with anisotropic temperature factors for the non-H atoms. The H atoms were positioned geometrically. Their coordinates were refined with isotropic temperature factors. Final refinement yielded $R = 0{\cdot}046$ and $R_w = 0{\cdot}036$. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/\sigma^2(F)$. Neutral-atom scattering factors were from *International Tables for X-ray Crystallography* (1974) with anomalous-dispersion corrections for Pd, S and Cl.

Table 1. *Positional parameters and* B_{eq} (Å^2) *values for the non-*H *atoms with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*
Pd	0	0	0	2·75 (7)
S(1)	0·0268 (2)	−0·2329 (2)	0·0402 (2)	4·0 (2)
S(2)	0·2056 (2)	−0·4566 (2)	−0·0224 (2)	5·0 (2)
S(3)	0·0339 (2)	−0·0731 (2)	−0·2773 (2)	3·6 (2)
S(4)	−0·0443 (2)	−0·3117 (2)	−0·5442 (2)	4·5 (2)
S(5)	0·4937 (2)	−0·3570 (2)	0·4081 (2)	4·2 (2)
S(6)	0·2890 (2)	−0·1695 (2)	0·4981 (3)	5·1 (2)
Cl	0·2980 (2)	0·1431 (2)	−0·0642 (2)	4·3 (2)
N(1)	0·2612 (5)	−0·1974 (7)	−0·0632 (6)	3·4 (5)
N(2)	−0·1588 (5)	−0·2675 (7)	−0·2699 (7)	3·2 (5)
N(3)	0·4584 (6)	−0·1161 (7)	0·3044 (8)	4·3 (6)
C(1)	0·1680 (6)	−0·2785 (7)	−0·0181 (7)	3·2 (6)
C(2)	0·3643 (9)	−0·4051 (11)	−0·0457 (12)	5·2 (9)
C(3)	0·3751 (9)	−0·2695 (12)	−0·1129 (13)	4·8 (9)
C(4)	−0·0630 (5)	−0·2166 (7)	−0·3464 (7)	2·9 (5)
C(5)	−0·1873 (8)	−0·4213 (12)	−0·5299 (11)	4·9 (9)
C(6)	−0·2260 (11)	−0·3989 (12)	−0·3556 (11)	5·4 (10)
C(7)	0·4239 (6)	−0·2140 (7)	0·3906 (7)	2·8 (5)
C(8)	0·3850 (8)	0·0046 (10)	0·3072 (11)	4·2 (8)
C(9)	0·2768 (11)	−0·0099 (14)	0·4184 (20)	7·1 (12)

* $B_{eq} = \frac{1}{3}\sum B_{ii}$.

Table 2. *Positional parameters and isotropic thermal parameters* (Å^2) *for the* H *atoms*

	x	y	z	B_{iso}
H(21)	0·394 (6)	−0·479 (8)	−0·089 (9)	3·5 (22)
H(22)	0·405 (6)	−0·391 (6)	0·056 (8)	4·3 (16)
H(31)	0·450 (8)	−0·190 (9)	−0·081 (9)	8·5 (25)
H(32)	0·368 (7)	−0·289 (8)	−0·192 (8)	0·3 (22)
H(51)	−0·152 (7)	−0·515 (8)	−0·573 (9)	6·7 (23)
H(52)	−0·240 (6)	−0·370 (7)	−0·578 (8)	3·5 (17)
H(61)	−0·297 (8)	−0·363 (9)	−0·344 (10)	6·2 (30)
H(62)	−0·186 (7)	−0·472 (9)	−0·326 (10)	5·2 (26)
H(81)	0·361 (6)	−0·001 (8)	0·199 (9)	7·1 (22)
H(82)	0·435 (6)	0·092 (7)	0·339 (8)	4·1 (19)
H(91)	0·273 (9)	0·047 (10)	0·503 (11)	8·0 (35)
H(92)	0·212 (9)	0·000 (11)	0·372 (13)	15·3 (43)
H(N1)	0·245 (6)	−0·073 (7)	−0·049 (8)	6·2 (18)
H(N2)	−0·171 (6)	−0·226 (8)	−0·185 (8)	4·2 (21)
H(N3)	0·515 (7)	−0·136 (8)	0·242 (9)	4·7 (23)

All calculations were performed on a Nova 1200 computer with the Syntex *XTL* structure determination system. The final atomic parameters are listed in Tables 1 and 2.*

Discussion. A view of the molecule with the atomic numbering is shown in Fig. 1. Bond lengths and angles are in Table 3 and the relevant least-squares planes in Table 4.

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* Lists of structure factors, anisotropic thermal parameters, torsion angles and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36758 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

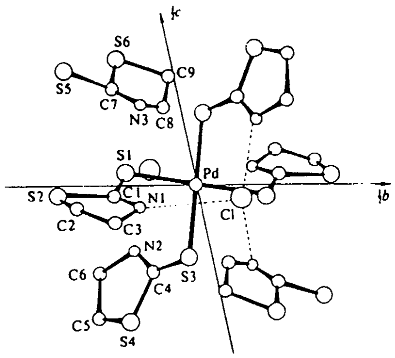

Fig. 1. Projection of the structure of $[Pd(C_3H_5NS_2)_4]$-$Cl_2.2(C_3H_5NS_2)$ along **a**.

