quinoline)$(OH_2)_2$], lengthens to 2.263 (5) Å.[13]

The coordination mode of $CH_3OCO_2^-$ also affects the Zn–O distance, and such a comparison is possible for the five-coordinate structures. The Zn–O length associated with unidentate $CH_3OCO_2^-$ (Zn–O(1) in **3** = 1.965 (3) Å) is slightly shorter than that involved in the bridge coordination (Zn(2)–O(2) in **2** = 2.034 (6) Å). The former value is close to Zn–O distance of 1.946 (6) Å found for a Zn(II) complex with unidentate $CH_3CO_2^-$, [2-(2-benzothiazolyl)-6-[2-(2-thiolophenyl)-2-azaethyl]pyridine](acetato)zinc(II).[14]

It has been suggested that there is a clear-cut difference in bond lengths between the tetahedral and octahedral Zn–O bond.[15] Yachandra et al. have also pointed out recently that there is a clear trend of increasing bond distance with increasing coordination number.[16] The structural data for the present series of monomethyl carbonato complexes show that the Zn–O bond lengthens in the following order, five-coordination with unidentate $CH_3OCO_2^-$ < five-coordination with bridging $CH_3OCO_2^-$ < pseudo-six-coordination < tetragonally distorted octahedral six-coordination.

Chemical Consequences of Coordination of Tetraazacycloalkanes to Zn^{2+} on CO_2 Uptake. Two types of basic structure have been found in this study: (i) a linear chain structure with bridging monomethyl carbonate (**1** and **2**); (ii) a mononuclear structure with a unidentate monoalkyl carbonato ligand (**3**). The cavity sizes of 14- and 15-membered macrocycles are apropriate to accommodate a Zn^{2+} ion in a planar fashion. To our knowledge, square-planar four-coordinate Zn(II) complexes are very rare and (phthalocyanato)- and (tetraphenylporphinato)zinc(II) are the only known examples.[17,18] In general, a Zn^{2+} ion in square-planar array of four nitrogens tends to take up additional ligands at axial positions to form either five- or six-coordinate complex. Therefore, when Zn^{2+} is accommodated into the cavity of the [14]aneN_4 or [15]aneN_4 macrocycle in a planar fashion, its vacant axial sites provide a strong driving force for the coordination of monoalkyl carbonates. Such stereochemical consequences of coordination environments about Zn^{2+} are considered to be responsible for the efficient and facile uptake of CO_2.

In the case of the Me_4[14]aneN_4 system, CO_2 is fixed into the Zn(II) complex as unidentate monomethyl carbonate. Steric constraint provided by four methyl groups prevents bridge coordination of monomethyl carbonate. However, the Me_4[14]aneN_4 ligand folds easily and is impossible to deform tetrahedrally. As a consequence, the complex attains a near trigonal-bipyramidal geometry by taking up $CH_3OCO_2^-$ at the fifth coordination site.

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Registry No. **1**, 94249-74-8; **2**, 94249-70-4; **3**, 94249-72-6.

Supplementary Material Available: Tables of hydrogen atomic coordinates, full bond lengths and angles, and structure factors and stereoscopic views of the crystal structures of complexes **1–3** (62 pages). Ordering information is given on any current masthead page.

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Structural Characterization and Infrared Studies of Tungsten Bromo Carbonyl Compounds

