tautomerism, but the data obtained thus far suggest that the open face of the *i*-B_9H_{15} cage is surrounded by bridging hydrogens and not by interconverting terminals and bridges. Rather long boron–boron distances around the periphery of the open face along with a slight asymmetry of B–H–B distances are proposed to account for a reduction in the severe nonbonded H–H interactions which would be expected in such a structure.

Acknowledgment. D.C.M. wishes to thank the Lubrizol Foundation for support in the form of a research fellowship. We gratefully acknowledge support from the National Science Foundation (Grant No. MPS 73 04669 A01).

Registry No. B_8H_{14}, 12008-46-7; *i*-B_9H_{15}, 12447-79-9.

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Notes

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Electronic Structure of Tungsten and Some of Its Borides, Carbides, Nitrides, and Oxides by X-Ray Electron Spectroscopy[1]

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Received April 15, 1975 AIC50263W

Results of an x-ray electron spectroscopic investigation of the core and valence electronic energy levels of tungsten and some of its borides, carbides, nitrides, and oxides are presented in this communication. This investigation stems from some of the recent interest in this laboratory dealing with studies of substoichiometric amorphous thin films of some transition metal oxides[2a] and of the catalytic behavior of tungsten carbide.[2b] It was concluded in the WC investigation[2b] that electron density shifts from W to C. In addition, we found it interesting to observe the shifts in electron density upon addition of nonmetal substituents (varying in the number of *p* electrons) to the tungsten matrix. We have just this situation in the series of compounds W, WB, WC, WN, WO_2, and WO_3.

Experimental Section

The samples studied in this investigation were W foil and WB, WC, W_2N + WN (mixture), WO_2, and WO_3 powders pressed into pellets. The tungsten oxides were obtained from RESEARCH Organic/Inorganic Chemical Corp. and the remaining samples from Ventron Corp., Alfa Inorganics. The W foil had a listed metallic purity of 99.95% and the WB and W_2N + WN (mixture) powders both had a listed purity of 99.5%. The purity of the WC powder was not reported. The WO_2 and WO_3 powders had a listed purity of 99 and 99.5%, respectively. X-ray diffraction patterns of WC, WO_2, and WO_3 showed that the samples were single phased with no detectable impurities. WB was found to actually exist as W_2B + WB (mixture) and W_2N + WN (mixture) was initially amorphous. In all cases, the photoelectron measurements revealed some oxide and carbon contamination.

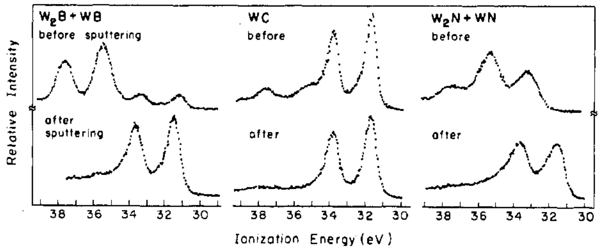

Figure 1. Photoelectron spectra of W_2B + WB, WC, and W_2N + WN 4*f* levels before and after sputtering with 500 V Ar ions.

Photoelectron spectra were recorded with a Hewlett-Packard 5950A ESCA spectrometer using monochromatized Al Kα (1486.6 eV) radiation. The instrumental resolution was ~0.55 eV measured as fwhm of the C 1s line of graphite. Samples were maintained at a temperature of 300°K and a vacuum of below 2×10^{-9} Torr during analysis. Charging effects were controlled by flooding the sample surface with a low flux (~0.4 mA) of zero kinetic energy electrons during analysis. Calibration was performed by vacuum evaporation of gold onto the sample surface and referencing the sample spectrum to the Au $4f_{7/2}$ peak at 83.8 eV.[3] The oxide impurity on the surface of the W foil was removed mechanically by a specially constructed grinding mechanism[4] designed to clean sample surfaces inside the high vacuum (below 2×10^{-8} Torr) sample preparation chamber. The W_2B + WB (mixture), WC, and W_2N + WN (mixture) samples were subjected to a "soft ion sputtering" procedure[5] utilizing 500 V Ar ions. Reduction of WO_2 to W was evident with the above procedure.[5] The WO_3 sample required no cleaning.