Table 3. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Pd–S(1)	2·327 (2)	S(1)–Pd–S(3)	92·7 (1)
Pd–S(3)	2·322 (2)	Pd–S(1)–C(1)	110·4 (2)
		Pd–S(3)–C(4)	109·2 (2)
S(1)–C(1)	1·666 (7)	S(1)–C(1)–N(1)	129·1 (5)
S(2)–C(1)	1·744 (7)	S(1)–C(1)–S(2)	119·1 (4)
N(1)–C(1)	1·312 (9)	S(2)–C(1)–N(1)	111·8 (5)
N(1)–C(3)	1·470 (12)	C(1)–S(2)–C(2)	91·6 (4)
C(3)–C(2)	1·497 (15)	S(2)–C(2)–C(3)	106·8 (7)
S(2)–C(2)	1·791 (10)	C(2)–C(3)–N(1)	106·3 (8)
		C(3)–N(1)–C(1)	116·9 (6)
C(4)–S(3)	1·675 (7)	S(3)–C(4)–N(2)	128·1 (5)
C(4)–S(4)	1·730 (6)	S(3)–C(4)–S(4)	119·4 (4)
C(4)–N(2)	1·312 (9)	S(4)–C(4)–N(2)	112·5 (5)
N(2)–C(6)	1·460 (13)	C(4)–S(4)–C(5)	92·3 (4)
S(4)–C(5)	1·823 (10)	S(4)–C(5)–C(6)	106·7 (7)
C(5)–C(6)	1·489 (13)	C(5)–C(6)–N(2)	108·2 (8)
		C(6)–N(2)–C(4)	117·4 (7)
C(7)–S(5)	1·641 (7)	S(5)–C(7)–N(3)	128·6 (5)
C(7)–S(6)	1·724 (7)	S(5)–C(7)–S(6)	121·5 (4)
C(7)–N(3)	1·313 (9)	S(6)–C(7)–N(3)	109·8 (5)
N(3)–C(8)	1·443 (12)	C(7)–S(6)–C(9)	94·2 (5)
S(6)–C(9)	1·792 (14)	S(6)–C(9)–C(8)	107·8 (9)
C(8)–C(9)	1·486 (17)	C(9)–C(8)–N(3)	107·7 (8)
		C(8)–N(3)–C(7)	120·5 (7)
Pd···Cl	3·504 (2)	S(1)–Pd–Cl	103·0 (1)
		S(3)–Pd–Cl	77·5 (1)

Hydrogen bonds

D–H	*A*	*D*···*A*	*A*···H	∠*DHA*
N(1)–HN(1)	Cl(x,y,z)	3·181 (7) Å	2·08 (7) Å	154 (5)°
N(2)–HN(2)	Cl($\bar{x},\bar{y},\bar{z}$)	3·163 (6)	2·46 (7)	155 (7)
N(3)–HN(3)	Cl($1-x,\bar{y},\bar{z}$)	3·251 (7)	2·46 (8)	168 (7)

Table 4. *Least-squares planes*

Values are given in the following order: atoms defining the plane, equation of plane, deviations of atoms from the plane (Å) with e.s.d.'s in parentheses.

Plane (1): Pd, S(1), S(3)

$$-0\cdot9686X-0\cdot2329Y-0\cdot0869Z=0$$

S(2) −1·547 (2), S(4) 1·423 (2), C(1) −1·396 (7), C(4) 1·305 (6), N(1) −2·467 (6), N(2) 2·322 (6)

Plane (2): Pd, S(1), C(1)

$$-0\cdot3286X-0\cdot2114Y-0\cdot9205Z=0$$

S(2) 0·199 (2), C(2) −0·293 (10), C(3) −0·061 (10), N(1) −0·141 (5)

Plane (3): Pd, S(3), C(4)

$$-0\cdot7324X+0\cdot6686Y-0\cdot1288Z=0$$

S(4) −0·249 (2), C(5) 0·124 (10), C(6) 0·105 (12), N(2) 0·217 (6)

Plane (4): S(1), C(1), N(1)

$$-0\cdot3096X-0\cdot0764Y-0\cdot9478Z+0\cdot3025=0$$

S(2) −0·012 (2), C(2) −0·396 (10), C(3) 0·037 (10)

Plane (5): S(3), C(4), N(2)

$$-0\cdot6483X+0\cdot6901Y-0\cdot3216Z-0\cdot4613=0$$

S(4) 0·069 (2), C(5) 0·272 (10), C(6) −0·057 (12)

Plane (6): S(1), S(2), N(1), C(1), C(2), C(3)

$$-0\cdot2939X-0\cdot0740Y-0\cdot9530Z+0\cdot2954=0$$

S(1) −0·006 (2), S(2) 0·012 (2), N(1) 0·038 (5), C(1) 0·020 (6), C(2) −0·342 (10), C(3) 0·097 (10)

