1728 *Inorg. Chem.* **1985**, *24*, 1728–1730

although the distortion is somewhat different because of the very different ligand arrangement.

Magnetic Properties. The electronic structure of $[Cr_4(OH)_4(mhp)_8]$ involves an antiferromagnetic spin-coupling regime among the four Cr(III) d^3 centers of the tetrameric unit. This interpretation is based on the room-temperature (298 K) magnetic moment of 3.18 μ_B per Cr atom, which is appreciably less than the value of 3.84 μ_B observed for simple $S = {}^3/_2$ paramagnets such as $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ and $K_3[Cr(C_2O_4)_3]$. The EPR spectrum of powdered $[Cr_4(OH)_4(mhp)_8]$ at 300 K displays a broad (ca. 250 G peak-to-peak line width) isotropic signal, with $g = 1.943$, at X-band frequency. The appearance of a weak feature of apparent g value 4.003 in this spectrum is indicative of a ground state with $S > {}^1/_2$. The comparative temperature variation of the second integral of the EPR signal intensity per unit gain for $[Cr_4(OH)_4(mhp)_8]$, $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$, and $K_3[Cr(C_2O_4)_3]$ is displayed in Figure 3. The form of the decrease in the EPR signal intensity with decreasing temperature for $[Cr_4(OH)_4(mhp)_8]$ contrasts with that for the other two compounds and is also consistent with the presence of antiferromagnetic exchange interactions within the cluster.

$[(C_5H_5)_4Cr_4O_4]$ also apears to involve antiferromagnetic coupling between the metal centers, but no EPR signal could be observed for this cubane-like cluster.[20]

Acknowledgment. We thank the Verband der Chemischen Industrie and the SERC for financial support.

Registry No. $[Cr_4(OH)_4(mhp)_8]$, 95693-74-6; $[Cr(CO)_6]$, 13007-92-6; $[Cr_2(mhp)_4]$, 67634-82-6.

Supplementary Material Available: Listings of structure factors, hydrogen atom positional parameters, and thermal parameters (12 pages). Ordering information is given on any current masthead page.

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Cluster Synthesis. 9. Importance of Triply Bridging Sulfido Ligands in the Synthesis of Mixed-Metal Clusters: Synthesis and Crystal and Molecular Structure of $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$

Richard D. Adams,*[1] István T. Horváth, and Suning Wang

Received July 24, 1984

Sulfido ligands have proven to be of great value for the synthesis of metal carbonyl cluster compounds.[2] Triply bridging sulfido ligands are particularly valuable because they contain a lone pair of electrons that can be used for donation to other unsaturated metal centers.[2-4] In our recent studies we have found that the compound $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**1**) readily adds unsaturated metal-containing fragments to form higher nuclearity[5,6] and mixed-metal cluster[7,8] compounds. Structural studies have shown that metal–metal bond formation has played a prominent role in the formation of all of these complexes.

Table I. Crystallographic Data

	General Data		
formula	$Os_3WS_2O_{14}C_{14}$		
space gp	$P2_1/c$	temp, °C	28
a, Å	13.716 (2)	V, Å^3	4719 (4)
b, Å	22.611 (9)	M_r	1210.7
c, Å	15.248 (4)	Z	8
β, deg	93.63 (2)	ρ_{calcd}, g/cm^3	3.41
	Measurement of Intensity Data		
radiation	Mo K$\bar{\alpha}$ (0.710 73 Å)		
monochromator	graphite		
detector aperture, mm			
horiz ($A + B \tan\theta$)			
A	3.0		
B	1.0		
vert	4.0		
cryst faces	$1\bar{1}\bar{1}$, 211, $\bar{1}10$, 121, 120, $0\bar{1}1$, $02\bar{1}$		
cryst size, mm	0.15 × 0.15 × 0.15		
reflcns measd	$+h, +k, \pm l$		
max 2θ, deg	47		
scan type	moving crystal		
ω-scan width ($A + 0.347 \tan\theta$) A, deg	1.00		
bkgd	$^1/_4$ addnl at each end of scan		
ω-scan rate (variable), deg/min			
max	10.0		
min	1.4		
data used ($F^2 \geqslant 3.0\sigma(F^2)$)	3345		
	Treatment of Data		
abs cor			
coeff, cm^{-1}	213.3		
grid	8 × 8 × 14		
transmiss coeff			
max	0.14		
min	0.06		
p factor	0.03		
final residuals: R_F	0.055		
R_{wF}	0.059		
esd of unit wt observn	1.80		
largest shift/error value of final cycle	0.39		
largest peak in final diff Fourier, e$_0$/Å^3	2.02		