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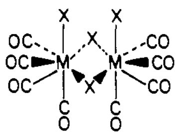
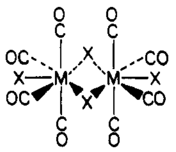
The syntheses of $[WBr(CO)_4]_2(\mu\text{-}Br)_2$ (**1**) and $(CO)_4W(\mu\text{-}Br)_3WBr(CO)_3$ (**2**) are described. Compound **1** crystallizes in the monoclinic space group *C*2/*m* with cell parameters a = 11.244 (9) Å, b = 8.172 (5) Å, c = 9.135 (7) Å, β = 94.58 (6)°, V = 837 (2) Å^3, and Z = 2. The general structure of **1** may be described as that of two edge-sharing capped octahedra having an overall C_{2h} point symmetry but with virtual C_{3v} symmetry about each metal center. Compound **2** crystallizes in space group *Pnma* with lattice parameters a = 20.249 (4) Å, b = 8.058 (2) Å, c = 9.670 (2) Å, V = 1578 (1) Å^3, and Z = 4. The complex has C_s symmetry, with three Br bridges between two W atoms, four CO groups on one end and three CO groups and a bromine atom on the other. In both compounds the metal atoms are seven-coordinate. In **1** the arrangement is that of a *fac*-$WBr_3(CO)_3$ octahedron capped by a CO on the $(CO)_3$ face, while in **2** there is a 4-3 arrangement, either $(CO)_4WBr_3$ or $(CO)_3BrWBr_3$, about each metal atom. The solution infrared spectra of these complexes are shown to be compatible with their solid-state structures.

Introduction

The halo carbonyls of the group 6[12] metals in their formal oxidation states of II, viz., $[MX_2(CO)_4]_x$ compounds with M = Mo or W and X = Cl, Br, or I, are useful starting materials in many interesting reactions.[1-3] Much of the pioneering work on the preparation of these compounds as well as early studies of their reactivity is due to Colton and co-workers.[4] If these compounds were to be formulated as mononuclear, they would be 16-electron species; dinuclear structures, with halogen bridges, such as a[5] and b[1] have therefore been suggested. However, there has still not been any definitive structural proof for any of these compounds, nor can it be said that infrared evidence has been invoked cogently in favor of any particular structure. In view of the fact that compounds of this class have been used in this laboratory for synthetic purposes on several occasions,[2,6] and because they are



a



b

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of rather basic interest, we have undertaken a few structural studies. We have focused on the bromo compounds of tungsten since these were available in connection with another study.[6] Our work has led to the structural characterization of the known compound $[WBr_2(CO)_4]_2$ (**1**) and also to the discovery and structural characterization of a new binuclear tungsten bromo carbonyl compound, $W_2Br_4(CO)_7$ (**2**).

Experimental Section

All syntheses were conducted on a Schlenk line. Isolated products were stored in a nitrogen-filled drybox or in Schlenk tubes. Methylene chloride was dried by refluxing over P_2O_5 under N_2. Hexane and toluene were dried by refluxing over benzophenone ketyl. $W(CO)_6$ was finely ground and stored in a disiccator over Drierite. All other reagents were used as received. IR spectra were obtained on Perkin-Elmer 283 or 783 spectrophotometers.

Syntheses. $W_2Br_4(CO)_8$ (1). The procedure used is based on that of Bowden and Colton.[4] Finely ground $W(CO)_6$ (5.05 g, 14.4 mmol) was suspended in 60 mL of CH_2Cl_2 in a three-neck round-bottom flask. After the suspension was cooled to −78 °C, 0.75 mL of Br_2 in 10 mL of CH_2Cl_2 was transferred via cannula to the stirred suspension. The red-orange solution was observed to be smoothly evolving CO. The solution, containing some undissolved $W(CO)_6$, was allowed to warm slowly with stirring to room temperature to give a dark orange solution, which was concentrated to ca. 5 mL during which time a red-orange microcrystalline precipitate formed. The dark green supernatant liquid was removed via cannula, and the orange precipitate was washed with toluene (10 mL) and then hexane (20 mL). The product was dried in vacuo and stored in a drybox; yield 4.60 g (70%). An infrared spectrum showed no indication of residual $W(CO)_6$ following this procedure. A portion of **1** freshly dissolved in CH_2Cl_2 was recrystallized at −20 °C. IR (CH_2Cl_2): 2095 (w), 2020 (s), 1935 (m) cm^{-1}.

