vacuum to yield a colourless viscous liquid. The addition of methanol (1 ml) followed by diethyl ether (3 ml) led to the formation of colourless crystals. Analytical data: calculated for $C_{12}H_{36}Cl_4Ga_2N_6O_2P_2$: C 22.5, H 5.76, N 13.1%; found: C 22.3, H 5.69, N 12.9%. The far IR spectra of the crystals exhibited strong bands at 324 and 344 cm^{-1} attributable to Ga—Cl stretching vibrations, and the Raman spectrum contained an intense peak at 254 cm^{-1} assignable to a Ga—Ga bond-stretching mode. A representative crystal was selected for the crystallographic investigation reported here.

Crystal data

[$Ga_2Cl_4(C_6H_{18}N_3OP)_2$]
$M_r = 639.65$
Monoclinic
$P2_1/n$
$a = 9.060\,(5)$ Å
$b = 11.4157\,(12)$ Å
$c = 14.058\,(4)$ Å
$\beta = 92.29\,(3)°$
$V = 1452.8\,(9)$ Å^3
$Z = 2$
$D_x = 1.462$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10–12°$
$\mu = 2.351$ mm^{-1}
$T = 293\,(2)$ K
Rectangular prism
$0.32 \times 0.22 \times 0.20$ mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.520$, $T_{max} = 0.651$
3357 measured reflections
2550 independent reflections

1312 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 24.97°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 13$
$l = -16 \rightarrow 16$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.117$
$S = 0.961$
2550 reflections
130 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.0517P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.324$ e Å^{-3}
$\Delta\rho_{min} = -0.300$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ga—O1	1.881 (4)	P1—O1	1.477 (4)
Ga—Cl2	2.189 (2)	P1—N2	1.611 (6)
Ga—Cl1	2.200 (2)	P1—N1	1.620 (6)
Ga—Ga^i	2.3919 (14)	P1—N3	1.621 (6)
P1—O1—Ga	150.0 (3)		
Ga^i—Ga—O1—P1	176.9 (6)		

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

The C atoms of the hexamethylphosphoramide groups show large displacement parameters indicative of disorder in these atoms. In one case, namely C2, the electron density could be resolved into two peaks and this atom was treated as two half-weighted atoms. In the remaining cases, the displacement parameters have been allowed to take up the disorder.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *Software*. Data reduction: local software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1238). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1216–1218

trans-Chlorodifluorotris(pyridine-*N*)-osmium(III)

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(*Received 13 October 1998; accepted 1 February 1999*)

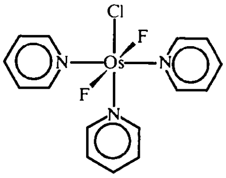
Abstract

The title compound, (*OC*-6-13)- or *trans*-[$OsClF_2(C_5H_5N)_3$], is a novel fluorine-containing threefold

mixed-ligand complex, with the central Os^{III} ion residing in a slightly distorted octahedron built up of three different axes, namely two symmetric F—Os—F and N—Os—N, and one asymmetric Cl—Os—N axis. Due to the stronger *trans* influence of the pyridine ligand in the asymmetrically coordinated axis, the Os—N bond is strengthened and the opposite Os—Cl bond is weakened. The pyridine rings are twisted from the N_3Cl ligand plane by angles of 76.1 (1), 59.0 (2) and 55.9 (1)°.

Comment

In the course of our studies on halogeno–pyridine–osmium complexes, many of them have been investigated by X-ray structure determination and characterized by their vibrational spectra (Kolf, 1998; Kolf & Preetz, 1997, 1999*a*). However, until now, only two species containing fluorine ligands, *i.e.* *trans*-$[OsF_2(C_5H_5N)_4]\cdot 4H_2O$ (Kolf & Preetz, 1997) and $[OsF(C_5H_5N)_5]BF_4\cdot H_2O\cdot CH_2Cl_2$ (Kolf & Preetz, 1999*b*), have been synthesized. We report herein the crystal structure of the title complex, (I), as a further example.



(I)

The molecular structure and atom-labelling scheme of (I) with its threefold mixed fluoro–chloro–pyridine ligand sphere is shown in Fig. 1. The structure shows a roughly octahedral geometry, with two *trans*-positioned F atoms, one Cl atom and three meridionally arranged pyridine ligands. The distances in the N—Os—N axis are 2.063 (4) and 2.099 (4) Å, and in the F—Os—F axis, both distances are 1.989 (3) Å. The asymmetrically coordinated Cl—Os—N3 axis exhibits the shortest Os—N bond [2.058 (4) Å], which is even shorter than the corresponding bond length in *mer*-$[OsCl_3(C_5H_5N)_3]$ (2.086 Å; Blake *et al.*, 1988). The Os—Cl bond *trans* to pyridine in *mer*-$[OsCl_3(C_5H_5N)_3]$ (2.376 Å) is significantly longer in comparison with the Os—Cl bonds in the Cl—Os—Cl axis (2.358 Å), and resembles the corresponding distance in (I) [2.368 (2) Å]. The reason for this is the stronger *trans* influence of the pyridine ligand compared with chlorine, causing a strengthening of the Os—N and a weakening of the Os—Cl bond. This holds for the Os^{II} complex $[OsF(C_5H_5N)_5]BF_4\cdot H_2O\cdot CH_2Cl_2$, with a strongly elongated Os—F distance of 2.064 Å due to the *trans* influence (Kolf & Preetz, 1999*b*), whereas in *trans*-$[OsF_2(C_5H_5N)_4]\cdot 4H_2O$, the average Os—F bond length of 1.974 Å is similar to that in (I). The pyridine ligands in (I) are individually planar, are coordinated end-on and are twisted about the Os—N bond axes by angles of 76.1 (1) (N1-containing ring), 59.0 (2) (N2) and 55.9 (1)° (N3) relative to the N1/N2/N3/Cl ligand plane. These values are higher than those found in other meridional pyridine complexes due to the affinity of the α-pyridine protons for the F atoms, resulting in short H···F distances ranging from 2.329 (3) (H15···F2) to 2.555 (3) Å (H35···F1). H···Cl distances are 3.120 (2) (H21···Cl) and 3.541 (1) Å (H15···Cl). Unlike other Os^{III} complexes featuring pyridine ligands in a meridional arrangement, *e.g.* *mer*-$[OsX_3(C_5H_5N)_3]$ (X = Br, I, NCS; Kolf & Preetz, 1998, 1999*a*), the *trans*-positioned pyridine ligands in (I) are nearly coplanar, with a torsion angle of 18.4 (2)°.

