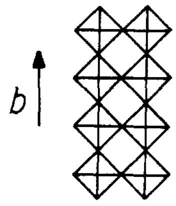
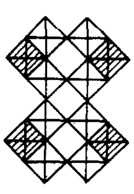
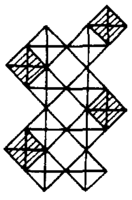


1

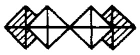


2a

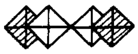


2b

shaded octahedra) to both sides of **1**. **3a** and **3b** are projection

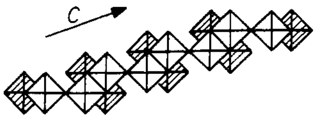


3a

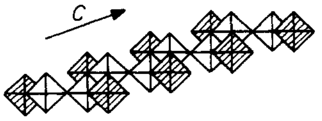


3b

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**



4a



4b

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.

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 $Cs_{0.25}MoO_3$.

Acknowledgment. This work was supported by the Scientific Affairs Division of NATO and also by the Office of Basic Sciences, Division of Materials Science, DOE, under Grant DE-FG05-86ER45259.

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