$W_2Br_4(CO)_7$ (2). Tungsten hexacarbonyl (6.31 g, 17.9 mmol) was dissolved in 60 mL of CH_2Cl_2 in a three-neck flask and the resultant mixture cooled to −60 °C. Br_2 (1.0 mL, 19 mmol) was added via syringe, and the suspension was allowed to warm to room temperature with stirring. The dark orange solution was evaporated to dryness and redissolved in 60 mL of fresh CH_2Cl_2. The solution was filtered through a pad of Celite during which copious gas evolution was observed. The filtrate was concentrated to 5 mL, and the supernatant liquid was removed via cannula. The orange product was washed with toluene (15 mL) and hexane (15 mL) and dried in vacuo; yield 2.61 g (33%). A portion of this product was recrystallized at −20 °C from CH_2Cl_2 to give **2** in ca. 40% yield. IR (CH_2Cl_2): 2110 (w), 2100 (w), 2050 (m), 2038 (s), 2025 (s), 1974 (m), 1950 (m) cm^{-1}.

$[NEt_4][WBr_3(CO)_4]\cdot CH_2Cl_2$ (3). Compound **1** (210 mg, 0.23 mmol) was mixed with anhydrous tetraethylammonium bromide (100 mg, 0.48 mmol) in a three-neck flask. CH_2Cl_2 (20 mL) was added via syringe. A clear yellow solution soon formed that turned orange over 1 h with stirring. The solution was evaporated to dryness, and the product was washed with hexane to give a yellow-green powder. A portion of this material was recrystallized at −20 °C to give yellow-green crystals of **3**. IR (CH_2Cl_2): 2085 (m), 2015 (s), 1925 (m) cm^{-1}. IR ($CHCl_3$): 2080 (m), 2010 (s), 1925 (m) cm^{-1}.

X-ray Crystallography. In all cases, the crystallographic work proceeded without any unusual problems and the experimental and computational procedures were those normally used in this laboratory.[7] Important crystallographic parameters are summarized in Table I.

Crystals of compound **1** typically had a very mosaic sort of appearance under a polarizing microscope, and a number of recrystallizations were carried out before a suitable crystal was obtained. The orange plate was mounted in a thin-walled glass capillary using epoxy cement. The cell dimensions were determined by a least-squares fit of 15 strong reflections in the range $20° < 2\theta < 30°$. Systematic absences showed only *C* centering; refinement was undertaken in space group *C*2/*m* (*C*2 and *Cm* being the other possibilities), and this choice was confirmed by successful refinement. On the basis of frequent checking of three reflections, no significant crystal decay (<1%) was noted. Absorption corrections initially were made empirically by employing ψ scans at χ values of 90° and 270 ± 15°;[8a] a further correction was applied according to the method of Walker and Stuart.[8b]

Table I. Crystallographic Parameters

	1	2
fw	911.40	883.41
space group	*C*2/*m*	*Pnma*
formula	$W_2Br_4C_8O_8$	$W_2Br_4O_7C_7$
a, Å	11.244 (9)	20.249 (4)
b, Å	8.172 (5)	8.058 (2)
c, Å	9.135 (7)	9.670 (2)
β, deg	94.58 (6)	
V, Å^3	837 (2)	1578 (1)
d_{calcd}, g/cm^{-3}	3.617	3.719
Z	2	4
cryst size, mm	0.1 × 0.2 × 0.25	0.1 × 0.2 × 0.25
radiation	Mo Kα with graphite monochromation	
diffractometer	Syntex P$\bar{1}$	CAD-4
μ(Mo Kα), cm^{-1}	246.7	249.5
range in 2θ, deg	5–50	4–50
no. of unique data	737	1496
no. of data with $F_o^2 > 3\sigma(F_o^2)$	573	964
no. of variables	60	103
R^a	0.0347	0.0364
R_w^b	0.0429	0.0420
quality of fit^c	0.893	1.168
largest shift/esd, final cycle	0.09	0.08