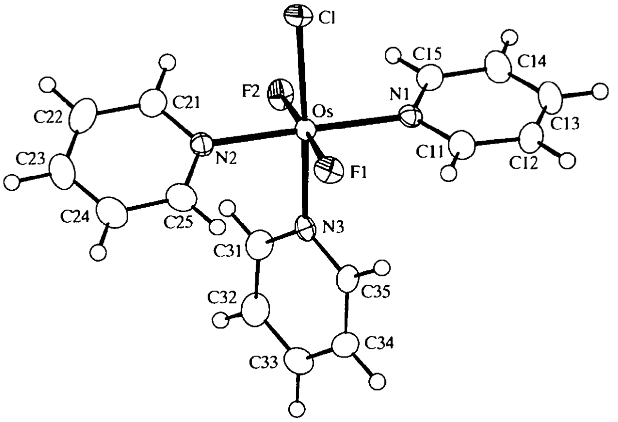


Fig. 1. View of the molecular structure of *trans*-$[OsF_2Cl(C_5H_5N)_3]$ showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary size.

Experimental

On refluxing for 24 h, the pale-yellow solution of a chloro–fluoro–Os^{IV} complex (0.2 g) (Preetz *et al.*, 1984) in pyridine/isoamyl alcohol (1:1, 10 ml) turned dark red. A crude product was precipitated by addition of *n*-hexane, which was purified by chromatography on silica gel using acetone/toluene (7:3) as the mobile phase, resulting in a 15% yield of (I). Orange single crystals were obtained by slow diffusion of diethyl ether from the gas phase into a dichloromethane solution.

Crystal data

$[OsClF_2(C_5H_5N)_3]$
M_r = 500.95
Monoclinic
$P2_1/c$
a = 8.217 (2) Å
b = 16.7363 (11) Å
c = 12.029 (4) Å
β = 100.53 (4)°
V = 1626.5 (7) $Å^3$
Z = 4
D_x = 2.046 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 2–25°
μ = 8.023 mm^{-1}
T = 208 (2) K
Prism
0.30 × 0.15 × 0.10 mm
Orange

Data collection

Enraf–Nonius CAD-4-Turbo four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.373$, $T_{max} = 0.448$
4011 measured reflections
2858 independent reflections
2455 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 24.98°$
$h = -1 \rightarrow 9$
$k = -2 \rightarrow 19$
$l = -14 \rightarrow 14$
3 standard reflections every 200 reflections intensity decay: 4.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.059$
$S = 0.934$
2858 reflections
200 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 6.4085P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.042$ e Å^{-3}
$\Delta\rho_{min} = -1.029$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Os—F1	1.989 (3)	Os—N2	2.063 (4)
Os—F2	1.989 (3)	Os—N1	2.099 (4)
Os—N3	2.058 (4)	Os—Cl	2.3681 (15)
F1—Os—F2	176.55 (11)	N3—Os—N1	92.35 (15)
F1—Os—N3	89.01 (14)	N2—Os—N1	178.66 (14)
F2—Os—N3	87.67 (14)	F1—Os—Cl	92.71 (9)
F1—Os—N2	89.80 (14)	F2—Os—Cl	90.56 (10)
F2—Os—N2	89.07 (14)	N3—Os—Cl	176.44 (11)
N3—Os—N2	86.44 (15)	N2—Os—Cl	90.45 (11)
F1—Os—N1	90.75 (13)	N1—Os—Cl	90.74 (11)
F2—Os—N1	90.31 (13)		

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: *DIAMOND* (Bergerhoff, 1995). Software used to prepare material for publication: *SHELXL97*.

Financial support from Fonds der Chemischen Industrie and Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1051). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1218–1220

{4,4′-Dimethyl-6,6′-bis(morpholinomethyl)-2,2′-[1,3-propanediylbis(nitrilomethylidene)]diphenolato-*O*,*N*,*N*′,*O*′}manganese(II) diperchlorate monohydrate

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(*Received 25 January 1999; accepted 6 April 1999*)

Abstract

In the title compound, $[Mn(C_{28}H_{36}N_4O_4)](ClO_4)_2 \cdot H_2O$, the morpholine rings adopt chair conformations. The geometry around the Mn^{II} ion is slightly distorted square planar. The dihedral angle between the N/Mn/N and O/Mn/O planes is 10.1 (1)°. In addition to van der Waals interactions, the molecules are stabilized by N—H···O and C—H···O hydrogen bonds.

Comment

The main line of defence in mammalian organisms for controlling extra- and intracellular superoxide radical anions is the series of Cu-, Zn-, Mn- and Fe-containing superoxide dismutase enzymes. A stable non-toxic and low molecular weight mononuclear manganese(II) or manganese(III) complex that catalyses the dismutation of a superoxide anion might be a suitable alternative for superoxide dismutase in clinical applications (Wada