*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.080$
$S = 1.144$
4023 reflections
116 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 2.81P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.28$ e Å$^{-3}$ (0.72 Å from I2)
$\Delta\rho_{min} = -0.89$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0229 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Co—S1 | 2.2742 (10) | I1—I2 | 2.8946 (10) |
| Co—S4 | 2.2959 (11) | I2—I3 | 2.9430 (11) |
| Co—S7 | 2.4088 (11) | | |
| S1—Co—S4 | 89.76 (4) | S4—Co—S7 | 89.09 (4) |
| S1—Co—S7 | 89.33 (5) | I1—I2—I3 | 177.934 (12) |

We were unable to apply the optimum method for absorption correction (numerical *via* face indexing) because it was necessary to coat the crystal in a film of perfluoropolyether oil (Hoechst RS3000) to prevent the loss of diiodine by sublimation. As a result, it was not possible to index the crystals faces or determine accurately their distances from a common point within the crystal. Corrections for absorption were therefore made using $\psi$ scans. H atoms were introduced at geometrically calculated positions; thereafter they were constrained to ride on their parent C atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). 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: AB1509). Services for accessing these data are described at the back of the journal.

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# Macrocyclic Thioether Complexes of Palladium with Dibromoiodide Anions


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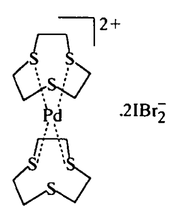
## Abstract

The structure of bis(1,4,7-trithiacyclononane)palladium(II) bis(dibromoiodide), $[Pd(C_6H_{12}S_3)_2](IBr_2)_2$, comprises ribbons in which neighbouring cations are linked by pairs of anions through S···Br contacts of 3.767 (5)–3.877 (5) Å. In (1,4,8,11-tetrathiacyclotetradecane)palladium(II) bis(dibromoiodide), $[Pd(C_{10}H_{20}S_4)](IBr_2)_2$, Pd···I, S···Br and S···I contacts link cations and anions into an infinite three-dimensional network.

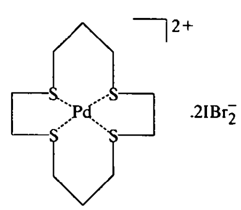

## Comment

Diiodine forms a range of adduct stoichiometries with uncomplexed homoleptic S-donor macrocyclic ligands (Blake, Cristiani *et al.*, 1997; Blake, Devillanova *et* *al.*, 1998; Blake, Li *et al.*, 1997), while with their metal complexes (Blake *et al.*, 1995), various polyiodide counter-anions such as $I_3^-$, $I_5^-$, $I_7^-$, $I_8^{2-}$, $I_9^-$, and $I_{12}^{2-}$ are observed. These anions can link together to give extended polyiodide arrays containing structural features such as spirals, belts, ribbons, chains, sheets and cages (Blake, Gould *et al.*, 1998), with the complex cation acting as a template for the formation of the polyiodide array. In other complexes, however, the polyiodide units are more isolated from each other, with no I···I contacts below *ca* 4.3 Å. However, in these cases, there are still interesting structural possibilities, including S···I interactions. We have already described one example, $[Co^{II}([9]aneS_3)_2]2I_3$, where cations and anions form infinite sheets *via* S···I contacts of 3.800 (2)–3.974 (2) Å (Blake, Lippolis *et al.*, 1998).

