Structure of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$. Single-crystal X-ray diffraction analysis of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$ establishes that the complex crystallizes in the centrosymmetric space group $P\bar{1}$ with one molecule per unit cell. The overall structure of the molecule, as shown in Figure 1, is similar to that of $I_2Os_3(CO)_{12}$.[26] It has approximate C_{2h} symmetry based on a linear arrangement of Os atoms. Since the central Os atom lies on the inversion center, the Os-Os-Os angle is 180°.

The molecule is disordered, the observed structure being 78.9% the structure shown in Figure 1 and 21.1% the structure in which the Br and C(5)-O(5) have interchanged positions. In the composite observed, the Br ligand of the minor isomer resides approximately midway between the C(5) and O(5) atoms (C(5)-Br(1′) = 0.61 (2) Å; O(5)-Br(1′) = 0.69 (2) Å). Similar bromine atom disorder was observed in $(\mu\text{-}H)(\mu\text{-}Br)Os_3(CO)_{10}$.[28]

Each Os atom has distorted octahedral coordination. As observed in $Re_2Pt(CO)_{12}$,[29] $I_2Os_3(CO)_{12}$,[26] and $Mn_3(CO)_{14}^-$,[30] the four carbonyl groups on the central Os atom are staggered with respect to the four equatorial ligands on the terminal Os atoms (the torsion angles C(2)-Os(1)-Os(2)-C(5), C(2)-Os(1)-Os(2)-Br(1), C(1)-Os(1)-Os(2)-C(5), and C(1)-Os(1)-Os(2)-C(3) are 45.3, 46.3, 43.7, and 46.1°, respectively). Selected bond distances and angles for the compound are contained in Tables IV and V. All the Os(1)-Os(2)-L(eq) (L = CO, Br) angles are less than 90°, ranging from 88.75 (6) to 83.1 (5)°, while the P(ax)-Os(2)-L(eq) (L = CO, Br) angles are all larger than 90°, ranging from 90.1 (5) to 99.0 (5)°. Thus, the equatorial CO groups and the bromide ligand on the terminal Os atom are bent slightly toward the central Os atom, as observed in other linear trinuclear carbonyl complexes, $Mn_3(CO)_{14}^-$,[30] $Mn_2Fe(CO)_{14}$,[31] $Re_2Pt(CO)_{12}$,[29] and $I_2Os_3(CO)_{12}$.[26] The Os-C-O bonds are all almost linear, with angles ranging from 171 (2) to 179 (1)°.

The Os-Os bond length of 2.916 (1) Å is similar to that found in $I_2Os_3(CO)_{12}$ (2.935 (2) Å)[26] and $(Cl_3Si)_2Os_3(CO)_{12}$ (2.912 (1) Å).[32] It is, however, longer than those found in $Os_3(CO)_{12}$ (2.877 (3) Å),[27] $Os_3(CO)_{11}(P(OCH_3)_3)$ (average 2.897 (10) Å),[33] $Os_3(CO)_{11}(CH_3CN)$ (average 2.870 (2) Å),[34] $Os_3(CO)_{10}(CH_3CN)_2$ (average 2.865 (2) Å),[34] $(\mu\text{-}H)(\mu\text{-}Br)Os_3(CO)_{10}$ (average 2.846 (1) Å),[28] and other triangular triosmium carbonyl complexes.[28] The average Os-CO and C-O distances (1.92 (2) and 1.42 (2) Å) are similar to those found in $Os_3(CO)_{12}$[27] and other osmium carbonyl complexes.[28,33,34] The Os-CO distance (1.87 (2) Å) for the carbonyl group trans to the Br atom is shorter than those (1.91-1.97 (2) Å) for other carbonyl groups presumably because of less competition by Br for π-bonding. The Os-Br distance (2.592 (3) Å) compares well with those found in $(\mu\text{-}H)(\mu\text{-}Br)Os_3(CO)_{10}$ (2.591 (2) and 2.583 (2) Å)[28] but is longer than those found in $[Os_2Br_{10}]^{2-}$ (average Os-Br(terminal) = 2.454 (5) Å)[35] and $OsBr_3(PPh_3)_2(CH_3CN)$ (average 2.493 (1) Å).[35] In $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$, the Os-P bond length (2.310 (4) Å) and the P-O distances in the $P(OMe)_3$ group are similar to those found in $Os_3(CO)_{11}[P(OMe)_3]$ (Os-P = 2.285 (5) Å)[33] and $Os_3(CO)_8(NO)_2[P(OMe)_3]$ (Os-P = 2.33 (1) Å).[36]

Since all the spectroscopic data recorded for $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$ in solution are similar to those of $Br_2Os_3(CO)_{10}(PPh_3)_2$ and $Br_2Os_3(CO)_{10}(PPh_2Me)_2$ and these data are consistent with the solid-state structure of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$, it appears that all three $Br_2Os_3(CO)_{10}L_2$ complexes have the same structure as the solid-state structure of $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$.

Registry No. $Br_2Os_3(CO)_2$, 21773-71-7; PPh_3, 603-35-0; $Os(CO)_4PPh_3$, 21192-24-5; $Br_2Os_3(CO)_{10}(PPh_3)_2$, 101033-34-5; $Br_2Os(CO)_2(PPh_3)_2$, 17456-72-3; PPh_2Me, 1486-28-8; $Os(CO)_4PPh_2Me$, 101033-35-6; $Br_2Os_3(CO)_{10}(PPh_2Me)_2$, 101033-36-7; $Br_2Os(CO)_2(PPh_2Me)_2$, 101033-37-8; $Br_2Os_3(CO)_{10}[P(OMe)_3]_2$, 101033-38-9.

Supplementary Material Available: Tables of anisotropic temperature factors for non-hydrogen atoms (Table 1) and observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Cluster Synthesis. 10. Reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with Trimethylamine *N*-Oxide Dihydrate. Syntheses and Structural Characterizations of $Os_3(CO)_8(NMe_3)(\mu\text{-}OH)(\mu_3\text{-}S)(\mu\text{-}H)$ and the Six-Atom-Chain Cluster $Os_6(CO)_{18}(\mu\text{-}OH)(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)$

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The reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with 2 equiv of $Me_3NO{\cdot}2H_2O$ leads to the formation of the compound $Os_3(CO)_8(NMe_3)(\mu\text{-}OH)(\mu_3\text{-}S)(\mu\text{-}H)$ (**1**) in 44% yield. Compound **1** was characterized by IR and ^1H NMR spectroscopies and by a single-crystal X-ray diffraction analysis. For **1** the space group is $P\bar{1}$, a = 9.703 (1) Å, b = 13.269 (2) Å, c = 8.057 (1) Å, α = 105.78 (1)°, β = 102.61 (1)°, γ = 77.80 (1)°, Z = 2, and ρ_{calcd} = 3.12 g/cm^3. The molecule consists of an open cluster of three osmium atoms with bridging hydroxyl and hydrido ligands, a triply bridging sulfido ligand, and one trimethylamine ligand. Compound **1** can be reacted with $Os_3(CO)_{10}(\mu_3\text{-}S)$ to give the hexanuclear cluster $Os_6(CO)_{18}(\mu\text{-}OH)(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)$ (**2**) in 43% yield. Compound **2** was characterized by IR and ^1H NMR spectroscopies and by a single-crystal X-ray diffraction analysis. For **2** the space group is $P\bar{1}$ with a = 12.127 (3) Å, b = 14.009 (6) Å, c = 9.155 (3) Å, α = 103.24 (3)°, β = 98.18 (2)°, γ = 90.00 (3)°, Z = 2, and ρ_{calcd} = 3.83 g/cm^3. Compound **2** consists of a chain of six osmium atoms connected by five osmium-osmium bonds. It also contains a quadruply bridging sulfido ligand, a triply bridging sulfido ligand, a bridging hydroxyl ligand, and a bridging hydrido ligand. The resonances of the protons on the hydroxyl ligands in both **1** and **2** are shifted upfield from Me_4Si.