In this report we describe the synthesis and structural characterization of the compound $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (**2**), which is formed when solutions of **1** and $W(CO)_6$ are exposed with UV radiation.

Experimental Section

$Os_3(CO)_9(\mu_3\text{-}S)_2$ was prepared as previously described.[9] $W(CO)_6$ was purchased from Strem Chemicals, Danvers, MA. UV irradiations were performed upon solutions in Pyrex glassware by using an external high-pressure mercury lamp. IR spectra were recorded on a Nicolet 5SX FT IR spectrophotometer.

Preparation of $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (2). A 0.042-g (0.05 mmol) portion of $Os_3(CO)_9(\mu_3\text{-}S)_2$ and 0.019 g (0.055 mmol) of $W(CO)_6$ were dissolved in 180 mL of hexane and the resultant mixture photolyzed for 45 min under an N_2 atmosphere. The yellow solution turned to orange-red. The solvent was removed in vacuo, and the residue was chromatographed on silica TLC plates. Elution with hexane/CH_2Cl_2 (90/10) separated the starting material (0.008 g) from the orange product $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (**2**): 0.040 g, (70%); IR (ν(CO) in hexane) 2087 (s), 2072 (m), 2066 (s), 2024 (s), 2019 (sh), 1947 (s) cm^{-1}. Anal. Found (calcd): C, 14.27 (13.89); H, 0.17 (0.00).

Crystallographic Analysis. Dark orange crystals of **2** suitable for X-ray diffraction measurements were grown from hexane/methylene chloride solutions by slow evaporation of the solvent at 4 °C. The data crystal was mounted in thin-walled glass capillary. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated dif-

