GABELA, F., KOJIĆ-PRODIĆ, B., ŠLJUKIĆ, M. & RUŽIĆ-TOROŠ, Z. (1977). *Acta Cryst.* B**33**, 3733–3736.
GAUDREAU, B. (1965). *Rev. Chim. Minér.* **2**, 1–52.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
KOJIĆ-PRODIĆ, B., GABELA, F., RUŽIĆ-TOROŠ, Z. & ŠLJUKIĆ, M. (1981). *Acta Cryst.* B**37**, 1963–1965.
WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.
WATERS, T. N. (1960). *J. Inorg. Nucl. Chem.* **15**, 320–328.

Acta Cryst. (1988). C**44**, 1701–1703

Structure of Tribenzylammonium 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-hydrido-2,3-μ-sulfonyl-*triangulo*-triosmium

BY G. D. JARVINEN,* E. M. LARSON, H. J. WASSERMAN, C. J. BURNS AND R. R. RYAN

Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545, *USA*

(*Received* 17 *August* 1987; *accepted* 25 *April* 1988)

Abstract. $[NH(CH_2C_6H_5)_3][Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SO_2)]$, $M_r = 1204{\cdot}16$, monoclinic, $P2_1$, $a = 9{\cdot}605\,(1)$, $b = 12{\cdot}809\,(4)$, $c = 15{\cdot}116\,(2)$ Å, $\beta = 105{\cdot}1\,(5)°$, $V = 1795{\cdot}82$ Å^3, $Z = 2$, $D_x = 2{\cdot}223$ g cm^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}7093$ Å, $\mu = 107{\cdot}1$ cm^{-1}, $F(000) = 1101$, $T = 298$ K, $R = 0{\cdot}034$ for 1523 reflections with $I \geq 2\sigma(I)$. The anion consists of a triangular array of osmium atoms with two unbridged edges [Os—Os 2·850 (3) and 2·864 (5) Å] and the third edge bridged by the hydride and SO_2 ligands [Os—Os 2·908 (7) Å]. A close contact [2·65 (4) Å] between the nitrogen of the cation and one of the SO_2 oxygens indicates hydrogen bonding between the tribenzylammonium cation and the cluster anion.

Introduction. Our recent investigations of reactions between metal hydride complexes and SO_2 have shown interesting reduction chemistry (Kubas & Ryan, 1986). Previously we reported on the structure of $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SO_2)$, one of a rather small number of metal complexes containing hydride and SO_2 ligands (Jarvinen & Ryan, 1984). The complex $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SO_2)$ is the first product observed by NMR or IR spectroscopy from the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ and SO_2, but additional products form at rates dependent on variables such as the solvent, temperature, and SO_2 concentration. Tertiary amines were added to the reaction mixture in an attempt to bind acidic protons that might be present. Addition of tribenzylamine gave the title compound, which formally results from the transfer of a proton from $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SO_2)$ to tribenzylamine.

