| | | | |
|---|---|---|---|
| C(25)—C(26)—C(27) | 109.5 (6) | Fe(1)—C(27)—C(26) | 70.0 (4) |
| Fe(1)—C(27)—C(28) | 69.2 (3) | C(26)—C(27)—C(28) | 107.2 (6) |
| Fe(1)—C(28)—C(24) | 70.2 (2) | Fe(1)—C(28)—C(27) | 69.0 (3) |
| C(24)—C(28)—C(27) | 107.6 (5) | Sn(2)—C(29)—C(30) | 119.3 (3) |
| Sn(2)—C(29)—C(34) | 122.3 (3) | C(30)—C(29)—C(34) | 118.2 (4) |
| C(29)—C(30)—C(31) | 121.8 (5) | C(30)—C(31)—C(32) | 118.9 (6) |
| C(31)—C(32)—C(33) | 121.4 (6) | C(32)—C(33)—C(34) | 119.8 (7) |
| C(29)—C(34)—C(33) | 119.9 (6) | Sn(2)—C(35)—C(36) | 121.1 (3) |
| Sn(2)—C(35)—C(40) | 121.8 (3) | C(36)—C(35)—C(40) | 117.1 (4) |
| C(35)—C(36)—C(37) | 121.1 (5) | C(36)—C(37)—C(38) | 120.4 (5) |
| C(37)—C(38)—C(39) | 119.6 (5) | C(38)—C(39)—C(40) | 120.8 (5) |
| C(35)—C(40)—C(39) | 120.9 (4) | Sn(2)—C(41)—C(42) | 119.5 (3) |
| Sn(2)—C(41)—C(46) | 122.7 (3) | C(42)—C(41)—C(46) | 117.8 (4) |
| C(41)—C(42)—C(43) | 121.7 (5) | C(42)—C(43)—C(44) | 120.5 (5) |
| C(43)—C(44)—C(45) | 119.9 (6) | C(44)—C(45)—C(46) | 120.5 (6) |
| C(41)—C(46)—C(45) | 119.5 (5) | | |

### Table 5. Angles (°) between least-squares planes

Plane 1 is defined by atoms C(19) to C(23), plane 2 by C(24) to C(28), plane 3 by C(1) to C(6), plane 4 by C(7) to C(12) and plane 5 by C(13) to C(18). In each case the atoms are coplanar with the largest deviation being 0.006 Å.

| Angle between planes | Compound (1) | Compound (2) |
|---|---|---|
| 1 and 2 | 1.7 (2) | 1.4 (3) |
| 1 and 3 | 92.2 (2) | 93.0 (3) |
| 1 and 4 | 84.4 (2) | 132.2 (3) |
| 1 and 5 | 131.0 (2) | 61.7 (3) |
| 2 and 3 | 91.4 (2) | 92.6 (3) |
| 2 and 4 | 86.5 (2) | 131.0 (3) |
| 2 and 5 | 132.4 (2) | 60.6 (3) |
| 3 and 4 | 112.7 (2) | 97.1 (3) |
| 3 and 5 | 80.0 (2) | 105.2 (3) |
| 4 and 5 | 55.7 (2) | 70.6 (3) |

Structure (1) was solved by direct methods, structure (2) by Patterson methods and both structures were refined by full-matrix least-squares methods. All H atoms were located from difference Fourier maps. The *SHELXTL/PC* (Sheldrick, 1990) program package was used for all calculations.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Dipyridiniomethane *cis*-Dichlorotetrafluoroosmate(IV)

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## Abstract

The structure of dipyridiniomethane *cis*-dichlorotetrafluoroosmate(IV) {or $N,N$-methylenedipyridinium dichlorotetrafluoroosmate(IV), *cis*-[$(C_5H_5N)_2CH_2$][$OsF_4Cl_2$]}, has been determined by single-crystal X-ray diffraction at room temperature. The complex anions are completely ordered in the lattice. As a result of the *trans* influence in the two asymmetric axes Cl—Os—F, the Os—F distances of 1.941 (4) and 1.953 (5) Å are slightly lengthened compared to those of the symmetric F—Os—F axis of 1.931 (5) and 1.934 (4) Å. Correspondingly, the Os—Cl distances of 2.324 (2) and 2.335 (2) Å are shortened in comparison with those of 2.364 Å in the octahedral complex anion of $K_2[OsCl_6]$.

