Data collection

Stoe Stadi-4 four-circle diffractometer
ω/θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\min} = 0.364$, $T_{\max} = 0.629$
2600 measured reflections
2384 independent reflections
1911 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 25.03°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 10$
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$^{\rm i}$	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$^{\rm i}$—Pd—S4	173.44 (5)	S4—Pd—I3	98.85 (3)
S1$^{\rm i}$—Pd—N7	86.53 (13)	N7—Pd—I3	75.99 (12)
S4—Pd—N7	86.99 (13)	I1—I2—I3	174.55 (2)
S1$^{\rm i}$—Pd—I3	80.53 (3)	Pd—I3—I2	109.66 (2)
C9$^{\rm i}$—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$^{\rm i}$	−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 $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(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.

We thank EPSRC for provision of a four-circle diffractometer and for a post-doctoral award (WSL), and the University of Nottingham for support.

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-κ^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.

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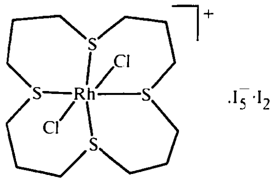
Comment

Recently, we have been investigating the use of complex metal cations containing thioether macrocyclic ligands as templating agents for the synthesis of extended polyiodide arrays (Blake *et al.*, 1995, 1996; Blake, Devillanova *et al.*, 1998). Numerous polyiodide networks have been synthesized featuring structural motifs such as spirals, belts, ribbons, chains, sheets and cages (Blake, Devillanova *et al.*, 1998; Blake, Gould *et al.*, 1998). Other examples of polyiodide salts of complex cations include $[Cu(dafone)_3]I_{12}$ (dafone is 4,5-diazafluoren-9-one; Menon & Rajasekharan, 1997), Fc_3I_{29} (Fc is ferrocenium; Tebbe & Buchem, 1997), $[Pd(TAAB)]I_8$ (TAAB is tetraazabenzo[*b,f,j,n*]-[1,5,9,13]tetraazacyclohexadecine; Jircitano *et al.*, 1981) and diiodotetrakis[tris(dimethylamido)phosphine oxide]-bismuth(III) pentaiodide (Farrugia *et al.*, 1998), in which the I_5^- anion is disordered.

The ultimate aim of this work is to control the geometrical features of the polyiodide matrix by tuning the size, charge and shape of the template cation. In general, spherical metal–macrocycle cations appear to be good templating agents for cage-like polyiodide structures; however, when the metal ion within the complex cation has free coordination sites, $M\cdots I$ as well as $S\cdots I$ interactions can play a major role and unpredictable geometrical motifs are found in the polyiodide network (Blake, Li, Lippolis & Schröder, 1998; Blake, Lippolis *et al.*, 1998; Blake, Li, Lippolis, Parsons & Schröder, 1998). To investigate this further, we determined the structure, (I), of the polyiodide array obtained using the $[RhCl_2([16]aneS_4)]^+$ cation ($[16]aneS_4$ is 1,5,9,13-tetrathiacyclohexadecane) as the cationic template. This cation possesses an overall spherical shape, with its two chloride ligands preventing any direct interaction of the metal centre with I atoms. On the basis of the arguments advanced above, we would predict a cage-like arrangement for the surrounding polyiodide architecture.



(I)