Results and Discussion

Data from the photoelectron measurements made in this laboratory on some core levels of W, W_2B + WB, WC, W_2N + WN, WO_2, and WO_3 are presented in Table I. They are grossly consistent with some of those previously reported by several authors.[6–12] Table I lists the energies for the W $4f_{7/2}$ and $4f_{5/2}$ levels plus their respective splitting (ΔW 4*f*) for each of the samples studied. Reproducibility of the W 4*f* binding energies is between ±0.1 and 0.2 eV and that for the observed splitting is ±0.05 eV. In addition, energies for the nonmetal 1s line are given and where applicable the energy for the contaminant line is also given. The reproducibility of these lines is ±0.2 eV. For the cases where two sets of data are given for one sample, the set labeled "NS" represents data taken on a sample that has not been Ar ion sputtered as opposed to those labeled "S" representing samples that have been Ar ion sputtered. Figure 1 shows the W 4*f* levels of these samples before and after Ar ion sputtering. Note the shift in binding energy for all cases and the disappearance of the high-binding-energy peaks after sputtering. These higher-energy peaks are due to tungsten oxide contamination of the surface. The tungsten boride spectrum shows that the surface is composed primarily of tungsten oxide before sputtering; this oxide is effectively removed by sputtering. These shifts clearly

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Table I. Data from Photoelectron Measurements (eV) on Some Core Levels of W, W_2B + WB, WC, W_2N + WN, WO_2, and WO_3[a]

	W	W_2B + WB		WC		W_2N + WN		WO_2	WO_3
Levels	G	NS	S	NS	S	NS	S	NS	NS
W $4f_{7/2}$	31.2	31.2	31.4	31.6	31.7	33.3	31.6	32.5	35.5
W $4f_{5/2}$	33.4	33.3	33.6	33.7	33.9		33.8		37.6
ΔW 4*f*	2.19	2.12	2.17	2.12	2.17		2.22		2.14
Nonmetal 1s		193.4	188.0	282.6	282.8	397.3	397.5	530.2	530.3
C 1s contaminant				284.4	284.4				
N 1s contaminant						399.5	399.5		

[a] G = mechanically ground in vacuum; S = sample sputtered by 500 V Ar ions; NS = sample not sputtered (used as received).

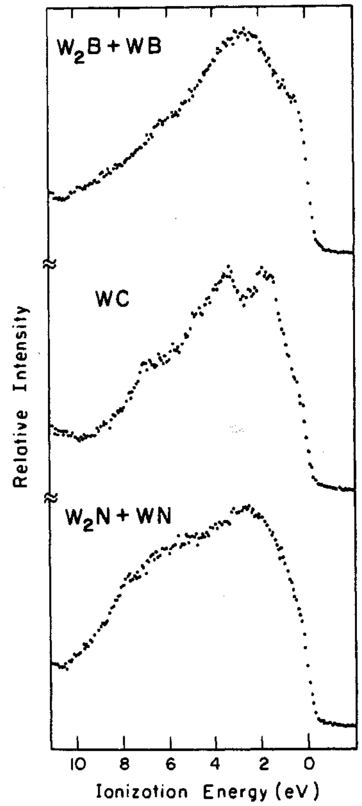

Figure 2. Photoelectron valence band spectra of W_2B + WB, WC, and W_2N + WN after sputtering with 500 V Ar ions.

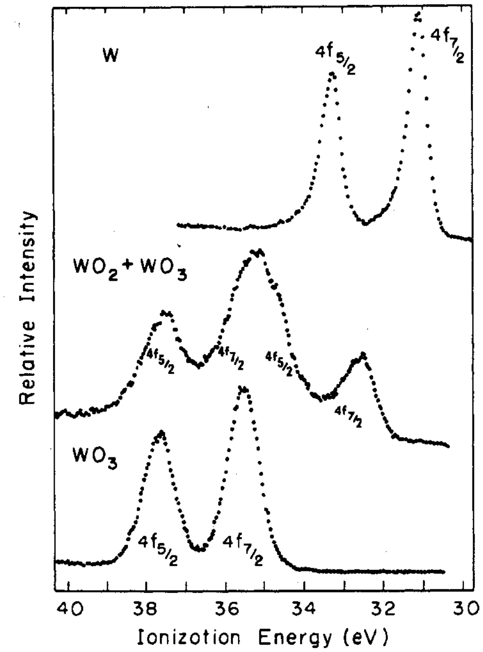

Figure 3. Photoelectron spectra of W foil, WO_2 + WO_3, and WO_3 4*f* levels.

