References

ALLEN, V. F., MASON, R. & HITCHCOCK, P. B. (1977). *J. Organomet. Chem.* **140**, 297–307.

CHURCHILL, M. R., HOLLANDER, F. J., SHAPLEY, J. R. & KEISTER, J. B. (1980). *Inorg. Chem.* **19**, 1272–1277.

CHURCHILL, M. R. & LASHEWYCZ, R. A. (1979). *Inorg. Chem.* **18**, 1926–1930.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

IWASAKI, F., MAYS, M. J., RAITHBY, P. R., TAYLOR, P. L. & WHEATLEY, P. J. (1981). *J. Organomet. Chem.* **213**, 185–206.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

SHELDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.

1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-hydrido-2,3-μ-trifluoroethylideneamido-*triangulo*-triosmium

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Abstract. [Os₃H(CO)₁₀N(CHCF₃)], M_r = 947·6, monoclinic, $P2_1/n$, a = 7·321 (5), b = 29·21 (1), c = 9·364 (5) Å, β = 100·55 (5)°, V = 1968·9 Å³, D_c = 3·196, D_m = 3·20 (5) Mg m⁻³, Z = 4, μ(Mo $K\alpha$) = 20·63 mm⁻¹. R = 0·103 for 2763 observed data. The Os atoms form a triangle of one Os(CO)₄ group and two Os(CO)₃ groups. The N of the CF₃CN molecule bridges the two Os(CO)₃ groups. One H is attached to the C of the nitrile group, the second is presumed to remain as an Os–H–Os bridge.

Introduction. Reaction of [H₂Os₃(CO)₁₀] with the nitrile CF₃CN yields two isomeric compounds of stoichiometry [H₂Os₃(CO)₁₀(CF₃CN)]. The ¹H NMR spectrum of the major product (I) contains only one metal hydride resonance and a one-proton quartet assignable to a CHCF₃ proton, suggesting that a hydride transfer has taken place. To ascertain the precise mode of bonding of the CF₃–CHN group to the Os₃ triangle, a crystallographic study of (I) was undertaken.

(I)
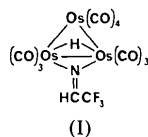
Suitable crystals were obtained by cooling a saturated hexane solution to 268 K. Data were collected from a crystal 0·3 × 0·3 × 0·3 mm on a Philips

four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å) for 3° < θ < 25° and index k ≤ 30. The small separation between reflexions caused by the long b axis prevented individual backgrounds being measured for each reflexion, so the background correction was based entirely on the value of the angle θ. Of 3461 reflexions measured, 2763 were classed as observed [I > 2·0σ(I)].

The intensities of the three standard reflexions dropped by about 7% during the course of data collection. Because of this decomposition and the imprecision of the background correction, only Lorentz and polarization corrections were applied to the intensities. A temperature-sharpened Patterson map (Lipson & Cochran, 1966) gave the coordinates of the three Os atoms, and subsequent Fourier maps yielded the coordinates of the lighter atoms. The structure was refined by block-diagonal least squares with the three Os atoms assigned anisotropic temperature factors. Weighting was proportional to $1/\sigma(F)$. Scattering factors were for neutral atoms (*International Tables for X-ray Crystallography*, 1962); that of Os was corrected for anomalous dispersion. The H atoms could not be located. The final R was 0·103 for 2763 observed data.* The relatively high value of R is to

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Table 1. *Fractional atomic coordinates* (×10⁴, *except for the Os y coordinates which are* ×10⁵) *and thermal parameters*

