well as in Pb[II] saccharinate (Jovanovski, Hergold-Brundić & Kamenar, 1988), Hg[II] saccharinate (Kamenar, Jovanovski & Grdenić, 1982) and chloromercury (II) saccharinate (Jovanovski, Kamenar, Ferguson & Kaitner, 1988). Since a complete comparison is difficult, we focused our attention on the interatomic distances and angles within the thiazole ring of the thiosaccharinate ion in the present compound and the corresponding values in the analogous structures of (I) and (II) (see Table 3). In spite of the general similarity, there are small differences in some bond lengths and angles. Namely, in (I) and (II) the C(7)—N bonds are longer than in the Na thiosaccharinate, while the N—S(1) bonds are shorter and the C(6)—C(7)—N angles are smaller. These differences are probably mainly due to the substitution of the O atom from the C=O group in the saccharinate ion by the S atom in the analogous thiosaccharinate ion.

References

CHUPRUNOV, B. V., GRUMILOV, S. A., STOLYAROVA, N. B., TARKHOVA, T. N. & BELOV, N. V. (1982). *Kristallografiya*, **27**, 1108–1111.
COTTON, F. A., LEWIS, G. E., MURILLO, C. A., SCHWOTZER, W. & VALLE, G. (1984). *Inorg. Chem.* **23**, 4038–4041.
DOMENICANO, A., SPAGNA, R. & VACIAGO, A. (1969). *Atti Acad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.* **47**, 331–336.
HAIDER, S. Z., MALIK, K. M. A., AHMED, K. J., HESS, H., RIFFEL, H. & HURSTHOUSE, M. B. (1983). *Inorg. Chim. Acta*, **72**, 21–27.
HAIDER, S. Z., MALIK, K. M. A., DAS, S. & HURSTHOUSE, M. B. (1984). *Acta Cryst.* C40, 1147–1150.
JOVANOVSKI, G., HERGOLD-BRUNDIČ, A. & KAMENAR, B. (1988). *Acta Cryst.* C44, 63–66.
JOVANOVSKI, G. & KAMENAR, B. (1982). *Cryst. Struct. Commun.* **11**, 247–255.
JOVANOVSKI, G., KAMENAR, B., FERGUSON, G. & KAITNER, B. (1988). *Acta Cryst.* C44, 616–618.
KAMENAR, B. & JOVANOVSKI, G. (1982). *Cryst. Struct. Commun.* **11**, 257–261.
KAMENAR, B., JOVANOVSKI, G. & GRDENIĆ, D. (1982). *Cryst. Struct. Commun.* **11**, 263–268.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
MALIK, K. M. A., HAIDER, S. Z., HOSSAIN, M. A. & HURSTHOUSE, M. B. (1984). *Acta Cryst.* C40, 1696–1698.
SHELDRICK, G. M. (1976). *SHELX76. Program for crystal structure determination.* Univ. of Cambridge, England.

Structure of Tetrakis(2,3-dihydro-1,3-thiazole-2-thione)palladium(II) Dichloride 2,3-Dihydro-1,3-thiazole-2-thione Solvate

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Abstract. [Pd(C$_3$H$_3$NS$_2$)$_4$]Cl$_2$.C$_3$H$_3$NS$_2$, $M_r = 763.2$, monoclinic, $P2_1/c$, $a = 11.546$ (1), $b = 17.749$ (2), $c = 13.724$ (2) Å, $\beta = 100.91$ (1)°, $V = 2761.6$ Å^3, $Z = 4$, $D_x = 1.835$, $D_m = 1.83$ (1) Mg m^{-3}, $F(000) = 1520$, $T = 295$ K, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.60$ mm^{-1}, $R = 0.0252$ for 4086 observed reflections. Thiazoline-2-thione, tztH, is monodentate S-donating to Pd[II] in the [Pd(tztH)$_4$]$^{2+}$ cation with a mean Pd—S distance of 2.336 (1) Å and a mean S—Pd—S angle of 90.2 (1)°. The chloride ions form an extensive H-bonding network involving the imido (NH) groups of the ligands and the solvated tztH molecule with NH⋯Cl distances ranging from 3.051 to 3.561 Å.

