$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 4.29P]$ where $P = (F_o^2 + 2F_c^2)/3$	Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Fe1—N1	1.664 (3)	Fe2—S1	2.2245 (9)
Fe1—S1	2.2114 (9)	Fe2—Fe3^{i}	2.6488 (6)
Fe1—S3	2.2235 (9)	Fe3—N3	1.666 (3)
Fe1—S2	2.2256 (9)	Fe3—S3	2.2163 (9)
Fe1—Fe2	2.6384 (6)	Fe3—S2^{i}	2.2184 (9)
Fe1—Fe3	2.6398 (6)	Fe3—S1	2.2214 (9)
Fe2—N2	1.664 (3)	N1—O1	1.186 (4)
Fe2—S2	2.2125 (9)	N2—O2	1.180 (4)
Fe2—S3^{i}	2.2218 (9)	N3—O3	1.187 (4)
N1—Fe1—S1	110.76 (10)	N3—Fe3—S1	109.95 (10)
N1—Fe1—S3	111.03 (11)	S3—Fe3—S1	106.91 (3)
S1—Fe1—S3	107.01 (3)	S2^{i}—Fe3—S1	113.68 (3)
N1—Fe1—S2	108.68 (11)	Fe1—S1—Fe3	73.10 (3)
S1—Fe1—S2	107.01 (3)	Fe1—S1—Fe2	72.99 (3)
S3—Fe1—S2	112.28 (3)	Fe3—S1—Fe2	110.31 (3)
N2—Fe2—S2	112.84 (10)	Fe2—S2—Fe3^{i}	73.42 (3)
N2—Fe2—S3^{i}	108.97 (10)	Fe2—S2—Fe1	72.95 (3)
S2—Fe2—S3^{i}	106.64 (3)	Fe3^{i}—S2—Fe1	111.80 (3)
N2—Fe2—S1	107.66 (10)	Fe3—S3—Fe2^{i}	73.28 (3)
S2—Fe2—S1	107.02 (3)	Fe3—S3—Fe1	72.96 (3)
S3^{i}—Fe2—S1	113.81 (3)	Fe2^{i}—S3—Fe1	111.50 (3)
N3—Fe3—S3	111.81 (10)	O1—N1—Fe1	172.9 (3)
N3—Fe3—S2^{i}	107.89 (11)	O2—N2—Fe2	175.6 (3)
S3—Fe3—S2^{i}	106.62 (3)	O3—N3—Fe3	173.9 (3)

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

Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analyzing the duplicate reflections. No decay was observed. H atoms were placed geometrically and refined with a riding model (with 60° torsion angles for methyl groups) and with U_{iso} constrained to be $1.2U_{eq}$ of the carrier atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *XPREP* in *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1352). Services for accessing these data are described at the back of the journal. A hard-copy ellipsoid plot has also been archived.

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Bis(1,4,7-trithiacyclononane-*S*,*S*′,*S*″)-cobalt(II) Bis(triiodide)

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Abstract

In the title compound, $[Co(C_6H_{12}S_3)_2](I_3)_2$, the cations and anions are linked into infinite sheets through interion S···I contacts of 3.800 (2)–3.989 (2) Å.

Comment

We have been studying the interactions of diiodine with both free homoleptic S-donor macrocyclic ligands (Blake, Cristiani *et al.*, 1997; Blake, Devillanova *et al.*, 1998; Blake, Li *et al.*, 1997) and their metal complexes (Blake *et al.*, 1995, 1996). In the former, a range of adduct stoichiometries is observed and for those with lower iodine–macrocycle ratios, we have established relationships between iodine content and observed structural features. With metal complexes, various polyiodide counter-anions such as I_3^-, I_5^-, I_7^- and I_9^- are observed, the anions producing extended polyiodide arrays containing features such as spirals, belts, ribbons, chains, sheets and cages (Blake *et al.*, 1998*a*,*b*). The metal complexes act as templates for the polyiodide lattices, as shown by the excellent matching of their size and shape with the surrounding polyiodide environments. In some cases, the polyiodide units are more isolated from each other and there are no I···I contacts below *ca* 4.3 Å. However, there is still the possibility of S···I interactions as described below.