[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 = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations for $W_2Br_4(CO)_8$ (1)

atom	*x*	*y*	*z*	*B*,^{a} Å^2
W(1)	0.40638 (7)	0.000	0.1816 (1)	2.29 (1)
Br(1)	0.500	0.2174 (2)	0.000	2.96 (4)
Br(2)	0.6132 (2)	0.000	0.3339 (3)	3.47 (4)
C(1)	0.277 (1)	0.000	0.015 (2)	2.8 (4)
C(2)	0.249 (2)	0.000	0.262 (3)	3.6 (5)
C(3)	0.403 (1)	0.203 (2)	0.312 (2)	3.3 (3)
O(1)	0.203 (1)	0.000	−0.073 (2)	3.5 (3)
O(2)	0.157 (1)	0.000	0.314 (2)	5.1 (4)
O(3)	0.399 (1)	0.319 (2)	0.378 (1)	4.8 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

A crystal of compound **2** was also mounted in a capillary with epoxy cement, and the unit cell dimensions were derived from a least-squares fit to 25 reflections in the range $20° < 2\theta < 30°$. The systematic absences were indicative of space groups *Pnma* or *Pna*2$_1$. Refinement was carried out successfully in the former. Monitoring of three check reflections showed that 12% decay, apparently linear and isotropic, had occurred during data collection, and a suitable correction was made. Absorption corrections were made by the same methods used for compound **1**.

The two structures were solved similarly. The positions of the tungsten atoms were determined by inspection of Patterson functions. The remaining atoms were determined in subsequent difference Fourier syntheses. Refinement of the structures by full-matrix least-squares techniques led to the residuals listed in Table I. Anisotropic thermal parameters were used for all atoms in **1**. All atoms in **2** were treated anisotropically, except for C(1), which was treated isotropically.

Inspection of final difference Fourier maps showed no peaks of structural significance. Final fractional coordinates are listed in Tables II and III, and structure factor tables are available as supplementary material.

Results and Discussion

Structures. $W_2Br_4(CO)_8$ (1). This compound is formed of discrete dinuclear molecules having the structure shown in Figure 1. The molecules reside on crystallographic sites of 2/*m* (C_{2h}) symmetry. The molecular structure is similar to the previously proposed structure a but differs in having a centrosymmetric, transoid arrangement of bromine atoms. Table IV lists the bond distances and the important bond angles.

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Table III. Positional Parameters and Their Estimated Standard Deviations for $W_2Br_4(CO)_7$ (2)

atom	*x*	*y*	*z*	*B*,[a] Å^2
W(1)	0.40440 (4)	0.250	0.1497 (1)	2.20 (2)
W(2)	0.35579 (4)	0.250	−0.2160 (1)	2.15 (2)
Br(1)	0.3030 (1)	0.250	0.3183 (3)	3.87 (6)
Br(2)	0.33758 (7)	0.4626 (2)	−0.0119 (2)	3.78 (3)
Br(3)	0.47185 (9)	0.250	−0.0885 (3)	3.80 (6)
O(1)	0.4558 (6)	0.250	−0.458 (2)	4.5 (4)
O(2)	0.3313 (5)	0.574 (1)	−0.390 (1)	4.8 (3)
O(3)	0.2036 (7)	0.250	−0.281 (2)	4.6 (4)
O(4)	0.5520 (6)	0.250	0.233 (2)	6.0 (5)
O(5)	0.4259 (5)	0.557 (2)	0.338 (1)	5.2 (3)
C(1)	0.4160 (8)	0.250	−0.374 (2)	2.2 (4)*
C(2)	0.3409 (7)	0.460 (2)	−0.328 (2)	3.7 (4)
C(3)	0.2561 (9)	0.250	−0.260 (2)	2.9 (5)
C(4)	0.498 (1)	0.250	0.200 (3)	4.7 (7)
C(5)	0.4190 (7)	0.441 (2)	0.270 (2)	3.6 (4)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table IV. Bond Distances and Selected Angles in $W_2Br_4(CO)_8$ (1)

