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# Dipyridiniomethane *trans*-Dichloro-tetrafluoroosmate(IV) Hydrate, *trans*-[(C₅H₅N)₂CH₂][OsF₄Cl₂].H₂O

CLEMENS BRUHN AND WILHELM PREETZ

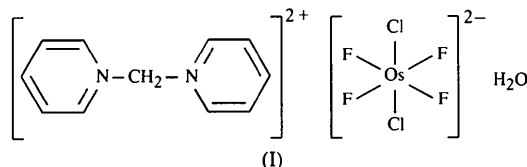*Institut für Anorganische Chemie, Universität Kiel, Olshausenstrasse 40, 24098 Kiel, Germany*

## Abstract

The X-ray diffraction study of dipyridiniomethane *trans*-dichlorotetrafluoroosmate(IV) hydrate [or *N,N*-methyl-enedipyridinium dichlorotetrafluoroosmate(IV) hydrate] at room temperature revealed the complete ordering of the complex anions, *i.e. trans*-[OsF₄Cl₂]²⁻, into *AB*-type salts with the doubly charged dipyridiniomethane cation [(C₅H₅N)₂CH₂]²⁺. A water molecule is linked to the F atoms by hydrogen bridges, resulting in the formation of chains. Hydrogen-bridged F atoms show Os—F distances of 1.938 (3) and 1.944 (3) Å compared with non-bridged F atoms of the anion exhibiting Os—F distances of 1.924 (3) and 1.938 (3) Å. The Os—Cl bond lengths are 2.341 (2) and 2.334 (2) Å.

## Comment

Octahedrally coordinated halide complexes of platinum group metals are well studied prototype species that have a variety of applications in spectroscopy. Mixed-ligand complex ions of the type $[OsF_nCl_{6-n}]^{2-}$ ($n$ = 0–6) have been synthesized systematically by stereospecific substitution reactions in order to examine the effects of altered symmetry on NMR, UV–Vis and vibrational spectra (Preetz, Ruf & Tensfeldt, 1984; Parzich, Peters & Preetz, 1993; Alyoubi, Greenslade, Foster & Preetz, 1990). Unfortunately, single-crystal structure analyses of alkali metal and alkylammonium salts revealed partial or complete statistical arrangement of the mixed halogeno complexes in the anion sublattices (Keller & Homborg, 1976). The bent and doubly charged dipyridiniomethane cation (Brüdgam & Hartl, 1986) provides an *AB*-type lattice of low symmetry in which the complex sublattice is perfectly ordered (Bruhn & Preetz, 1994*a,b*; Bruhn, Drews, Meynhardt & Preetz, 1995). In the course of our work on mixed F/Cl complexes of $Os^{IV}$, we isolated the title compound, (I), by ion-exchange chromatography.



(I)

In the triclinic unit cell, two inequivalent Os atoms reside on special positions [Os1 at 0,0,0 and Os2 at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$]. Due to the location of the Os atoms on inversion centers, the F and Cl atoms form linear F—Os—F and Cl—Os—Cl axes, respectively, with Os—F bond lengths Os1—F11 1.924 (3), Os1—F12 1.938 (3), Os2—F21 1.938 (3) and Os2—F22 1.944 (3) Å, and Os—Cl bond distances Os1—Cl1 2.341 (2) and Os2—Cl2 2.334 (2) Å. These axes are almost orthogonal, close to the ideal value of 90° in octahedral complexes, with a maximum deviation of 1.5°. One of the F—Os—F axes is bridged to a water molecule and the bridging H atoms are linked to the complex ions forming chains with F···O distances O···F12 2.897 (7) and O···F22 2.845 (7) Å, and F···O···F angles of 103.5 (2)°. The bridging H atoms are not collinear with F···O, forming angles of 144 (9)° for O—H1···F12 and 161 (13)° for O—H2···F22 (Fig. 1).

