absorption and ESR spectral properties identical with those shown by solutions containing the electrochemically generated anion. The electrochemical properties of 7 confirmed its identity. A CV showed that it possessed the expected two one-electron oxidations and a one-electron reduction, together with a couple at –0.90 V due to cobaltocene/cobaltocenium.[12]

Note that, in the preparative procedure used to obtain the neutral complex 6 (see Experimental Section), we found some reduction to the monoanion occurred in the reaction mixture. Hence we added a quantity of tropylium hexafluorophosphate[13] to reoxidize the anion back to the neutral complex and thereby enhance its yield.

Our attempts to develope the redox chemistry of 6 further by generating the monocation upon oxidizing its solutions in 0.2 M TBAH–CH_2Cl_2 at +1.40 V led to decomposition to give unidentified species.

Concluding Remarks

The reactions of several pyridine ligands (py, 4-Mepy, 4-Phpy, or Hhp) with $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2$ give the doubly bonded ditungsten(IV) complexes $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2L_2$, where L = py, 4-Mepy, or 4-Phpy, and $W_2Cl_4(\mu\text{-OEt})_2(hp)_2$, which exhibit well-defined redox chemistry. In the case of $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2L_2$, electrochemical oxidation to the paramagnetic monocations can be achieved, whereas $W_2Cl_4(\mu\text{-OEt})_2(hp)_2$ is easily reduced (chemically and electrochemically) to its monoanion. The oxidation to $[W_2Cl_4(\mu\text{-OEt})_2(OEt)_2L_2]^+$ represents, on the basis of the Fenske–Hall molecular orbital treatment of molecules of this type,[4] the loss of an electron from the π-bonding HOMO and a configuration change from $\sigma^2\pi^2$ (double bond) to $\sigma^2\pi^1$. Thus, such cations may represent examples of W–W bonds of order 1.5. On the other hand, reduction of $W_2Cl_4(\mu\text{-OEt})_2(hp)_2$ to $[W_2Cl_4(\mu\text{-OEt})_2(hp)_2]^-$, if this involves the addition of an electron to a δ^* orbital (the predicted LUMO),[4] also represents formally the formation of a W–W bond of order 1.5, although one that is clearly of a different type, viz. $\sigma^2\pi^2\delta^{*1}$.

Acknowledgment. Support from the National Science Foundation (Grant No. CHE82-06117) is gratefully acknowledged. The Varian XL-200 spectrometer was purchased from funds provided by the National Science Foundation (Grant No. CHE80-04246 to Purdue).

Registry No. 1, 78350-74-0; 3, 91551-22-3; 3 (monocation), 91551-28-9; 4, 91551-23-4; 4 (monocation), 91551-29-0; 5, 91551-24-5; 5 (monocation), 91551-30-3; 6, 91551-25-6; 7, 91551-27-8; $W_2Cl_4(\mu\text{-OEt})_2(O\text{-}i\text{-Pr})_2(i\text{-PrOH})_2$, 85202-62-6; W, 7440-33-7.

---

[13] Tropylium hexafluorophosphate is, on the basis of its electrochemical properties, a suitable oxidant for this purpose. See footnote 11 in: Conner, K. A.; Walton, R. A. *Organometallics* **1983**, *2*, 169.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

New Bromo Complexes of Osmium(IV) and Osmium(III): $[Os_2Br_{10}]^{2-}$ and $OsBr_3(PPh_3)_2(CH_3CN)$