Introduction

The inactivity of many transition-metal carbonyl compounds toward CO replacement has been a major impediment in the development of these compounds for use both in stoichiometric and in catalytic metal-promoted transformations of small molecules.[1] The problem has been particularly acute for osmium carbonyl cluster compounds.[2] Numerous methods for activating metal carbonyl compounds have been developed. One of the more successful of these has involved the use of trimethylamine *N*-oxide.[3] This reagent converts CO ligands into CO_2 by oxygen atom transfer, and the CO_2 is then released from the complex. A vacant site is generated on the metal atom and reaction solvents or selected reagents can be readily coordinated.[3] In poorly donating solvents and in the absence of donor reagents, the trimethylamine produced in the reaction can become coordinated.[4] In this report we describe our studies of the reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with trimethylamine *N*-oxide dihydrate.

Experimental Section

Although the reagents and the products are air-stable, the reactions were performed under a nitrogen atmosphere. Trimethylamine *N*-oxide dihydrate was purchased from Aldrich Chemical Co. and was used without further purification. $Os_3(CO)_{10}(\mu_3\text{-}S)$ was prepared from $HOs_3(CO)_{10}(\mu\text{-}SPh)$ as previously described.[5] Reagent grade solvents CH_2Cl_2 and hexane were used without further purification. Infrared spectra were recorded on a Nicolet 5 DXB FT-IR spectrometer. ^1H NMR spectra were recorded on an IBM NR-80 spectrometer. Elemental analyses were performed at MIC Anal., Tucson, AZ.

A. Reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with 2 equiv of $Me_3NO{\cdot}2H_2O$. A 19-mg (0.0215-mmol) sample of $Os_3(CO)_{10}(\mu_3\text{-}S)$ was dissolved in 10 mL of CH_2Cl_2 and placed in a dropping funnel on a 100-mL 3-necked round-bottom flask that contained 100 mL of CH_2Cl_2 solvent. A 4.3-mg (0.039-mmol) sample of $Me_3NO{\cdot}2H_2O$ was dissolved in 10 mL of CH_2Cl_2 and placed in a second dropping funnel on the round-bottom flask. Both reagent solutions were slowly added to the reaction flask at 25 °C over a period of 10 min. There appeared to be a rapid reaction as evidenced by the disappearance of the IR absorptions of $Os_3(CO)_{10}(\mu_3\text{-}S)$. However, the yields of **1** on workups shortly after mixing are very low. After the mixture was stirred for several hours at 25 °C, the IR absorptions due to **1** became prominent. After a total of 20 h, the solvent was removed and the residue was chromatographed by TLC on silica gel with 30/70, CH_2Cl_2/hexanes solvent. Only one yellow band eluted. This yielded 8.3 mg (44%) of **1**. A considerable amount of green material remained on the baseline of the TLC plate and could not be eluted. IR for **1** (ν(CO) in hexane solvent, cm^{-1}): 2083 (m), 2046 (vs), 2024 (vs), 1997 (s), 1988 (s), 1970 (m), 1952 (m). ^1H NMR for **1** (ppm in $CDCl_3$): 3.34 (9 H, $N(CH_3)_3$), −3.55 (1 H, br, OH) −19.43 (1 H, OsH). Anal. Calcd for **1**: C, 14.60; H, 1.23; N, 1.54. Found: C, 15.54; H, 1.48; N, 1.50.

B. Reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with 1 equiv of $Me_3NO{\cdot}2H_2O$. A 15-mg (0.017-mmole sample of $Os_3(CO)_{10}(\mu_3\text{-}S)$ was dissolved in 5 mL of CH_2Cl_2 at 25 °C in a 100-mL round-bottom flask equipped with a dropping funnel. A 2-mg (0.018-mmol) sample of $Me_3NO{\cdot}2H_2O$ was dissolved in 20 mL of CH_2Cl_2 and was added to the solution of $Os_3(CO)_{10}(\mu_3\text{-}S)$ from the dropping funnel over a period of 20 min. The reaction solution was allowed to stir at 25 °C for 21 h. The solvent was removed in vacuo, and the residue was chromatographed by TLC on silica gel with 20/80 CH_2Cl_2/hexane solvent. In order of elution the following bands were observed: trace of an unidentified colorless (UV sensitive) band; 1.0 mg of yellow $Os_3(CO)_9(\mu_3\text{-}S)_2$;[6] 8.0 mg of unreacted $Os_3(CO)_{10}(\mu_3\text{-}S)$; 1.6 mg of orange **2** (11% yield, 23% yield based on $Os_3(CO)_{10}(\mu_3\text{-}S)$ consumed); 2.4 mg of yellow **1** (16% yield).

C. Reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with 1. An 8.0-mg (0.009-mmol) sample of $Os_3(CO)_{10}(\mu_3\text{-}S)$ and 8.0 mg (0.0089 mmol) of $Os_3(CO)_8(NMe_3)(\mu_3\text{-}S)(\mu\text{-}OH)(\mu\text{-}H)$ were dissolved at 25 °C in 25 mL of hexane in a 100-mL round-bottom flask equipped with a reflux condenser. The solution was refluxed for 5 h. The solvent was removed in vacuo, and the red residue was chromatographed by TLC on silica plates with a 40/60 CH_2Cl_2/hexane solvent mixture. A small yellow band of $Os_3(CO)_9(\mu_3\text{-}S)_2$ was eluted first. This was followed by unreacted $Os_3(CO)_{10}(\mu_3\text{-}S)$ (1.7 mg), orange **2** (6.5 mg (43%)), unreacted **1** (0.9 mg), and an unidentified red compound (1.1 mg). Anal. Calcd for **2**: C, 12.51; H, 0.12. Found: C, 12.67; H, 0.21. IR (νCO in hexane, cm^{-1}): 2122 (m), 2102 (m), 2082 (vs), 2071 (s), 2052 (w), 2040 (m), 2032 (w), 2017 (m), 2007 (s), 1992 (s), 1968 (m). ^1H NMR (in $CDCl_3$, ppm): −2.99 (s, OH) −13.31 (s, OsH).