Experimental. The compound was prepared by dissolving 152·7 mg of $Os_3(CO)_{10}(\mu\text{-}H)_2$ and 53·7 mg of tribenzylamine in 28 ml of 3:1 heptane/chloroform under N_2. Sulfur dioxide was bubbled through the purple solution which was then left overnight. The resulting clear yellow solution was placed in a freezer and a small amount of powdery solid formed. The solution was warmed to room temperature and the $CHCl_3$ was partially evaporated by passing N_2 over the solution. The flask was again placed in a freezer where crystals formed, 57·4 mg, 26%. Analysis: calc. for $C_{31}H_{23}NO_{12}Os_3S$: C, 30·92; H, 1·93; N, 1·16; O, 15·94; S, 2·66%. Found: C, 30·84; H, 2·02; N, 1·12; O, 16·62; S, 2·77%. A yellow crystal having a length of about 0·1 mm was mounted on a standard goniometer. Data were collected by θ–2θ scans ($2\theta_{\max} = 40°$) on a CAD-4 automated diffractometer using Mo $K\alpha$ radiation and a graphite monochromator. Cell dimensions were determined by least-squares refinement of 25 centered reflections ($12° \leq \theta \leq 35°$). The space group was chosen on the basis of systematically absent reflections and a subsequent successful refinement. Reflections in a quadrant with Miller indices $h = 0$–9, $k = 0$–12 and $l = 0 \pm 14$ were collected and averaged to yield 1523 reflections with $I \geq 2\sigma(I)$. The R value based on F_o^2 for the merge of equivalent reflections was 0·024. Data correction including a combination of spherical and φ absorption corrections was made (max. transmission 0·484, min. 0·284) and corrections for Lorentz and polarization factors were performed as previously (Ryan & Swanson, 1974). The structure was solved by standard Patterson methods and refined by full-matrix least squares employing the Los Alamos *Generalized Crystal Structure Analysis System* (Larson & Von Dreele, 1986). All atoms except the metals and SO_2 group were modeled as having isotropic thermal motion. The function minimized was $\sum w(F_o^2 - F_c^2)^2$ and weights were determined by $w = 1/(\sigma F_o^2)^2$ and $\sigma F_o^2 = [I + B + 0{\cdot}01I^2]T\text{Lp}$. The final residuals were $R = 0{\cdot}034$ and $wR = 0{\cdot}031$ for the 1523 reflections having $I \geq 2\sigma(I)$. $(\Delta/\sigma)_{\max} = 0{\cdot}51$. Hydrogens were placed several times after successive refinements and

---

* Author to whom correspondence should be addressed: Group INC-4, MS C346, Los Alamos National Laboratory.

0108-2701/88/101701-03$03.00

Table 1. *Atom parameters*

	x	y	z	$U_{iso}(\times 10^2$ Å$^2)$
Os(1)	0·0267 (2)	−0·0018 (1)	0·3936 (1)	5·84*
Os(2)	0·1637 (1)	0·1945 (1)	0·3885 (1)	5·29*
Os(3)	−0·1486 (1)	0·1811 (1)	0·3486 (1)	5·08*
S(1)	−0·008 (1)	0·2199 (7)	0·2471 (6)	5·16*
O(1)	−0·017 (2)	0·153 (2)	0·166 (1)	6·29*
O(2)	−0·019 (3)	0·334 (2)	0·219 (2)	5·08*
N(1)	−0·078 (2)	0·375 (2)	0·041 (1)	3·9 (5)
C(1)	0·028 (5)	0·031 (3)	0·510 (4)	10·4 (12)
O(3)	0·018 (4)	0·053 (3)	0·587 (2)	10·2 (7)
C(2)	0·034 (3)	−0·029 (3)	0·272 (2)	8·2 (9)
O(4)	0·049 (2)	−0·061 (2)	0·199 (1)	8·3 (6)
C(3)	0·193 (5)	−0·079 (4)	0·440 (3)	9·8 (11)
O(5)	0·298 (5)	−0·130 (4)	0·466 (2)	10·6 (8)
C(4)	−0·123 (6)	−0·094 (5)	0·380 (3)	13·3 (15)
O(6)	−0·227 (4)	−0·148 (3)	0·370 (2)	14·1 (10)
C(5)	0·303 (5)	0·144 (4)	0·338 (3)	11·6 (13)
O(7)	0·382 (3)	0·099 (2)	0·301 (2)	11·2 (7)
C(6)	0·227 (6)	0·322 (5)	0·385 (4)	11·2 (14)
O(8)	0·266 (4)	0·416 (3)	0·386 (2)	13·1 (9)
C(7)	0·272 (3)	0·170 (3)	0·508 (2)	8·0 (8)
O(9)	0·333 (3)	0·141 (2)	0·586 (2)	10·7 (7)
C(8)	−0·228 (4)	0·313 (4)	0·336 (2)	6·3 (9)
O(10)	−0·276 (3)	0·402 (2)	0·316 (2)	8·7 (6)
C(9)	−0·285 (5)	0·112 (4)	0·260 (3)	10·6 (12)
O(11)	−0·368 (3)	0·069 (2)	0·200 (2)	12·3 (8)
C(10)	−0·232 (3)	0·148 (3)	0·451 (2)	6·5 (8)
O(12)	−0·307 (5)	0·128 (4)	0·501 (2)	11·8 (9)
C(11)	0·037 (2)	0·317 (2)	0·006 (2)	4·8 (7)
C(12)	0·185 (3)	0·365 (3)	0·047 (2)	6·2 (8)
C(13)	0·248 (5)	0·424 (3)	−0·009 (3)	6·2 (9)
C(14)	0·457 (4)	0·438 (3)	0·115 (2)	8·5 (10)
C(16)	0·397 (5)	0·378 (4)	0·168 (3)	10·0 (11)
C(17)	0·263 (3)	0·336 (3)	0·134 (2)	6·9 (8)
C(18)	−0·218 (3)	0·316 (2)	0·011 (1)	4·7 (6)
C(19)	−0·270 (3)	0·295 (3)	−0·086 (2)	5·2 (8)
C(20)	−0·360 (4)	0·357 (3)	−0·155 (2)	7·0 (8)
C(21)	−0·398 (4)	0·324 (4)	−0·247 (2)	8·3 (10)
C(22)	−0·359 (3)	0·242 (14)	−0·274 (2)	8·2 (15)
C(23)	−0·287 (4)	0·177 (4)	−0·212 (3)	10·9 (10)
C(24)	−0·248 (4)	0·203 (3)	−0·120 (2)	6·9 (8)
C(25)	−0·083 (3)	0·487 (3)	0·012 (2)	5·1 (6)
C(26)	−0·171 (4)	0·553 (2)	0·058 (2)	5·1 (7)
C(27)	−0·133 (3)	0·567 (3)	0·152 (2)	6·3 (7)
C(28)	−0·210 (4)	0·636 (3)	0·189 (2)	9·0 (10)
C(29)	−0·329 (3)	0·689 (3)	0·137 (2)	7·1 (7)
C(30)	−0·364 (3)	0·676 (3)	0·046 (2)	6·6 (7)
C(31)	−0·285 (4)	0·614 (3)	0·005 (3)	5·9 (9)