F. ALBERT COTTON,*[1a] STAN A. DURAJ,[1a] CONRAD C. HINCKLEY,*[1b] MAREK MATUSZ,[1b]
and WIESLAW J. ROTH[1a]

Received December 13, 1983

When $(n\text{-Bu}_4N)_2[OsBr_6]$ is refluxed in trifluoroacetic acid for several hours, it is converted in about 80% yield to $(n\text{-Bu}_4N)_2[Os_2Br_{10}]$ (1). When 1 is warmed in acetonitrile containing additional PPh_3, $OsBr_3(PPh_3)_2(CH_3CN)$ (2) is obtained in yields around 30%. Compound 1, a black crystalline solid, has been shown by X-ray crystallography to contain edge-sharing bioctahedral $[Br_4Os(\mu\text{-Br})_2OsBr_4]^{2-}$ anions. These reside on crystallographic inversion centers and have essentially D_{2h} symmetry. The Os–Os distance is 3.788 (3) Å, and other important average dimensions are Os–(μ-Br) = 2.544 [4] Å, Os–Br(terminal) = 2.454 [5] Å, and Os–Br–Os = 96.3 (1)°. The structure indicates that Os–Os bonding does not occur although the compound is only feebly paramagnetic. Compound 1 crystallizes in space group $P2_1/n$ with unit cell dimensions a = 12.186 (4) Å, b = 16.528 (4) Å, c = 12.908 (4) Å, β = 103.02 (2)°, V = 2532 (3) Å^3, and Z = 2. Compound 2 consists of approximately octahedral molecules in which the bromine atoms are meridional and the Ph_3P ligands occupy trans positions above and below the $OsBr_3(CH_3CN)$ plane. The important bond distances are Os–Br = 2.481 (1), 2.499 (1) (trans Br's), 2.499 (1) Å (trans to CH_3CN), Os–P = 2.418 (2), 2.419 (2) Å, and Os–N = 2.024 (10) Å. Compound 2 crystallizes in space group $P2_1/n$ with the following unit cell dimensions: a = 10.210 (2) Å, b = 15.308 (3) Å, c = 23.122 (3) Å, β = 91.15 (3)°, V = 3613 (2) Å^3, Z = 4.

Introduction

The hexahaloosmates(IV) and their derivatives play a leading role in the chemistry of tetravalent osmium,[2,3] and for this reason the $[OsX_6]^{2-}$ ions have already been extensively studied both chemically and physically. In spite of this, it has not previously been observed that $[OsX_6]^{2-}$ ions can dimerize with attendant loss of halide ions to give a binuclear product. We report here the preparation and characterization of the $[Os_2Br_{10}]^{2-}$ ion. In the course of studying the chemical reactivity of this new complex anion, we have found that it reacts wth triphenylphosphine in acetonitrile to give the osmium(III) complex $OsBr_3(PPh_3)_2(CH_3CN)$, the chloro analogue of which is already known.[4-6] In this paper we present full preparative and crystallographic details for the two new compounds $(n\text{-Bu}_4N)_2[Os_2Br_{10}]$ (1) and $OsBr_3(PPh_3)_2(CH_3CN)$ (2).

Experimental Section

Preparation of $(n\text{-Bu}_4N)_2[Os_2Br_{10}]$ (1). The starting material, $(n\text{-Bu}_4N)_2[OsBr_6]$, was prepared by a method in the literature.[3] Two grams (1.73 mmol) of $(n\text{-Bu}_4N)_2[OsBr_6]$ and 15 mL of trifluoroacetic acid were placed in a 50-mL round-bottom flask equipped with a condenser and stirring bar. The mixture was heated to reflux, and a black solid began to form. Refluxing was continued for about 2 h at which time there appeared to be no further formation of precipitate, and the supernatant liquid was either pale yellow or pale red. The black solid was isolated by filtration and dried under vacuum.

---

[1] (a) Texas A&M University. (b) Southern Illinois University.

[2] Gulliver, D. J.; Levason, W. *Coord. Chem. Rev.* **1982**, *46*, 1.

[3] Griffith, W. P.; Raub, C. J. "Gmelin Handbuch der Anorganischen Chemie"; Springer-Verlag: New York, Suppl. Vol. 1.

[4] Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2379.

[5] Parker, R. L.; Payne, N. C.; Sherman, E. O. *Can. J. Chem.* **1980**, *58*, 1042.

[6] Goeden, G. V.; Haymore, B. L. *Inorg. Chim. Acta* **1983**, *71*, 239.