Table I. Crystallographic Data for X-ray Diffraction Studies

	1	2
	(A) Crystal Data	
formula	$Os_3SO_9NC_{11}H_{11}$	$Os_6S_2O_{19}C_{18}H_2$
temp, °C	25 ± 3	23 ± 3
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.703 (1)	12.127 (3)
b, Å	13.269 (2)	14.009 (6)
c, Å	8.057 (2)	9.155 (3)
α deg	105.78 (1)	103.24 (3)
β deg	102.61 (1)	98.18 (2)
γ deg	77.80 (1)	90.00 (3)
V, Å^3	961.3 (5)	1498 (2)
M_r	903.88	1727.5
Z	2	2
ρ_{calcd}, g/cm^3	3.12	3.83
	(B) Measurement of Intensity Data	
radiation	Mo K$\bar{\alpha}$ (0.71073 Å)	Mo K$\bar{\alpha}$ (0.71073 Å)
monochromator	graphite	graphite
detector aperture, mm		
horizontal ($A + B \tan \theta$)		
A	3.0	2.0
B	1.2	1.0
vertical	4.0	2.0
cryst faces:	$011, 0\bar{1}\bar{1}, 010, 0\bar{1}0, 100, \bar{1}00, 10\bar{1}, \bar{1}01$	$001, 00\bar{1}, 1\bar{1}0, \bar{1}10, 110, \bar{1}\bar{1}0$
cryst size, mm	0.09 × 0.15 × 0.47	0.10 × 0.17 × 0.19
crystal orientation: direction; deg for ϕ axis	*a**; 23.7	[221]; 2.1
reflcns measd	$h,\pm k,\pm l$	$h,\pm k,\pm l$
max 2θ, deg	50	50
scan type	moving crystal–stationary counter	moving crystal–stationary counter
ω-scan width ($A + 0.347 \tan \theta$), deg	1.00	0.70
bkgd	$^1/_4$ addnl scan at each end of scan	$^1/_4$ addnl scan at each end of scan
ω-scan rate (variable)		
max, deg/min	10.0	20.0
min, deg/min	1.5	2.5
no. of reflcns measd	3350	5254
no. of data used ($F^2 \geq 3.0\sigma(F^2)$)	2458	3832
	(C) Treatment of Data	
abs corr		
coefficient, cm^{-1}	199.5	256.1
grid	18 × 8 × 10	12 × 10 × 12
transmission coeff		
max	0.254	0.131
min	0.023	0.049
P factor	0.04	0.04
final residuals		
R_F	0.034	0.035
R_w	0.043	0.042
no. of variables	211	221
esd of unit wt observn	1.55	1.21
largest shift/error value of final cycle	0.04	0.06
largest peak in final difference Fourier, e/Å^3	1.54	1.68

D. Crystallographic Analyses. Yellow and red crystals of **1** and **2**, respectively, were grown by slow evaporation of solvent from benzene solutions at 5 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements on **1** were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer at the University of South Carolina. Diffraction measurements on **2** were performed on a CAD-4 diffractometer at the Molecular Structure Corp., College Station, TX. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a VAX 11/782 computer by using the Enraf-Nonius SDP program library. Absorption corrections of a

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Table II. Positional and Thermal Parameters for $Os_3(CO)_8(NMe_3)(\mu\text{-}OH)(\mu_3\text{-}S)(\mu\text{-}H)$ (**1**)[a]

atom	x	y	z	B, Å^2
Os(1)	0.45468 (5)	0.21397 (4)	0.25369 (6)	2.80 (1)
Os(2)	0.68782 (6)	0.15592 (4)	0.52400 (6)	3.05 (1)
Os(3)	0.79372 (5)	0.26165 (4)	0.33590 (6)	3.00 (1)
S	0.5928 (4)	0.3302 (3)	0.4871 (5)	3.52 (8)
N	0.336 (1)	0.3424 (9)	0.124 (2)	4.4 (3)
C(1)	0.373 (1)	0.1044 (9)	0.086 (2)	3.5 (3)
O(1)	0.319 (1)	0.375 (7)	−0.007 (1)	4.6 (3)
C(2)	0.320 (2)	0.225 (1)	0.392 (2)	4.5 (4)
O(2)	0.241 (1)	0.230 (1)	0.484 (2)	7.3 (4)
C(3)	0.830 (2)	0.187 (1)	0.729 (2)	4.7 (4)
O(3)	0.907 (1)	0.205 (1)	0.853 (1)	7.1 (4)
C(4)	0.570 (2)	0.119 (1)	0.655 (2)	4.6 (4)
O(4)	0.505 (1)	0.0936 (9)	0.731 (1)	6.2 (3)
C(5)	0.798 (1)	0.018 (1)	0.438 (2)	3.5 (3)
O(5)	0.862 (1)	−0.0592 (8)	0.385 (1)	5.7 (3)
C(6)	0.809 (2)	0.370 (1)	0.224 (2)	5.1 (4)
O(6)	0.829 (1)	0.4299 (9)	0.162 (2)	8.2 (4)
C(7)	0.936 (1)	0.151 (1)	0.245 (2)	3.8 (3)
O(7)	1.025 (1)	0.085 (1)	0.194 (1)	6.2 (3)
C(8)	0.926 (1)	0.316 (1)	0.529 (2)	4.1 (4)
O(8)	0.994 (1)	0.356 (1)	0.653 (2)	6.7 (4)
O(20)	0.6254 (8)	0.2084 (6)	0.124 (1)	2.9 (2)
C(9)	0.421 (3)	0.416 (2)	0.118 (3)	10.0 (7)*
C(10)	0.267 (3)	0.300 (2)	−0.051 (3)	10.8 (8)*
C(11)	0.230 (4)	0.411 (3)	0.221 (5)	15 (1)*
H(91)	0.4699	0.4482	0.2365	4*
H(92)	0.4924	0.3874	0.0472	4*
H(93)	0.3628	0.4781	0.0761	4*
H(101)	0.2056	0.2512	−0.0542	4*
H(102)	0.2021	0.3583	−0.1004	4*
H(103)	0.3317	0.2676	−0.1294	4*
H(111)	0.2773	0.4452	0.3452	4*
H(112)	0.1875	0.4762	0.1758	4*
H(113)	0.1562	0.3822	0.2348	4*

[a] B values denoted with an asterisk are for isotropically refined atoms. Hydrogen atoms were not refined. B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table III. Interatomic Distances (Å) with Esd's for $Os_3(CO)_8(NMe_3)(\mu\text{-}OH)(\mu_3\text{-}S)(\mu\text{-}H)$ (**1**)

Os(1)–Os(2)	2.9018 (6)	Os(3)–C(7)	1.899 (13)
Os(1)–S	2.430 (3)	Os(3)–C(8)	1.872 (12)
Os(1)–N	2.221 (9)	Os(3)–O(20)	2.165 (7)
Os(1)–C(1)	1.876 (12)	N–C(9)	1.43 (2)
Os(1)–C(2)	1.854 (14)	N–C(10)	1.44 (3)
Os(1)–O(20)	2.119 (7)	N–C(11)	1.44 (4)
Os(2)–Os(3)	2.7869 (6)	C(1)–O(1)	1.134 (13)
Os(2)–S	2.375 (3)	C(2)–O(2)	1.161 (15)
Os(2)–C(3)	1.918 (14)	C(3)–O(3)	1.114 (15)
Os(2)–C(4)	1.926 (15)	C(4)–O(4)	1.118 (15)
Os(2)–C(5)	1.947 (13)	C(5)–O(5)	1.105 (14)
Os(3)–S	2.408 (3)	C(6)–O(6)	1.121 (14)
Os(3)–C(6)	1.934 (13)	C(7)–O(7)	1.148 (14)
Os(1)···Os(3)	3.3707 (6)	C(8)–O(8)	1.130 (15)

Table IV. Interatomic Angles (deg) with Esd's for $Os_3(CO)_8(NMe_3)(\mu\text{-}OH)(\mu_3\text{-}S)(\mu\text{-}H)$ (**1**)