The $[Pd([9]aneS_3)_2]^{2+}$ and $[Pd([14]aneS_4)]^{2+}$ cations (where $[9]aneS_3$ is 1,4,7-trithiacyclononane and [14]-$aneS_4$ is 1,4,8,11-tetrathiacyclotetradecane) have been structurally characterized with non-interacting hexafluorophosphate anions (Blake *et al.*, 1987; Bell *et al.*, 1987). The centrosymmetric $[Pd([9]aneS_3)_2]^{2+}$ cation in bis(1,4,7-trithiacyclononane)palladium(II) bis(dibromoiodide), (1), has a geometry similar to that observed in the $PF_6^-$ salt, with equatorial Pd—S distances of 2.315 (5) and 2.324 (5) Å, and a long-range apical interaction to the third S atom of each trithia macrocycle of 2.997 (6) Å, slightly longer than the value of 2.952 (4) Å in the $PF_6^-$ salt. However, the $[Pd([14]aneS_4)]^{2+}$ cation in (1,4,8,11-tetrathiacyclotetradecane)palladium(II) bis(dibromoiodide), (2), has crystallographically imposed inversion symmetry and the metal therefore lies exactly in the plane defined by the four S atoms: this is in contrast to the ligand conformation in the $PF_6^-$ salt, where the metal atom lies 0.038 Å out of the $S_4$ plane, in the opposite direction to all the methylene groups. In both salts, the five- and six-membered chelate rings adopt $C_2$ twist and boat conformations, respectively: the differences arise from the disposition of these rings (*syn* or *anti*) with respect to the $S_4$ plane and demonstrate that different anions can exert differing influences on macrocyclic conformation. In (2), two S-atom lone pairs point up and two point down in contrast with the corresponding $PF_6^-$ salt (Bell *et al.*, 1997), where all four point in the same direction. The $IBr_2^-$ anions may also exert their influence sterically as the conformation seen in the $PF_6^-$ salt would require a *cis* arrangement of the two Pd···$IBr_2$ interactions (see below).




(1)




(2)

In (1), cations are bridged on each side by pairs of $IBr_2^-$ anions through S···Br contacts of 3.767 (5)–3.877 (5) Å (Fig. 1). Only Br2 participates in these, Br1 and I1 having no close interactions. Each Br2 participates in three such contacts: one to an S atom in each $[9]aneS_3$ ring of one cation, providing an intra-

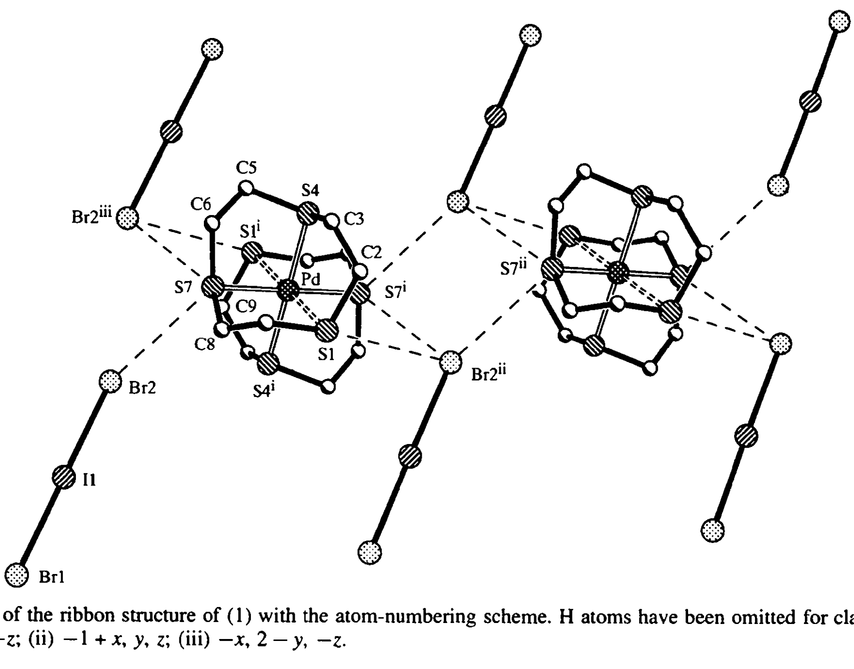



Fig. 1. A view of part of the ribbon structure of (1) with the atom-numbering scheme. H atoms have been omitted for clarity. Symmetry codes: (i) $-1-x, 2-y, -z$; (ii) $-1+x, y, z$; (iii) $-x, 2-y, -z$.