## Comment

We are currently studying the effects of altered symmetry in octahedral mixed-ligand complex ions of the type $[MX_nY_{6-n}]^{2-}$ ($M$ = Re, Tc, Os, Ir, Pt; $X \neq Y$ = F, Cl, Br, I) on the chemical and physical properties. The main emphasis is placed on vibrational and NMR spectra of compounds containing F ligands (Preetz, Ruf & Tensfeldt, 1984; Parzich, Peters & Preetz, 1993; Alyoubi, Greenslade, Foster & Preetz, 1986). Bond interactions resulting from the mutual *trans* influence between different ligands may be described by force-field calculations if the structural parameters are known (Erlhöfer & Preetz, 1989; Preetz & Irmer, 1990). Unfortunately, up to now most of the structure analyses have failed because of the statistical arrangement of the mixed-halogeno complex ions in lattices of high symmetry and, consequently, no detailed information about bond lengths and angles has been available. Total or partial disorder has been observed in complex

salts containing alkaline cations (De, 1972; Keller & Homburg, 1976) and also with alkylammonium ions. This problem is overcome using the dication dipyridin-iomethane, $[(C_5H_5N)_2CH_2]^{2+}$ (Brüdgam & Hartl, 1986), which forms completely ordered $AB$-type salts with mixed-ligand complex dianions.

By reaction of $K_2[OsCl_6]$ with $BrF_3$ at room temperature a mixture containing several compounds of the series $[OsF_nCl_{6-n}]^{2-}$ is formed, from which cis-$[OsF_4Cl_2]^{2-}$ has been separated by ion-exchange chromatography on diethylaminoethylcellulose (Preetz, Ruf & Tensfeldt, 1984). cis-$[(C_5H_5N)_2CH_2][OsF_4Cl_2]$ was precipitated from an $N,N$-dimethylformamide solution of the tetra-$n$-butylammonium complex salt with dipyri-diniomethane dibromide and recrystallized from water/acetone forming suitable single crystals. A view of the title compound (I) with atom labelling is shown in Fig. 1.



(I)
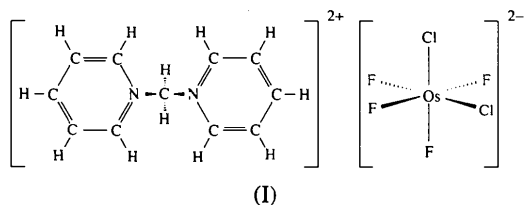
The slightly distorted octahedral complex ion with nearly $C_{2v}$ point symmetry is characterized by two asymmetric F—Os—Cl axes and one symmetric F—Os—F axis. As a result of the stronger *trans* influence of Cl compared to F in the asymmetric axes the
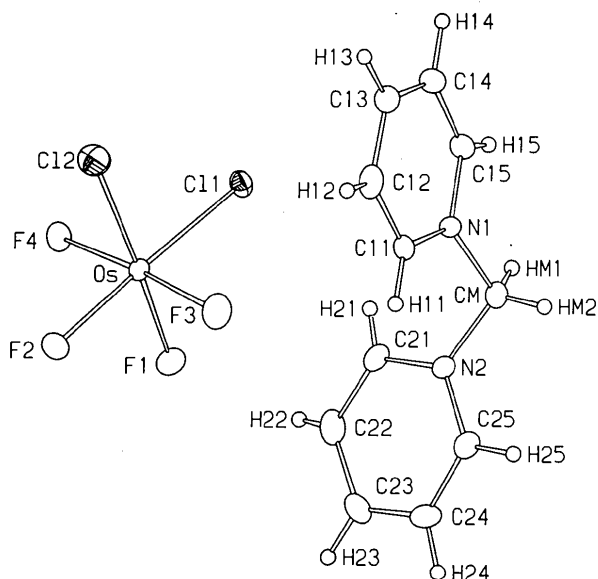
Os—F bonds are weakened and the Os—Cl bonds are strengthened. This means that the determined Os—F distances of 1.941 (4) and 1.953 (5) Å are slightly lengthened in comparison with those of the symmetric F—Os—F axis of 1.931 (5) and 1.934 (4) Å. The Os—Cl bond lengths of 2.324 (2) and 2.335 (2) Å are significantly shorter than those in the homoleptic compound $K_2[OsCl_6]$ (2.364 Å; McCullough, 1936).