Os(2)–Os(1)–S	51.85 (7)	Os(2)–Os(3)–C(6)	160.1 (4)
Os(2)–Os(1)–N	145.9 (3)	Os(2)–Os(3)–C(7)	99.2 (4)
Os(2)–Os(1)–C(1)	118.0 (3)	Os(2)–Os(3)–C(8)	93.2 (4)
Os(2)–Os(1)–C(2)	91.3 (4)	Os(2)–Os(3)–O(20)	85.0 (2)
Os(2)–Os(1)–O(20)	82.7 (2)	S–Os(3)–C(6)	106.4 (5)
S–Os(1)–N	94.5 (3)	S–Os(3)–C(7)	152.6 (4)
S–Os(1)–C(1)	169.7 (3)	S–Os(3)–C(8)	94.0 (4)
S–Os(1)–C(2)	91.8 (4)	S–Os(3)–O(20)	81.1 (2)
S–Os(1)–O(20)	81.5 (2)	C(6)–Os(3)–C(7)	100.4 (6)
N–Os(1)–C(1)	95.4 (4)	C(6)–Os(3)–C(8)	90.0 (6)
N–Os(1)–C(2)	95.9 (5)	C(6)–Os(3)–O(20)	90.1 (4)
N–Os(1)–O(20)	87.0 (4)	C(7)–Os(3)––C(8)	91.7 (5)
C(1)–Os(1)–C(2)	90.0 (6)	C(7)–Os(3)–O(20)	93.4 (4)
C(1)–Os(1)–O(20)	96.2 (4)	C(8)–Os(3)–O(20)	174.9 (4)
C(2)–Os(1)–O(20)	172.9 (4)	Os(1)–S–Os(2)	74.57 (9)
Os(1)–Os(2)–Os(3)	72.49 (2)	Os(1)–S–Os(3)	88.3 (1)
Os(1)–Os(2)–S	53.57 (7)	Os(2)–S–Os(3)	71.27 (8)
Os(1)–Os(2)–C(3)	153.5 (4)	Os(1)–N–C(9)	114 (1)
Os(1)–Os(2)–C(4)	95.9 (4)	Os(1)–N–C(10)	112 (1)
Os(1)–Os(2)–C(5)	111.1 (3)	Os(1)–N–C(11)	112 (1)
Os(3)–Os(2)–S	54.91 (8)	C(9)–N–C(10)	109 (2)
Os(3)–Os(2)–C(3)	94.1 (4)	C(9)–N–C(11)	101 (2)
Os(3)–Os(2)–C(4)	163.0 (4)	C(10)–N–C(11)	108 (2)
Os(3)–Os(2)–C(5)	95.2 (3)	Os(1)–C(1)–O(1)	176 (1)
S–Os(2)–C(3)	100.0 (4)	Os(1)–C(2)–O(2)	177 (1)
S–Os(2)–C(4)	108.2 (4)	Os(2)–C(3)–O(3)	176 (1)
S–Os(2)–C(5)	148.1 (3)	Os(2)–C(4)–O(4)	177 (1)
C(3)–Os(2)–C(4)	91.3 (5)	Os(2)–C(5)–O(5)	177 (1)
C(3)–Os(2)–C(5)	92.4 (5)	Os(3)–C(6)–O(6)	174 (1)
C(4)–Os(2)–C(5)	100.7 (5)	Os(3)–C(7)–O(7)	178 (1)
Os(2)–Os(3)–S	53.81 (7)	Os(3)–C(8)–O(8)	172 (1)
		Os(1)–O(20)–Os(3)	103.7 (3)

Gaussian integration type were done for each structure. Neutral-atom scattering factors were calculated by the standard procedures.[7a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[7b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Both compounds crystallized in the triclinic crystal system. Space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of both structures. The structures were solved by a combination of Patterson and difference Fourier techniques. Except for the methyl carbon atoms all the non-hydrogen atoms in **1** were refined with anisotropic thermal parameters. The hydrogen atom positions on the methyl carbon atoms were calculated by assuming idealized geometry. These positions were not refined. For **2** only the atoms heavier than oxygen were refined anisotropically. The hydroxyl hydrogen atom was not observed in the structure of **1** and was subsequently ignored in the calculations. A peak of approximately the size of a hydrogen was observed at 0.85 Å from the hydroxyl oxygen atom in **2**. This was assumed to be the hydroxyl hydrogen atom and its contribution was added to the structure factor calculation, but it was not refined. Error analyses were calculated from the inverse matrix obtained in the final cycle of refinement for each structure. See the supplementary material for the tables of structure factor amplitudes and the values of the anisotropic thermal parameters.

Results

A reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with 2 equiv of $Me_3NO\cdot 2H_2O$ appeared to occur rapidly at 25 °C; however, the yellow product identified as $Os_3(CO)_8NMe_3(\mu\text{-}OH)(\mu_3\text{-}S)(\mu\text{-}H)$ (**1**, vide infra) was formed very slowly. After a period of 20 h, compound **1** was obtained in 44% yield. Attempts to isolate suspected intermediates were unsuccessful. Compound **1** was characterized by IR and ^1H NMR spectroscopies and by elemental and single-crystal X-ray diffraction analyses. Compound **1** contains a bridging hydroxyl ligand, which shows a characteristic IR absorption at 3622 cm^{-1} and a broad ^1H NMR signal at −3.55 ppm. When CD_3CD_2OD was added to the NMR sample of **1**, the resonance at −3.55 disappeared.

When $Os_3(CO)_{10}(\mu_3\text{-}S)$ was allowed to react with 1 equiv of $Me_3NO\cdot 2H_2O$ for 21 h, the yield of **1** decreased markedly to 16% and over half of the starting cluster was recovered. A new orange compound identified as $Os_6(CO)_{18}(\mu\text{-}OH)(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)$ (**2**) was isolated in 11% yield. Compound **2** also contains a bridging hydroxyl ligand. The IR absorption frequency of this ligand was not observed; however, its characteristic ^1H NMR signal was observed at −2.99 ppm.

Compound **2** was believed to be a product of the coupling of **1** with $Os_3(CO)_{10}(\mu_3\text{-}S)$, and this was confirmed by an independent synthesis. When 1 equiv of **1** was reacted with 1 equiv of $Os_3(CO)_{10}(\mu_3\text{-}S)$ for 5 h in refluxing hexane, compound **2** was obtained in 43% yield.

Description of the Structures

An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. Final fractional atomic coordinates are given in Table

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(7) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

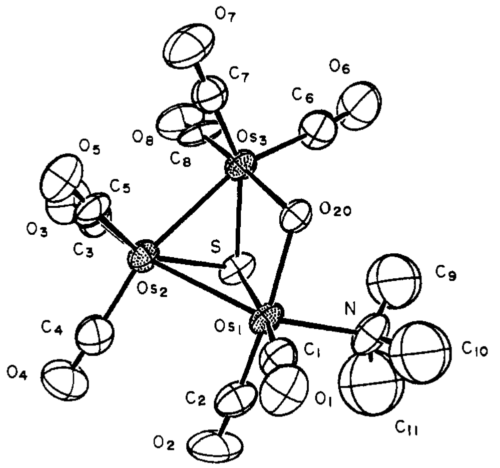

Figure 1. ORTEP diagram of $Os_3(CO)_8(NMe_3)(\mu\text{-}OH)(\mu_3\text{-}S)(\mu\text{-}H)$ (**1**) showing 50% probability thermal ellipsoids.