The structure determination shows the compound to have the formulation $[RhCl_2([16]aneS_4)]I_7$ (Fig. 1). As in the analogous PF_6^- complex (Blake & Schröder, 1990), the Rh^{III} ion has a slightly distorted octahedral geometry, being bonded to all four S-donors of [16]-aneS$_4$ in an equatorial plane, with the chloride ligands in the axial positions [Rh—S 2.352 (4)–2.361 (4) and Rh—Cl 2.330 (3) Å]. There are two long $S\cdots I$ contacts of 3.892 (4) Å for $S13\cdots I2$ and 3.913 (4) Å for $S5\cdots I2(-1+x,\ y,\ z)$ which are mutually *trans* and may help to orient the cation within the anionic framework. These distances are similar to some of the longer distances seen in bis(1,4,7-trithiacyclononane-*S,S′,S″*)-cobalt(II) bis(triiodide) (Blake, Lippolis *et al.*, 1998). There are no other $S\cdots I$ contacts shorter than 4.11 Å. The three-dimensional polyiodide matrix is composed of I_5^- anions and slightly elongated I_2 molecules [I6—I7 2.732 (2) Å]. The I_5^- ions consist of asymmetric I_3^- anions [I3—I4 2.962 (2) and I4—I5 2.884 (2) Å] interacting with diiodine molecules [I1—I2 2.752 (2) Å] through $I\cdots I$ contacts of 3.172 (2) Å; the I2—I3—I4 angle is 103.01 (5)°. Infinite puckered anionic layers can be identified within the polyiodide network in the crystal lattice (Fig. 2). They are composed of the I6—I7 diiodine molecules and the I_3^- moiety of the I_5^- ions, and form centrosymmetric four-, ten- and 12-membered polyiodide rings through $I\cdots I$ interactions of 3.336 (2)–4.133 (2) Å. These infinite two-dimensional sheets are stacked along the *c* axis such that the ten-membered rings in one layer are facing the 12-membered rings of the layers located above and below. The I1—I2 diiodine molecules from the I_5^- fragments link consecutive anionic layers *via* $I\cdots I$ bridging interactions of 4.106 (2) Å, forming the very distorted cages which host the $[RhCl_2([16]aneS_4)]^+$ cation (Fig. 3). The four edges of each cage are each composed of a bridging I_2 unit, whereas the upper and lower faces consist of one four- and one ten-membered ring of an anionic layer and one four- and one 12-membered ring of the successive layer, respectively. The cages have approximate dimensions 11 × 9 × 8 Å.

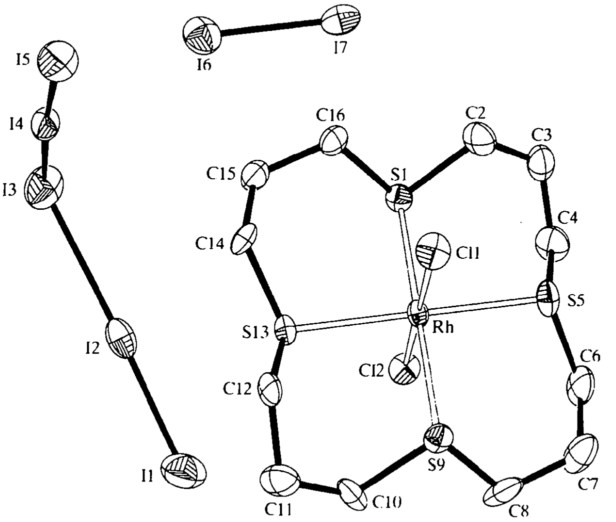


Fig. 1. A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.

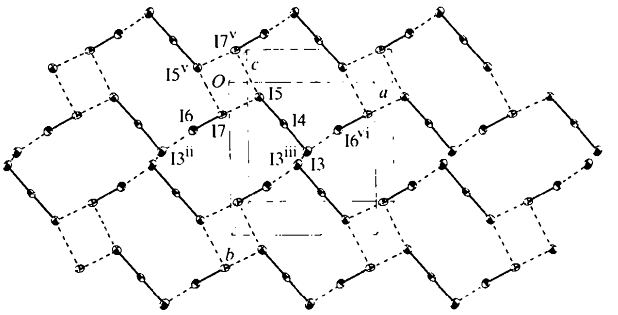


Fig. 2. A single puckered anionic layer lying perpendicular to **c** within the polyiodide network, showing fused four-, ten- and 12-membered rings. Solid lines indicate the bonds within I_3^- anions and I_2 molecules. Each I_3^- combines with a perpendicular diiodine molecule to form an I_5^- anion. [Symmetry codes: (ii) $x-1, y, z$; (iii) $1-x, 1-y, -z$; (v) $-x, -y, -z$; (vi) $1+x, y, z$.]