For steric reasons, the F1—Os—F2 angle is narrowed to 86.8 (2)°, the Cl—Os—Cl angle is widened to 92.5 (7)° and the F3—Os—F4 axis is bent to 175.4 (2)°. In the dication, the normals to the pyridine rings are almost perpendicular forming an angle of 93.8 (1)°. Its low symmetry forces the ordering of the mixed complex ions in the monoclinic unit cell, shown in Fig. 2.
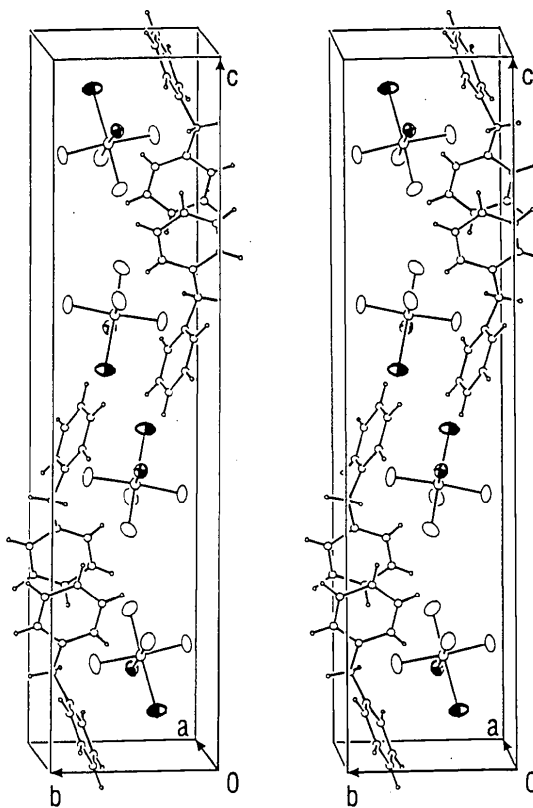


Fig. 2. Stereoview of the crystal packing along the $a$ axis.



Fig. 1. View of the cis-$[OsF_4Cl_2]^{2-}$ anion and the $[(C_5H_5N)_2CH_2]^{2+}$ cation. Displacement ellipsoids are drawn at the 50% probability level, except for the H atoms which are drawn as spheres of arbitrary radius.

## Experimental

*Crystal data*

$[(C_5H_5N)_2CH_2][OsF_4Cl_2]$
$M_r = 509.33$
Monoclinic
$P2/n$
$a = 6.9689\ (3)$ Å
$b = 6.7658\ (3)$ Å
$c = 28.994\ (2)$ Å
$\beta = 90.172\ (5)°$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 6.490–11.897°$
$\mu = 9.754$ mm$^{-1}$
$T = 293\ (2)$ K
Prismatic

$V = 1367.07$ (14) Å$^3$
$Z = 4$
$D_x = 2.475$ Mg m$^{-3}$

0.3 × 0.2 × 0.2 mm
Orange

### Data collection

CAD-4-Turbo four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ($\psi$ scans)
$T_{min} = 0.69$, $T_{max} = 0.99$
2612 measured reflections
2402 independent reflections
2150 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0437$
$\theta_{max} = 24.97°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 8$
$l = -34 \rightarrow 34$
3 standard reflections frequency: 240 min intensity variation: none

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.0294$
$wR(F^2) = 0.0846$
$S = 1.159$
2384 reflections
220 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0600P)^2 + 3.3849P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$

$\Delta\rho_{max} = 1.410$ e Å$^{-3}$
$\Delta\rho_{min} = -2.181$ e Å$^{-3}$
Extinction correction: SHELXL93 (Sheldrick, 1994)
Extinction coefficient: 0.0363 (12)
Atomic scattering factors from International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Os | 0.89761 (3) | 0.38209 (3) | 0.364512 (8) | 0.0197 (2) |
| Cl1 | 0.5903 (3) | 0.3930 (2) | 0.39527 (7) | 0.0280 (4) |
| Cl2 | 1.0352 (3) | 0.3050 (4) | 0.43582 (7) | 0.0446 (5) |
| F1 | 0.7927 (7) | 0.4366 (7) | 0.3038 (2) | 0.0410 (10) |
| F2 | 1.1490 (7) | 0.3737 (6) | 0.3350 (2) | 0.0391 (12) |
| F3 | 0.9363 (7) | 0.6619 (7) | 0.3739 (2) | 0.0430 (11) |
| F4 | 0.8684 (7) | 0.1044 (5) | 0.3503 (2) | 0.0344 (10) |
| CM | 0.2936 (10) | 0.9645 (11) | 0.3684 (3) | 0.0300 (15) |
| C11 | 0.5836 (10) | 0.9009 (9) | 0.4141 (3) | 0.0245 (14) |
| C12 | 0.6680 (12) | 0.8394 (11) | 0.4554 (3) | 0.034 (2) |
| C13 | 0.5558 (11) | 0.7548 (11) | 0.4890 (3) | 0.032 (2) |
| C14 | 0.3625 (11) | 0.7249 (11) | 0.4815 (3) | 0.034 (2) |
| C15 | 0.2857 (10) | 0.7840 (11) | 0.4405 (3) | 0.0282 (15) |
| N1 | 0.3935 (9) | 0.8748 (7) | 0.4088 (2) | 0.0209 (13) |
| C21 | 0.4069 (11) | 0.7326 (11) | 0.3100 (3) | 0.031 (2) |
| C22 | 0.4790 (11) | 0.6955 (12) | 0.2672 (3) | 0.037 (2) |
| C23 | 0.5291 (11) | 0.8499 (13) | 0.2384 (3) | 0.036 (2) |
| C24 | 0.5131 (11) | 1.0410 (12) | 0.2548 (3) | 0.034 (2) |
| C25 | 0.4464 (11) | 1.0736 (11) | 0.2979 (3) | 0.032 (2) |
| N2 | 0.3900 (8) | 0.9216 (9) | 0.3248 (2) | 0.0240 (12) |