Introduction. Thioamides coordinate readily with divalent palladium and platinum generally producing complexes of formula [ML_2Cl$_2$] and [ML_4]Cl$_2$, although compounds with other stoichiometries have also been reported (Raper, 1985). Structural details are limited to the *cis* isomer of [Pd(thiazolidine-2-thione)$_2$Cl$_2$], for the [ML_2Cl$_2$] compounds (Kubiak, 1985). The situation is slightly better for the [PdL_4]Cl$_2$ series where structures have been reported for thiourea (tu) (Berta, Spofford, Boldrini & Amma, 1970), 1-methylimidazoline-2-thione (mimntH) (Butler, Creighton, Oughtred, Raper & Nowell, 1983) and thiazolidine-2-thione (tztdH) (Kubiak &

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{eq}(\text{Å}^2)$
Pd	0·49804 (2)	0·10163 (1)	0·24193 (1)	0·03686 (7)
Cl(1)	0·84174 (8)	0·36497 (4)	0·13197 (5)	0·0526 (3)
Cl(2)	0·14146 (8)	0·36475 (5)	0·37645 (6)	0·0587 (3)
S(21)	0·61811 (8)	0·19900 (5)	0·20456 (5)	0·0537 (3)
S(11)	0·52596 (7)	0·14003 (5)	−0·00396 (5)	0·0479 (2)
S(22)	0·62103 (7)	0·01174 (5)	0·18948 (5)	0·0527 (3)
S(12)	0·71305 (7)	0·03517 (5)	0·41008 (5)	0·0503 (2)
S(23)	0·36522 (7)	0·19204 (5)	0·27781 (5)	0·0494 (2)
S(13)	0·45166 (7)	0·13057 (5)	0·48623 (5)	0·0513 (2)
S(24)	0·38721 (7)	0·00478 (5)	0·29456 (5)	0·0501 (2)
S(14)	0·29956 (7)	0·02166 (5)	0·07240 (5)	0·0496 (2)
S(25)	0·95302 (10)	0·17540 (7)	0·40387 (7)	0·0757 (4)
S(15)	1·04292 (13)	0·08678 (7)	0·24779 (10)	0·0858 (5)
C(21)	0·6181 (2)	0·1934 (2)	0·0812 (2)	0·0382 (8)
N(31)	0·6897 (2)	0·2332 (1)	0·0361 (2)	0·0440 (8)
C(41)	0·6737 (3)	0·2242 (2)	−0·0646 (2)	0·0516 (11)
C(51)	0·5891 (3)	0·1751 (2)	−0·0988 (2)	0·0520 (11)
C(22)	0·7178 (2)	−0·0047 (2)	0·2979 (2)	0·0401 (9)
N(32)	0·8086 (2)	−0·0519 (1)	0·3064 (2)	0·0471 (8)
C(42)	0·8742 (3)	−0·0582 (2)	0·4002 (2)	0·0536 (11)
C(52)	0·8346 (3)	−0·0157 (2)	0·4666 (2)	0·0581 (11)
C(23)	0·3611 (2)	0·1847 (2)	0·4404 (2)	0·0402 (9)
N(33)	0·2884 (2)	0·2242 (1)	0·4448 (2)	0·0478 (8)
C(43)	0·3029 (3)	0·2136 (2)	0·5460 (2)	0·0567 (12)
C(53)	0·3873 (3)	0·1650 (2)	0·5808 (2)	0·0565 (11)
C(24)	0·2937 (2)	−0·0157 (2)	0·1861 (2)	0·0401 (9)
N(34)	0·2052 (2)	−0·0645 (1)	0·1786 (2)	0·0471 (8)
C(44)	0·1416 (3)	−0·0742 (2)	0·0840 (2)	0·0543 (11)
C(54)	0·1812 (3)	−0·0326 (2)	0·0168 (2)	0·0554 (11)
C(25)	0·9906 (3)	0·1672 (2)	0·2937 (2)	0·0498 (10)
N(35)	0·9863 (3)	0·2204 (2)	0·2243 (2)	0·0656 (11)
C(45)	1·0203 (3)	0·1996 (3)	0·1370 (3)	0·0695 (14)
C(55)	1·0547 (4)	0·1301 (3)	0·1373 (3)	0·0789 (16)

