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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1361). Services for accessing these data are described at the back of the journal.

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Dipyridiniomethane *cis*-Dibromotetrafluoroosmate(IV), *cis*-[(C₅H₅N)₂CH₂]-[OsBr₂F₄]

MATTHIAS HÖHLING AND WILHELM PREETZ

Institut für Anorganische Chemie, Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany. E-mail: sunac024@talos.ac.uni-kiel.de

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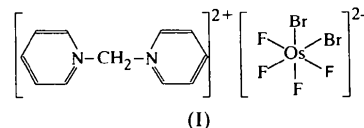
Abstract

The title compound is an *AB*-type salt with a completely ordered anion sublattice. Because of the strong *trans* influence of the Br ligands, both Os—Br bonds, of 2.466 (1) and 2.468 (1) Å, are shortened compared with those reported for K₂[OsBr₆] (2.51 Å). However, only one of the two F ligands coordinated *trans* to a Br

ligand exhibits a longer Os—F distance [1.968 (4) Å] than those along the symmetrically coordinated F—Os—F axis [1.930 (4) and 1.929 (4) Å].

Comment

Until recently, species of mixed octahedral hexahalogeno complexes of transition metals have been characterized mainly by their spectroscopic properties (IR, Raman, UV-visible, NMR). Data from X-ray structure determinations have not been available in most cases because of partial or total disorder of the complex anions (Keller & Homborg, 1976). In the past few years, this problem was overcome by studying salts with the dipyridiniomethane dication [(C₅H₅N)₂CH₂]²⁺. *AB*-type salts of this doubly-charged cation with a doubly-charged heteroleptic anion usually have ordered sublattices of both the dications and dianions. This has been attributed to the high steric flexibility of the dication. Thus, it has been possible to determine the structures of nearly all species of the well known mixed chloro-fluoroosmates(IV) (Preetz *et al.*, 1984) and chloro-fluoroplatinate(IV) (Preetz & Erhlöfer, 1989; Parzich *et al.*, 1993) by single-crystal X-ray structure diffraction (Bruhn, 1995; Bruhn & Preetz, 1994*a,b*, 1995, 1996; Bruhn *et al.*, 1995).



This is the first report of a completely ordered structure of a mixed bromofluoroosmate(IV) which has already been characterized by NMR and vibrational spectroscopy (Höhling, 1996). The complex anion was separated by ion-exchange chromatography from a mixture of bromofluoroosmates(IV), which was obtained by a stereospecific oxidative ligand-exchange reaction of hexabromoosmate(IV) with BrF₃ or KBrF₄. The structure of (I) is isotypic with the structure of dipyridiniomethane *cis*-dichlorotetrafluoroosmate(IV) (Bruhn & Preetz, 1994*a*); the dimensions of the monoclinic unit cell are only slightly different. The asymmetric unit with its labelling scheme is presented in Fig. 1.

The octahedral complex anion has approximately C_{2v} local symmetry. Since the *trans* influence of Br ligands is greater than that of F ligands, the Os—Br distances of 2.466 (1) and 2.468 (1) Å are shortened compared with those reported for K₂[OsBr₆] (2.51 Å; McCullough, 1934). However, only one of the two F ligands coordinated *trans* to a Br ligand exhibits a longer Os—F bond [Os—F2 1.968 (4) Å] compared with the lengths of 1.930 (4) and 1.929 (4) Å for the distances along the symmetrically coordinated F3—Os—F4 axis; in contrast, the Os—F1 distance of 1.928 (4) Å is very

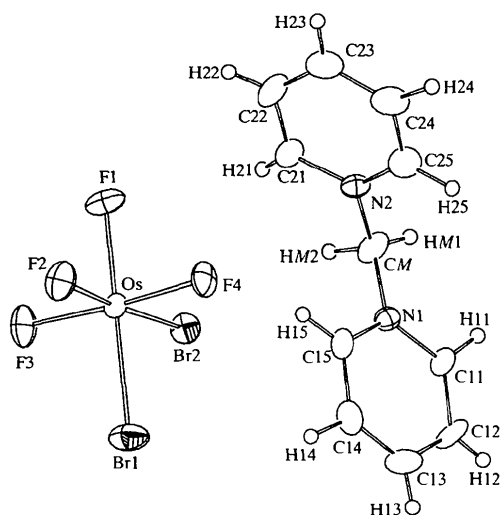


Fig 1. View of the asymmetric unit of *cis*-[(C_5H_5N) $_2CH_2$][$OsBr_2F_4$] showing 50% probability displacement ellipsoids (H atoms are shown as spheres of arbitrary size).