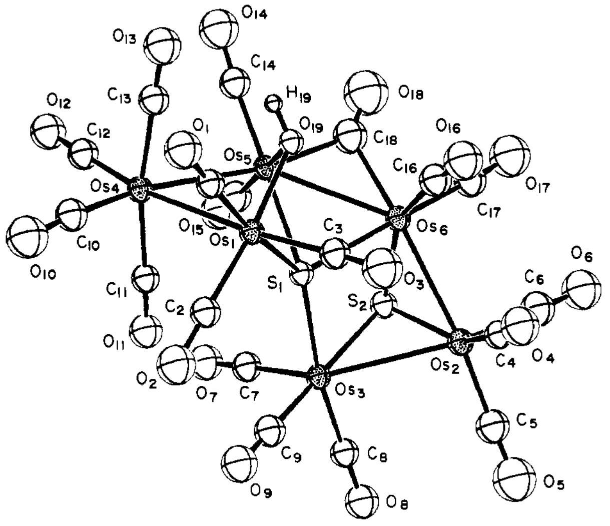

Figure 2. ORTEP diagram of $Os_6(CO)_{18}(\mu\text{-}OH)(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)$ (**2**) showing 50% probability thermal ellipsoids.

II, and interatomic distances and angles are listed in Tables III and IV, , respectively. The molecule consists of an open triangular clusters of three osmium atoms. The Os(2)–Os(3) bonding distance of 2.7869 (6) Å is about 0.025 Å shorter the Os–Os bonding distances found in the bis(sulfido)-bridged compound $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**3**), which contains a similarly arranged open cluster.[6] The Os(1)–Os(2) distance at 2.9018 (6) Å is significantly longer than the Os(2)–Os(3) distance but is still well within the normal bonding range. The Os(1)···Os(3) separation of 3.3707 (6) Å probably contains very little direct bonding. Although this distance is considerably shorter than the nonbonding interaction in **3**, which is 3.662 (1) Å, the shorter distance in **1** could be attributed to the smaller size of the hydroxyl ligand that bridges Os(1) and Os(3). The compound $Os_3(CO)_{10}(\mu\text{-}OMe)_2$ contains two methoxyl ligands bridging a nonbonding osmium–osmium interaction that is contracted to 3.078 (3) Å.[8] Compound **1** contains one triply bridging sulfido ligand. The osmium–sulfur distances span a significant range, 2.375 (3)–2.430 (3) Å, but similar distances were observed in **3**. Compound **1** contains one bridging hydrido ligand, which was verified by a ^1H NMR resonance at −19.43 ppm. This ligand was not located crystallographically, but it is believed to bridge the elongated Os(1)–Os(2) metal–metal bond.[9] A hydroxyl ligand bridges atoms Os(1) and Os(3). The Os(1)–O(20) and Os(3)–O(20) distances of 2.119 (7) and 2.165 (7) Å, respectively, are similar in length. Hydroxyl ligands have been structurally characterized in the osmium clusters $Os_4(CO)_{12}(\mu\text{-}OH)(\mu\text{-}H)_4{}^+$ [10] and $Os_3(CO)_9(\mu\text{-}C{=}C{=}CPh_2)(\mu\text{-}OH)(\mu\text{-}H)$,[11] and show Os–O bonding distances similar to those in **1**. The hydroxyl hydrogen atom was not observed crystallographically. The molecule contains eight linear terminal carbonyl ligands arranged such that Os(2) and Os(3) each have three and Os(1) has only two. Os(1) contains a trimethylamine ligand. The Os(1)–N distance of 2.221 (9) Å is statistically equal to the Os–N distance of 2.22 (2) Å observed in the trimethylamine complex $Os_3(CO)_9(NO)_2(NMe_3)$.[4]

Table V. Positional and Isotropic Thermal Parameters for $Os_6(CO)_{18}(\mu\text{-}OH)(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)$ (**2**)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Os(1)	0.45599 (5)	0.83592 (4)	0.19561 (6)	1.92 (1)
Os(2)	0.00677 (5)	0.76642 (5)	−0.06414 (7)	2.32 (1)
Os(3)	0.17319 (5)	0.61236 (4)	−0.05927 (7)	2.05 (1)
Os(4)	0.53290 (5)	0.70604 (4)	0.38669 (7)	2.15 (1)
Os(5)	0.30650 (5)	0.75578 (4)	0.41072 (6)	1.97 (1)
Os(6)	0.11427 (5)	0.81644 (5)	0.23551 (7)	2.11 (1)
S(1)	0.2775 (3)	0.7400 (3)	0.1423 (4)	1.98 (8)
S(2)	0.0288 (3)	0.6562 (3)	0.0991 (5)	2.60 (8)
C(1)	0.588 (1)	0.911 (1)	0.271 (2)	2.4 (3)*
O(1)	0.669 (1)	0.9575 (9)	0.325 (1)	4.1 (3)*
C(2)	0.525 (1)	0.765 (1)	0.038 (2)	2.8 (3)*
O(2)	0.565 (1)	0.718 (1)	−0.063 (1)	4.7 (3)*
C(3)	0.393 (1)	0.927 (1)	0.084 (2)	2.8 (3)*
O(3)	0.367 (1)	0.985 (1)	0.012 (1)	4.8 (3)*
C(4)	0.055 (1)	0.885 (1)	−0.110 (2)	2.5 (3)*
O(4)	0.085 (1)	0.957 (1)	−0.127 (1)	4.7 (3)*
C(5)	−0.072 (2)	0.707 (1)	−0.256 (2)	3.8 (4)*
O(5)	−0.118 (1)	0.677 (1)	−0.380 (2)	6.5 (4)*
C(6)	−0.130 (2)	0.819 (1)	−0.014 (2)	4.1 (4)*
O(6)	−0.217 (1)	0.845 (1)	0.018 (2)	5.5 (3)*
C(7)	0.212 (1)	0.502 (1)	0.029 (2)	3.0 (3)*
O(7)	0.230 (1)	0.432 (1)	0.080 (1)	4.4 (3)*
C(8)	0.080 (1)	0.530 (1)	−0.221 (2)	2.8 (3)*
O(8)	0.025 (1)	0.4839 (9)	−0.329 (1)	4.0 (3)*
C(9)	0.291 (1)	0.593 (1)	−0.180 (2)	3.2 (3)*
O(9)	0.361 (1)	0.582 (1)	−0.250 (1)	4.3 (3)*
C(10)	0.675 (1)	0.696 (1)	0.329 (2)	3.2 (3)*
O(10)	0.760 (1)	0.683 (1)	0.283 (2)	5.3 (3)*
C(11)	0.472 (1)	0.602 (1)	0.217 (2)	2.6 (3)*
O(11)	0.439 (1)	0.5372 (9)	0.116 (1)	3.8 (3)*
C(12)	0.557 (1)	0.627 (1)	0.531 (2)	3.1 (3)*
O(12)	0.574 (1)	0.580 (1)	0.623 (1)	4.3 (3)*
C(13)	0.570 (1)	0.825 (1)	0.543 (2)	2.9 (3)*
O(13)	0.591 (1)	0.895 (1)	0.635 (1)	4.4 (3)*
C(14)	0.351 (1)	0.786 (1)	0.619 (2)	3.2 (3)*
O(14)	0.373 (1)	0.807 (1)	0.752 (2)	5.4 (3)*
C(15)	0.259 (1)	0.630 (1)	0.413 (2)	3.3 (3)*
O(15)	0.229 (1)	0.553 (1)	0.420 (1)	4.6 (3)*
C(16)	0.156 (1)	0.948 (1)	0.253 (2)	3.3 (3)*
O(16)	0.173 (1)	1.027 (1)	0.253 (1)	4.7 (3)*
C(17)	−0.020 (2)	0.863 (1)	0.305 (2)	3.5 (4)*
O(17)	−0.101 (1)	0.888 (1)	0.355 (2)	6.0 (4)*
C(18)	0.154 (2)	0.806 (1)	0.463 (2)	4.0 (4)*
O(18)	0.108 (1)	0.825 (1)	0.570 (2)	7.0 (4)*
O(19)	0.3778 (8)	0.8915 (7)	0.390 (1)	2.0 (2)*
H(19)	0.4179	0.9179	0.4726	4*

