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# Dichloro($\mu$-[18]aneN$_2$S$_4$)dipalladium(II) Bis(triiodide)

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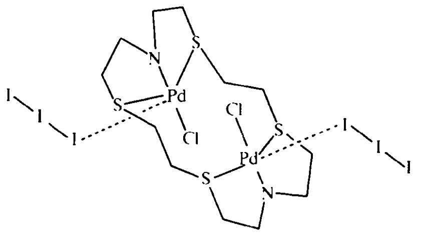
## Abstract

In the title compound, $\mu$-(1,4,10,13-tetrathia-7,16-diazacyclooctadecane)-$S^4$,$N^7$,$S^{10}$:$S^1$,$N^{16}$,$S^{13}$-bis[chloropalladium(II)] bis(triiodide), $[Pd_2Cl_2(C_{12}H_{26}N_2S_4)](I_3)_2$, the $I_3^-$ anions are linked together through I···I contacts of 4.0236 (6) Å to form infinite sinusoidal chains. These chains are linked by dinuclear palladium complex units *via* Pd···I contacts of 3.5429 (6) Å to form undulating sheets.

## Comment

On the grounds that large cations tend to stabilize large anions, we have been interested in ascertaining whether metal–thioether macrocycle cations could be used as templating agents for the self-assembly of extended polyiodide arrays (Blake *et al.*, 1995, 1996; Blake, Devillanova *et al.*, 1998). In this context, numerous polyiodide networks have been synthesized, featuring spirals, belts, ribbons, chains, sheets and cages as their motifs (Blake, Devillanova *et al.*, 1998; Blake, Gould *et al.*, 1998). In some cases, the basic polyiodide units ($I_3^-$, $I_5^-$, $I_7^-$, $I_8^{2-}$, $I_9^-$ and $I_{12}^{2-}$), which act as the building blocks for the construction of these extended multidimensional anionic networks, are more isolated from each other and no I···I interactions below *ca* 4.2 Å are observed in the lattice. Nevertheless, S···I and metal···I contacts frequently lead to interesting patterns in the organization of metal cations and polyiodide anions (Blake, Li *et al.*, 1998; Blake, Lippolis *et al.*, 1998), and the title compound, (I), is one example of this.



(I)

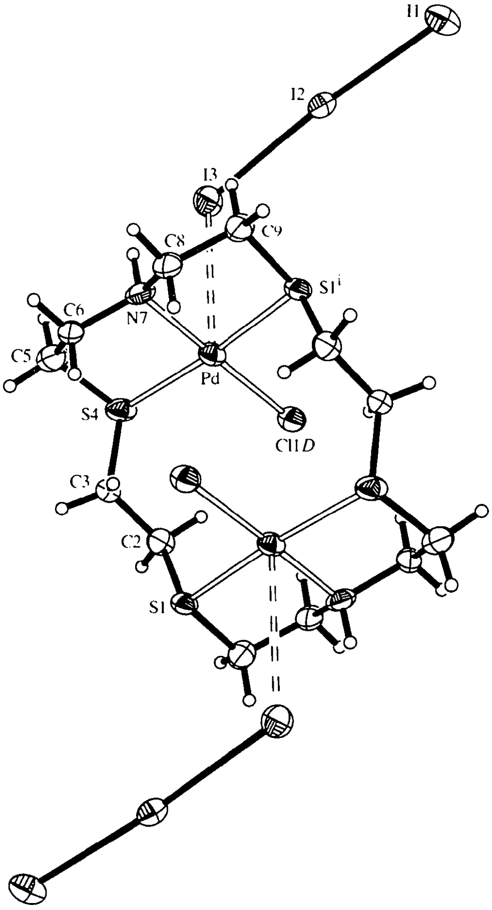


Fig. 1. A view of the title compound showing the atom-numbering system. The dication lies across a crystallographic inversion centre which also relates the two triiodides. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii. Only one of the four components (Cl*D*) of the disordered chloride is shown. Double dashed lines indicate Pd···I distances of 3.5429 (6) Å. [Symmetry code: (i) $2 - x, 1 - y, 1 - z$.]