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} (i = 1\text{–}3)$.

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

Os(1)—Os(2)	2·850 (3)	Os(2)—Os(1)—Os(3)	61·18 (13)
Os(1)—Os(3)	2·864 (5)	Os(1)—Os(2)—Os(3)	59·64 (7)
Os(2)—Os(3)	2·908 (7)	Os(1)—Os(3)—Os(2)	59·18 (15)
Os(2)—S(1)	2·36 (2)	S(1)—Os(2)—Os(3)	85·8 (3)
Os(3)—S(1)	2·35 (1)	S(1)—Os(3)—Os(2)	85·7 (3)
		Os(2)—S(1)—Os(3)	76·4 (3)
S(1)—O(1)	1·47 (2)	O(1)—S(1)—O(2)	110·5 (2)
S(1)—O(2)	1·51 (3)	O(1)—S(1)—Os(2)	119·8 (11)
		O(2)—S(1)—Os(3)	111·8 (16)
Os(1)—C(1)	1·82 (6)	Os(1)—C(1)—O(3)	175· (5)
Os(1)—C(2)	1·89 (4)	Os(1)—C(2)—O(4)	169· (4)
Os(1)—C(3)	1·85 (5)	Os(1)—C(3)—O(5)	177· (4)
Os(1)—C(4)	1·84 (8)	Os(1)—C(4)—O(6)	175· (5)
Os(2)—C(5)	1·82 (6)	Os(2)—C(5)—O(7)	171· (5)
Os(2)—C(6)	1·76 (7)	Os(2)—C(6)—O(8)	176· (6)
Os(2)—C(7)	1·87 (4)	Os(2)—C(7)—O(9)	171· (4)
Os(3)—C(8)	1·85 (5)	Os(3)—C(8)—O(10)	171· (4)
Os(3)—C(9)	1·83 (6)	Os(3)—C(9)—O(11)	176· (5)
Os(3)—C(10)	1·97 (4)	Os(3)—C(10)—O(12)	168· (4)
C(1)—O(3)	1·23 (6)		
C(2)—O(4)	1·22 (4)		
C(3)—O(5)	1·19 (6)		
C(4)—O(6)	1·19 (6)		
C(5)—O(7)	1·20 (6)		
C(6)—O(8)	1·25 (7)		
C(7)—O(9)	1·23 (4)		
C(8)—O(10)	1·23 (5)		
C(9)—O(11)	1·18 (5)		
C(10)—O(12)	1·21 (5)		
N(1)—O(2)	2·65 (4)		
N(1)—C(11)	1·54 (4)	C(11)—N(1)—C(18)	109·0 (2)
N(1)—C(18)	1·51 (4)	C(18)—N(1)—C(25)	115·8 (3)
N(1)—C(25)	1·50 (5)	C(11)—N(1)—C(25)	109·0 (2)

