*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.134$
$S = 1.068$
1862 reflections
151 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0690P)^2 + 0.0869P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.015$
$\Delta\rho_{\max} = 0.230$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.251$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.2300 (19) | N4—O3 | 1.2265 (19) |
| N2—C2 | 1.359 (2) | N4—O4 | 1.237 (2) |
| N2—C1 | 1.394 (2) | N4—O2 | 1.2400 (19) |
| N3—C1 | 1.324 (2) | | |
| C2—N2—C1 | 125.93 (14) | N1—C2—N2 | 120.39 (14) |
| O1—C1—N3 | 124.50 (16) | N1—C2—C3 | 118.35 (15) |
| O1—C1—N2 | 121.18 (15) | N2—C2—C3 | 121.26 (15) |
| N3—C1—N2 | 114.32 (15) | | |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—HN1···O1 | 0.85 (2) | 1.95 (2) | 2.6221 (19) | 135.1 (18) |
| N1—HN1···O1$^{i}$ | 0.85 (2) | 2.34 (2) | 2.9417 (18) | 127.9 (17) |
| N2—HN2···O2 | 0.86 (2) | 1.97 (2) | 2.820 (2) | 168 (2) |
| N3—HN31···O4 | 0.88 (2) | 2.10 (2) | 2.971 (2) | 168.0 (17) |
| N3—HN32···O3$^{ii}$ | 0.89 (2) | 2.33 (2) | 3.210 (2) | 171.7 (17) |
| N3—HN32···O2$^{ii}$ | 0.89 (2) | 2.47 (2) | 3.155 (2) | 134.8 (16) |

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

H atoms were localized from difference Fourier maps and refined with fixed $U_{\rm iso} = 0.0506$ Å$^2$.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Manual*. Data reduction: *DATARED* (Vassilev, unpublished). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1296). Services for accessing these data are described at the back of the journal.

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# A dithiadiazolylium chloride salt from the reaction of 4-phenyl-1,2,3,5-dithiadiazolyl with gold(I) chloride

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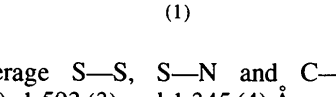
## Abstract

4-Phenyl-1,2,3,5-dithiadiazolyl reacts with AuCl·THT (THT is tetrahydrothiophene) to produce 4-phenyl-1,2,3,5-dithiadiazolylium chloride and elemental gold. The structure of the dichloromethane hemisolvate, $C_7H_5N_2S_2^+ \cdot Cl^- \cdot 0.5CH_2Cl_2$ or $PhCNSSN^+ \cdot Cl^- \cdot 0.5CH_2Cl_2$, contains one $Cl^-$ anion per dithiadiazolylium cation. The $Cl^-$ anion sits approximately equidistant from each of the S atoms of the $CN_2S_2$ fragment, and lies almost directly in the heterocyclic ring plane. The solvent molecule is well ordered, forming weak interactions with the dithiadiazolium and $Cl^-$ ions.

## Comment

Recently, we have been investigating the oxidative addition reactions of 4-phenyl-1,2,3,5-dithiadiazolyl radicals to late transition metal elements (Banister *et al.*, 1998), in which the dithiadiazolyl is bound directly to the metal following sulfur–sulfur bond cleavage of the ligand. The reaction of 4-phenyl-1,2,3,5-dithiadiazolyl with AuCl·THT (THT is tetrahydrothiophene) in dichloromethane produced a yellow crystalline solid, which was identified by a single-crystal X-ray diffraction study as $PhCNSSN^+ \cdot Cl^- \cdot 0.5CH_2Cl_2$, (1).



(1)

The average S—S, S—N and C—N distances [2.0115 (13), 1.593 (3) and 1.345 (4) Å, respectively] are the same within experimental error as those found previously in the toluene solvate structure (Hazell & Hazell, 1988), and are shorter than those found in the corresponding dithiadiazolyl radical (Vegas *et al.*, 1980). Each chloride anion is closely associated with a dithiadiazolylium cation and the chloride ion lies in front of the S—S bridge, and within 1° of the plane of the planar CNSSN ring. Whilst the average S···Cl distance of 2.948 (5) Å is considerably less than the sum of the van der Waals radii (around 3.18 Å; Nyburg & Faerman, 1985), molecular-orbital calculations indicate that the interaction is almost entirely electrostatic at that distance (Rawson & Smith, 1998).