Distances, Å

W(1)-Br(1)	2.701 (2)	C(1)-O(1)	1.12 (3)
-Br(2)	2.613 (2)	C(2)-O(2)	1.17 (3)
-C(1)	2.02 (3)	C(3)-O(3)	1.12 (2)
-C(2)	1.97 (2)		
-C(3)	2.04 (2)		

Angles, deg

Br(1)-W(1)-Br(1)′	82.27 (7)	C(2)-W(1)-C(1)	71 (1)
-Br(2)	87.31 (4)	-C(3)	74.0 (6)
W(1)-Br(1)-W(1)′	97.73 (7)	C(1)-W(1)-C(3)	113.2 (5)
Br(1)-W(1)-C(2)	129.4 (4)	C(3)-W(1)-C(3)′	108.5 (9)
Br(2)-W(1)-C(2)	126.2 (8)	W(1)-C(1)-O(1)	177 (2)
		-C(2)-O(2)	178 (2)
		-C(3)-O(3)	177 (2)

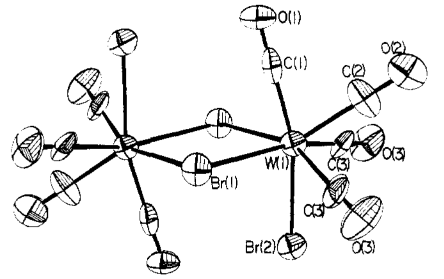

Figure 1. $W_2Br_4(CO)_8$ molecule in compound **1**. Atoms are represented by thermal ellipsoids at the 50% level. There is an inversion center relating unlabeled atoms to labeled ones.

The complete structure can be regarded as the result of taking two capped octahedral $WBr_3(CO)_4$ units, in which the *fac*-$WBr_3(CO)_3$ octahedron is capped by a CO group on the $(CO)_3$ face, and joining them, centrosymmetrically, by having them share one Br···Br edge. Figure 2 gives another view of the molecule looking approximately down the line O(2)–C(2)–W(1), which would be the threefold symmetry axis of an ideal capped octahedral $WBr_3(CO)_4$ unit. In the actual structure there are, of course, deviations from C_{3v} local symmetry, as may be seen in Table IV. For example, the angles made by the W–Br bonds with the W–C(2) bond (the approximate C_3 symmetry axis) are ca. 129, 129, and 126°, and the angles from the W–C(2) bond to the other three W–C bonds are ca. 71, 74, and 74°.

The capped octahedral structure of half of the $W_2Br_4(CO)_8$ molecule is very similar to the structure of the anion in $[NEt_4][WBr_3(CO)_4]$, which has been reported briefly by Drew and Wolters.[9] The $[WBr_3(CO)_4]^-$ ion has virtual C_{3v} symmetry, with distances and angles very similar to those found in each half of compound **1**. The small differences that are observed can clearly be attributed to the fact that in **1** two of the Br atoms are bridging while in the $[WBr_3(CO)_4]^-$ ion they are all terminal.

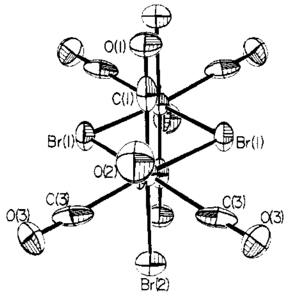

Figure 2. Another view of the $W_2Br_4(CO)_8$ molecule looking down the CO group that is the capping ligand in one of the capped octahedral moieties.

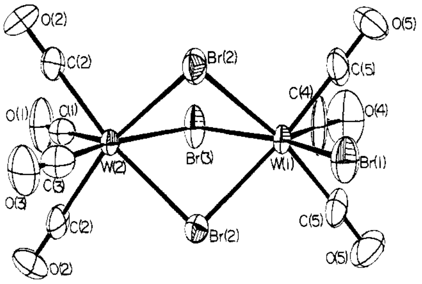

Figure 3. $W_2Br_4(CO)_7$ molecule in compound **2**. Atoms are represented by thermal ellipsoids at the 50% level.