In the dipyridiniomethane dication, the normals to the pyridine rings are almost perpendicular, making an angle of 85.9 (2)° with respect to one another. The interplanar angles of the pyridine rings with the plane through atoms *CM*, N1 and N2 are 56.8 (4) and 69.8 (4)°. All the atoms of the cation lie in general positions. The packing in the triclinic unit cell is shown in Fig. 2.
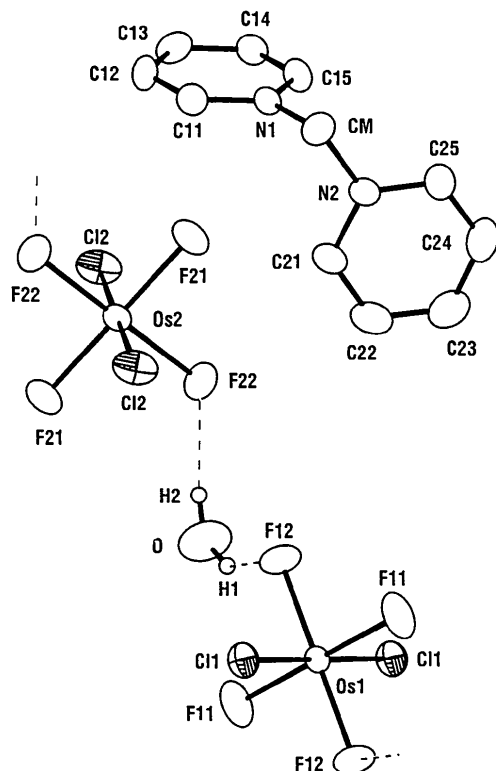
Fig. 1. A perspective view of the *trans*-$[OsF_4Cl_2]^{2-}$ anions and the $[(C_5H_5N)_2CH_2]^{2+}$ dication. Displacement ellipsoids are drawn at the 50% probability level except for the water H atoms, which are drawn as spheres of arbitrary radii. Dication H atoms are omitted for clarity.
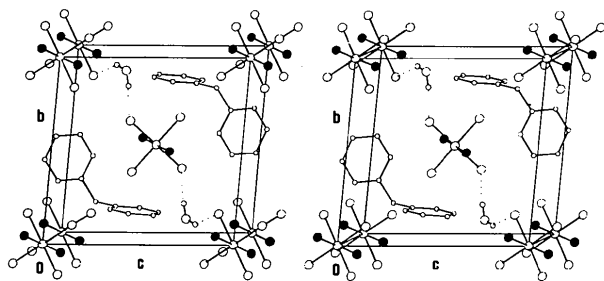


Fig. 2. Stereoview of the crystal packing almost along the $a$ axis. Dication H atoms are omitted for clarity.

## Experimental

The reaction of $K_2[OsCl_6]$ with $BrF_3$ at room temperature results in a mixture containing several compounds of the series $[OsF_nCl_{6-n}]^{2-}$ ($n$ = 0–6), from which $[OsF_5Cl]^{2-}$ has been separated by ion-exchange chromatography on diethylaminoethylcellulose and finally isolated as its tetra-$n$-butylammonium (TBA) salt. This salt is converted by stereo-specific ligand exchange with HCl gas in dichloromethane at 278 K to *trans*-$[OsF_4Cl_2]^{2-}$ in 40% yield (Preetz, Ruf & Tensfeldt, 1984). *trans*-$[(C_5H_5N)_2CH_2][OsF_4Cl_2].H_2O$ was precipitated from an $N,N$-dimethylformamide solution of the

TBA complex salt using dipyridiniomethane dibromide and recrystallized from water/acetone solution to give suitable single crystals.

