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Comparison between Mo–Mo and W–W Bonding in Oxide Clusters: Crystal Structure of $Zn_2MoW_2O_8$ Determined by Time-of-Flight Powder Neutron Diffraction

Metal clusters are a common feature of mixed-metal oxides of molybdenum in which the Mo is present in a low formal oxidation state. The first reported example was $Zn_2Mo_3O_8$,[1] which contains triangular Mo_3O_{13} clusters (Figure 1) with a Mo–Mo single-bond distance of 2.532 Å, but many other examples have been reported in the last 10 years. These include $NaMo_4O_6$,[2] with an infinite chain of fused, edge-sharing Mo_6 octahedra, $In_{11}Mo_{40}O_{62}$,[3] which contains finite chains of four and five edge-sharing octahedra, and $LaMo_5O_8$,[4] in which double octahedral Mo_{10} units are linked by further metal–metal bonding. By contrast, our own attempts, and those of others, to prepare tungsten analogues of these phases have been unsuccessful, with the exception of a report of a metastable form of $Zn_2W_3O_8$,[5] which decomposes according to

$$Zn_2W_3O_8 \rightarrow 2ZnWO_4 + W \qquad (1)$$

The tungsten compound is apparently isomorphous with the molybdenum analogue and forms a continuous solid solution with it. In the present work, we have refined the structure of a solid solution with the composition $Zn_2MoW_2O_8$ and shown that, in spite of the apparent instability of the tungsten compound, the W–W bond in this system is almost identical with, and probably shorter than, the M–M contact in the molybdenum end-member.

We were unable to synthesize a pure sample of metastable $Zn_2W_3O_8$ by the method of Tourne and Czeskleba,[5] but we were able to replace two-thirds of the molybdenum by tungsten in the solid-solution $Zn_2Mo_{3-x}W_xO_8$. The reaction involved heating stoichiometric proportions of ZnO, MoO_3, WO_3, and W metal at 500 °C for 15 h and 900 °C for 28 h, followed by regrinding and firing at 900 °C for a further 48 h. Sample homogeneity and the cation ratios were confirmed by analytical electron microscopy, and the Mo/W ratio of 1/2 was fixed in the subsequent structural refinement. The lattice parameters were carefully determined by powder X-ray diffraction with an internal standard: a = 5.7891 (8) Å and c = 9.941 (1) Å, in the hexagonal cell ($P6_3mc$ given by McCarroll et al.[1]). A sample of $Zn_2Mo_3O_8$, which was run immediately following the title compound, gave lattice parameters a = 5.7770 (8) Å and b = 9.923 (1) Å, in excellent agreement with the values reported by McCarroll et al.[1] (a = 5.775 (5) Å and c = 9.915 (10) Å) but somewhat larger than the values given in a more recent examination of the $Zn_2Mo_3O_8$ structure (a = 5.759 (5) Å and c = 9.903 (5) Å).[6]

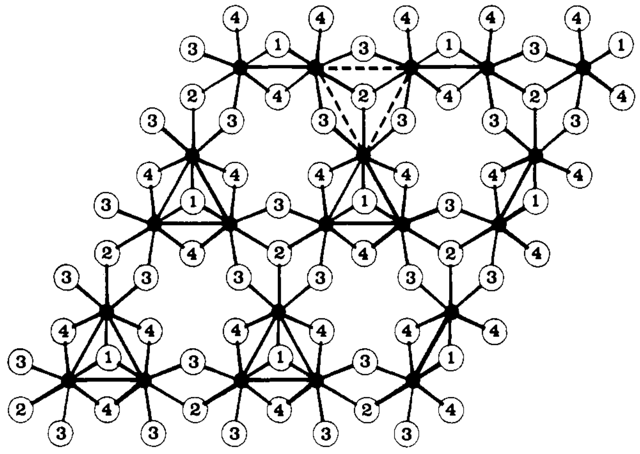

Figure 1. Crystal structure of $Zn_2Mo_3O_8$, viewed down [001]. The Mo atoms are shaded, the oxygen atoms (open circles) are numbered, and the Zn atoms are omitted for clarity. The structure of the title compound is essentially identical.