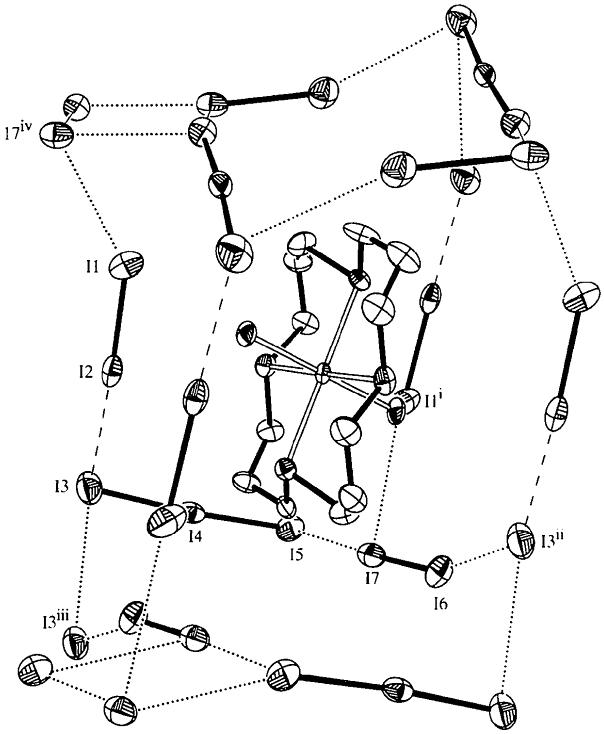


Fig. 3. A view of a single complex cation with a surrounding cage comprising diiodine molecules and parts of I_5^- anions. Dashed lines indicate the short I···I contacts of 3.172 (2) Å within I_5^- anions, while dotted lines denote I···I contacts in the range 3.336 (2)–4.133 (2) Å. [Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x-1, y, z$; (iii) $1-x, 1-y, -z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.]

The FT–Raman spectrum of the solid compound shows characteristic ν(I–I) peaks at 172, 126 and 107 cm^{-1}, indicating the presence of slightly elongated I_2 molecules and slightly asymmetric I_3^- ions (Deplano *et al.*, 1992).

Experimental

For the preparation of the title compound, $[RhCl_2(C_{12}H_{24}S_4)]PF_6$ (14.68 mg, 0.024 mmol) and I_2 (18.28 mg, 0.072 mmol) were dissolved in MeCN (5 ml) and allowed to stand for several days, during which time dark block-like crystals (yield 218 mg, 64%) formed by slow evaporation of the solvent. Elemental analysis: found (calculated for $C_{12}H_{24}Cl_2I_7RhS_4$): C 10.50 (10.60), H 1.82% (1.78%). FT–Raman spectrum in the range 500–50 cm^{-1}, ν(I–I): 172 (*s*), 126 (*w*), 107 (*w*) cm^{-1}.

Crystal data

$[RhCl_2(C_{12}H_{24}S_4)](I_5)\cdot I_2$
$M_r = 1358.7$
Monoclinic
$P2_1/n$
$a = 11.632 (3)$ Å
$b = 11.835 (2)$ Å
$c = 22.412 (4)$ Å
$\beta = 100.28 (3)°$
$V = 3035.8 (11)$ Å^3
$Z = 4$
$D_x = 2.973$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 44 reflections
$\theta = 14.0–17.5°$
$\mu = 8.134$ mm^{-1}
$T = 210 (2)$ K
Block
0.35 × 0.26 × 0.20 mm
Dark red

Data collection

Stoe Stadi-4 four-circle diffractometer
ω/θ scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1995*b*)
$T_{min} = 0.193$, $T_{max} = 0.258$
5328 measured reflections
5328 independent reflections

