standing, with a simultaneous decrease in the strength of the δ(Zn–H) and ν(CO) bands in the IR spectra. These spectra and the elemental analysis suggest the *tert*-butoxy groups remained intact in the solid. This evidence, along with the presence of metallic copper on the walls of the reaction vessel, implicates a reduction of the Cu(I) species with the simultaneous release of carbon monoxide.

Because Tsuda et al.[11] had shown that PPh_3 would displace CO from $[(CH_3)_3COCu(CO)]_4$, we thought that the phosphine complex might not dissociate when combined with the alkoxyzinc hydride. Hydride transfer had been reported between $[(CH_3)_3COCu(PPh_3)]_4$ and $HZnO(CH_2)_2NMe_2$.[6] The reddish orange copper compound produced from **1** and $[(CH_3)_3COCu(PPh_3)]_4$ showed the presence of a hydride and a PPh_3 in the ^1H NMR spectrum. If similar hydride transfer from zinc to copper were to have happened with **1** and $[(CH_3)_3COCu(CO)]_4$, CO would be displaced and the resulting alkoxycopper hydride might undergo an internal redox reaction giving the observed copper metal and *tert*-butyl alcohol.

Acknowledgment. We are grateful to the Cornell University Materials Science Center and the Department of Chemistry for financial support and to the National Institutes of Health for major equipment grants (No. DHHSO8SORR02002A) for the NMR spectrometer and the mass spectrometer (No. RR03520).

Registry No. **1**, 119656-28-9; $[(CH_3)_3COCu(PPh_3)]_4$, 79811-70-4; $[(CH_3)_3COCu]_4$, 60842-00-4; $[HCuPPh_3]_6$, 33636-93-0; $[(CH_3)_3COCu(CO)]_4$, 85479-93-2.

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Crystal Symmetry Governing the Metallic vs Semiconducting Properties of Cesium Molybdenum Bronzes Cs_xMoO_3 ($x \cong 0.25, 0.33$)

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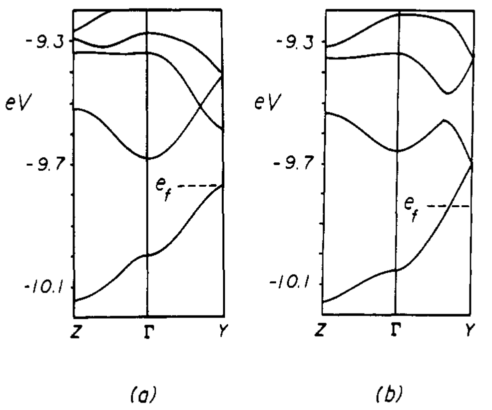
Alkali-metal molybdenum oxides have three well-characterized phases:[1] blue bronzes $A_{0.3}MoO_3$,[2] purple bronzes $A_{0.9}Mo_6O_{17}$,[3] and red bronzes $A_{0.33}MoO_3$.[4] At room temperature, the blue and purple bronzes are metals while the red bronzes are semiconductors. Recent band electronic structure studies[5,6] have shown that the red bronzes $A_{0.33}MoO_3$ (A = Li, K, Rb, Cs, Tl) are regular semiconductors, which have a band gap as a consequence of the O–Mo···O bond alternations in their crystal structures. Cesium molybdenum bronze $Cs_{0.25}MoO_3$[7] does not belong to any of these molybdenum bronze classes but is closely related in structure to the red bronze $Cs_{0.33}MoO_3$.[4a] However, our band structure calculations[8] predict $Cs_{0.25}MoO_3$ to be a pseudo-one-dimensional metal. In this note, we report how and why the two cesium bronzes $Cs_{0.33}MoO_3$ and $Cs_{0.25}MoO_3$ differ in their electronic structures concerning the metallic vs semiconducting properties.



(a) (b)

Figure 1. Bottom portion of the t_{2g}-block bands calculated for (a) the Mo_6O_{18} layer **4a** of $Cs_{0.33}MoO_3$ and (b) the Mo_6O_{18} layer **4b** of $Cs_{0.25}MoO_3$. The wave vectors Γ, Y, and Z are defined as Γ = (0, 0), Y = ($b^*/2$, 0), and Z = (0, $c^*/2$), where the reciprocal vectors b^* and c^* are related to the repeat vectors of the Mo_6O_{18} layer defined in **1** and **4**.

The crystal structures of $Cs_{0.33}MoO_3$ and $Cs_{0.25}MoO_3$ may be constructed by beginning with the Mo_2O_9 chain **1**, which is made up of corner-shared MoO_6 octahedra. The Mo_6O_{24} chains **2a** and **2b** are obtained by adding extra MoO_6 octahedra (i.e., the

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(8) Tight-binding band calculations[9] based upon the extended Hückel method[10] employed in ref 5 and 6. The atomic parameters used in the present work were taken from ref 5 and 6, and a modified Wolfsberg–Helmholz formula was used to calculate the off-diagonal H_{ij}.[11]

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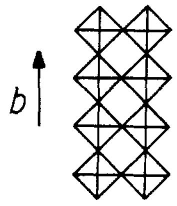
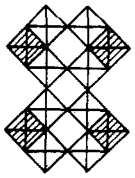
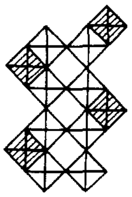