### Crystal data

| | |
|---|---|
| $[(C_5H_5N)_2CH_2][OsF_4Cl_2].$$H_2O$ | Mo $K\alpha$ radiation |
| $M_r$ = 527.34 | $\lambda$ = 0.71069 Å |
| Triclinic | Cell parameters from 25 |
| $P\overline{1}$ | reflections |
| $a$ = 7.834 (2) Å | $\theta$ = 4.18–12.64° |
| $b$ = 10.0520 (10) Å | $\mu$ = 8.998 mm⁻¹ |
| $c$ = 10.4670 (10) Å | $T$ = 293 (2) K |
| $\alpha$ = 82.818 (8)° | Prismatic |
| $\beta$ = 68.423 (8)° | 0.2 × 0.2 × 0.1 mm |
| $\gamma$ = 75.53 (2)° | Dark pink |
| $V$ = 741.7 (2) Å³ | |
| $Z$ = 2 | |
| $D_x$ = 2.361 Mg m⁻³ | |

### Data collection

| | |
|---|---|
| Enraf–Nonius CAD-4-Turbo four-circle diffractometer | $R_{int}$ = 0.0211 |
| | $\theta_{max}$ = 24.97° |
| $\omega/2\theta$ scans | $h$ = 0 → 9 |
| Absorption correction: | $k$ = −11 → 11 |
| empirical *via* $\psi$ scans | $l$ = −11 → 12 |
| $T_{min}$ = 0.69, $T_{max}$ = 1.0 | 3 standard reflections |
| 2817 measured reflections | frequency: 240 min |
| 2607 independent reflections | intensity decay: 0.5% |
| 1984 observed reflections | |
| $[I > 2\sigma(I)]$ | |

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.0202
$wR(F^2)$ = 0.0484
$S$ = 1.055
2607 reflections
250 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 1.1760P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 1.428 e Å⁻³
$\Delta\rho_{min}$ = −1.007 e Å⁻³
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0257 (8)
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* (Å²)

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

| | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|
| Os1 | 0 | 0 | 0 | 0.02184 (13) |
| Cl1 | −0.2585 (2) | 0.0610 (2) | −0.07368 (15) | 0.0335 (3) |
| F11 | −0.1468 (5) | 0.1101 (4) | 0.1579 (4) | 0.0462 (10) |
| F12 | 0.0946 (5) | 0.1578 (4) | 0.9003 (4) | 0.0426 (9) |
| Os2 | 1/2 | 1/2 | 1/2 | 0.02423 (13) |
| Cl2 | 0.1863 (2) | 0.4828 (2) | 0.6025 (2) | 0.0439 (4) |
| F21 | 0.5450 (5) | 0.3509 (4) | 0.3826 (4) | 0.0387 (8) |
| F22 | 0.5584 (5) | 0.3703 (4) | 0.6401 (3) | 0.0408 (9) |
| CM | 0.3783 (9) | 0.2019 (7) | 0.2206 (6) | 0.0331 (13) |
| N1 | 0.2155 (7) | 0.1876 (5) | 0.3445 (5) | 0.0268 (10) |
| C11 | 0.2291 (9) | 0.1793 (7) | 0.4694 (6) | 0.0336 (13) |
| C12 | 0.0776 (10) | 0.1655 (7) | 0.5838 (7) | 0.038 (2) |
| C13 | −0.0888 (9) | 0.1603 (6) | 0.5728 (6) | 0.0351 (14) |

| | | | |
|---|---|---|---|
| C14 | −0.1041 (8) | 0.1702 (6) | 0.4443 (6) | 0.0301 (13) |
| C15 | 0.0502 (8) | 0.1818 (6) | 0.3313 (7) | 0.0299 (13) |
| N2 | 0.3264 (6) | 0.3269 (5) | 0.1408 (5) | 0.0259 (10) |
| C21 | 0.2972 (9) | 0.4508 (6) | 0.1926 (7) | 0.0351 (14) |
| C23 | 0.2309 (9) | 0.5593 (7) | −0.0040 (7) | 0.044 (2) |
| C24 | 0.2604 (10) | 0.4317 (8) | −0.0536 (7) | 0.045 (2) |
| C22 | 0.2480 (10) | 0.5683 (7) | 0.1208 (8) | 0.043 (2) |
| C25 | 0.3089 (9) | 0.3160 (7) | 0.0198 (6) | 0.0351 (14) |
| O | 0.4692 (8) | 0.1066 (7) | 0.6944 (7) | 0.0597 (15) |
| H1 | 0.378 (11) | 0.083 (9) | 0.754 (8) | 0.07 (3) |
| H2 | 0.473 (19) | 0.188 (9) | 0.675 (13) | 0.14 (5) |