Table 2. *Bond lengths (Å) and angles (°)*

Pd—S(21)	2·332 (1)	Pd—S(22)	2·338 (1)
Pd—S(23)	2·336 (1)	Pd—S(24)	2·338 (1)
S(21)—C(21)	1·696 (3)	C(21)—S(11)	1·711 (3)
C(21)—N(31)	1·326 (4)	S(11)—C(51)	1·724 (4)
N(31)—C(41)	1·369 (4)	C(41)—C(51)	1·327 (5)
S(22)—C(22)	1·709 (3)	C(22)—S(12)	1·705 (3)
C(22)—N(32)	1·330 (4)	S(12)—C(52)	1·725 (3)
N(32)—C(42)	1·369 (4)	C(42)—C(52)	1·328 (5)
S(23)—C(23)	1·697 (3)	C(23)—S(13)	1·713 (3)
C(23)—N(33)	1·327 (4)	S(13)—C(53)	1·724 (4)
N(33)—C(43)	1·380 (4)	C(43)—C(53)	1·322 (5)
S(24)—C(24)	1·705 (3)	C(24)—S(14)	1·708 (3)
C(24)—N(34)	1·328 (4)	S(14)—C(54)	1·728 (3)
N(34)—C(44)	1·377 (4)	C(44)—C(54)	1·328 (5)
S(25)—C(25)	1·657 (4)	C(25)—S(15)	1·761 (4)
C(25)—N(35)	1·335 (5)	S(15)—C(55)	1·728 (5)
N(35)—C(45)	1·380 (5)	C(45)—C(55)	1·297 (7)
S(21)—Pd—S(22)	91·0 (1)	S(21)—Pd—S(23)	88·8 (1)
S(22)—Pd—S(23)	174·3 (1)	S(21)—Pd—S(24)	174·7 (1)
S(22)—Pd—S(24)	89·6 (1)	S(23)—Pd—S(24)	91·2 (1)
Pd—S(21)—C(21)	106·8 (1)	S(21)—C(21)—S(11)	126·6 (2)
S(21)—C(21)—N(31)	123·6 (2)	S(11)—C(21)—N(31)	109·8 (2)
C(21)—S(11)—C(51)	91·1 (1)	C(21)—N(31)—C(41)	115·6 (2)
N(31)—C(41)—C(51)	112·5 (3)	S(11)—C(51)—C(41)	111·0 (2)
Pd—S(22)—C(22)	100·6 (1)	S(22)—C(22)—S(12)	126·0 (2)
S(22)—C(22)—N(32)	124·0 (2)	S(12)—C(22)—N(32)	110·0 (2)
C(22)—S(12)—C(52)	91·5 (2)	C(22)—N(32)—C(42)	114·8 (3)
N(32)—C(42)—C(52)	113·5 (3)	S(12)—C(52)—C(42)	110·2 (2)
Pd—S(23)—C(23)	107·4 (1)	S(23)—C(23)—S(13)	126·6 (2)
S(23)—C(23)—N(33)	123·6 (2)	S(13)—C(23)—N(33)	109·7 (2)
C(23)—S(13)—C(53)	91·4 (2)	C(23)—N(33)—C(43)	115·1 (3)
N(33)—C(43)—C(53)	113·1 (3)	S(13)—C(53)—C(43)	110·7 (2)
Pd—S(24)—C(24)	100·4 (1)	S(24)—C(24)—S(14)	126·0 (2)
S(24)—C(24)—N(34)	123·8 (2)	S(14)—C(24)—N(34)	110·2 (2)
C(24)—S(14)—C(54)	91·3 (2)	C(24)—N(34)—C(44)	114·8 (3)
N(34)—C(44)—C(54)	113·2 (3)	S(14)—C(54)—C(44)	110·5 (2)
S(25)—C(25)—S(15)	125·4 (2)	S(25)—C(25)—N(35)	127·4 (3)
S(15)—C(25)—N(35)	107·2 (3)	C(25)—S(15)—C(55)	92·5 (2)
C(25)—N(35)—C(45)	116·8 (3)	N(35)—C(45)—C(55)	112·9 (4)
S(15)—C(55)—C(45)	110·5 (3)		

Głowiak, 1982). All of the complexes contain square-planar $[PdL_4]^{2+}$ cations with monodentate S-donating ligands and ionic chlorides.