	x	y	z	B (Å²)
Os(1)	1826 (2)	13751 (5)	1186 (2)	*
Os(2)	1092 (2)	17514 (5)	3817 (2)	*
Os(3)	2605 (2)	8574 (5)	3746 (2)	*
N	696 (46)	798 (11)	1909 (36)	4·4 (7)
F(1)	-1226 (71)	498 (18)	-934 (56)	14·8 (16)
F(2)	-3031 (83)	872 (20)	-82 (64)	17·6 (19)
F(3)	-2951 (74)	122 (18)	-30 (58)	15·2 (16)
C(1)	-751 (52)	491 (13)	1644 (41)	3·5 (8)
C(2)	-1841 (102)	519 (25)	334 (78)	10·3 (19)
C(11)	-355 (58)	1693 (14)	115 (45)	4·0 (8)
C(12)	2267 (56)	1077 (14)	-466 (44)	4·0 (8)
C(13)	3389 (61)	1896 (15)	1011 (47)	4·5 (9)
C(21)	-1211 (71)	1497 (17)	3302 (56)	5·7 (11)
C(22)	234 (85)	2359 (21)	3042 (66)	7·9 (16)
C(23)	1227 (46)	1802 (12)	5805 (36)	2·6 (6)
C(24)	3634 (85)	2007 (21)	4188 (66)	7·9 (15)
C(31)	1213 (69)	620 (18)	5030 (56)	6·1 (12)
C(32)	3639 (67)	301 (16)	3433 (53)	5·4 (11)
C(33)	4476 (66)	1017 (18)	5263 (53)	5·7 (11)
O(11)	1519 (47)	1867 (12)	-526 (36)	6·3 (8)
O(12)	2907 (63)	890 (16)	-1554 (51)	10·2 (13)
O(13)	4491 (58)	2142 (15)	957 (47)	9·1 (11)
O(21)	-2681 (61)	1315 (14)	3013 (48)	9·0 (11)
O(22)	-302 (61)	2698 (15)	2673 (48)	9·0 (11)
O(23)	776 (50)	1820 (12)	6941 (38)	6·7 (8)
O(24)	5105 (46)	2098 (12)	4312 (36)	6·2 (8)
O(31)	315 (56)	468 (14)	5812 (44)	8·7 (11)
O(32)	4593 (49)	-35 (12)	3218 (38)	6·9 (9)
O(33)	5778 (46)	1156 (11)	6176 (35)	6·0 (7)

* Anisotropic thermal parameters for the osmium atoms:

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Os(1)	0·0157 (3)	0·00066 (2)	0·0066 (2)	0·0005 (1)	0·0067 (4)	0·00005 (9)
Os(2)	0·0196 (4)	0·00060 (2)	0·0075 (2)	0·0011 (1)	0·0086 (4)	-0·00050 (10)
Os(3)	0·0175 (3)	0·00049 (2)	0·0088 (2)	0·0002 (1)	0·0070 (4)	0·00041 (9).

The form of the expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.
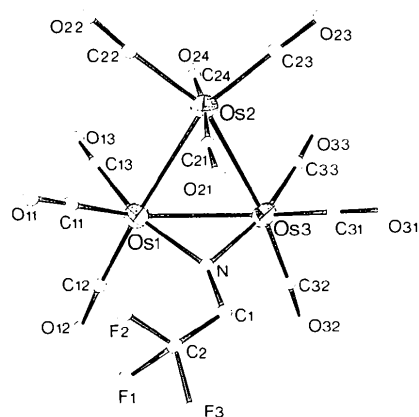

Fig. 1. A projection of the molecule showing the numbering system. If the CHCF₃ group is discounted, the molecule has an approximate mirror plane of symmetry perpendicular to Os(1)—Os(3) and passing through Os(2).

some extent due to the lack of an absorption correction,* but it is mainly caused by the radiation damage and consequent broadening of the diffraction peaks. The decomposition likewise is the cause of the general imprecision of the Os—C and C—O bond lengths and the large values of B, especially for the atoms of the CF₃ group. There was no evidence for disorder in the CF₃ group.