Plane (7): S(3), S(4), N(2), C(4), C(5), C(6)

$$-0\cdot6501X+0\cdot7008Y-0\cdot2938Z-0\cdot3912=0$$

S(3) 0·004 (2), S(4) −0·006 (2), N(2) −0·011 (6), C(4) −0·024 (6), C(5) 0·191 (10), C(6) −0·098 (12)

Plane (8): S(5), S(6), N(3), C(7), C(8), C(9)

$$-0\cdot5122X-0\cdot4052Y-0\cdot7573Z+3\cdot9999=0$$

S(5) −0·001 (2), S(6) 0·000 (2), N(3) −0·002 (7), C(7) 0·016 (6), C(8) −0·008 (9), C(9) 0·000 (15)

Interplanar angles (°); e.s.d.'s are 0·5–1·5°

(1)–(2)	63·4	(2)–(4)	8·0
(1)–(3)	55·6	(2)–(6)	8·3
(1)–(6)	67·4	(3)–(5)	12·1
(1)–(7)	60·5	(3)–(7)	10·7
		(6)–(7)	65·2

The crystal structure consists of $[Pd(ttz)_4]^{2+}$ cations, Cl^- anions and free ttz solvent molecules.

The ttz ligand is monodentate and S-bonded to the metal. The Pd atom occupies a crystallographic centre of symmetry and is bound to four ligand molecules *via* four S donors in a strictly planar MS_4 array, with an S–Pd–S angle of 92·7 (1)°. The Pd–S distances [2·322 (2) and 2·327 (2) Å] are comparable to the values found in other square-planar Pd compounds (Berta, Spofford, Boldrini & Amma, 1970). The Pd–S–C angles [109·2 (2) and 110·4 (2)°] and the dihedral angles between the Pd, S, C plane and the mean plane of the ligands [8·3 and 10·7 (15)°] indicate that the S atom is largely sp^3 in character (Spofford & Amma, 1976; Raper & Nowell, 1979).

There are three crystallographically independent ttz molecules with different structural functions. Two are bound to the metal through the exocyclic S atom, and the third, uncoordinated molecule stabilizes the crystal structure.

Their geometry is essentially the same (Table 3). The exocyclic C–S bond lengths range from 1·641 (7) to

1·675 (7) Å, typical of exocyclic thiones (Form, Raper & Downie, 1976). The endocyclic S—C(sp^2) and S—C(sp^3) distances range from 1·724 (7) to 1·744 (7) Å and from 1·791 (10) to 1·823 (10) Å, respectively. They agree well with the corresponding data found for similar systems (Stanković, Ribár, Kálmár & Argay, 1980).

The C—N and C—C distances and bond angles for both coordinated and uncoordinated molecules are similar to each other and to those found in 3-(*p*-bromobenzyl)-1,3-thiazolidine-2-thione (Bryan, Hartley, Peckler, Fujita, Nagao & Seno, 1980). The bond lengths suggest the thione form for all the ttz molecules in our structure. However, the very short N(1)—C(1), N(2)—C(4) and N(3)—C(7) bonds, and the near equality of the exocyclic and endocyclic S—C(sp^2) bonds point to some contribution also from the thiol form.

Though the three independent ttz rings in the unit cell are very similar in their geometry, significant differences occur in their conformation.

The two coordinated ligands have the twist form with C(2), C(3) and C(5), C(6) deviating significantly from the plane defined by the remaining atoms of their respective rings (Table 4). The thiazolidine ring of the solvating molecule is, however, strictly planar. These differences in conformation are presumably due to packing effects and to the coordination of ligand to metal ion. The crystal packing is illustrated in Fig. 1.

The Cl^- ion is hydrogen bonded to the N atom of each of the three independent ttz molecules. The N—H···Cl angles (154–168°) and N···Cl distances (3·16–3·25 Å) are in good agreement with published data for such hydrogen bonds (Hamilton & Ibers, 1968).

The Cl^- anions which are relatively close to the Pd atom [3·504 (2) Å] complete the psuedooctahedral coordination sphere around the metal.

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Tricarbonyl[2–5-η-(methyl 3,5-dimethoxy-1α-methyl-2,4-cyclohexadiene-1β-carboxylate)]iron(0)

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Abstract. $C_{14}H_{16}FeO_7$, $M_r = 352·13$, triclinic, $P\bar{1}$, $a = 7·590\,(1)$, $b = 8·445\,(1)$, $c = 12·175\,(1)$ Å, $\alpha = 81·49\,(1)$, $\beta = 85·30\,(1)$, $\gamma = 82·85\,(1)°$ (293 K), $U = 764·2$ Å^3, $Z = 2$, $D_c = 1·531$ Mg m^{-3}, $F(000) = 364$, μ(Mo $K\alpha$) = 1·049 mm^{-1}. Refinement converged with $R = 0·028$, $R_w = 0·045$ for 2582 diffractometer data [$I \geq 3\sigma(I)$]. The metal–ligand bonding follows the expected pattern for 1,3-dienetricarbonyliron(0) complexes.

Introduction. Substituent directive effects in the reactions of substituted cyclohexadienes with iron carbonyls have been studied extensively in these

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