Table I

formula	$Os_2Br_{10}N_2C_{32}H_{72}$	$OsBr_3P_2NC_{38}H_{33}$
fw	1664.43	995.57
space group	$P2_1/n$	
syst absences	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$	
a, Å	12.186 (4)	10.210 (2)
b, Å	16.528 (4)	15.308 (3)
c, Å	12.908 (4)	23.122 (3)
α, deg	90.0	90.0
β, deg	103.02 (2)	91.15 (3)
γ, deg	90.0	90.0
V, Å^3	2532 (3)	3613 (2)
Z	2	4
d_{calcd}, g/cm^3	2.182	1.830
cryst size, mm	0.15 × 0.2 × 0.4	0.1 × 0.3 × 0.3
μ(Mo Kα), cm^{-1}	128.580	69.348
data collcn instrum	Syntex P$\bar{1}$	CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)	
no. of orientation reflcns; range (2θ), deg	15; $20.26 \leq 2\theta \leq 30.30$	25; $14.34 \leq 2\theta \leq 31.12$
temp, °C	ambient	
scan method	$\omega-2\theta$	
data collcn range (2θ), deg	$4 \leq 2\theta \leq 50$	
no. of unique data	1089	4314
$F_o^2 > 3\sigma(F_o^2)$	923	3386
no. of parameters refined	123	406
transmissn factors: max, min	0.9992, 0.8182	0.9991, 0.8661
R[a]	0.0374	0.0385
R_w[b]	0.0487	0.0452
quality-of-fit indicator[c]	0.990	1.078
largest shift/esd, final cycle	0.0	0.06
largest peak, e/Å^3	0.518	0.726

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2 / (N_{observns} - N_{parameters})]^{1/2}$.

Yield: 1.11 g, 0.68 mmol (ca. 80%). Anal. Calcd for $C_{32}H_{72}N_2Br_{10}Os_2$: C, 23.09; H, 4.36; N, 1.68; Br, 48.00. Found: C, 23.3; H, 4.38; N, 1.66; Br, 48.1. The compound is insoluble in water but dissolves in most common organic solvents. It is stable toward air as a solid, but solutions exposed to air slowly decompose.

A well-crystallized product was obtained within a few hours by placing the reaction mixture in an apparatus designed to cycle the temperature back and forth between set limits, which in this case were 37 and 42 °C, with a cycle time of ca. 1 h. In view of this result, it seems likely that the reflux temperature (ca. 72 °C) of trifluoroacetic acid is not necessary. We have not attempted to find the optimum conditions for the reaction.

Preparation of $OsBr_3(Ph_3P)_2(CH_3CN)$ (2). Compound **1** (0.22 g, 0.13 mmol) was dissolved in 30 mL of acetonitrile, and triphenylphosphine (0.30 g, 1.1 mmol) was added. The mixture was maintained at 45–50 °C for 24 h. Black crystals that precipitated from the solution were separated by filtration, washed with acetonitrile, followed by diethyl ether, and dried in air. Yields were somewhat variable but were typically about 30% (ca. 0.070 g). Anal. Calcd for $C_{38}H_{33}NP_2Br_3Os$: C, 45.80; H, 3.34; P, 6.22; Br, 24.07. Found: C, 45.0; H, 3.50; P, 6.15; Br, 21.7. The low halogen analysis is not unusual for compounds of this type: see, for example, the analysis for $OsCl_4(PPh_3)_2$ in ref 4.

Better yields (>50%) may be obtained by reacting $(n\text{-}Bu_4N)_2[OsBr_6]$ with Ph_3P in acetonitrile. $OsBr_3(Ph_3P)_2(CH_3CN)$ is insoluble in most common solvents but slightly soluble in CH_2Cl_2.

Magnetic Measurements. The magnetic susceptibility of compound **1** was determined at 296 K on a Faraday balance. The molar susceptibility after correction for diamagnetism was 27 × 10^{-6} cgsu, from which a magnetic moment of 0.26 μ_B is calculated. As a check on the apparatus and procedure the susceptibility of K_2OsBr_6 was measured, and the value of μ_B found, 1.0 μ_B, is in good agreement with the literature data.[7]

X-ray Crystallography. General procedures have been described previously.[8] Basic information about data collection and structure refinement for both **1** and **2** are summarized in Table I. Polarization, Lorentz, and absorption corrections were applied to the intensity data.