Ring (1)
C(11)—C(12) 1·52 (4)

Ring contains C(12) to C(17)
Mean C—C 1·37 Mean C—C—C 120

Ring (2)
C(18)—C(19) 1·46 (4)

Ring contains C(19) to C(24)
Mean C—C 1·35 Mean C—C—C 119

Ring (3)
C(25)—C(26) 1·49 (4)

Ring contains C(26) to C(31)
Mean C—C 1·38 Mean C—C—C 120

given a thermal parameter ($U = 0{\cdot}063$ Å^2) which was not refined. The total number of parameters, including positional and thermal variables plus a scale and extinction coefficient ($5{\cdot}89 \times 10^{-8}$) (Larson, 1970; Zachariasen, 1967) was 224 for the 1523 observations. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). To check the chirality of the structure, the signs of the f'' were changed and a refinement attempted with 1–2% less successful results. In a final Fourier map no significant peaks were observed.

Discussion. An *ORTEP* drawing (Johnson, 1976) of the ion pair is presented as Fig. 1. Table 1 gives the positional and thermal parameters for the cation and anion.* Table 2 lists selected distances and angles.

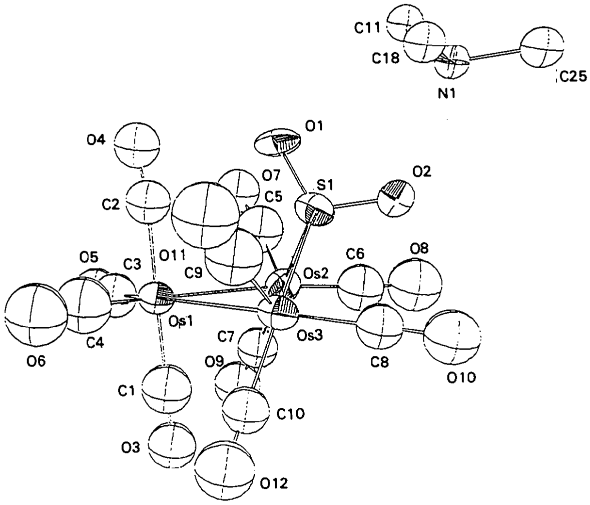

Fig. 1. *ORTEP* drawing of title compound.

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44982 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A triangular array of osmium atoms forms the framework of the anion with the Os(2)—Os(3) edge bridged by the SO_2 and hydride ligands and the other two edges unbridged. The structure of the anion is quite similar to that of the neutral dihydride except for the Os—Os edge bridged only by a hydride in $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SO_2)$. Removing this proton to give the anion yields an Os(1)—Os(2) distance of 2·850 (3) *vs* 3·068 (1) Å for the corresponding distance in the dihydride. The other Os—Os distances in the anion are closer to those found for the hydride–SO_2-bridged edge [2·895 (1) Å] and unbridged edge [2·848 (1) Å] of $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SO_2)$. The bridging hydride was not located, but its approximate position can be inferred from the arrangement of the carbonyl and SO_2 ligands about Os(2) and Os(3), *i.e. trans* to both C(5) and C(9). The bridging hydride resonance appears as a sharp singlet at δ −14·9 in the ^{1}H NMR spectrum of the compound in $CDCl_3$.