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

| | | | |
|---|---|---|---|
| Os1—F11 | 1.924 (3) | C12—C13 | 1.364 (9) |
| Os1—F12$^i$ | 1.938 (3) | C13—C14 | 1.383 (8) |
| Os1—Cl1 | 2.341 (2) | C14—C15 | 1.363 (8) |
| Os2—F21 | 1.938 (3) | N2—C25 | 1.344 (8) |
| Os2—F22 | 1.944 (3) | N2—C21 | 1.353 (7) |
| Os2—Cl2 | 2.334 (2) | C21—C22 | 1.368 (9) |
| C*M*—N1 | 1.469 (7) | C23—C22 | 1.376 (10) |
| C*M*—N2 | 1.475 (8) | C23—C24 | 1.378 (10) |
| N1—C11 | 1.340 (8) | C24—C25 | 1.363 (10) |
| N1—C15 | 1.367 (8) | F12···O | 2.897 (7) |
| C11—C12 | 1.363 (9) | F22···O | 2.845 (7) |
| | | | |
| F11—Os1—F12$^i$ | 89.9 (2) | F21—Os2—Cl2$^{iv}$ | 90.67 (11) |
| F11—Os1—F12$^{ii}$ | 90.1 (2) | F21—Os2—Cl2 | 89.33 (11) |
| F11—Os1—Cl1$^{iii}$ | 91.41 (11) | F22—Os2—Cl2$^{iv}$ | 91.32 (12) |
| F11—Os1—Cl1 | 88.58 (11) | F22—Os2—Cl2 | 88.68 (12) |
| F12$^i$—Os1—Cl1 | 91.00 (11) | N1—C*M*—N2 | 109.3 (5) |
| F12$^{ii}$—Os1—Cl1 | 89.00 (11) | F22···O···F12 | 103.5 (2) |
| F21—Os2—F22$^{iv}$ | 89.0 (2) | H1—O—H2 | 122 (10) |
| F21—Os2—F22 | 91.0 (2) | | |

Symmetry codes: (i) $x, y, z − 1$; (ii) $−x, −y, 1 − z$; (iii) $−x, −y, −z$; (iv) $1 − x, 1 − y, 1 − z$.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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# Three Polymorphs of Potassium 4-Sulfonatobenzoic Acid

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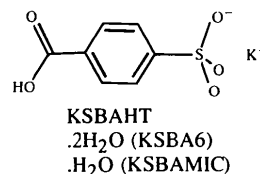
## Abstract

The structures of the dihydrate, monohydrate and anhydrous forms of $K^+.CO_2H(C_6H_4)SO_3^-$ have been solved. Each $K^+$ cation interacts with nine O atoms in the dihydrate and with seven in the other two structures. Electrostatic forces and hydrogen bonds hold the layered structures together.

## Comment

Many instances of polymorphism in organic salts have become evident during a study of solid-state reactivity. For example, five crystalline forms of magnesium hydrogen phthalate have been observed (Kariuki & Jones, 1989, 1992). While investigating salts of derivatives of benzoic acid, three polymorphs of potassium 4-sulfonatobenzoic acid have been obtained, $K^+.C_7H_5O_5S^-.2H_2O$ (KSBA6), $K^+.C_7H_5O_5S^-.H_2O$ (KSBAMIC) and $K^+.C_7H_5O_5S^-$ (KSBAHT).



KSBAHT
.2H₂O (KSBA6)
.H₂O (KSBAMIC)

In the anions, the interplanar angles between the phenyl rings and carboxylate ($CO_2$) groups are 1.87 (28)° for KSBA6, 1.18 (7)° for KSBAMIC and