Table II. Positional and Isotropic Equivalent Thermal Parameters for $(n\text{-}Bu_4N)_2[Os_2Br_{10}]$ (1)[a]

atom	x	y	z	B, Å^2
Os	−0.1196 (1)	−0.00684 (6)	0.0712 (1)	3.89 (2)
Br(1)	0.0946 (2)	0.0015 (2)	0.1187 (2)	4.39 (7)
Br(2)	−0.1262 (3)	−0.0115 (2)	0.2602 (3)	6.66 (9)
Br(3)	−0.3253 (3)	−0.0146 (2)	0.0070 (3)	6.6 (1)
Br(4)	−0.1299 (3)	0.1415 (2)	0.0744 (3)	5.86 (9)
Br(5)	−0.1054 (3)	−0.1541 (2)	0.0691 (3)	5.72 (9)
N	0.518 (2)	0.262 (1)	0.032 (2)	3.4 (5)*
C(1)	0.400 (2)	0.267 (2)	0.049 (3)	5.1 (7)*
C(2)	0.526 (2)	0.190 (2)	−0.048 (2)	4.2 (6)*
C(3)	0.542 (2)	0.345 (2)	−0.013 (3)	5.6 (8)*
C(4)	0.605 (2)	0.243 (2)	0.137 (2)	4.0 (7)*
C(11)	0.376 (3)	0.330 (2)	0.127 (3)	6.4 (9)*
C(12)	0.255 (3)	0.320 (2)	0.147 (3)	7 (1)*
C(13)	0.252 (3)	0.242 (2)	0.213 (3)	8 (1)*
C(21)	0.450 (2)	0.202 (2)	−0.158 (2)	5.0 (7)*
C(22)	0.493 (3)	0.129 (2)	−0.219 (3)	7.2 (9)*
C(23)	0.434 (3)	0.136 (3)	−0.337 (4)	11 (1)*
C(31)	0.656 (2)	0.343 (2)	−0.042 (2)	4.8 (7)*
C(32)	0.683 (3)	0.434 (2)	−0.068 (3)	6.1 (8)*
C(33)	0.791 (3)	0.437 (2)	−0.108 (3)	6.9 (9)*
C(41)	0.569 (3)	0.174 (2)	0.201 (3)	6.3 (9)*
C(42)	0.666 (3)	0.153 (2)	0.295 (3)	6.1 (8)*
C(43)	0.630 (3)	0.091 (2)	0.362 (3)	8 (1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

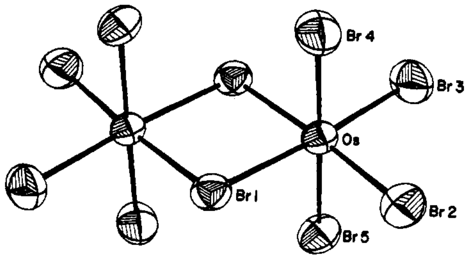

Figure 1. ORTEP drawing of the $[Os_2Br_{10}]^{2-}$ ion. The thermal ellipsoids enclose 50% of electron density. There is a crystallographic inversion center relating the halves of the ion.

In each case the position of the osmium atom was obtained from a three-dimensional Patterson function.[9] The remainder of each structure was developed by a series of least-squares refinements and difference Fourier syntheses. For **1** anisotropic thermal parameters were assigned only to Os and Br atoms.[10] For **2** the refinement was carried out with all atoms having anisotropic parameters.

Tables of structure factors and anisotropic thermal parameters are available as supplementary material.

Results and Discussion

Positional and isotropic equivalent thermal parameters for compounds **1** and **2** are presented in Tables II and III, respectively. The bond distances and bond angles in the $[Os_2Br_{10}]^{2-}$ ion are listed in Table IV. Table V provides important interatomic dimensions for **2**. Complete lists of bond distances and angles for both complexes are included in the supplementary material.