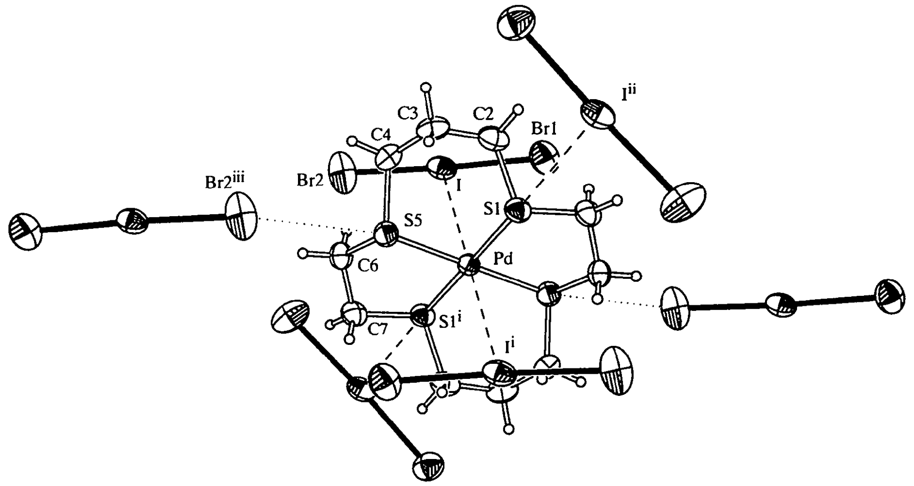



Fig. 2. A representation of part of the infinite three-dimensional network in (2). Displacement ellipsoids represent 50% probability surfaces and H atoms are shown as spheres of arbitrary radii. The anions shown participate in further contacts to an outer shell of cations (not shown). Symmetry codes: (i) $2-x, -y, 2-z$; (ii) $\frac{1}{2}+x, -y, z$; (iii) $2-x, -1-y, 2-z$.

cation bridge, and one to a ring of a neighbouring cation, providing the inter-cation link. The thia donor atom S7 forms two interactions with symmetry-related Br2 acceptors. The contacts link cations and anions into essentially discrete infinite ribbons running parallel to (100).

In (2), there are Pd···I/I$^{i}$ [4.020 (1) Å] and S1···I$^{ii}$ [3.870 (2) Å], as well as S5···Br2$^{iii}$ [3.684 (2) Å], interactions [symmetry codes: (i) $2-x, -y, 2-z$; (ii) $\frac{1}{2}+x, -y, z$; (iii) $2-x, -1-y, 2-z$]. The Pd···I contacts are apical, conferring a [4+2] coordination on the Pd$^{II}$ centre. Each cation in (2) is surrounded by a shell of six $IBr_2^-$ anions: each of these participates in a complementary interaction with an outer shell of cations, thereby linking cations and anions into an infinite three-dimensional network, part of which is shown as Fig. 2.

## Experimental

A solution of $^{n}Bu_4NIBr_2$ was prepared by mixing equivalent amounts of $^{n}Bu_4NI$ and $Br_2$ in MeCN. Compounds (1) and (2) were obtained in 40–50% yield by slow evaporation from an MeCN solution containing the corresponding $PF_6^-$ salt and $^{n}Bu_4NIBr_2$ in a 1:2 molar ratio. Elemental analysis: found (calculated for $C_{12}H_{24}Br_4I_2PdS_6$): C 13.70 (13.85), H 2.40 (2.32), S 18.65 (18.49)%; found (calculated for $C_{10}H_{20}Br_4I_2PdS_4$): C 12.50 (12.66), H 2.25 (2.12), S 13.45 (13.52)%. Crystals of (1) gave broad (>2°) misshapen reflection profiles at ambient temperature and these became even worse when cooling was attempted.