similar to the latter. For steric reasons, the *cis*-F—Os—F angles are smaller (average 88.0°) than the *cis*-F—Os—Br angles (91.3°) and the Br1—Os—Br2 angle [$92.18(4)^\circ$].

In the dication, the planes through the pyridine rings form angles of $43.6(5)$ and $62.8(6)^\circ$ with the plane through N1, CM and N2.

Experimental

The title compound was precipitated by adding an aqueous solution of [(C_5H_5N) $_2CH_2$] Br_2 to *cis*-[($n-C_4H_9$) $_4N$] $_2[OsBr_2F_4]$ dissolved in acetone. Single crystals were grown from water-acetone at 279 K.

Crystal data

$(C_{11}H_{12}N_2)[OsBr_2F_4]$

$M_r = 598.25$

Monoclinic

$P2_1/n$

$a = 7.080(3) \text{ \AA}$

$b = 6.8203(5) \text{ \AA}$

$c = 29.473(4) \text{ \AA}$

$\beta = 90.32(3)^\circ$

$V = 1423.1(6) \text{ \AA}^3$

$Z = 4$

$D_x = 2.792 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 6.336\text{--}12.013^\circ$

$\mu = 14.610 \text{ mm}^{-1}$

$T = 208(2) \text{ K}$

Prism

$0.30 \times 0.15 \times 0.10 \text{ mm}$

Red

Data collection

Enraf-Nonius CAD-4-Turbo
four-circle diffractometer

ω - 2θ scans

Absorption correction:

ψ scan (North *et al.*,
1968)

$T_{\min} = 0.17$, $T_{\max} = 0.23$

2084 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 25.07^\circ$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 8$

$l = -34 \rightarrow 34$

2718 measured reflections

2501 independent reflections

3 standard reflections

frequency: 250 min

intensity decay: 4.5%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.073$

$S = 1.170$

2501 reflections

183 parameters

H-atom parameters

constrained (riding)

$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2$

$+ 6.689P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 1.036 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.453 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL97 (Sheldrick,
1997)

Extinction coefficient:

0.0054 (2)

Scattering factors from

*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Os—F1	1.928 (4)	Os—F2	1.968 (4)
Os—F4	1.929 (4)	Os—Br1	2.466 (1)
Os—F3	1.930 (4)	Os—Br2	2.468 (1)
F1—Os—F4	88.1 (2)	F3—Os—Br1	92.4 (2)
F1—Os—F3	89.1 (2)	F2—Os—Br1	91.4 (2)
F4—Os—F3	175.6 (2)	F1—Os—Br2	90.3 (2)
F1—Os—F2	86.1 (2)	F4—Os—Br2	91.1 (1)
F4—Os—F2	88.1 (2)	F3—Os—Br2	92.2 (2)
F3—Os—F2	88.4 (2)	F2—Os—Br2	176.4 (1)
F1—Os—Br1	177.1 (1)	Br1—Os—Br2	92.18 (4)
F4—Os—Br1	90.4 (1)	N1—CM—N2	112.2 (6)

Data collection: *CAD-4-PC* (Enraf-Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1992). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1245). Services for accessing these data are described at the back of the journal.