indicate the problem associated with surface characterization. Is the sample surface representative of the bulk or just an artifact of the sputtering process? It is known that preferential sputtering of lighter elements may take place, that Ar ions may be implanted, and that crystalline solids may become disordered. These problems are the subject of a forthcoming communication.[4] A similar shift in the B 1s level (spectrum not shown) was observed by Mavel et al.[10] between what they termed their "oxidized form" and "nonoxidized form" for WB; however, no mention was given on how they obtained these forms. Figure 2 shows the photoelectron measurements on the valence bands of these Ar ion sputtered samples. Note the enhancement of intensity in the 4–8-eV region of the valence bands as one precedes from top to bottom in Figure 2. This is the expected energy region for the nonmetal 2p band. The intensity increase is in accord with the increase in photoionization cross section as $B < C < N < O$ for 2p orbitals.[13,14] The broadened and diffuse nature of these valence bands resembles that of the valence band of a sputtered W foil[4] (not shown), especially for the W_2B + WB and W_2N + WN samples in the 0–5-eV region. These observations combined with the observed core level shifts may be an indication of sample surface amorphousness.[4,15]

Figure 3 shows the W $4f_{7/2}$ and $4f_{5/2}$ core levels of W, WO_2 + WO_3, and WO_3 samples. Note the large chemical shifts observed for W with 0, +4, and +6 "formal oxidation states". This feature is nicely reflected in the valence region of W, WO_2 + WO_3, and WO_3 (Figure 4). These valence band spectra clearly indicate that the tungsten 5d and 6s bands are occupied (containing 6 electrons) in W metal, partially occupied (containing 2 electrons) in WO_2, and completely empty in WO_3.

Since 6s and 5d electrons of W have a much larger x-ray photoionization cross section[13,14] than do 2p electrons of B, C, or N (e.g., $\sigma W_{5d}/\sigma C_{2p} \sim 141$ and $\sigma W_{6s}/\sigma C_{2p} \sim 25$ per electron), the area ratio of the valence band to a tungsten core band in W_2B + WB, WC, W_2N + WN, or WO_2 + WO_3 (WO_3 was not used since its W 5d and 6s bands are empty), compared with a similar area ratio in W, can help elucidate the nature of the occupied valence bands of W_2B + WB, WC, W_2N + WN, and WO_2. From our experimental data for *nonsputtered* samples, the area ratios of the valence band to W 4*f* lines in W_2B + WB, WC, and WO_2 + WO_3 are found to be less (~4, ~7, and ~2.5%, respectively) and in W_2N + WN greater (~3%) when compared with the similar area ratio in elemental W. This indicates for the W_2B + WB, WC, and WO_2 samples that there has been a shift of electron density from the W valence bands to the nonmetal 2p band. Chemical shifts in the core levels of the W_2B + WB, WC, and WO_2 (and W_2N + WN) relative to elemental W and nonmetal substituents reflect a charge transfer from W to the nonmetal atom(s). These observations for W_2B + WB, WC, and WO_2 are consistent with the direction of charge transfer found experimentally and theoretically in some other transition metal carbides.[6,7] The data for W_2N + WN are in conflict. Initially, the W_2N + WN sample was found to be amorphous.

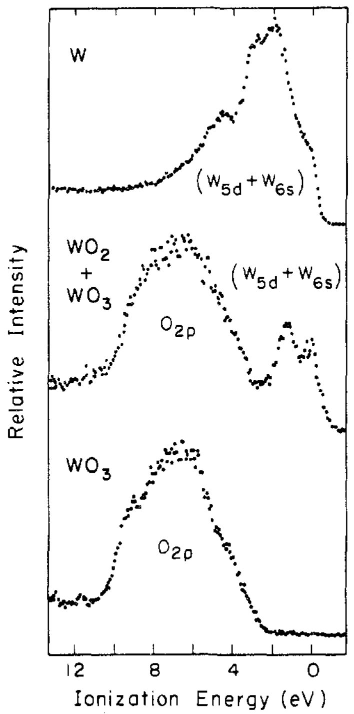

Figure 4. Photoelectron valence band spectra of W foil, WO_2 + WO_3, and WO_3. The surface of the W foil was mechanically ground in vacuum.