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Table II. Final Fractional Atomic Coordinates with Esds for $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (**2**)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Os(1)	0.9577 (1)	0.17032 (8)	0.9182 (1)	O(23)	0.688 (3)	0.248 (2)	0.730 (3)
Os(2)	1.0146 (1)	0.23586 (7)	0.7739 (1)	O(24)	0.469 (3)	0.343 (2)	0.566 (2)
Os(3)	1.1425 (1)	0.11834 (7)	0.9042 (1)	O(25)	0.340 (3)	0.494 (2)	0.711 (2)
Os(4)	0.5513 (1)	0.32558 (7)	0.9700 (1)	O(26)	0.386 (3)	0.484 (2)	0.435 (2)
Os(5)	0.3659 (1)	0.37415 (7)	0.9236 (1)	O(27)	0.624 (2)	0.519 (1)	0.867 (2)
Os(6)	0.5047 (1)	0.25411 (7)	0.8247 (1)	O(28)	0.765 (3)	0.374 (2)	0.712 (2)
W(1)	0.9522 (1)	0.44320 (7)	1.1790 (1)	C(1)	0.848 (4)	0.119 (2)	0.904 (3)
W(2)	0.5515 (1)	0.43085 (8)	0.7139 (1)	C(2)	0.875 (3)	0.236 (2)	0.927 (3)
S(1)	0.0238 (8)	0.3682 (5)	0.2873 (6)	C(3)	0.973 (4)	0.151 (2)	1.040 (3)
S(2)	0.1143 (8)	0.2777 (5)	0.4095 (7)	C(4)	0.912 (2)	0.235 (1)	0.682 (2)
S(3)	0.4896 (8)	0.1415 (4)	0.3260 (6)	C(5)	0.986 (3)	0.315 (2)	0.805 (3)
S(4)	0.3972 (8)	0.2295 (5)	0.4417 (7)	C(6)	1.107 (3)	0.255 (2)	0.693 (3)
O(1)	0.776 (3)	0.089 (2)	0.898 (2)	C(7)	1.216 (4)	0.115 (2)	1.011 (3)
O(2)	0.829 (2)	0.280 (1)	0.930 (2)	C(8)	1.251 (4)	0.115 (2)	0.841 (3)
O(3)	0.989 (2)	0.139 (1)	1.114 (2)	C(9)	1.131 (4)	0.034 (2)	0.909 (3)
O(4)	0.854 (2)	0.233 (1)	0.629 (2)	C(10)	0.989 (3)	0.113 (2)	0.584 (3)
O(5)	0.970 (2)	0.364 (1)	0.815 (2)	C(11)	0.823 (3)	0.096 (2)	0.677 (3)
O(6)	1.168 (2)	0.265 (1)	0.642 (2)	C(12)	0.903 (3)	0.500 (2)	1.092 (3)
O(7)	1.254 (3)	0.118 (2)	1.081 (2)	C(13)	0.914 (3)	0.004 (2)	0.784 (2)
O(8)	1.321 (3)	0.115 (2)	0.800 (2)	C(14)	1.081 (4)	0.015 (2)	0.679 (3)
O(9)	1.119 (3)	−0.015 (1)	0.921 (2)	C(15)	0.667 (3)	0.372 (2)	0.962 (3)
O(10)	1.009 (3)	0.144 (2)	0.523 (2)	C(16)	0.623 (3)	0.259 (2)	1.008 (2)
O(11)	0.743 (3)	0.115 (1)	0.678 (2)	C(17)	0.536 (3)	0.357 (2)	1.083 (3)
O(12)	0.868 (3)	0.532 (2)	1.039 (2)	C(18)	0.286 (3)	0.373 (2)	1.025 (2)
O(13)	0.896 (2)	−0.026 (1)	0.835 (2)	C(19)	0.259 (3)	0.375 (2)	0.847 (2)
O(14)	1.162 (3)	−0.008 (2)	0.677 (2)	C(20)	0.385 (3)	0.457 (2)	0.922 (3)
O(15)	0.737 (3)	0.402 (1)	0.956 (2)	C(21)	0.416 (3)	0.231 (2)	0.729 (2)
O(16)	0.664 (2)	0.218 (1)	1.030 (2)	C(22)	0.527 (3)	0.173 (2)	0.857 (3)
O(17)	0.516 (2)	0.378 (1)	1.150 (2)	C(23)	0.617 (4)	0.254 (2)	0.759 (3)
O(18)	0.246 (2)	0.374 (1)	1.085 (2)	C(24)	0.503 (4)	0.378 (2)	0.622 (3)
O(19)	0.190 (2)	0.376 (1)	0.795 (2)	C(25)	0.421 (3)	0.473 (2)	0.708 (2)
O(20)	0.614 (2)	0.491 (1)	1.073 (2)	C(26)	0.588 (3)	0.485 (2)	0.621 (3)
O(21)	0.363 (3)	0.226 (1)	0.668 (2)	C(27)	0.599 (3)	0.488 (2)	0.808 (3)
O(22)	0.541 (2)	0.125 (1)	0.877 (2)	C(28)	0.683 (3)	0.392 (2)	0.713 (3)