[a] *B* values for isotropically refined atoms are denoted with an asterisk. Hydrogen atoms were not refined. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

An ORTEP drawing of the molecular structure of **2** is shown in Figure 2. Final fractional atomic coordinates are given in Table V. Interatomic distances and selected interatomic angles are given in Tables VI and VII, respectively. The most interesting feature of this cluster is the arrangement of metal atoms, which consists

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(10) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Zuccaro, C. *J. Chem. Soc., Dalton Trans.* **1980**, 716.

(11) Aime, S.; Deeming, A. J.; Hursthouse, M. B.; Backer-Dirks, J. D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1625.

Table VI. Interatomic Distances (Å) with Esd's for $Os_6(CO)_{18}(\mu\text{-}OH)(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)$ (**2**)

Os(1)–Os(4)	2.871 (1)	Os(5)–(18)	2.06 (2)
Os(1)–S(1)	2.472 (3)	Os(5)–O(19)	2.146 (9)
Os(1)–C(1)	1.864 (15)	Os(6)–S(1)	2.422 (4)
Os(1)–C(2)	1.858 (15)	Os(6)–S(2)	2.452 (4)
Os(1)–C(3)	1.91 (2)	Os(6)–C(16)	1.87 (2)
Os(1)–O(19)	2.124 (9)	Os(6)–C(17)	1.90 (2)
Os(1)···Os(5)	3.231 (1)	Os(6)–C(18)	2.11 (2)
Os(2)–Os(3)	2.962 (1)	C(1)–O(1)	1.16 (2)
Os(2)–Os(6)	2.795 (1)	C(2)–O(2)	1.18 (2)
Os(2)–S(2)	2.374 (4)	C(3)–O(3)	1.17 (2)
Os(2)–C(4)	1.910 (15)	C(4)–O(4)	1.13 (2)
Os(2)–C(5)	1.88 (2)	C(5)–O(5)	1.17 (2)
Os(2)–C(6)	1.89 (2)	C(6)–O(6)	1.17 (2)
Os(3)–S(1)	2.453 (3)	C(7)–O(7)	1.18 (2)
Os(3)–S(2)	2.422 (4)	C(8)–O(8)	1.16 (2)
Os(3)–C(7)	1.93 (2)	C(9)–O(9)	1.13 (2)
Os(3)–C(8)	1.876 (15)	C(10)–O(10)	1.16 (2)
Os(3)–C(9)	1.91 (2)	C(11)–O(11)	1.16 (2)
Os(4)–Os(5)	2.861 (1)	C(12)–O(12)	1.18 (2)
Os(4)–C(10)	1.87 (2)	C(13)–O(13)	1.14 (2)
Os(4)–C(11)	1.932 (15)	C(14)–O(14)	1.17 (2)
Os(4)–C(12)	1.90 (2)	C(15)–O(15)	1.16 (2)
Os(4)–C(13)	1.94 (2)	C(16)–O(16)	1.13 (2)
Os(5)–Os(6)	2.881 (1)	C(17)–O(17)	1.16 (2)
Os(5)–S(1)	2.391 (3)	C(18)–O(18)	1.18 (2)
Os(5)–C(14)	1.86 (2)	O(19)–H(19)	0.85
Os(5)–C(15)	1.85 (2)		

of a chain of six osmium atoms Os(1)–Os(4)–Os(5)–Os(6)–Os(2)–Os(3) that folds back upon itself such that the termini of the chain, Os(1) and Os(3), which are both bonded to the bridging sulfido ligand S(1), are only 4.625 (1) Å apart. Compound **2** is very similar to the compound $Os_6(CO)_{18}(\mu_4\text{-}S)(\mu\text{-}H)_2$ (**4**) reported previously,[12] except that **2** contains a bridging hydroxyl ligand across the Os(1)···Os(5) separation where **4** contained a bridging hydrido ligand. The osmium–osmium bond distances in **2** range from 2.795 (1) to 2.962 (1) Å and correspond individually very closely to those observed in **4**. The exception to this is the Os(1)···Os(5) nonbonding separation of 3.231 (1) Å in **2**, which is a hydrido-bridged separation of 2.945 (1) Å in **4**.[13] Compound **2** contains a quadruply bridging sulfido ligand S(1) that is bonded to Os(1), Os(3), Os(5), and Os(6) in a distorted tetrahedral geometry. This ligand serves as a six-electron donor. The sulfido ligand, S(2), is a triple bridge that serves as a four-electron donor. The osmium-sulfur distances to both sulfido ligands span considerable ranges, 2.391 (3)–2.472 (3) Å for S(1), and 2.374 (4)–2.452 (4) Å for S(2), but these distances also correspond very closely to those observed in **4**. Unlike **4** compound **2** contains a bridging hydroxyl ligand across the atoms Os(1) and Os(5). The Os(1)–O(19) and Os(5)–O(19) distances are 2.124 (9) and 2.146 (9) Å, respectively, and are very similar to those observed in **1** (vide supra). A peak of appropriate size and position was "observed" near the hydroxyl oxygen atom O(19) in a difference Fourier analysis and was assigned as the hydroxyl hydrogen atom. Compound **2** contains one hydrido ligand, with a ^1H NMR resonance at −13.31 ppm. This ligand was not observed crystallographically, but is believed to serve as a bridge across the long Os(2)–Os(3) bond.[9] There are 17 linear terminal carbonyl ligands distributed among the six metal atoms as shown in Figure 2, and there is one symmetrical bridging carbonyl ligand, C(18)–O(18), that spans the Os(5)–Os(6) bond.