1

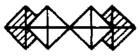


2a

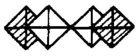


2b

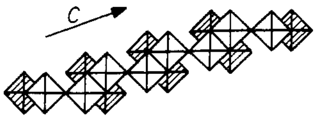
shaded octahedra) to both sides of **1**. **3a** and **3b** are projection views of **2a** and **2b** along the chain direction, respectively. The Mo_6O_{18} layers **4a** and **4b** are derived from the Mo_6O_{24} chains **3a** and **3b**, respectively, upon sharing the octahedral edges and corners. It is the Mo_6O_{18} layers **4a** and **4b** that are found in $Cs_{0.33}MoO_3$ and $Cs_{0.25}MoO_3$, respectively. In both bronzes, the Mo_6O_{18} layers are separated by the layers of Cs^+ ions. Thus, $Cs_{0.33}MoO_3$ and $Cs_{0.25}MoO_3$ differ essentially in the way the hump octahedra (i.e., those shaded in **2–4**) are added to the Mo_2O_9 chain **1**. The chains **2b** of $Cs_{0.25}MoO_3$ have a symmetry element of 2-fold screw rotation, while the chains **2a** of $Cs_{0.33}MoO_3$ do not.



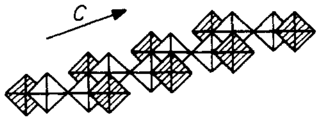
3a



3b



4a



4b

The bottom portion of the t_{2g}-block bands calculated for the Mo_6O_{18} layer **4a** of $Cs_{0.33}MoO_3$[6] is shown in Figure 1a, and that for the Mo_6O_{18} layer **4b** of $Cs_{0.25}MoO_3$ is shown in Figure 1b. In Figure 1, the t_{2g}-block bands are represented primarily by the orbitals of the Mo_2O_9 chains **1**, which are common to **2a** and **2b**. A detailed analysis of the nature of such bands in $Cs_{0.33}MoO_3$ and $Li_{0.33}MoO_3$ has already been given elsewhere.[5,6] Note that the bands of **4b** are paired up (Figure 1b), while this is not the case with the bands of **4a** (Figure 1a). This difference, essential for the semiconducting properties of $Cs_{0.33}MoO_3$, originates from the fact that the chain **2b** has a 2-fold screw rotation but the chain **2a** does not.

Figure 1 shows that the layer **4a** leads to a band gap but the layer **4b** does not. From the viewpoint of the electronic energy stabilization associated with a band-gap opening, therefore, $Cs_{0.33}MoO_3$ (which has two electrons to fill the t_{2g}-block bands) would be expected to adopt the layer structure **4a** instead of **4b**, as found experimentally. To obtain a cesium bronze Cs_xMoO_3 having the layer structure **4b**, it would be necessary to have less than two electrons to fill the bands, thereby removing the possibility of electronic energy stabilization by a band gap opening at the zone edge. That is, a cesium bronze Cs_xMoO_3 with the layer structure **4b** would be more accessible for x smaller than $^1/_3$. This is consistent with the original observation of $x \cong 0.25$ by Mumme and Watts[7] and may be one of the reasons their phase has not been reproduced so far.[1a]

Figure 1b suggests that any cesium molybdenum bronze Cs_xMoO_3 ($x < {}^1/_3$) consisting of the Mo_6O_{18} layers **4b** would be a pseudo-one-dimensional metal and hence would exhibit a charge density wave phenomenon. It will be of interest to characterize the physical properties of $Cs_{0.25}MoO_3$.

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Additions and Corrections

1988, Volume 27

James P. Collman,* James M. Garner, Kimoon Kim, and James A. Ibers*: Synthesis of Rhenium(II) Porphyrin Complexes and Crystal Structure of Bis(trimethylphosphine)(tetra-*p*-tolylporphyrinato)rhenium(II)–Toluene.

Page 4516. In the Registry paragraph, "(TPP)" should be changed to "(TTP)" in the three places it occurs. That is, the Registry No. should read exactly as follows: PEt_3, 554-70-1; PMe_3, 594-09-2; Re(OEP)(O)(Cl), 117201-90-8; Re(TTP)(O)(Cl), 117201-86-2; Re(OEP)$(PMe_3)_2$, 117201-87-3; Re(TTP)$(PMe_3)_2 \cdot C_6H_5CH_3$, 117201-89-5; Re(OEP)$(PEt_3)_2$, 117201-91-9; Re(TTP)$(PEt_3)_2$, 117201-92-0.—James P. Collman

1989, Volume 28

Paul J. Toscano,* Allen L. Seligson, Matthew T. Curran, Andrew T. Skrobutt, and David C. Sonnenberger*: Cobalt–Carbon Bond Disruption Enthalpies: The First Reliable Measurement of a Co–Methyl BDE via Solution Thermochemical Methods.

Page 167. In Table I, the correct order for the data in the column headed by ΔH_{soln} is as follows: 2.6 for the methyl complex, 2.7 for the benzyl complex, and 2.9 for the isopropyl complex. In addition, footnote *d* in Table I should read $\Delta H_{reacn} = 2\Delta H_4$. The remainder of the data and calculated numbers in Table I are correct as presented.—Paul J. Toscano