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

| | | | |
|---|---|---|---|
| Os—F3 | 1.931 (5) | C12—C13 | 1.376 (11) |
| Os—F4 | 1.934 (4) | C13—C14 | 1.379 (11) |
| Os—F1 | 1.941 (4) | C14—C15 | 1.361 (11) |
| Os—F2 | 1.953 (5) | C15—N1 | 1.338 (9) |
| Os—Cl1 | 2.324 (2) | C21—N2 | 1.355 (9) |
| Os—Cl2 | 2.335 (2) | C21—C22 | 1.362 (12) |
| CM—N2 | 1.461 (9) | C22—C23 | 1.383 (12) |
| CM—N1 | 1.492 (9) | C23—C24 | 1.383 (12) |
| C11—N1 | 1.345 (10) | C24—C25 | 1.350 (11) |
| C11—C12 | 1.395 (12) | C25—N2 | 1.351 (9) |

| | | | |
|---|---|---|---|
| F3—Os—F4 | 175.4 (2) | N1—C11—C12 | 118.1 (7) |
| F3—Os—F1 | 89.6 (2) | C13—C12—C11 | 119.5 (7) |
| F4—Os—F1 | 87.3 (2) | C12—C13—C14 | 120.4 (7) |
| F3—Os—F2 | 88.0 (2) | C15—C14—C13 | 118.5 (7) |
| F4—Os—F2 | 88.4 (2) | N1—C15—C14 | 120.9 (7) |
| F1—Os—F2 | 86.8 (2) | C15—N1—C11 | 122.5 (6) |
| F3—Os—Cl1 | 92.48 (15) | C15—N1—CM | 117.7 (6) |
| F4—Os—Cl1 | 90.92 (14) | C11—N1—CM | 119.6 (6) |
| F1—Os—Cl1 | 89.83 (15) | N2—C21—C22 | 119.7 (7) |
| F2—Os—Cl1 | 176.6 (2) | C21—C22—C23 | 120.3 (8) |
| F3—Os—Cl2 | 92.2 (2) | C24—C23—C22 | 118.5 (8) |
| F4—Os—Cl2 | 90.8 (2) | C25—C24—C23 | 119.9 (7) |
| F1—Os—Cl2 | 177.00 (15) | C24—C25—N2 | 120.8 (7) |
| F2—Os—Cl2 | 90.9 (2) | C25—N2—C21 | 120.6 (7) |
| Cl1—Os—Cl2 | 92.51 (7) | C25—N2—CM | 119.0 (6) |
| N2—CM—N1 | 112.6 (6) | C21—N2—CM | 120.2 (6) |

Data collection and cell refinement were performed using *CAD-4-PC* software (Enraf–Nonius, 1993). *MolEN* (Fair, 1990) was used for data reduction. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990). Refinement was carried out by full-matrix least-squares methods using the program *SHELXL*93 (Sheldrick, 1994). Absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Table 4.2.4.2). Individual anisotropic displacement parameters were used for all non-H atoms. Planes were calculated with *XANADU* (Roberts & Sheldrick, 1975). Molecular graphics were prepared using *ORTEP*II (Johnson, 1976) and the material for publication was produced using *SHELXL*93.

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