Table III. Selected Interatomic Distances with Esds for $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (**2**)

molecule 1		molecule 2	
atoms	dist, Å	atoms	dist, Å
Os(1)–Os(2)	2.804 (2)	Os(4)–Os(5)	2.818 (2)
Os(1)–Os(3)	2.815 (2)	Os(4)–Os(6)	2.784 (2)
Os(1)–S(1)	2.407 (8)	Os(4)–S(3)	2.419 (7)
Os(1)–S(2)	2.459 (9)	Os(4)–S(4)	2.467 (8)
Os(2)–S(1)	2.364 (8)	Os(5)–S(3)	2.354 (8)
Os(2)–S(2)	2.426 (8)	Os(5)–S(4)	2.396 (8)
Os(3)–S(1)	2.357 (8)	Os(6)–S(3)	2.370 (8)
Os(3)–S(2)	2.384 (8)	Os(6)–S(4)	2.414 (9)
W–S(1)	2.522 (8)	W(2)–S(3)	2.550 (8)
Os–C	1.82 (5)–1.92 (4)	Os–C	1.81 (3)–1.95 (3)
W–C	1.94 (3)–2.09 (3)	W–C	1.93 (4)–2.02 (3)
C–O	1.08 (3)–1.23 (4)	C–O	1.09 (3)–1.23 (4)

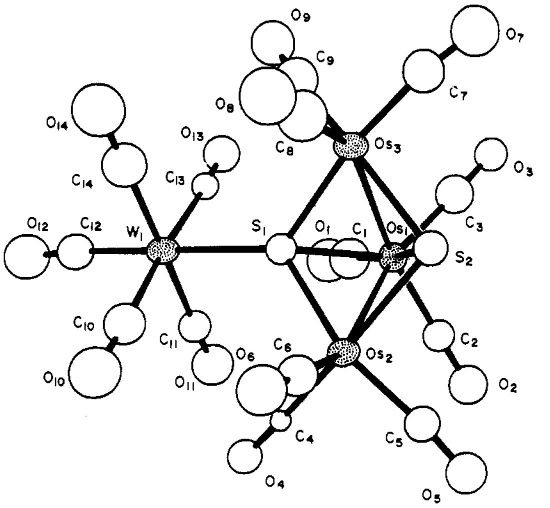

Figure 1. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (**2**) showing 50% probability thermal ellipsoids.

fractometer and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters are listed in Table I. All data processing was performed on a Digital Equipment Corp. PDP 11/45 computer using the Enraf-Nonius SDP program library (version 18). An absorption correction of a Gaussian integration type was applied to all data. Neutral-atom scattering factors were calculated by the standard procedures.[10a] Anomalous dispersion corrections were applied to all atoms.[10b]

The structure was solved by combination of direct methods and dif-

Table IV. Selected Interatomic Angles with Esds for $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (**2**)

molecule 1		molecule 2		molecule 1		molecule 2	
atoms	angle, deg	atoms	angle, deg	atoms	angle, deg	atoms	angle, deg
Os(2)–Os(1)–Os(3)	82.21 (5)	Os(5)–Os(4)–Os(6)	82.44 (5)	S(1)–Os(1)–S(2)	75.7 (3)	S(3)–Os(4)–S(4)	75.6 (3)
Os(1)–S(1)–Os(2)	72.0 (2)	Os(4)–S(3)–Os(5)	72.4 (2)	S(1)–Os(1)–C(1)	91.1 (12)	S(3)–Os(4)–C(15)	91.1 (10)
Os(1)–S(1)–Os(3)	72.4 (2)	Os(4)–S(3)–Os(6)	71.1 (2)	S(1)–Os(1)–C(2)	127.2 (10)	S(3)–Os(4)–C(16)	132.4 (9)
Os(1)–S(1)–W(1)	129.4 (3)	Os(4)–S(3)–W(2)	133.9 (3)	S(1)–Os(1)–C(3)	134.5 (12)	S(3)–Os(4)–C(17)	131.3 (1)
Os(2)–S(1)–Os(3)	103.0 (3)	Os(5)–S(3)–Os(6)	102.8 (3)	S(2)–Os(1)–C(1)	166.6 (12)	S(4)–Os(4)–C(15)	166.2 (10)
Os(2)–S(1)–W(1)	126.6 (3)	Os(5)–S(3)–W(2)	127.7 (3)	S(2)–Os(1)–C(2)	99.4 (10)	S(4)–Os(4)–C(16)	94.1 (10)
Os(3)–S(1)–W(1)	129.0 (3)	Os(6)–S(3)–W(2)	126.9 (3)	S(2)–Os(1)–C(3)	97.0 (12)	S(4)–Os(4)–C(17)	101.8 (11)
Os(1)–S(2)–Os(2)	70.1 (2)	Os(4)–S(4)–Os(5)	70.8 (2)	Os–C–O	172 (4)–178 (3)	Os–C–O	169 (4)–179 (2)
Os(1)–S(2)–Os(3)	71.0 (2)	Os(4)–S(4)–Os(6)	69.5 2)	W–C–O	175 (3)–177 (4)	W–C–O	173 (3)–177 (3)
Os(2)–S(2)–Os(3)	100.3 (3)	Os(5)–S(4)–Os(6)	100.3 (3)				