When the W_2B + WB or WC samples were made amorphous by Ar ion sputtering, their area ratios changed significantly. In these cases the area ratio becomes greater due to the increase in area of the broadened and diffuse valence bands. Perhaps the conflict for the W_2N + WN sample lies within its amorphous nature or is due to the fact that it is a mixture. Unfortunately, a more reliable numerical result along this line has to be deferred until a later time.

Acknowledgment. The authors express their gratitude to the National Science Foundation for a grant (GP-37724) which made acquisition of the electron spectrometer possible.

Registry No. W, 7440-33-7; W_2B + WB, 57016-62-3; WC, 12070-12-1; W_2N + WN, 57016-63-4; WO_2, 12036-22-5; WO_3, 1314-35-8; WO_2 + WO_3, 57016-64-5.

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Vibrational Spectra of Binuclear Molybdenum Sulfate Complexes of High Bond Order

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Received May 30, 1975 AIC50497F

Numerous molybdenum(II) compounds discovered in the last decade have a Mo-to-Mo quadruple bond. The central group in all these compounds, $Mo–Mo^{4+}$, is coordinated to monodentate ligands, such as chloride[1] (in $Mo_2Cl_8{}^{4-}$), or bidentate bridging ligands, such as acetate[2] (in $Mo_2(CH_3COO)_4$) or sulfate[3,4] (in $Mo_2(SO_4)_4{}^{4-}$). Most of the relevant information on these binuclear molybdenum(II) compounds was derived from x-ray crystallography. The very short metal–metal bond length in $Mo_2{}^{4+}$ (2.10 to 2.15 Å), in conjunction with other structural data and theoretical considerations,[1,5] furnished the main evidence for the existence of a quadruple bond between the two metal atoms.

The use of vibrational spectroscopy, mainly Raman scattering, in the study of binuclear Mo(II) species was mainly oriented toward the characterization of the metal–metal stretching fundamental ν_1. This frequency was found to be in most compounds between 406 cm^{-1} (in the tetraacetate) and 335 cm^{-1} (in the octabromide ion).[4,6,7] The overtones $n\nu_1$ of this fundamental were observed in $Mo_2Cl_8{}^{4-}$ by resonance Raman spectroscopy.[4,8,9] Observation of an overtone progression in ν_1 out to $5\nu_1$ enables the deduction of the harmonic frequency ω_1 and the anharmonicity constant X_{11}.

Cotton, Frenz, and Webb[10,11] discovered the remarkable compound $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ in which the Mo-to-Mo bond order is 3.5. They carried out an extensive x-ray crystallographic study of the pink $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ and the blue $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$. The important structural unit in each compound is the $Mo_2(SO_4)_4{}^{n-}$ ion, in which four bidentate sulfate ions, related by a fourfold axis, serve as bridges across the strongly bonded pair of molybdenum atoms. Thus, in spite of the difference in color, and in oxidation state, caused by the removal of one electron from the quadruple bond, the two complex ions have qualitatively identical structures.

The vibrational spectra of $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ and the newly reported spectra of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ have been recorded. A variation of the experimental procedures of their preparations[12] enabled us to obtain crystalline samples suitable for Raman spectroscopy. The ir spectrum of the Mo(II) compound is in general agreement with that reported by Bowen and Taube.[3] In addition to assigning the Mo–Mo frequency in the $Mo_2{}^{5+}$ complex, the spectra of both compounds are interpreted in terms of the various skeletal and ligand modes. Spectroscopic evidence is provided for the existence of two crystallographically[11] distinct species in the $Mo_2{}^{5+}$ complex. The effects of stresses present in the ring structures of both these compounds are also discussed.

Experimental Section

$K_4Mo_2(SO_4)_4 \cdot 2H_2O$ was prepared from a solution of $K_4Mo_2Cl_8 \cdot 2H_2O$ in 2 *M* H_2SO_4 by precipitation with saturated K_2SO_4.[3] $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ was prepared as described previously.[12] Both substances are obtained by these procedures as a finely powdered