The structure of the PhCNSSN$^+$ cation has also been determined in a number of other salts, including [PhCNSSN][AsF$_6$] (Scholz *et al.*, 1989), [PhCNSSN]$_2$-[Pt(mnt)$_2$] (mnt is maleonitriledithiolate; Clegg *et al.*, 1994), [PhCNSSN][S$_3$N$_3$] and [PhCNSSN]$_2$Cl-[S$_3$N$_3$] (Banister *et al.*, 1990), and [PhCNSSN]I and [PhCNSSN][I$_3$] (Bryan *et al.*, 1994). The variation of S—S distances in these structures has been attributed to differing degrees of charge transfer from anion to cation in the solid state (Rawson *et al.*, 1995).

In the toluene solvate structure, the solvent molecule is disordered and appears to act merely as a space-filling unit within the crystal (Hazell & Hazell, 1988). In this structure, the dichloromethane molecule lies on a special position and is well ordered due to weak hydrogen bonds [C9—H9*A* 0.98, H9*A*···Cl2$^{ii}$ 2.65 Å and C9—H9*A*···Cl2$^{ii}$ 156°; symmetry code: (ii) $1-x, y, \frac{1}{2}-z$] coupled with out-of-plane interactions between dichloromethane Cl atoms and cation S atoms [Cl1···S2$^{iii}$ 3.526 (5) Å; symmetry code: (iii) $x, 1-y, \frac{1}{2}-z$]. An additional close S···Cl contact occurs between Cl2 and S1$^{ii}$ at a distance of 3.119 (5) Å.

Instead of the anticipated oxidative addition reaction of PhCNSSN to Au$^I$ to form an Au$^{III}$ complex, the PhCNSSN radical acts as a dechlorinating agent (Adamson *et al.*, 1993), forming PhCNSSN$^+$·Cl$^-$ and Au$^0$ (which precipitates as elemental gold). Competition between halogen abstraction and oxidative addition is likely to be a common feature of these types of reactions between low oxidation state metal–halogen fragments and dithiadiazolyl radicals. Careful matching of the redox potentials of the two species will be required if further dithiadiazolyl–metal complexes are to be obtained.

## Experimental

The reaction of AuCl·THT (115 mg, 0.50 mmol) and 4-phenyl-1,2,3,5-dithiadiazole (90 mg, 0.50 mmol) was carried out by stirring in dichloromethane (15 ml) at room temperature. The