Final positional and thermal parameters are given in Table 1. Selected bond lengths and angles are in Table 2. The stereochemistry and numbering systems are shown in Fig. 1.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Os(1)—Os(3)	2·803 (5)	N—C(1)	1·38 (5)
Os(1)—Os(2)	2·838 (5)	C(1)—C(2)	1·34 (5)
Os(2)—Os(3)	2·842 (5)	C(2)—F(1)	1·35 (5)
Os(1)—N	2·05 (3)	C(2)—F(2)	1·36 (5)
Os(3)—N	2·02 (3)	C(2)—F(3)	1·42 (5)
Os(1)—C(11)	1·96 (3)	C(11)—O(11)	1·08 (5)
Os(1)—C(12)	1·85 (3)	C(12)—O(12)	1·32 (5)
Os(1)—C(13)	1·93 (3)	C(13)—O(13)	1·09 (5)
Os(2)—C(21)	1·83 (3)	C(21)—O(21)	1·19 (5)
Os(2)—C(22)	1·98 (3)	C(22)—O(22)	1·10 (5)
Os(2)—C(23)	1·85 (3)	C(23)—O(23)	1·17 (5)
Os(2)—C(24)	1·98 (3)	C(24)—O(24)	1·10 (5)
Os(3)—C(31)	1·85 (3)	C(31)—O(31)	1·16 (5)
Os(3)—C(32)	1·84 (3)	C(32)—O(32)	1·24 (5)
Os(3)—C(33)	1·84 (3)	C(33)—O(33)	1·23 (5)
Os(1)—Os(2)—Os(3)	59·1 (3)	Os(1)—N—C(1)	145 (1)
Os(2)—Os(1)—Os(3)	60·5 (3)	Os(3)—N—C(1)	127 (1)
Os(2)—Os(3)—Os(1)	60·3 (3)	N—C(1)—C(2)	116 (2)
Os(1)—N—Os(3)	87·3 (5)	C(21)—Os(2)—C(24)	174 (1)
N—Os(1)—Os(3)	45·9 (5)	C(22)—Os(2)—C(23)	105 (1)
N—Os(3)—Os(1)	46·8 (5)	C(11)—Os(1)—C(13)	91 (1)
Os(1)—Os(3)—C(31)	135·1 (5)	C(11)—Os(1)—C(12)	93 (1)
Os(2)—Os(3)—C(32)	171·6 (5)	C(12)—Os(1)—C(13)	96 (1)
Os(3)—Os(1)—C(11)	135·5 (5)	C(31)—Os(3)—C(33)	91 (1)
Os(2)—Os(1)—C(12)	174·8 (5)	C(31)—Os(3)—C(32)	94 (1)
Os(1)—Os(2)—C(22)	97·3 (5)	C(32)—Os(3)—C(33)	94 (1)
Os(3)—Os(2)—C(23)	98·5 (5)		

Discussion. One hydrogen bridge has been attacked by the N of the nitrile group with the transfer of a H atom to the C atom and the formation of an Os—N—Os bridge. The length N—C(1), 1·38 Å, and the angle N—C(1)—C(2), 116°, indicate that the bonding is suitably described as N=CH—CF₃ with C(1) sp^2-hybridized. Similar geometric bridging arrangements have been found in [Mn₂{N=C(CF₃)₂}], N—C = 1·26 Å (Churchill & Lin, 1975), and [Re₂{N=CHCH₃}], N—C = 1·39 Å (Mays, Prest & Raithby, 1980). The second H atom is assumed to remain in the bridge between Os(1) and Os(3), and the Os(1)—Os(3) length of 2·803 Å thus corresponds to a doubly-bridged bond.

The angle Os(1)—N—C(1) is opened up to relieve intramolecular compressions between the CF₃ group and the carbonyls (11) and (12) on Os(1). Atoms Os(1), Os(3), N, C(1) and C(2) are closely coplanar,

* Experience with similar compounds in the past has shown that omission of an absorption correction has little effect on the final positional parameters. The error is taken up in the thermal parameters.

and the angle between this plane and that of the three Os atoms is 109°.

The Os—Os bond lengths (2·803, 2·838, 2·842 Å) are similar to those found previously; *e.g.* in [HOs₃(CO)₁₀(CHCH=NEt₂)] the analogous lengths were 2·785, 2·866 and 2·870 Å (Shapley, Tachikawa, Churchill & Lashewycz, 1978). Os(2) has coordination number 6, while Os(1) and Os(3) have coordination number 7 (including the hydrogen bridge). All three Os atoms obey the effective-atomic-number rule; Os(1)—Os(2), Os(3)—Os(2) have a formal metal–metal bond order of 1. Os(1)—Os(3) is shortened by the two bridging groups, as was found in |H₂Os₃(CO)₁₀| itself where the bond lengths are 2·683, 2·814, 2·815 Å (Broach & Williams, 1979).