Experimental. Burgundy-red crystals from an acidified (*M*.HCl) solution of K_2PdCl_4 (1 mmol) and excess of tztH; crystal dimensions $0·31 \times 0·35 \times 0·58$ mm, D_m by flotation in CCl_4/CH_3I. Stoe–Siemens AED-2 diffractometer. Unit-cell parameters from 32 centred reflections ($20 < 2\theta < 25°$). 4885 unique reflections measured ($3 < 2\theta < 50°$), index ranges h −13 to 13, k 0 to 21, l 0 to 16. Scanning mode ω/θ, variable scanning range and time with on-line profile fitting (Clegg, 1981), no significant variation in three standard reflections, semi-empirical absorption correction, transmission 0·36–0·47. 4086 observed reflections with $F > 4\sigma_c(F)$ and $\sigma_c(F)$ from counting statistics only. Structure solved by direct methods and difference-Fourier methods, refined by blocked-cascade least squares on F to a minimum of $\sum w\Delta^2$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 1 + 52G - 18G^2 - 4S + 4S^2 - 65GS$ with $G = F_c/F_{max}$ and $S = \sin\theta/\sin\theta_{max}$ (Wong & Robertson, 1985). Anisotropic thermal parameters for all non-H atoms; ligand aromatic H atoms located on external bisectors of ring angles,

$C—H = 0·96$ Å, $N—H = 0·87$ Å, $U(H) = 1·2U_{eq}$ (C or N). Isotropic extinction parameter $x = 1·8$ (2) $\times 10^{-7}$ $[F_c = F_c/(1 + xF_c^2/\sin\theta)^{1/4}]$. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149), 299 parameters, $R = 0·0252$, $wR = 0·0288$, $\Delta/\sigma_{max} = 0·030$, mean $= 0·008$. Largest peak in final difference synthesis $+0·45$ e Å^{-3}, largest hole $-0·43$ e Å^{-3}, goodness of fit 1·07. *SHELXTL* (Sheldrick, 1985), and local programs.

Discussion. Atomic coordinates and U_{eq}'s are given in Table 1, bond lengths and angles are in Table 2.* The structure of the complex cation, with the chloride ions and the solvate tztH molecule, together with the atomic numbering scheme, are shown in Fig. 1. Unit-cell contents, in c projection, are in Fig. 2.

Significant perturbation in the thione region of the IR spectrum of the ligand (800–500 cm^{-1}) together with the presence of ν(Pd—S) at 355 cm^{-1} suggested

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the ligand to be thione-S donating in the complex (Raper, Britton & Creighton, 1989). The absence of $\nu(Pd$—Cl) activity indicated the presence of ionic chloride and the broad strong $\nu(N$—H) band at $3100\ cm^{-1}$ suggested substantial H bonding in the complex.

The structure consists of $[Pd(tztH)_4]^{2+}$ cations, chloride anions and uncoordinated tztH molecules. There are four independent tztH ligands in the complex cation each of which is monodentate thione-S donating to the metal. The planar PdS_4 core of the cation is essentially regular with an average S—Pd—S angle of 90·2 (1)° and the largest atomic displacement from the PdS_4 mean plane being S(23) at $-0·113\ Å$. The Pd—S distances range from 2·332 (1) to 2·338 (1) Å [mean 2·336 (1) Å]. Angles (Pd—S—C) at the thione-S atom range from 100·4 (1) to 107·4 (1)° [mean 103·3 (1)°]. The ligands 'twist' about their corresponding Pd—S—C planes with dihedral angles ranging from 1·7 to 10·7° and also 'tilt' about the PdS_4 plane with dihedral angles in the range 63·3 to 111·2°. Such angles define the ligand orientations in the $[Pd(LH)_4]^{2+}$ cation and are a consequence of a number of factors including metal–

ligand bonding, H-bonding requirements as well as steric and packing factors (Butler et al., 1983).

The mean Pd—S distances reported for other $[Pd(LH)_4]^{2+}$ cations are: 2·334 (3) Å ($LH = tu$, Berta et al., 1970); 2·363 (2) Å ($LH = mimtH$, Butler et al., 1983); and 2·325 (2) Å ($LH = tztdH$, Kubiak & Głowiak, 1982). These distances are sufficiently close to each other to suggest a common conventional σ-bonding mode for the thione-S donating ligands in this series of complexes.