The $[Os_2Br_{10}]^{2-}$ Ion. Compound **1** is composed of discrete $[Os_2Br_{10}]^{2-}$ anions and tetra-n-butylammonium cations. The dinuclear anion is represented in Figure 1 by its ORTEP

---

(7) Reference 3, p 153.

(8) See, for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(9) All crystallographic computations were carried out on the departmental VAX computer using a local version of the Enraf-Nonius structure determination package.

(10) The relatively small number of statistically valid reflections for compound **1** is not indicative of any abnormality (i.e., disorder); these crystals are simply rather poor scatterers.

Table III. Positional and Isotropic Equivalent Parameters for $OsBr_3(PPh_3)_2(CH_3CN)$ (2)[a]

atom	x	y	z	B, Å^2
Os	0.04200 (4)	0.22826 (3)	0.34863 (2)	2.166 (7)
Br(1)	0.1939 (1)	0.35398 (8)	0.36587 (5)	3.08 (2)
Br(2)	−0.1388 (1)	0.31797 (9)	0.30477 (5)	3.38 (3)
Br(3)	0.1942 (1)	0.11643 (9)	0.38899 (5)	3.64 (3)
P(1)	0.1331 (3)	0.2010 (2)	0.2546 (1)	2.37 (6)
P(2)	−0.0510 (3)	0.2490 (2)	0.4430 (1)	2.54 (7)
N	−0.0807 (8)	0.1264 (6)	0.3343 (4)	2.8 (2)
C(1)	−0.149 (1)	0.0689 (8)	0.3246 (5)	3.1 (3)
C(2)	−0.233 (1)	−0.0072 (9)	0.3149 (6)	4.6 (3)
C(3)	0.051 (1)	0.1076 (8)	0.2193 (4)	3.0 (3)
C(4)	0.091 (1)	0.0229 (8)	0.2371 (6)	4.6 (3)
C(5)	0.027 (2)	−0.047 (1)	0.2109 (8)	7.4 (4)
C(6)	−0.077 (1)	−0.033 (1)	0.1711 (7)	7.9 (4)
C(7)	−0.120 (1)	0.051 (1)	0.1581 (6)	6.8 (4)
C(8)	−0.055 (1)	0.122 (1)	0.1822 (6)	4.8 (3)
C(9)	0.124 (1)	0.2866 (8)	0.1997 (5)	3.1 (3)
C(10)	0.109 (1)	0.3748 (8)	0.2168 (5)	3.0 (3)
C(11)	0.109 (1)	0.4432 (8)	0.1760 (5)	3.4 (3)
C(12)	0.125 (1)	0.4223 (9)	0.1175 (5)	3.5 (3)
C(13)	0.140 (1)	0.3346 (9)	0.1003 (5)	4.0 (3)
C(14)	0.137 (1)	0.2661 (9)	0.1408 (5)	4.1 (3)
C(15)	0.308 (1)	0.1711 (8)	0.2489 (4)	2.8 (2)
C(16)	0.350 (1)	0.1177 (9)	0.2040 (5)	3.9 (3)
C(17)	0.484 (1)	0.104 (1)	0.1956 (6)	4.9 (3)
C(18)	0.576 (1)	0.145 (1)	0.2328 (6)	4.9 (3)
C(19)	0.531 (1)	0.1962 (9)	0.2787 (6)	4.0 (3)
C(20)	0.399 (1)	0.2105 (7)	0.2869 (5)	3.1 (3)
C(21)	0.055 (1)	0.2341 (8)	0.5082 (5)	3.4 (3)
C(22)	0.191 (1)	0.2490 (7)	0.5047 (5)	3.4 (3)
C(23)	0.269 (1)	0.2405 (9)	0.5574 (6)	4.9 (3)
C(24)	0.210 (2)	0.2186 (9)	0.6075 (6)	6.0 (4)
C(25)	0.076 (2)	0.205 (1)	0.6107 (6)	5.8 (4)
C(26)	−0.002 (1)	0.2137 (9)	0.5602 (5)	5.0 (4)
C(27)	−0.130 (1)	0.3526 (8)	0.4607 (5)	3.3 (3)
C(28)	−0.090 (1)	0.4303 (8)	0.4363 (5)	3.3 (3)
C(29)	−0.143 (1)	0.5111 (8)	0.4553 (6)	4.1 (3)
C(30)	−0.235 (1)	0.513 (1)	0.4987 (5)	5.0 (4)
C(31)	−0.276 (2)	0.434 (1)	0.5228 (6)	7.3 (4)
C(32)	−0.226 (2)	0.352 (1)	0.5050 (7)	7.6 (4)
C(33)	−0.178 (1)	0.1664 (9)	0.4516 (4)	3.2 (3)
C(34)	−0.307 (1)	0.184 (1)	0.4331 (5)	4.9 (3)
C(35)	−0.399 (1)	0.111 (1)	0.4359 (6)	5.2 (4)
C(36)	−0.357 (1)	0.029 (1)	0.4551 (6)	5.6 (4)
C(37)	−0.228 (2)	0.015 (1)	0.4735 (6)	5.4 (4)
C(38)	−0.139 (1)	0.0852 (9)	0.4727 (5)	4.0 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table IV. Bond Distances (Å) and Angles (deg) in the $[Os_2Br_{10}]^{2-}$ Anion[a]