Table I. Neutron Diffraction Data Collection and Analysis

data range	30 000–130 000 μs (d = 0.62–2.69 Å) collcd 36 000–124 000 μs (d = 0.75–2.57 Å) analyzed 160 contributing reflcns 23 variables
sample can	flat-plate aluminum can with thin vanadium windows
scattering lengths[7]	Zn: 5.680 fm Mo: 6.950 fm W: 4.770 fm O: 5.805 fm
refinement	Rietveld method;[8] program VDELSQ[9]
background	three-term Chebychev polynomial
function minimized	$\sum_i w_i(y_i(\text{obs}) - y_i(\text{calc}))^2$ with $w_i = 1/\sigma_i^2$ (σ_i based on tot. count)
peak shape	Voigt convoluted with a double exponential[9]

Powder neutron diffraction data were collected by time-of-flight methods on the high-resolution powder diffractometer (HRPD) at the ISIS facility (Rutherford-Appleton Laboratory); details of the data collection and structure refinement are given in Table I. The initial structural model for a Rietveld profile analysis[8] was taken from ref 1. Atomic coordinates and isotropic tem-

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Table II. Important Bond Lengths/Å and Bond Angles/deg in $Zn_2Mo_3O_8$ and $Zn_2MoW_2O_8$

	$Zn_2Mo_3O_8$	$Zn_2MoW_2O_8$
(a) Coordination around Mo and Mo/W		
M-O(1)	2.00 (3)	2.022 (4)
M-O(2)	2.13 (3)	2.135 (3)
M-O(3) × 3	2.06 (1)	2.085 (2)
M-O(4) × 3	1.93 (2)	1.954 (2)
mean M-O	2.01	2.034
M-M (within cluster)	2.532 (2)	2.523 (3)
M-O(1)-M	78.2 (8)	77.2 (2)
M-O(4)-M	81.8 (5)	80.4 (1)
(b) Coordination around Zn		
Zn(1)-O(2)	1.99 (3)	2.015 (8)
Zn(1)-O(3) × 3	1.98 (1)	1.965 (3)
Zn(2)-O(3) × 3	2.12 (1)	2.176 (4)
Zn(2)-O(4) × 3	2.07 (2)	2.024 (4)

perature factors for Zn, W/Mo, and O were refined: $R_p = 9.15\%$, $R_{wp} = 10.33\%$, and $\chi^2 = 1.06$. In Table II, some important bond lengths in the $Zn_2MoW_2O_8$ structure are compared with the corresponding values in $Zn_2Mo_3O_8$. For this comparison, the fractional coordinates given in ref 6 were used, together with the more accurate lattice parameters obtained in the present work.

The most striking feature of our refinement is that the metal-metal single bond in the mixed triangular cluster is almost identical with, and probably slightly shorter than, the Mo-Mo distance in $Zn_2Mo_3O_8$. Extrapolating our results to the pure tungsten end-member, we would predict a W-W bond length of 2.518 Å. This trend is in agreement with the metal-metal distances in the distorted MO_2 rutile structures, with Mo-Mo = 2.5106 (5) Å[10] and W-W = 2.475 Å,[11] and with thermochemical estimates which suggest that W-W bonds are stronger than their molybdenum analogues.[12] The single-bond M-M distances in the triangular alkoxide clusters, $M_3O(OR)_{10}$ with R = *i*-Pr, which yield Mo-Mo = 2.534 (5) Å[13] and W-W = 2.540 (6) Å,[14] are also in good agreement with our results. On the other hand, it is interesting to recall that Mo-Mo bonds become significantly shorter than their W-W counterparts in complexes containing triple or quadruple M-M bonds.[15]

The similarity between the Mo-Mo and W-W bond lengths in the $Zn_2Mo_{3-x}W_xO_8$ system can be contrasted with the overall increase in cell volume, which reflects the fact that the W-O bonds are longer than Mo-O bonds. The marginal shortening of the M-M bond and the lengthening of M-O distances in the title compound result in the M-O(1)-M and M-O(4)-M angles becoming more acute (Table II); O(1) lies centrally above the cluster, and O(4) bridges the edges of the cluster.