ference Fourier techniques and refined by the method of full-matrix least squares. Only the metal atoms were refined with anisotropic thermal parameters.

Results and Discussion

The compound $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ (**2**) is formed in 70% yield when solutions of **1** and $W(CO)_6$ are exposed to UV irradiation. The molecular structure of **2** was determined by a single-crystal X-ray diffraction analysis. The compound crystallizes with 2 independent molecules in the asymmetric crystal unit. Both molecules are structurally similar, and an ORTEP diagram of one of these is shown in Figure 1. Final fractional atomic coordinates are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV, respectively.

The molecule consists of an $Os_3(CO)_9(\mu_3\text{-}S)_2$ moiety linked to a $W(CO)_5$ unit via a donor–acceptor bond from one of the triply bridging sulfido ligands in the osmium cluster to the tungsten atom. The W–S distances in the two molecules are 2.522 (8) and 2.550 (8) Å. These distances are very similar to the W–S distance of 2.547 (6) Å observed in the compound $Fe_3(CO)_9(\mu_3\text{-}P\text{-}t\text{-}Bu)(\mu_4\text{-}S)[W(CO)_5]$ in which a $Fe_3(CO)_9(\mu_3\text{-}P\text{-}t\text{-}Bu)(\mu_3\text{-}S)$ cluster is ligated to a $W(CO)_5$ unit.[3] No metal–metal bonds are made in the formation of **2**. The structure of the $Os_3(CO)_9S_2$ moiety in **2** is very similar to that of the isolated cluster.[11] The quadruply bridging sulfido ligand serves as a six-electron donor, and all the metal atoms attain 18-electron configurations. Interestingly, the heptacoordinate osmium atom in **2** adopts a structure in which a carbonyl ligand lies approximately trans to the triply bridging sulfido ligand. This seems to suggest, as might be expected, that the triply bridging sulfido ligand donates more electron density to Os(1) than the quadruply bridging sulfido ligand.

In contrast to the reaction of **1** with $W(CO)_6$, which yields the product **2** that has no new metal–metal bonds, the reaction of **1** with $W(CO)_5PMe_2Ph$ gives a number of compounds, all of which contain osmium–tungsten bonds.[7,12]

Acknowledgment. This work was supported by the National Science Foundation. We thank Engelhard Industries for a loan of osmium tetroxide.

Registry No. **1**, 72282-40-7; **2**, 95912-77-9; $W(CO)_6$, 14040-11-0.

Supplementary Material Available: Tables of interatomic distances and angles, thermal parameters, and observed and calculated structure factors for **2** (21 pages). Ordering information is given on any current masthead page.

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

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Additions and Corrections

1984, Volume 23

Thomas P. E. Auf der Heyde* and Luigi R. Nassimbeni: Reaction Pathways from Structural Data: Dynamic Stereochemistry of Nickel Compounds.

Page 4529. Reference 20b (cited as: Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257) should read: Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318. The former refers to a review article, while the latter is the original reference.—Thomas P. E. Auf der Heyde