	Distances		
Os–Os′	3.788 (3)[b]	Os–Br(3)	2.460 (4)
–Br(1)	2.548 (3)	–Br(4)	2.456 (4)
–Br(1)′	2.540 (3)	–Br(5)	2.441 (4)
–Br(2)	2.460 (4)		

	Angles		
Br(1)–Os–Br(1)′	83.7 (1)	Br(1)′–Os–Br(5)	90.0 (2)
–Br(2)	91.4 (1)	Br(2)–Os–Br(3)	94.3 (2)
–Br(3)	174.4 (1)	–Br(4)	90.1 (2)
–Br(4)	89.7 (1)	–Br(5)	89.9 (2)
–Br(5)	89.2 (2)	Br(3)–Os–Br(4)	90.3 (2)
Br(1)′–Os–Br(2)	175.1 (1)	–Br(5)	90.8 (2)
–Br(3)	90.6 (1)	Br(4)–Os–Br(5)	178.9 (2)
–Br(4)	89.9 (2)	Os–Br(1)–Os′	96.3 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Nonbonding contact.

Table V. Important Bond Distances (Å) and Angles (deg) in **2**[a]

	Distances		
Os–Br(1)	2.499 (1)	Os–P(1)	2.418 (3)
–Br(2)	2.499 (1)	–P(2)	2.419 (3)
–Br(3)	2.481 (1)	–N	2.024 (10)

	Angles		
Br(1)–Os–Br(2)	95.32 (5)	Br(3)–Os–P(1)	88.27 (8)
–Br(3)	95.12 (4)	–P(2)	90.31 (8)
–P(1)	91.56 (8)	–N	88.2 (3)
–P(2)	90.48 (8)	P(1)–Os–P(2)	177.6 (1)
–N	180.0 (6)	–N	88.2 (3)
Br(2)–Os–Br(3)	169.56 (5)	P(2)–Os–N	89.8 (3)
–P(1)	91.40 (8)		
–P(2)	89.65 (8)		
–N	84.7 (3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

drawing, which also defines the labeling scheme. The anion resides on a crystallographic inversion center and has a structure typical for M_2X_{10} species, namely, two octahedra sharing an edge in such a way as to have idealized D_{2h} symmetry. Each $OsBr_6$ unit deviates but slightly from perfect octahedral symmetry. However, the most noticeable deviations that do exist are almost entirely of the sort that indicate a repulsive force between the metal atoms. Thus, the central rhombus consisting of Os, Os′, Br(1), and Br(1)′ is stretched along the Os–Os′ direction, so that the Os–Br(1)–Os′ angle, 96.3 (1)°, is greater than the ideal value of 90° and the Br(1)–Os–Br(1)′ angle, 83.7(1)°, is less than 90°. The four bridge bonds are equal within experimental error, with a mean distance, 2.544 [4] Å, that is somewhat longer than any of the terminal Os–Br distances, which range from 2.441 (4) to 2.460 (4) Å.