Table V. Bond Distances and Selected Angles in $W_2Br_4(CO)_7$ (2)

Distances, Å

W(1)-Br(1)	2.622 (2)	W(2)-C(1)	1.95 (2)
-Br(2)	2.684 (2)	-C(2)	2.03 (2)
-Br(3)	2.677 (2)	-C(3)	2.06 (2)
W(2)-Br(2)	2.639 (2)	C(1)-O(1)	1.15 (2)
W(2)-Br(3)	2.654 (2)	C(2)-O(2)	1.11 (2)
W(1)-C(4)	1.96 (2)	C(3)-O(3)	1.08 (2)
-C(5)	1.95 (2)	C(4)-O(4)	1.14 (2)
		C(5)-O(5)	1.15 (2)

Angles, deg

W(1)-Br(2)-W(2)	87.17 (5)	C(5)-W(1)-C(5)′	104 (1)
-Br(3)-W(2)	87.01 (6)	C(4)-W(1)-C(5)	72.9 (6)
Br(2)-W(1)-Br(2)′	79.30 (8)	C(1)-W(2)-C(3)	116.8 (8)
-Br(3)	75.91 (5)	C(2)-W(2)-C(2)′	113.0 (9)
-W(2)-Br(2)′	80.94 (8)	C(1)-W(2)-C(2)	71.2 (5)
-Br(3)	77.08 (5)	C(2)-W(2)-C(3)	75.3 (5)
C(4)-W(1)-Br(1)	127.3 (7)		

$W_2Br_4(CO)_7$ (2). The structure of this unsymmetrical molecule is shown in Figure 3. It resides on a crystallographic mirror plane, and this is, indeed, the highest symmetry it can have. In this molecule, as in **1**, it is evident that a coordination number of seven is preferred by the tungsten(II) atoms. However, it is achieved in a different way and results in a different type of coordination polyhedron about the metal atoms. For each tungsten atom there is a 4-3 arrangement of ligands, with the set of three for each one being the three bromine atoms that are shared as μ-Br bridges. On one end, W(2), the set of four ligands is made up entirely of CO groups while on the other end, W(1), there are three CO groups and a bromine atom. The principal bond lengths and angles are listed in Table V.

The imbalance in the distribution of terminal ligands would, by itself, tend to make W(1) effectively more oxidized than W(2). However, there seems to be a compensatory effect in the bonding to the bridging bromine atoms. The W(1) to bridge atoms bonds are about 0.25–0.45 Å longer than those to W(2). The errors in the W–C and C–O distances are large enough that a search for systematic variations is fruitless.

There are two previous structures with which that of **2** might be compared. The closest comparison can be made with the

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[9] Drew, M. G. B.; Wolters, A. P. *J. Chem. Soc., Chem. Commun.* **1972**, 457.

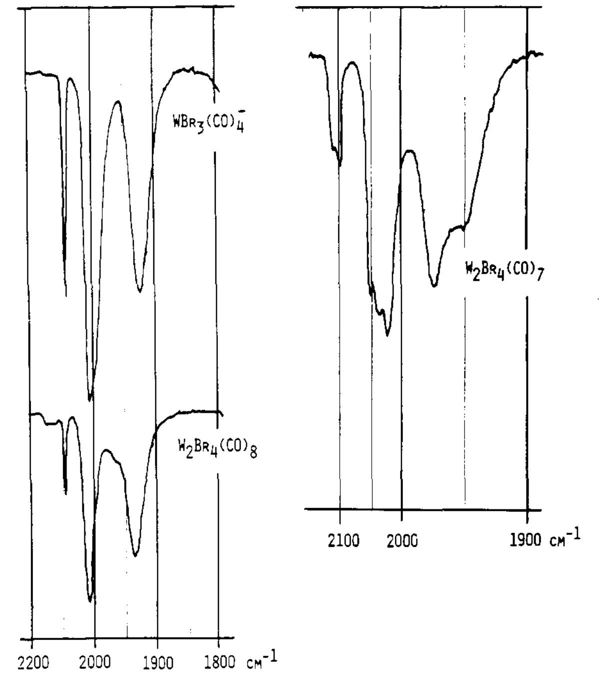

Figure 4. Infrared spectra in CH_2Cl_2 solutions of the two dinuclear compounds and, for comparison, of the $[WBr_3(CO)_4]^-$ ion.