Table VII. Interatomic Angles (deg) with Esd's for $Os_6(CO)_{18}(\mu\text{-}OH)(\mu_4\text{-}S)(\mu_3\text{-}S)(\mu\text{-}H)$ (**2**)

Os(4)–Os(1)–S(1)	85.93 (8)	Os(4)–Os(5)–O(19)	78.3 (2)
Os(4)–Os(1)–C(1)	88.1 (4)	Os(6)–Os(5)–S(1)	53.73 (8)
Os(4)–Os(1)–C(2)	91.7 (5)	Os(6)–Os(5)–C(14)	129.9 (5)
Os(4)–Os(1)–C(3)	173.4 (5)	Os(6)–Os(5)–C(15)	100.5 (5)
Os(4)–Os(1)–O(19)	78.4 (2)	Os(6)–Os(5)–C(18)	47.0 (5)
S(1)–Os(1)–C(1)	170.0 (4)	Os(6)–Os(5)–O(19)	82.7 (2)
S(1)–Os(1)–C(2)	98.9 (5)	S(1)–Os(5)–C(14)	168.7 (5)
S(1)–Os(1)–C(3)	91.1 (5)	S(1)–Os(5)–C(15)	98.5 (5)
S(1)–Os(1)–O(19)	76.2 (3)	S(1)–Os(5)–C(18)	100.4 (5)
C(1)–Os(1)–C(2)	89.4 (7)	S(1)–Os(5)–O(19)	77.6 (2)
C(1)–Os(1)–C(3)	93.9 (6)	C(14)–Os(5)–C(15)	91.3 (7)
C(1)–Os(1)–O(19)	94.7 (5)	C(14)–Os(5)–C(18)	85.2 (7)
C(2)–Os(1)–C(3)	94.6 (7)	C(14)–Os(5)–O(19)	91.9 (6)
C(2)–Os(1)–O(19)	169.1 (5)	C(15)–Os(5)–C(18)	89.1 (7)
C(3)–Os(1)–O(19)	95.2 (5)	C(15)–Os(5)–O(19)	172.3 (6)
Os(3)–Os(2)–Os(6)	77.46 (2)	C(18)–Os(5)–O(19)	98.2 (6)
Os(3)–Os(2)–S(2)	52.6 (1)	Os(2)–Os(6)–Os(5)	137.23 (3)
Os(3)–Os(2)–C(4)	116.6 (4)	Os(2)–Os(6)–S(1)	87.33 (8)
Os(3)–Os(2)–C(5)	95.9 (5)	Os(2)–Os(6)–S(2)	53.32 (9)
Os(3)–Os(2)–C(6)	149.5 (6)	Os(2)–Os(6)–C(16)	100.8 (5)
Os(6)–Os(2)–S(2)	55.91 (9)	Os(2)–Os(6)–C(17)	90.9 (5)
Os(6)–Os(2)–C(4)	94.0 (4)	Os(2)–Os(6)–C(18)	157.0 (5)
Os(6)–Os(2)–C(5)	167.9 (5)	Os(5)–Os(6)–S(1)	52.74 (8)
Os(6)–Os(2)–C(6)	93.9 (5)	Os(5)–Os(6)–S(2)	100.34 (9)
S(2)–Os(2)–C(4)	148.3 (4)	Os(5)–Os(6)–C(16)	100.0 (5)
S(2)–Os(2)–C(5)	112.0 (6)	Os(5)–Os(6)–C(17)	127.1 (5)
S(2)–Os(2)–C(6)	98.3 (6)	Os(5)–Os(6)–C(18)	45.6 (5)
C(4)–Os(2)–C(5)	98.1 (7)	S(1)–Os(6)–S(2)	81.2 (1)
C(4)–Os(2)–C(6)	92.9 (7)	S(1)–Os(6)–C(16)	98.7 (5)
C(5)—Os(2)–C(6)	86.7 (8)	S(1)–Os(6)–C(17)	174.1 (5)
Os(2)–Os(3)–S(1)	83.11 (8)	S(1)–Os(6)–C(18)	98.0 (5)
Os(2)–Os(3)–S(2)	51.14 (9)	S(2)–Os(6)–C(16)	154.1 (5)
Os(2)–Os(3)–C(7)	142.1 (5)	S(2)–Os(6)–C(17)	93.2 (5)
Os(2)–Os(3)–C(8)	88.5 (5)	S(2)–Os(6)–C(18)	105.2 (5)
Os(2)–Os(3)–C(9)	124.2 (5)	C(16)–Os(6)–C(17)	87.1 (7)
S(1)–Os(3)–S(2)	81.2 (1)	C(16)–Os(6)–C(18)	100.5 (7)
S(1)–Os(3)–C(7)	97.5 (5)	C(17)–Os(6)–C(18)	81.5 (7)
S(1)–Os(3)–C(8)	171.2 (5)	Os(1)–S(1)–Os(3)	139.4 (2)
S(1)–Os(3)–C(9)	94.0 (5)	Os(1)–S(1)–Os(5)	83.3 (1)
S(2)–Os(3)–C(7)	91.3 (5)	Os(1)–S(1)–Os(6)	119.4 (1)
S(2)–Os(3)–C(8)	95.4 (5)	Os(3)–S(1)–Os(5)	129.6 (2)
S(2)–Os(3)–C(9)	173.5 (5)	Os(3)–S(1)–Os(6)	95.4 (1)
C(7)–Os(3)–C(8)	90.6 (7)	Os(5)–S(1)–Os(6)	73.5 (1)
C(7)–Os(3)–C(9)	93.7 (7)	Os(2)–S(2)–Os(3)	76.3 (1)
C(8)–Os(3)–C(9)	88.7 (7)	Os(2)–S(2)–Os(6)	70.98 (1)
Os(1)–Os(4)–Os(5)	68.64 (2)	Os(3)–S(2)–Os(6)	95.4 (1)
Os(1)–Os(4)–C(10)	94.6 (5)	Os(1)–O(19)–Os(5)	98.3 (4)
Os(1)–Os(4)–C(11)	85.6 (4)	Os(1)–C(1)–O(1)	177 (1)
Os(1)–Os(4)–C(12)	168.2 (5)	Os(1)–C(2)–O(2)	178 (2)
Os(1)–Os(4)–C(13)	85.1 (5)	Os(1)–C(3)–O(3)	172 (1)
Os(5)–Os(4)–C(10)	163.2 (5)	Os(2)–C(4)–O(4)	175 (1)
Os(5)–Os(4)–C(11)	85.8 (4)	Os(2)–C(5)–O(5)	174 (2)
Os(5)–Os(4)–C(12)	99.8 (5)	Os(2)–C(6)–O(6)	176 (2)
Os(5)–Os(4)–C(13)	85.1 (5)	Os(3)–C(7)–O(7)	176 (1)
C(10)–Os(4)–C(11	92.3 (7)	Os(3)–C(8)–O(8)	175 (1)
C(10)–Os(4)–C(12)	97.0 (7)	Os(3)–C(9)–O(9)	179 (1)
C(10)–Os(4)–C(13)	94.6 (7)	Os(4)–C(10)–O(10)	174 (2)
C(11)–Os(4)–C(12)	96.3 (7)	Os(4)–C(11)–O(11)	177 (1)
C(11)–Os(4)–C(13)	168.8 (6)	Os(4)–C(12)–O(12)	178 (1)
C(12)–Os(4)–C(13)	91.6 (7)	Os(4)–C(13)–O(13)	179 (2)
Os(4)–Os(5)–Os(6)	139.96 (3)	Os(5)–C(14)–O(14)	175 (2)
Os(4)–Os(5)–S(1)	87.69 (9)	Os(5)–C(15)–O(15)	178 (2)
Os(4)–Os(5)–C(14)	85.9 (5)	Os(6)–C(16)–O(16)	173 (2)
Os(4)–Os(5)–C(15)	95.0 (5)	Os(6)–C(17)–O(17)	175 (2)
Os(4)–Os(5)–C(18)	170.4 (5)	Os(5)–C(18)–O(18)	138 (2)
		Os(6)–C(18)–O(18)	134 (2)

Discussion

The reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with $Me_3NO{\cdot}2H_2O$ leads to the removal of 2 mol of CO and the addition of 1 mol of Me_3N and 1 mol of H_2O, which is transformed into hydroxyl and hydrido ligands. There is a net loss of four ligand electrons from the two expelled carbonyl ligands and a gain of six electrons from the addition of Me_3N, OH, and H ligands. As a consequence, in order to preserve 18-electron configurations on all the metal atoms, the closed cluster structure observed in $Os_3(CO)_{10}(\mu_3\text{-}S)$ is converted into the open cluster observed in **1** through the cleavage of one metal–metal bond.