4073 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.04°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 60 min
intensity decay: 8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.134$
$S = 1.235$
5328 reflections
236 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 66.9P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.76$ e Å^{-3}
$\Delta\rho_{min} = -1.13$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00024 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Rh—Cl1	2.330 (3)	I1—I2	2.752 (2)
Rh—Cl2	2.330 (3)	I2—I3	3.172 (2)
Rh—S1	2.361 (4)	I3—I4	2.962 (2)
Rh—S5	2.352 (4)	I4—I5	2.884 (2)
Rh—S9	2.355 (4)	I6—I7	2.732 (2)
Rh—S13	2.355 (3)		
Cl1—Rh—Cl2	179.85 (14)	S1—Rh—S5	89.31 (13)
Cl1—Rh—S1	91.61 (13)	S1—Rh—S9	179.64 (13)
Cl1—Rh—S5	88.33 (14)	S1—Rh—S13	91.23 (13)
Cl1—Rh—S9	88.32 (13)	S5—Rh—S9	90.34 (13)
Cl1—Rh—S13	91.64 (13)	S5—Rh—S13	179.46 (14)
Cl2—Rh—S1	88.35 (13)	S9—Rh—S13	89.12 (13)
Cl2—Rh—S5	91.52 (14)	I1—I2—I3	176.93 (5)
Cl2—Rh—S9	91.73 (13)	I2—I3—I4	103.01 (5)
Cl2—Rh—S13	88.50 (13)	I3—I4—I5	175.18 (5)

Table 2. *I$\cdots$I and S$\cdots$I contact distances (Å)*

$I7\cdots I1^{i}$	4.106 (2)	$I3\cdots I6^{vi}$	3.776 (2)
$I6\cdots I3^{ii}$	3.776 (2)	$I5\cdots I7$	3.336 (2)
$I3\cdots I3^{iii}$	3.871 (2)	$S5\cdots I2^{ii}$	3.913 (4)
$I1\cdots I7^{iv}$	4.106 (2)	$S13\cdots I2$	3.892 (4)
$I5\cdots I7^{v}$	4.133 (2)		

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

H atoms were included at geometrically calculated positions 0.98 Å from their parent C atoms, and during refinement were constrained to ride on these with $U_{iso}(H) = 1.2U_{eq}(C)$. The highest difference electron-density peak lay 0.99 Å from I2, while the deepest trough was located 0.74 Å from I6; these therefore possess no chemical significance.

Data collection: *STADI4* (Stoe & Cie, 1995*a*). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe & Cie, 1995*b*). Program(s) used to solve structure: *SHELXS96* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL96*.

We thank EPSRC for provision of a four-circle diffractometer and for a post-doctoral award (to WSL), and the University of Nottingham for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1058). Services for accessing these data are described at the back of the journal.

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Ferrocene, Ferrocenium and a Bis(maleonitriledithiolate) Complex of Nickel

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Abstract

The crystal structure of the title compound, diferrocenium bis{bis[1,2-dimercaptoethene-1,2-dicarbonitrilato(2−)-*S*,*S*′]nickel(III)} ferrocene, is a 2:3 complex of $[Ni\{C_2S_2(CN)_2\}_2]$ and $[Fe(C_5H_5)_2]$. The structural data suggest that the formula for this compound can be written as $[Fe(C_5H_5)_2]_2[Ni\{C_2S_2(CN)_2\}_2]_2.[Fe(C_5H_5)_2]$.

Comment

Organometallic charge-transfer complexes have attracted attention in recent years, since some of them exhibit interesting electronic or magnetic properties (Green *et al.*, 1988). The $[M(mnt)_2]^{n-}$ anions $\{M$ = Ni, Pd or Pt; mnt = maleonitriledithiolate, *i.e.* $[C_2S_2(CN)_2]^{2-}\}$ have a delocalized π-electron system, and their redox potentials vary depending on the metal. They are considered electron acceptors and have formed quasi-one-dimensional conductors, such as $Li_{0.75}[Pt(mnt)_2].2H_2O$ (Underhill & Armad, 1981). On the other hand, ferrocene and alkyl-substituted ferrocenes may be regarded as interesting electron donors and can form charge-transfer salts with various electron acceptors. Some such salts are mixed-valence systems, with segregated stacks of donors and acceptors, giving rise to conducting solids such as $[Fe(\eta\text{-}C_5H_4Me)_2](TCNQ)_2$ (Wilson *et al.*, 1979), where TCNQ is tetracyanoquinodimethane. Other crystals may consist of mixed stacks of alternating $D^+A^-D^+A^-$ (D = donor and A = acceptor), resulting in insulators which may exhibit interesting cooperative magnetic phenomena; an example is the ferromagnetic salt $[Fe(\eta\text{-}C_5Me_5)_2](TCNE)$

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