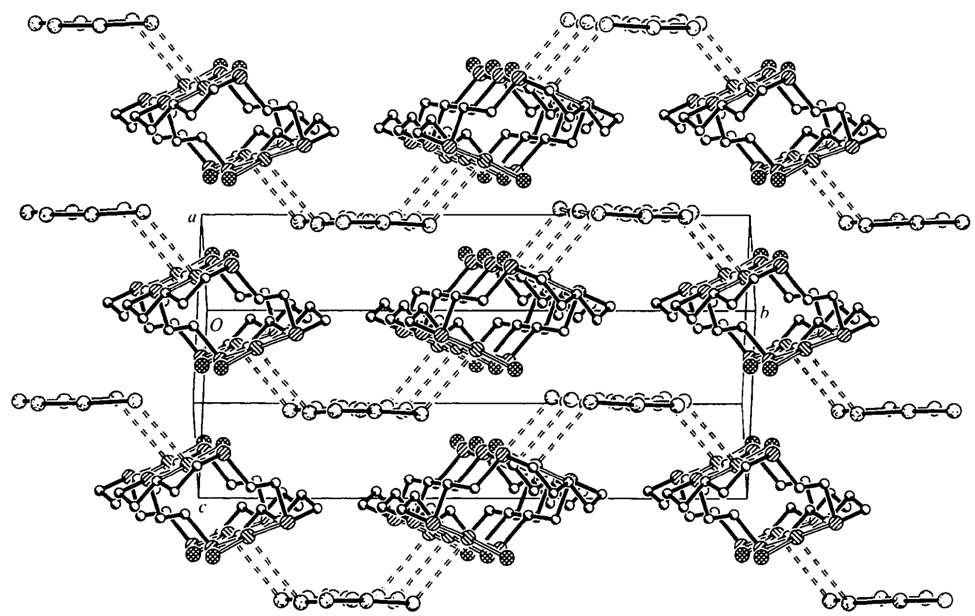


Fig. 2. An orthogonal view showing the sheet undulations and the relationship between adjacent sheets.

The metathesis reaction between $[Pd_2Cl_2([18]ane\text{-}N_2S_4)](PF_6)_2$ (Blake *et al.*, 1990), where $[18]aneN_2S_4$ is 1,4,10,13-tetrathia-7,16-diazacyclooctadecane, gives the title compound as red–brown elongated plates. Its structure consists of a crystallographically centrosymmetric $[Pd_2Cl_2(C_{12}H_{26}N_2S_4)]^{2+}$ dication and two symmetry-related and slightly asymmetric $I_3^-$ anions [I1—I2 2.8649 (6), I2—I3 2.9889 (5) Å and I1—I2—I3 174.55 (2)°] (Fig. 1). The geometry of the dinuclear $Pd^{II}$ complex is similar to that observed in $[Pd_2Cl_2(C_{12}H_{26}N_2S_4)](PF_6)_2$ (Blake *et al.*, 1990). The two $Pd^{II}$ ions are each coordinated to one N- and two S-donor atoms, with a disordered $Cl^-$ ligand completing the square-planar coordination [Pd—S1$^i$ 2.3175 (13), Pd—S4 2.3153 (14), Pd—N7 2.040 (4) and Pd—Cl 2.374 (1) Å; symmetry code: (i) $2-x$, $1-y$, $1-z$; Cl represents the mean position of the chloride disorder components Cl*A*, Cl*B*, Cl*C* and Cl*D*]. The two coordination planes are related by an inversion centre and therefore lie exactly parallel to each other, 3.817 Å apart, with the overall binuclear dication adopting a stepped conformation. The $I_3^-$ ions form polymeric sinusoidal chains in the crystal lattice *via* head-to-tail $I_3^- \cdots I_3^-$ contacts of 4.0236 (6) Å involving I1 and the symmetry equivalent of I3 generated by the *c*-glide operation ($1+x$, $\frac{3}{2}-y$, $\frac{1}{2}+z$). These chains are linked by dinuclear palladium complex units *via* Pd···I contacts of 3.5429 (6) Å. The dications alternate on either side of the poly-$I_3^-$ chains, building up infinite two-dimensional undulating layers (Fig. 2). In this compound, therefore, both metal···I and I···I interactions contribute to the extended structure.

Interestingly, the black faceted prismatic crystals produced from the same reaction mixture show a structure comprising a more complex polyiodide network involving ladders and 14- and 24-membered polyiodide rings (Blake, Devillanova *et al.*, 1998).