There are two previously published examples of cobalt complexes of 1,4,7-trithiacyclononane ([9]-aneS$_3$), namely $[Co^{III}([9]aneS_3)_2](ClO_4)_3$, (2) (Kuppers *et al.*, 1986), and $[Co^{II}([9]aneS_3)_2](BF_4)_2.2CH_3NO_2$, (3) (Setzer *et al.*, 1983). Comparison of the geometries of the cations in the title complex, (1) (Fig. 1), and (3)

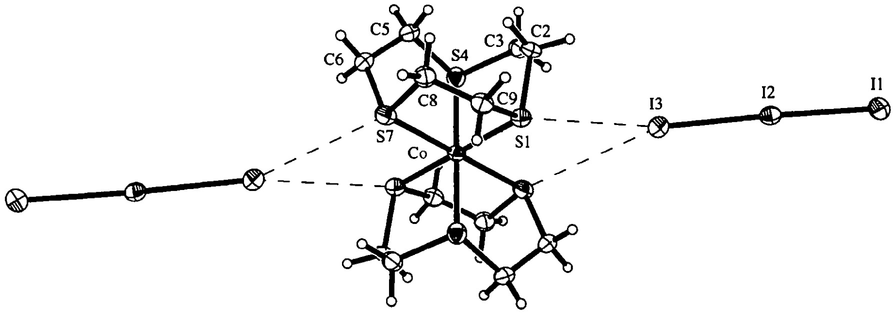
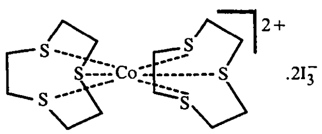


Fig. 1. View of two asymmetric units comprising one complex cation and two triiodide anions. Displacement ellipsoids enclose 50% electron probability and H atoms are shown as small spheres with an arbitrary radius. The cation lies across, and the two anions are related by, the same inversion centre.



(1)

shows that in both cases, the Co^{II} ion adopts a fairly regular octahedral coordination, with S—Co—S angles near 90°. In both (1) and (3), the metal ion occupies a crystallographic inversion centre. However, the Co—S distances in (1) do not follow the same pattern as seen in (3), the values being 2.2742 (10)/2.2959 (11)/2.4088 (11) and 2.240 (7)/2.356 (6)/2.367 (5) Å, respectively (*i.e.* two short/one long *versus* one short/two long bonds). All the S-donor atoms in (1) participate in long-range S···I contacts (Fig. 2).

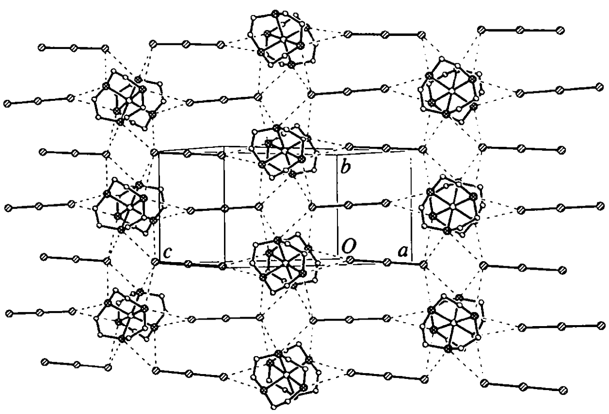


Fig. 2. Part of an infinite sheet of cations and triiodide anions linked by S···I interactions. H atoms have been omitted for clarity.

The triiodide anions are slightly asymmetric [I1—I2 2.8946 (10), I2—I3 2.9430 (11) Å and I1—I2—I3 177.934 (12)°] and each terminal I atom participates in two (I3) or four (I1) S···I contacts to one and two cations, respectively. These contacts (Fig. 2) [3.806 (2), 3.908 (2), 3.971 (2) and 3.989 (2) Å to I1, and 3.800 (2) and 3.975 (2) Å to I3] link anions and cations into infinite flat sheets which lie in the (101) plane. The sheets are well separated and there are no close contacts between them.

Experimental

The title compound was prepared by mixing $[Co([9]\text{-}aneS_3)_2](PF_6)_2$ (20 mg, 0.028 mmol) and $^{n}Bu_4NI_3$ (34.90 mg, 0.056 mmol) in MeCN (10 ml). Dark block-like crystals were formed by slow evaporation of the solvent. Elemental analysis: found (calculated for $C_{12}H_{24}CoI_6S_6$): C 12.10 (12.20), H 1.98% (2.05%). FT Raman (500–10 cm^{-1}): ν(I—I) 109 cm^{-1}.

Crystal data

$[Co(C_6H_{12}S_3)_2](I_3)_2$
M_r = 1181.00
Monoclinic
$P2_1/c$
a = 9.421 (2) Å
b = 9.081 (2) Å
c = 16.310 (4) Å
β = 98.14 (4)°
V = 1381.2 (6) Å^3
Z = 2
D_x = 2.840 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 34 reflections
θ = 15–18°
μ = 7.781 mm^{-1}
T = 150 (2) K
Faceted prismatic block
0.51 × 0.38 × 0.31 mm
Dark red

Data collection

Stoe Stadi-4 four-circle diffractometer with Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
T_{min} = 0.038, T_{max} = 0.090
5395 measured reflections
4023 independent reflections

3621 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 30.01°
h = −13 → 13
k = 0 → 12
l = 0 → 22
3 standard reflections
frequency: 60 min
intensity variation: ±2%

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 ψ 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*