Since 2 mol of Me_3NO are presumably consumed in the reaction with $Os_3(CO)_{10}(\mu_3\text{-}S)$, some $Os_3(CO)_{10}(\mu_3\text{-}S)$ remains when the reaction is conducted with a 1/1 stoichiometry. We have shown previously that $Os_3(CO)_{10}(\mu_3\text{-}S)$ readily engages in con-

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densation reactions to yield higher nuclearity clusters.[5,13] This apparently occurred in these solutions also, and 1 mol of **1** combined with 1 mol of $Os_3(CO)_{10}(\mu_3\text{-}S)$ to yield **2**. This was supported by the results of an independent reaction of **1** with $Os_3(CO)_{10}(\mu_3\text{-}S)$, which gave **2** in 43% yield.

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Registry No. **1**, 101032-85-3; **2**, 101032-86-4; $Os_3(CO)_{10}(\mu_3\text{-}S)$, 93426-79-0; $Me_3NO{\cdot}2H_2O$, 62637-93-8.

Supplementary Material Available: Tables of structure factor amplitudes and general temperature factor expressions for both structures (67 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Crystal Structure of a Hexaaza Macrocyclic Complex of Lutetium(III)

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A compound of formula $Lu(C_{22}H_{26}N_6)(CH_3COO)(OH)(ClO_4)(CH_3OH)(H_2O)_{0.5}$ was obtained by the metal-templated cyclic condensation of 1,2-diaminoethane with 2,6-diacetylpyridine, and its structure was determined by a single-crystal X-ray diffraction analysis. The compound crystallized in the triclinic space group $P\bar{1}$ with $Z = 2$, in a unit cell having $a = 13.051$ (3) Å, $b = 11.351$ (2) Å, $c = 11.400$ (2) Å, $\alpha = 108.95$ (3)°, $\beta = 104.63$ (3)°, and $\gamma = 100.40$ (3)°. Its structure was ionic, with the complex cation consisting of 9-coordinate Lu(III) linked to the six N-donor atoms of the $C_{22}H_{26}N_6$ macrocycle, to a bidentate chelating acetate, and to either a water or methanol molecule. Noncoordinated OH^- and ClO_4^- balanced the residual cationic charges; clathrated methanol was also present. Thermogravimetric measurements and NMR (^1H and ^{13}C) spectra showed the compound to be thermally stable in the solid state as well as inert toward metal release in solution.

Introduction

It was recently established that the trivalent lanthanides can act as templating agents in the formation of polyaza macrocyclic systems of appropriate cavity size. Several series of complexes containing the hexaaza hexadentate, 18-member macrocyclic cations L_A and L_B (Figure 1)[1–6] were obtained with all elements from lanthanum to lutetium (except radioactive promethium) in the presence of O-donor counterions. Closely related lanthanide derivatives were described for a dioxatetraaza tetradentate analogue of L_A containing two furan rings instead of two pyridines. Complexation of the hexaaza, 14-member macrocycle L_C acting as a tetradentate ligand was reported for the smaller lanthanides, terbium to lutetium.[7] Compounds of La(III), Ce(III), and Nd(III) nitrates with the rigid, 18-member macrocyclic system obtained from the (2 + 2) Schiff-base condensation of 1,2-diaminoethane and 2,6-diacetylpyridine were also described.[8,9] Crystal structures were reported for two polyaza macrocyclic lanthanide complexes: A lanthanum(III) species, $[LaL_A(NO_3)_2]$, was found to be 12-coordinate,[1] and a samarium(III) species, $[SmL_B(OH)(NO_3)H_2O]NO_3{\cdot}2CH_3OH$, was 10-coordinate;[2] both contained bidentate chelating NO_3^- groups. However limited, this evidence suggested that the decrease in ionic radii along the $4f^n$ series, while not drastically affecting the ability of the metal ions to function as templating agents and to complex with the resulting macrocyclic ligands, may tend to lower their total coordination number.

The structural data for La(III) and Sm(III)—two of the larger lanthanides—did not, however, permit one to assess how a decrease in the ionic radius of the metal might influence the structural features and spatial arrangement of the macrocyclic entity itself. This question was particularly relevant to an understanding of the striking inertness of these complexes toward transmetalation[1,2] and metal release[4] in solution. To provide some insight on this question, we have synthesized a complex of the smallest lanthanide, lutetium(III), with the six-nitrogen macrocyclic ligand L and report here its properties and crystal structure.

Experimental Section

Synthesis and Characterization of the Complex. Lutetium(III) acetate (Alfa Products, 1 mmol, 0.389 g dissolved in 45 mL of anhydrous methanol), 2,6-diacetylpyridine (Aldrich Chemical Co., 2 mmol, 0.3265 g dissolved in 10 mL of methanol) and 1,2-diaminoethane (2 mmol, 5.0 mL of an 0.40 M methanol solution[4]) were refluxed together with 6 h. The pale yellow solution was allowed to cool, filtered over cotton, evaporated to 30 mL over mild heat and treated with $LiClO_4$ (10 mmol, 0.904 g dissolved in 10 mL of methanol). The mixture was heated at 50 °C for 1 h and then kept at room temperature overnight. A minute amount of a pale lavender crystalline precipitate formed and was filtered off. (Its infrared spectrum showed it to be nearly anhydrous lutetium(III) perchlorate). After the filtered solution was allowed to stand loosely covered for several days, well-formed light amber crystals were deposited, which were filtered, washed with methanol and diethyl ether, and dried in an oven at 70 °C. Yields: 30–40%.

Anal. Calcd for $Lu(C_{22}H_{26}N_6)(CH_3COO)(OH)(ClO_4)(CH_3OH)(H_2O)_{0.5}$: C, 39.18; H, 4.60; N, 11.22; O, 17.75. Found: C, 38.00; H, 4.05; N, 10.65; O, 17.57. The compound was moderately soluble in dimethyl sulfoxide, sparingly soluble in chloroform, and very nearly insoluble in other common solvents. The IR spectrum (4000–200 cm^{-1}) was taken in a combination of Nujol and hexachlorobutadiene mulls. The ^1H and ^{13}C NMR spectra were recorded in Me_2SO solution. Thermogravimetric measurements were carried out under a dry He flow of 50 mL/min. The PYR-GC-mass spectrum was recorded with the pyrolysis furnace set at 195 °C. Relevant results from these measurements are reported in the Results and Discussion section.

X-ray Measurements and Structure Determination. The crystal and refinement data for $LuL(CH_3COO)(OH)(ClO_4){\cdot}CH_3OH{\cdot}0.5H_2O$ (pale yellow transparent regular prisms) are summarized in Table I. A prismatic single crystal of 0.32 × 0.20 × 0.12 mm was lodged in a Lindeman glass capillary and centered on a four-circle Philips PW1100

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