## Experimental

To a solution of $[Pd_2Cl_2(C_{12}H_{26}N_2S_4)](PF_6)_2$ (20.2 mg, 0.0224 mmol) in MeCN (4 ml) was added a solution of $^nBu_4NI_3$ in MeCN obtained by mixing $^nBu_4NI$ (16.55 mg, 0.0448 mmol) and $I_2$ (11.38 mg, 0.0448 mmol) in MeCN (4 ml). An orange–brown precipitate formed immediately and was recovered by filtration (15.5 mg). Recrystallization of this solid (5 mg) from hot MeCN/MeNO$_2$ (1:1, 5 ml) gave red–brown elongated plates (3.42 mg, 35% yield) of the title compound. Elemental analysis: found (calculated for $C_{12}H_{26}Cl_2I_6N_2Pd_2S_4$): C 10.78 (10.50), H 2.12 (1.91), N 2.38% (2.04%); FT-Raman (range 500–50 cm$^{-1}$), $\nu$(I–I): 130 (*s*), 108 (*w*), 99 (*w*) cm$^{-1}$. From the same reaction mixture a very small number of black faceted prismatic crystals were also isolated (see above). Loss of iodine by sublimation was prevented by encapsulating a crystal of the title compound in a film of perfluoropolyether (Hoechst RS3000).

*Crystal data*

$[Pd_2Cl_2(C_{12}H_{26}N_2S_4)](I_3)_2$
$M_r = 1371.69$
Monoclinic
$P2_1/c$
$a = 7.2501\ (5)$ Å
$b = 22.9170\ (2)$ Å
$c = 9.1648\ (7)$ Å
$\beta = 92.443\ (9)°$
$V = 1521.35\ (16)$ Å$^3$
$Z = 2$
$D_x = 2.994$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 48 reflections
$\theta = 14–16°$
$\mu = 7.727$ mm$^{-1}$
$T = 220\ (2)$ K
Lath
0.54 × 0.16 × 0.06 mm
Red–brown

*Data collection*

Stoe Stadi-4 four-circle diffractometer
$\omega/\theta$ scans
Absorption correction: $\psi$ scans (North *et al.*, 1968)
$T_{min} = 0.364$, $T_{max} = 0.629$
2600 measured reflections
2384 independent reflections
1911 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 25.03°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 60 min
random variation: ±5%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.087$
$S = 1.030$
2384 reflections
141 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 6.29P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 1.34$ e Å$^{-3}$
$\Delta\rho_{min} = -0.77$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00020 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Pd—S1$^i$ | 2.3175 (13) | Pd—I3 | 3.5429 (6) |
| Pd—S4 | 2.3153 (14) | I1—I2 | 2.8649 (6) |
| Pd—N7 | 2.040 (4) | I2—I3 | 2.9889 (5) |
| S1$^i$—Pd—S4 | 173.44 (5) | S4—Pd—I3 | 98.85 (3) |
| S1$^i$—Pd—N7 | 86.53 (13) | N7—Pd—I3 | 75.99 (12) |
| S4—Pd—N7 | 86.99 (13) | I1—I2—I3 | 174.55 (2) |
| S1$^i$—Pd—I3 | 80.53 (3) | Pd—I3—I2 | 109.66 (2) |
| C9$^i$—S1—C2—C3 | 178.2 (4) | S4—C5—C6—N7 | 54.9 (5) |
| S1—C2—C3—S4 | 148.3 (3) | C5—C6—N7—C8 | −178.4 (4) |
| C2—C3—S4—C5 | −179.3 (4) | C6—N7—C8—C9 | 178.5 (4) |
| C3—S4—C5—C6 | 75.6 (5) | N7—C8—C9—S1$^i$ | −54.6 (5) |

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

The chloride ligand was found to be disordered equally over four adjacent sites. This disorder was modelled by applying extensive restraints and constraints; the four Pd—Cl distances were restrained to be of equal length, the Cl anisotropic displacement parameters were constrained to be identical, and the four occupancies were restrained to sum to unity. H atoms were placed geometrically at distances of 0.92 and 0.98 Å from N and C, respectively, with $U_{iso}(H) = 1.2U_{eq}$(parent atom), and a riding model was used in their refinement. The highest peak in the final difference Fourier synthesis (1.34 e Å$^{-3}$) was located 0.47 Å from Cl*B* and 2.52 Å from Pd; it represents residual disorder in the region of the chloride ligand.

Data collection: *STADI*4 (Stoe & Cie, 1995*a*). Cell refinement: *STADI*4. Data reduction: *X-RED* (Stoe & Cie, 1995*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). 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: FG1461). Services for accessing these data are described at the back of the journal.

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# *trans*-Dichloro([16]aneS$_4$)rhodium(III) Pentaiodide Diiodine

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## Abstract

In the title compound, *trans*-dichloro(1,5,9,13-tetrathiacyclohexadecane-$\kappa^4S$)rhodium(III) pentaiodide diiodine, $[RhCl_2(C_{12}H_{24}S_4)](I_5)\cdot I_2$, the complex cations are embedded in a three-dimensional polyiodide matrix composed of cages of $I_5^-$ ions and $I_2$ molecules interacting *via* I···I contacts which range from 3.336 (2) to 4.133 (2) Å.