### Compound (1)

*Crystal data*

$[Pd(C_6H_{12}S_3)_2](IBr_2)_2$
$M_r = 1040.51$
Monoclinic
$P2_1/n$
$a = 9.253$ (8) Å
$b = 12.88$ (2) Å
$c = 12.455$ (10) Å
$\beta = 109.69$ (7)°
$V = 1398$ (3) Å$^3$
$Z = 2$
$D_x = 2.473$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 36 reflections
$\theta = 15.5–16.0°$
$\mu = 9.039$ mm$^{-1}$
$T = 295$ (2) K
Block
0.58 × 0.44 × 0.28 mm
Dark red

*Data collection*

Stoe Stadi-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scans (North *et al.*, 1968), and then refined from $\Delta F$ (Walker & Stuart, 1983)
$T_{min} = 0.010$, $T_{max} = 0.062$
2478 measured reflections
2435 independent reflections

1740 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity variation: ±2%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.094$
$wR(F^2) = 0.288$
$S = 1.065$
2435 reflections
116 parameters
H atoms: riding model
$w = 1/[\sigma^2(F_o^2) + (0.192P)^2 + 20.95P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 3.46$ e Å$^{-3}$ (0.30 Å from Br2)
$\Delta\rho_{min} = -3.56$ e Å$^{-3}$ (0.89 Å from I1)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Pd—S1 | 2.997 (6) | I1—Br1 | 2.819 (4) |
| Pd—S4 | 2.313 (5) | I1—Br2 | 2.850 (4) |
| Pd—S7 | 2.323 (5) | | |
| Br1—I1—Br2 | 178.18 (7) | | |

**Compound (2)**

*Crystal data*

$[Pd(C_{10}H_{20}S_4)](IBr_2)_2$
$M_r = 948.34$
Monoclinic
$I2/a$
$a = 14.651$ (2) Å
$b = 9.3117$ (7) Å
$c = 16.7648$ (11) Å
$\beta = 93.468$ (10)°
$V = 2282.9$ (4) Å$^3$
$Z = 4$
$D_x = 2.759$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 48 reflections
$\theta = 13$–14°
$\mu = 10.877$ mm$^{-1}$
$T = 293$ (2) K
Plate
0.43 × 0.35 × 0.04 mm
Red

*Data collection*

Stoe Stadi-4 four-circle diffractometer
$\omega/\theta$ scans
Absorption correction: $\psi$ scans (North *et al.*, 1968)
$T_{min} = 0.176$, $T_{max} = 0.694$
2523 measured reflections
1894 independent reflections

1564 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25°$
$h = -17 \rightarrow 17$
$k = -11 \rightarrow 0$
$l = -19 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.110$
$S = 1.055$
1878 reflections
98 parameters
H-atom parameters constrained with $U_{iso}(H) = 1.2U_{eq}(C)$
$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 29.01P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.12$ e Å$^{-3}$ (0.89 Å from Br2)
$\Delta\rho_{min} = -1.07$ e Å$^{-3}$ (0.84 Å from Br2)
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00123 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Pd—S1 | 2.290 (2) | S5—Br2$^{ii}$ | 3.684 (2) |
| Pd—S5 | 2.292 (2) | I—Br1 | 2.6981 (12) |
| S1—I$^{i}$ | 3.870 (2) | I—Br2 | 2.6827 (13) |
| S1—Pd—S5 | 89.74 (8) | Br1—I—Br2 | 177.10 (5) |

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

In order to prevent the loss of diiodine by sublimation, it was necessary to coat the crystals in films of perfluoropolyether oil (Hoechst RS3000). An absorption correction was essential, but the optimum method (numerical by means of face-indexing) was not practicable because we could neither identify the faces nor obtain reliable measurements of their distances from a common point within the crystal. It is clear from the results that the correction made is not completely adequate.

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1992*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990) for (1); *SIR*92 (Altomare *et al.*, 1994) for (2). Program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997) for (1); *SHELXL*93 (Sheldrick, 1993) for (2). For both compounds, molecular graphics: *SHELXTL/PC* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXL*97 for (1); *SHELXL*93 for (2).

We thank EPSRC for provision of a four-circle diffractometer and for a post-doctoral award (to SP). We are also grateful to The University of Nottingham for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1202). Services for accessing these data are described at the back of the journal.

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