$[Mo(CO)_2L_2]_2(\mu\text{-}Cl)_3^+$ ion,[10] where L = $P(OMe)_3$. While there were some technical difficulties in the crystallographic work, the model refined by Drew and Wilkins, as well as the proposed charge of 1+ on the cation, appears to be correct, and the structure is then obviously a forerunner of our $W_2Br_4(CO)_7$ structure. Exactly the same fusion of two 4-3 seven-coordinate units on a common set of three bridging halogen atoms is seen. The mean Cl–Mo–Cl angle (76°) is within the range of Br–W–Br angles, 76–81°, that we have found. The $[W_2Br_9]^{2-}$ ion also contains a set of three bridging bromine atoms,[11] but it differs considerably since there is a direct W–W bond and this leads to much more acute W–Br–W angles (ca. 60°) and much larger Br–W–Br angles (ca. 97°) although the W–Br distances (ca. 2.60 Å) are comparable to those in $W_2Br_4(CO)_7$.

Infrared Spectra. The infrared spectra of the three compounds whose structures have been discussed, as well as that of $[NEt_4][WBr_3(CO)_4]$, are shown in Figure 4. Exact frequencies have been listed in the Experimental Section. The spectrum of the $[WBr_3(CO)_4]^-$ ion is in accord with its structure, assuming that ideal C_{3v} symmetry prevails. There should be three infrared-active modes: (1) one mode of A_1 type arising from the unique CO group along the threefold molecular axis; (2) a second mode of A_1 type arising in the set of three equivalent CO groups; (3) a mode of E symmetry also arising in the set of three. Presumably the two higher frequency bands are the A_1 modes and the lowest frequency band is the E mode.

The spectrum of $W_2Br_4(CO)_8$ is very similar to that of the $[WBr_3(CO)_4]^-$ ion. This is in good accord with the structure, which, as discussed above, consists of two equivalent halves that are each slightly perturbed forms of the $[WBr_3(CO)_4]^-$ ion. Previously, Bowden and Colton[4] had reported a four-band spectrum for "$WBr_2(CO)_4$" that included three bands at about the positions of those we find and in addition a strong band at 1980 cm^{-1}. The latter band is clearly due to an impurity (apparently present in substantial quantities) that we suggest is probably $W(CO)_6$.

The infrared spectrum of $W_2Br_4(CO)_7$ exhibits at least seven bands. For the structure we have found, seven bands are to be expected.

Origin of $W_2Br_4(CO)_7$. Neither this compound nor any other $M_2X_4(CO)_7$ compound has previously been reported. Obviously it could arise from $W_2Br_4(CO)_8$ by loss of CO, and we believe that this is, in fact, how it is formed. In the preparation of this compound there are two points of difference compared to the procedure for obtaining $W_2Br_4(CO)_8$. After the bromination of $W(CO)_6$ has been carried out, the solution is evaporated to dryness in the procedure for $W_2Br_4(CO)_7$. The solid is then redissolved and the solution filtered through Celite, during which process gas evolution is observed. Surely in the second of these steps and perhaps in both, CO is lost in the conversion of $W_2Br_4(CO)_8$ to $W_2Br_4(CO)_7$.

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Registry No. 1, 94668-00-5; 2, 94570-82-8; 3, 18129-64-1; $W(CO)_6$, 14040-11-0.

Supplementary Material Available: Listings of bond angles not included in the paper, anisotropic thermal parameters, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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(11) Templeton, J. L.; Jacobson, R. A.; McCarley, R. E. *Inorg. Chem.* **1977**, *16*, 3320.

(12) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.