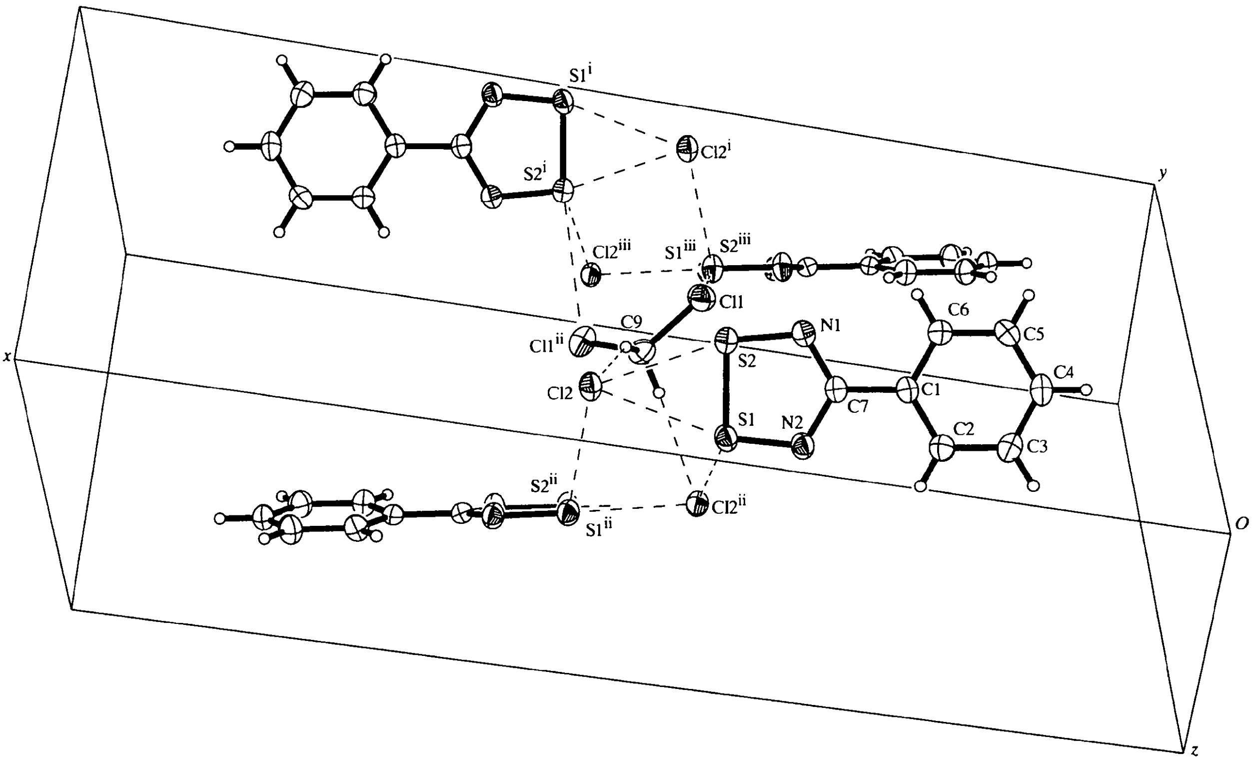


Fig. 1. The packing of PhCNSSN$^+$·Cl$^-$·0.5CH$_2$Cl$_2$, illustrating the S···Cl and H···Cl interactions, and the atom-labelling scheme. Symmetry transformations are: (i) $1-x, 1-y, -z$; (ii) $1-x, y, \frac{1}{2}-z$; (iii) $x, 1-y, \frac{1}{2}+z$.

product, 4-phenyl-1,2,3,5-dithiadiazolylium chloride, began to form almost immediately. Yellow crystals suitable for single-crystal X-ray diffraction were grown by cooling a saturated solution to 253 K for 14 d [yield: 85 mg (79%)].

### *Crystal data*

$C_7H_5N_2S_2^+ \cdot Cl^- \cdot 0.5CH_2Cl_2$
$M_r = 259.17$
Monoclinic
$C2/c$
$a = 25.119\,(3)$ Å
$b = 11.104\,(4)$ Å
$c = 7.570\,(3)$ Å
$\beta = 103.53\,(2)°$
$V = 2052.8\,(11)$ Å$^3$
$Z = 8$
$D_x = 1.677$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3.10\text{–}27.49°$
$\mu = 0.993$ mm$^{-1}$
$T = 150$ K
Block
0.2 × 0.2 × 0.2 mm
Orange

### *Data collection*

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (Molecular Structure Corporation, 1988)
$T_{\min} = 0.740$, $T_{\max} = 0.820$
2411 measured reflections
2361 independent reflections

1767 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.080$
$\theta_{\max} = 27.49°$
$h = 0 \rightarrow 32$
$k = 0 \rightarrow 14$
$l = -9 \rightarrow 9$
3 standard reflections every 200 reflections intensity decay: 1.2%

### *Refinement*

Refinement on $F^2$
$R(F) = 0.044$
$wR(F^2) = 0.102$
$S = 1.123$
2357 reflections
124 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 0.9247P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.471$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.389$ e Å$^{-3}$
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0001 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| S1 | 0.43293 (3) | 0.09227 (7) | 0.05106 (11) | 0.0291 (2) |
| C1 | 0.27914 (11) | 0.1498 (3) | −0.1565 (4) | 0.0241 (6) |
| N1 | 0.36590 (11) | 0.2282 (3) | −0.1993 (4) | 0.0334 (6) |
| S2 | 0.43124 (3) | 0.22113 (8) | −0.13695 (11) | 0.0324 (2) |
| N2 | 0.36852 (10) | 0.0786 (2) | 0.0161 (4) | 0.0288 (6) |
| C2 | 0.25144 (12) | 0.0605 (3) | −0.0848 (4) | 0.0311 (7) |
| Cl2 | 0.54541 (3) | 0.16806 (7) | 0.04159 (11) | 0.0307 (2) |
| C3 | 0.19466 (13) | 0.0595 (3) | −0.1275 (5) | 0.0359 (8) |
| C4 | 0.16585 (13) | 0.1468 (3) | −0.2399 (4) | 0.0333 (7) |
| C5 | 0.19299 (13) | 0.2361 (3) | −0.3109 (5) | 0.0323 (7) |
| C6 | 0.24967 (13) | 0.2375 (3) | −0.2701 (4) | 0.0301 (7) |
| C7 | 0.33929 (11) | 0.1525 (3) | −0.1128 (4) | 0.0249 (6) |
| C9 | 1/2 | 0.4239 (4) | 1/4 | 0.0323 (10) |
| Cl1 | 0.44654 (3) | 0.51370 (9) | 0.12338 (12) | 0.0410 (2) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| S1—N2 | 1.585 (2) | N1—S2 | 1.600 (3) |
| S1—S2 | 2.0115 (13) | N2—C7 | 1.353 (4) |
| N1—C7 | 1.337 (4) | | |
| N2—S1—S2 | 95.65 (11) | N1—C7—N2 | 119.1 (3) |
| C7—N1—S2 | 114.9 (2) | N1—C7—C1 | 120.6 (3) |
| N1—S2—S1 | 95.40 (11) | N2—C7—C1 | 120.4 (3) |
| C7—N2—S1 | 115.0 (2) | | |

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1280). Services for accessing these data are described at the back of the journal.

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