We must now address the question as to why the tungsten oxide cluster compounds are unstable, in spite of the fact that W-W single bonds are apparently as short as, and therefore probably stronger than, Mo-Mo bonds. In this regard, it is instructive to examine the energetics of the disproportionation of MoO_2 and WO_2 according to the following equation:

$$3MO_2 \rightarrow 2MO_3 + M \qquad (2)$$

From thermochemical data for the corresponding dioxides and trioxides,[16,17] it can be shown that the heat of disproportionation of MoO_2 (+92.2 kJ mol^{-1}) is considerably higher than that of WO_2 (+27.5 kJ mol^{-1}), even though their heats of formation are almost identical. This result and the structural findings in the present work point to the conclusion that the instability of tungsten oxide cluster compounds stems not from the weakness of the W-W bonds but from the high sublimation energy of W metal and the relative ease with which tungsten is oxidized to the +VI oxidation state. These factors are consistent with decomposition pathways of the type shown in eq 1. If the behavior in the solid state is analogous to that in the coordination complexes, we would also expect that tungsten oxide clusters are even less likely to be found in phases that would require multiply bonded W-W interactions.

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Supplementary Material Available: Table SI, listing atomic coordinates and isotropic temperature factors for Zn, Mo/W, and O (1 page). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of the First Gallacarborane Sandwich

We recently described a unique synthetic route leading to the *commo*-aluminacarborane sandwich, Tl[*commo*-3,3′-Al(3,1,2-$AlC_2B_9H_{11})_2$] (**1**).[1] As part of our continuing research effort with main-group metallacarboranes, we have attempted to expand this procedure to other group 13 metals. We now report the synthesis and single-crystal X-ray diffraction study of the first *commo*-gallacarborane sandwich, Tl[*commo*-3,3′-Ga(3,1,2-$GaC_2B_9H_{11})_2$] (**2**). Although minor differences exist between the preparative routes that lead to **1** and **2**, the results presented here support the mechanism proposed in the initial communication.

The addition of a toluene solution containing 2 molar equiv of gallium(III) chloride to a suspension of 1 molar equiv of $Tl_2[7,8\text{-}C_2B_9H_{11}]$ in toluene formed **2** in 100% yield based on carborane as determined by ^{11}B FTNMR. During the course of the reaction, the mixture became colorless and free of suspended solids. The product **2** was isolated in only 55% yield due to difficulties inherent in its separation from the other reaction products. Fractional crystallization of the reaction solution using heptane as the countersolvent first produced $TlGaCl_4$, followed by **2**.[2] The crystals of **2** obtained by this means proved to be suitable for a single-crystal X-ray diffraction study. The ^{11}B FTNMR, ^1H FTNMR, and IR spectra of **2** were characteristic of a compound that contains a single type of symmetric carborane cage. The formulation $Tl[Ga(C_2B_9H_{11})_2]$ was confirmed by elemental

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(2) $GaCl_3$ (325 mg, 1.85 mmol) was dissolved in approximately 100 mL of toluene in the glovebox. This solution was added to a suspension of $Tl_2(7,8\text{-}C_2B_9H_{11})$ (500 mg, 0.92 mmol) in toluene and the mixture stirred. After 1 h, the solution became homogeneous and colorless. The final product was isolated by fractional crystallization using heptane as the countersolvent. The composition of the material isolated was monitored by mass spectroscopy (the disappearance of the *m/e* peaks due to $TlGaCl_4$) and IR spectroscopy (the appearance of the B-H stretching vibration due to the carborane cage of **2** at 2522 cm^{-1}). When $TlGaCl_4$ was no longer observable the product was washed with heptane yielding 136 mg (55%) of colorless, crystalline **2**.