The separation between the osmium atoms is large, 3.788 (3) Å. This, together with the distortion indicative of a repulsive force between them, leads to the conclusion that no direct Os–Os bonding exists in this complex. The very weak, almost zero, paramagnetic moment observed must therefore be explained in some other way, but we would not wish to hazard any specific proposal. If we note, however, that even for an isolated hexabromoosmate(IV) ion the magnetic moment is only ca. 1.0 μ_B, it does not seem unreasonable that a little further spin coupling through the bridging bromide ions might result in an almost complete quenching of electron spin-based paramagnetism.

The absence of Os–Os bonding in this case is not to be considered surprising in the light of prior knowledge. It was shown several years ago[11] that $OsCl_4$ crystallizes to form infinite chains in which $OsCl_6$ octahedra share opposite edges, with all Os–Os separations the same at a nonbonding distance of 3.560 (1) Å. The $[Os_2Br_{10}]^{2-}$ ion is like a segment of such a chain in which, however, the chance for direct Os–Os bonding is further reduced by the larger size of the bridging atoms. In comparing the two structures in more detail, we note that corresponding types (i.e., axial and bridging) of Os–X bonds in the two compounds differ by 0.16–0.19 Å, which may be compared with the difference by 0.15 Å suggested by Pauling single-bond radii.[12]

It is somewhat surprising that the existence of the $[Os_2Br_{10}]^{2-}$ has not been discovered earlier, especially since Os(IV) halide complexes have been very extensively studied. The compound we have made is quite stable and presents no difficulty during its isolation and handling. It is possible that a very special environment is required to promote the formation of sufficient quantities of $[Os_2Br_{10}]^{2-}$, via the equilibrium

$$2[OsBr_6]^{2-} \rightleftarrows [Os_2Br_{10}]^{2-} + 2Br^-$$

There is no obvious reason why trifluoroacetic acid should be

---

(11) Cotton, F. A.; Rice, C. E. *Inorg. Chem.* **1977**, *16*, 1865.

(12) Pauling, L. "The Nature of the Chemical Bond"; 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 224.

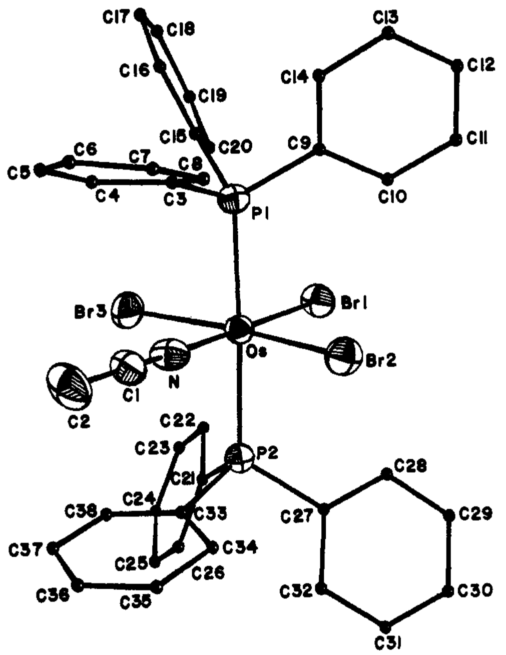

Figure 2. ORTEP drawing of the $OsBr_3(PPh_3)_2(CH_3CN)$ molecule. The thermal ellipsoids enclose 50% of electron density. Carbon atoms in the phenyl rings were assigned arbitrarily small thermal ellipsoids.

especially favorable, unless it is because it is a good solvent for the $[OsBr_6]^{2-}$ ion and a poor one for the desired product ion. Clearly, the preparation, properties, and factors favoring the stability of this and perhaps other such $[M_2X_{10}]^{2-}$ ions will require, and merit, further study.