The uncoordinated tztH molecule adopts the thione tautomeric form with dimensions similar to the related thiazole-thione derivatives, benzthiazoline-2-thione (Chesick & Donohue, 1971) and thiazolidine-2-thione (Raper, Oughtred & Nowell, 1983). In tztH the exocyclic C—$S_{(thione)}$ distance, 1·657 (4) Å, corresponds to 50% π character (Trinajstic, 1968). This distance is lengthened, in the complex cation, to an average value of 1·702 (4) Å, which corresponds to about 42% π character in the C—$S_{(thione)}$ bond (Trinajstic, 1968). An increase in the C—$S_{(thione)}$ distance upon coordination is a common characteristic of thione-S donating ligands (Raper, Creighton, Oughtred & Nowell, 1983).

The chloride ions, Cl(1) and Cl(2), form an extensive H-bonded network of NH···Cl contacts with the imido NH groups of all the ligands as well as that of the uncoordinated tztH molecule. The Cl(1) ion forms contacts with N(31) (3·055); N(34) (3·015) and N(35) (3·173 Å) while the Cl(2) ion is in contact with N(32) (3·051 Å); N(33) (3·055 Å) and also forms a weak contact with N(35) (3·561 Å).
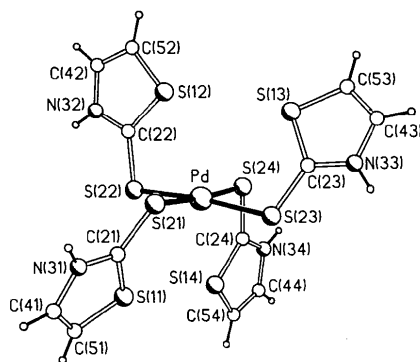

Fig. 1. Labelled perspective diagram of the complex cation showing the orientation of the ligands about the PdS_4 core.
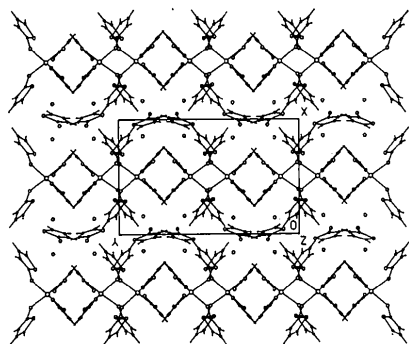

Fig. 2. Unit-cell contents in c projection with the H-bonded contacts omitted for reasons of clarity.

References

BERTA, D. A., SPOFFORD, W. A., BOLDRINI, P. & AMMA, E. L. (1970). Inorg. Chem. 9, 136–142.

BUTLER, L. M., CREIGHTON, J. R., OUGHTRED, R. E., RAPER, E. S. & NOWELL, I. W. (1983). Inorg. Chim. Acta, 75, 149–154.

CHESICK, J. P. & DONOHUE, J. (1971). Acta Cryst. B27, 1441–1444.

CLEGG, W. (1981). Acta Cryst. A37, 22–28.

KUBIAK, M. (1985). Proceedings of the School Symposium on Inorganic Biochemistry and Molecular Biophysics, Univ. of Wrocław, Karpacz, Poland, June 1985, pp. 175–181.

KUBIAK, M. & GŁOWIAK, T. (1982). Acta Cryst. B28, 2931–2936.

RAPER, E. S. (1985). Coord. Chem. Rev. 61, 118–184.

RAPER, E. S., BRITTON, A. M. & CREIGHTON, J. R. (1989). Thermochim. Acta, 40, 343–353.

RAPER, E. S., CREIGHTON, J. R., OUGHTRED, R. E. & NOWELL, I. W. (1983). Acta Cryst. B39, 355–366.

RAPER, E. S., OUGHTRED, R. E. & NOWELL, I. W. (1983). Inorg. Chim. Acta, 77, L89–L93.

SHELDRICK, G. M. (1985). SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. Revision 5. Univ. of Göttingen, Federal Republic of Germany.

TRINAJSTIC, N. (1968). Tetrahedron Lett. 12, 1529–1531.

WONG, H. & ROBERTSON, B. E. (1985). Structure and Statistics in Crystallography, edited by A. J. C. WILSON, pp. 125–137. New York: Adenine Press.