The arrangement of the CO groups about Os(2) of the Os(CO)₄ group is identical to that in [HOs₃(CO)₁₀(C₂H₃)] (Orpen, Rivera, Bryan, Pippard, Sheldrick & Rouse, 1978) and [HOs₃(CO)₁₀(p-CH₃C₆H₄—NC(H)O)] (Adams & Golembeski, 1979) but differs from that in [HOs₃(CO)₁₀(CF₃CCHCF₃)] (Laing, Sommerville, Dawoodi, Mays & Wheatley, 1978). In this latter compound, Os(2) is σ-bonded to a C atom, thus raising its coordination number to 7 while simultaneously forcing a change in orientation of the Os(CO)₄ moiety. The angle C(21)—Os(2)—C(23) in this compound clearly exceeds 90°, as does its geometric analogue in the present case, C(22)—Os(2)—C(23), which is 105°.

References

ADAMS, R. D. & GOLEMBESKI, N. M. (1979). *J. Organomet. Chem.* **171**, C21–C26.
BROACH, R. W. & WILLIAMS, J. M. (1979). *Inorg. Chem.* **18**, 314–318.
CHURCHILL, M. R. & LIN, K. G. (1975). *Inorg. Chem.* **14**, 1675–1680.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.
LAING, M., SOMMERVILLE, P., DAWOODI, Z., MAYS, M. J. & WHEATLEY, P. J. (1978). *Chem. Commun.* pp. 1035–1036.
LIPSON, H. & COCHRAN, W. (1966). *The Determination of Crystal Structures*, 3rd ed., pp. 165–169. London: Bell.
MAYS, M. J., PREST, D. W. & RAITHBY, P. R. (1980). *Chem. Commun.* pp. 171–173.
ORPEN, A. G., RIVERA, A. V., BRYAN, E. G., PIPPARD, D., SHELDRICK, G. M. & ROUSE, K. D. (1978). *Chem. Commun.* pp. 723–724.
SHAPLEY, J. R., TACHIKAWA, M., CHURCHILL, M. R. & LASHEWYCZ, R. A. (1978). *J. Organomet. Chem.* **162**, C39–C42.

The Structure of Calcium Methanedisulfonate Trihydrate

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Abstract. [Ca(CH₂O₆S₂)(H₂O)₃], CH₈CaO₉S₂, monoclinic, $P2_1/n$, $a = 5.777$ (1), $b = 19.469$ (4), $c = 7.748$ (2) Å, $\beta = 92.98$ (2)°, $V = 870.3$ Å³, $Z = 4$, $d_c = 2.05$, $d_m = 2.03$ Mg m⁻³, μ(Mo Kα) = 1·2 mm⁻¹, $R = 0.033$ and $R_w = 0.051$ for 1451 counter-collected reflections. The sevenfold, approximately pentagonal bipyramidal, coordination polyhedron around the Ca²⁺ ion consists of three water molecules and four sulfonate O atoms from three different methanedisulfonate ions. The methanedisulfonate ligand binds one Ca²⁺ ion forming a six-membered chelate ring and is linked to two other Ca²⁺ ions by unidentate bridging bonds. The ligand occurs in a conformation which has approximate C_{2v} symmetry.

Introduction. Colorless single crystals were readily grown by evaporation from an aqueous solution of the 1:1 salt. From indexed Weissenberg photographs the crystals were found to be monoclinic and the systematic absences $h + l$ odd for $h0l$ and k odd for $0k0$ indicated space group $P2_1/n$ |a non-standard setting for $P2_1/c$ with general positions $\pm(x,y,z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$|. A single crystal with approximate dimensions 0·3 × 0·3 × 0·2 mm was used to collect accurate unit-cell parameters as well as three-dimensional X-ray intensity data on an automated diffractometer. A total of 1578 data out to $2\theta = 50°$ were collected using Mo Kα radiation and the θ–2θ scan technique.

The raw intensity data were assigned e.s.d.'s from