To our knowledge the $[Os_2Br_{10}]^{2-}$ ion is only the second example of an anionic edge-sharing bioctahedron. That general type of structure is, of course, extremely common, but all previous examples, except for the $[Ti_2Cl_{10}]^{2-}$ ion,[13] are neutral molecules. A few are metal(V) halides, e.g., Nb_2Cl_{10}, Mo_2Cl_{10}, W_2Cl_{10}, and Re_2Cl_{10}. In other cases this structure is formed when metal(III) halides are complexed by neutral ligands, as in the following representative compounds: $Ta_2Cl_6(PMe_3)_4$, $Nb_2Cl_6(dppe)_2$, $Mo_2Cl_6(EtSCH_2CH_2SEt)_2$, $W_2Cl_6(py)_4$. In still other cases more varied sets of ligands are present, e.g., $W_2(\mu\text{-}S)_2(OR)_4(S_2CNEt_2)_2$, but still the substance contains neutral molecules rather than an anion. In fact, it would appear that when anions are to be formed, they prefer to have the confacial bioctahedral structure with a composition $[M_2X_9]^{n-}$.

The $OsBr_3(PPh_3)_2(CH_3CN)$ Molecule (2). The reaction by which this compound was obtained is of a type that is simultaneously well-known and poorly understood. The reduction of Os(IV) to Os(III) in the presence of triphenylphosphine in solvents such as ethanol[5] or a nitrile[4] has been observed a number of times before. It is probably the solvent rather than the phosphine that serves as the reductant, but, especially in the case of nitriles, the process has not been well studied. In view of this, the reaction of the $[Os_2Br_{10}]^{2-}$ ion in CH_3CN with Ph_3P to yield compound **2** cannot be considered surprising. It may well proceed through $OsBr_4(PPh_3)_2$ as an intermediate, in which case there would be a clear analogy to the reaction of $OsCl_4(PPh_3)_2$ with acetonitrile to yield $OsCl_3(PPh_3)_2(CH_3CN)$.[4] We have, in fact, shown that compound **2** can be obtained when $(n\text{-}Bu_4N)_2[OsBr_6]$ is used in place of the $[Os_2Br_{10}]^{2-}$ compound.

The molecule of **2** is shown in Figure 2. The molecular structure is very similar to that of the chloro analogue[5] and in fact the two compounds are crystallographically isomorphous.[14] Significant differences in molecular dimensions are few, or nonexistent. The Os–N distances differ by 0.014 (13) Å, which is clearly insignificant. The corresponding Os–Br distances exceed the Os–Cl distances by 0.133 (2), 0.135 (2), and 0.126 (2) Å. All of these are very close to the accepted difference[12] in the covalent radii of chlorine and bromine, 0.15 Å. Only for the Os–P bonds are there differences that are statistically real, viz., 0.014 (2) and 0.010 (2) Å. This slight difference could well be genuine and due to the fact that the effective charge on the osmium atom in the bromo compound is lower and thus the P → Os bond weaker. It could also be due to slightly greater nonbonded repulsive forces between the larger Br atoms and the PPh_3 ligands.

Acknowledgment. We are grateful to the National Science Foundation for support.

Registry No. **1**, 91670-29-0; **2**, 91670-30-3; $(n\text{-}Bu_4N)_2[OsBr_6]$, 3866-51-1.

Supplementary Material Available: Tables of anisotropic thermal vibration parameters, bond distances and bond angles, and observed and calculated structure factors for both compounds (29 pages). Ordering information is given on any current masthead page.

---

(13) Kistenmacher, T. J.; Stucky, G. D. *Inorg. Chem.* **1971**, *10*, 122.

(14) In ref 5 the structure of $OsCl_3(PPh_3)_2(CH_3CN)$ was handled in space group $P2_1/c$, whereas we have used $P2_1/n$ for the bromo compound. The two are simply alternate settings. Our preference for $P2_1/n$ was (and is) based on the fact that it gives a smaller β angle, i.e., 91.15 vs. 113°.