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(Phthalocyaninato)antimony Iodide

RYSZARD KUBIAK AND MARIOLA RAZIK

W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50–950 Wrocław, PO Box 937, Poland. E-mail: kubiak@highscreen.int.pan.wroc.pl

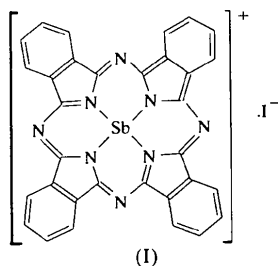
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Abstract

The asymmetric unit of the title complex, [SbPc]I (Pc = C₃₂H₁₆N₈), consists of an [SbPc]⁺ cation and an I[−] anion. A combination of ionic and acceptor–donor interactions links the [SbPc]I moieties to form pseudo-dimers in the unit cell. The pseudo-dimers are linked through I··H—C_{benzole} hydrogen-bond interactions to form a two-dimensional network. As a result of these interactions, the four Sb—N_{isoindole} bonds in the [SbPc]⁺ moiety are not equivalent and the symmetry of the Sb–N core is only close to C_s.

Comment

Previously, two kinds of antimony phthalocyanines have been prepared, which were characterized only by elemental analyses (Barrett *et al.*, 1938). Recently, the synthesis and spectral data of [SbPc]F and [SbPc(OH)₂]F have been reported (Knör, 1996). To our knowledge, this paper reports the first X-ray single-crystal structure determination of an antimony phthalocyanine, (I).



The asymmetric unit of the title compound consists of a saucer-shaped macrocyclic [SbPc]⁺ cation and an I[−] anion (Fig. 1). A combination of ionic and acceptor–donor interactions, *e.g.* Sb1··I1 [3.438 (1) Å], I1··Sb1ⁱ [3.474 (1) Å], I1··N7 [3.591 (4) Å] and I1··N1ⁱ [3.568 (4) Å] [symmetry code: (i) $-x, -y+1, -z+1$], link the [SbPc]I moieties to form pseudo-dimers in the unit cell. These pseudo-dimers are linked through I··H—C_{benzole} interactions, *e.g.* I1··H14ⁱⁱ [3.06 (5) Å] and I1ⁱ··H20ⁱⁱ [3.22 (5) Å] [symmetry code: (ii) $-x+1, -y+1, -z+1$], which could be considered as weak hydrogen-bond interactions, to form a two-dimensional network (Fig. 2).

The influence of these interactions is clearly manifested in the Sb—N_{isoindole} coordination. The four Sb—N_{isoindole} distances fall into two groups, *i.e.* the Sb1—N1 [2.203 (4) Å] and Sb1—N7 [2.202 (4) Å] distances are shorter than Sb1—N3 [2.236 (4) Å] and Sb1—N5 [2.211 (4) Å] (Fig. 1). As a consequence, the molecular symmetry of the Sb–N core is close to C_s and not to C_{4v}, which is possible for saucer-shaped M^{II}Pc macrocycles (Friedel *et al.*, 1970; Ukei, 1973; Iyechika *et al.*, 1982).

The average interatomic distances in the phthalocyanine ring are similar to those observed for other phthalocyanine structures. In contrast to fluorides of antimony(III) phthalocyanine and dihydroxoantimony(V) phthalocyanine complexes (Knör, 1996), the (phthalocyaninato)antimony iodide complex is not readily soluble, in particular in alcohols, acetone or acetonitrile.

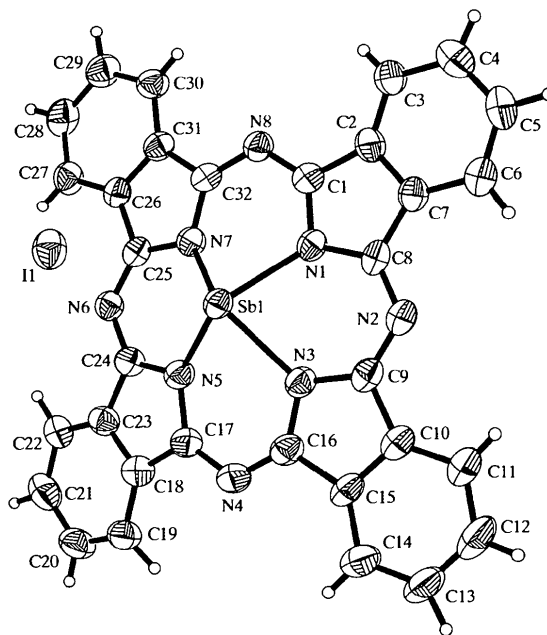


Fig. 1. The molecular structure of [SbPc]I with 50% probability ellipsoids.