The N(1)—O(2) distance of 2·65 (4) Å is indicative of a hydrogen bond between the N—H group of the cation and one oxygen atom of the SO_2 ligand (Hamilton & Ibers, 1968). A weak, broad peak at 2520 cm^{-1} in the infrared spectrum of a Nujol mull of the complex was assigned to the N—H stretch and also indicated a substantial hydrogen-bonding interaction. The longer S—O(2) distance of 1·51 (3) Å compared to S—O(1) of 1·47 (3) Å is probably a manifestation of the hydrogen bond, even though this difference is less than 2σ. The identity of the species that donates a proton to the amine during the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ and SO_2 is not clear at present. Addition of tribenzylamine does alter the reaction chemistry of the $Os_3(CO)_{10}(\mu\text{-}H)_2/SO_2$ system considerably. The tribenzylammonium salt is quite stable in solution for days near 298 K, whereas $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SO_2)$ reacts under these conditions to give a number of products as indicated by NMR and IR spectra. The binding of this acidic proton by the amine thus greatly inhibits further reactions of the cluster.

The authors are grateful to D. T. Cromer and Allen C. Larson for helpful discussions. This work was carried out under the auspices of the US Department of Energy, Office of Basic Energy Sciences.

References

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids*, p. 16. New York: Benjamin.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Jarvinen, G. D. & Ryan, R. R. (1984). *Organometallics*, **3**, 1434–1438.

Johnson, C. K. (1976). *ORTEPII. A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kubas, G. J. & Ryan, R. R. (1986). *Polyhedron*, **5**, 473–485.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 291–294. Copenhagen: Munksgaard.

Larson, A. C. & Von Dreele, R. B. (1986). *Generalized Structure Analysis System*. Report LAUR 86-748. Los Alamos National Laboratory, USA.

Ryan, R. R. & Swanson, B. I. (1974). *Inorg. Chem.* **13**, 1681–1684.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1988). C**44**, 1703–1707

Structures of Cadmium Magnesium Tetranitrite Dihydrate, Cadmium Calcium Tetranitrite Tetrahydrate and Cadmium Strontium Tetranitrite Tetrahydrate

By Tomonori Aoyama, Shigeru Ohba and Yoshihiko Saito

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, *Kohoku-ku, Yokohama* 223, *Japan*

(*Received* 12 *April* 1988; *accepted* 27 *May* 1988)

Abstract. $CdMg(NO_2)_4.2H_2O$ (I), $M_r = 356{\cdot}8$, monoclinic, $C2/c$, $a = 11{\cdot}441$ (2), $b = 6{\cdot}958$ (2), $c = 12{\cdot}017$ (2) Å, $\beta = 91{\cdot}70$ (2)°, $V = 956{\cdot}2$ (4) Å^3, $Z = 4$, $D_x = 2{\cdot}48$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 2{\cdot}39$ mm^{-1}, $F(000) = 688$, $T = 296$ (1) K, final $R = 0{\cdot}018$ for 933 observed unique reflections. $CaCd(NO_2)_4.4H_2O$ (II), $M_r = 408{\cdot}6$, trigonal, $P3_121$ or $P3_221$, $a = 7{\cdot}5003$ (6), $c = 18{\cdot}413$ (3) Å, $V = 897{\cdot}0$ (2) Å^3, $Z = 3$, $D_m(CCl_4/CH_3I) = 2{\cdot}28$ (1), $D_x = 2{\cdot}27$ Mg m^{-3}, $\mu = 2{\cdot}30$ mm^{-1}, $F(000) = 600$, $T = 296$ (1) K, final $R = 0{\cdot}035$ for 1327 reflections. $CdSr(NO_2)_4.4H_2O$ (III), $M_r = 456{\cdot}1$, trigonal, $P3_121$ or $P3_221$, $a = 7{\cdot}6379$ (7), $c = 18{\cdot}707$ (4) Å, $V = 945{\cdot}1$ (2) Å^3, $Z = 3$, D_m $(CCl_4/C_2H_2Br_4) = 2{\cdot}37$ (1), $D_x = 2{\cdot}40$ Mg m^{-3}, $\mu = 5{\cdot}85$ mm^{-1}, $F(000) = 654$, $T = 295$ (1) K, final $R = 0{\cdot}030$ for 1264 reflections. The structures of (II) and (III) are isomorphous. In (I), the Mg^{2+} ion is surrounded octahedrally by two water and

0108-2701/88/101703-05$03.00