$$\tfrac{1}{2}[\mathrm{PtH}(\mu\text{-}\mathrm{NH_2})(\mathrm{PPh_3})]_2 \xrightarrow{-\mathrm{NH_3}} \mathrm{Pt(PPh_3)_2} \xrightarrow{\mathrm{CDCl_3}} cis\text{-}\mathrm{PtCl_2(PPh_3)_2} \quad (4)$$

$$[\mathrm{PtH}(\mu\text{-}\mathrm{NH_2})(\mathrm{PEt_3})]_2 + 2\mathrm{PEt_3} \rightarrow \tfrac{4}{3}\mathrm{Pt(PEt_3)_3} + \tfrac{2}{3}\mathrm{Pt} + 2\mathrm{NH_3} \quad (5)$$

however, the observed product is $Pt(PEt_3)_3$ (eq 5), the reductive elimination product.[10] The elimination of NH_3 from the anti isomer of $[PtH(\mu\text{-}NH_2)(PEt_3)]_2$ is found to be faster than from the syn isomer because the hydride and amide ligands are mutually cis in the anti isomer. In our initial premise summarized in eq 1, we proposed that the first product of the reaction of the cationic complex *trans*-$[PtX(NH_3)L_2]ClO_4$ with strong bases was monomeric with a trans stereochemistry. We now find that such monomeric complexes *trans*-$PtX(NH_2)L_2$ (X = H, Me) can be readily prepared with a bulky ligand L, such as PCy_3 (eq 6).

$$trans\text{-}[\mathrm{PtX(NH_3)(PCy_3)_2}]\mathrm{ClO_4} + \mathrm{NaNH_2} \rightarrow trans\text{-}\mathrm{PtX(NH_2)(PCy_3)_2} + \mathrm{NaClO_4} + \mathrm{NH_3} \quad (6)$$

$$X = H, Me$$

Indeed, solutions of these sterically stabilized compounds *trans*-$PtX(NH_2)(PCy_3)_2$ *do not* undergo substitution dimerization or reductive elimination at 25 °C.

These results show that sterically stabilized monomeric hydride and alkyl amide platinum(II) complexes are thermodynamically stable and that the trans amide hydrides undergo substitution dimerization prior to the reductive elimination of ammonia.

Acknowledgment. We thank the graduate school of Tulane University for support (S.P.).

Registry No. *syn*-**1**, 110719-63-6; *anti*-**1**, 110771-97-6; *syn*-**2**, 110719-64-7; *anti*-**2**, 110771-98-7; *anti*-**3**, 110719-65-8; *syn*-**4**, 110719-67-0; *anti*-**4**, 110772-00-4; *syn*-**5**, 110771-99-8; *anti*-**5**, 110719-66-9; *trans*-$[PtH(NH_3)(PPh_3)_2]ClO_4$, 32109-33-4; *trans*-$[PtH(NH_3)(PEt_3)_2]ClO_4$, 110719-69-2; *trans*-$[PtMe(NH_3)(PPh_3)_2]ClO_4$, 110719-71-6; *trans*-$[PtMe(NH_3)(PEt_3)_2]ClO_4$, 110719-73-8; *trans*-$[PtMe(NH_3)(PMePh_2)_2]ClO_4$, 110719-75-0; *cis*-$PtMe(NH_2)(PPh_3)_2$, 110719-76-1; *cis*-$PtMe(NH_2)(PEt_3)_2$, 110719-77-2; *cis*-$PtMe(NH_2)(PMePh_2)_2$, 110719-78-3; *cis*-$PtCl_2(PPh_3)_2$, 15604-36-1; $Pt(PEt_3)_2$, 66916-63-0; *trans*-$[PtH(NH_3)(PCy_3)_2]ClO_4$, 110719-80-7; *trans*-$PtH(NH_2)(PCy_3)_2$, 110719-81-8; *trans*-$[PtMe(NH_3)(PCy_3)_2]ClO_4$, 110719-83-0; *trans*-$PtMe(NH_2)(PCy_3)_2$, 110719-84-1.

Supplementary Material Available: Atomic coordinates (Table 1S), bond distances (Table 2S), bond angles (Table 3S), anisotropic thermal parameters (Table 4S), and hydrogen atom coordinates (Table 5S) (4 pages); observed and calculated structure factors (Table 6S) (37 pages). Ordering information is given on any current masthead page.

Department of Chemistry
Tulane University
New Orleans, Louisiana 70118
Soonheum Park
D. Max Roundhill*

Department of Chemistry
University of Delaware
Newark, Delaware 19716
Arnold L. Rheingold

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(10) ^{195}Pt NMR shows a quartet (^1J(PtP) = 4209 Hz) at δ −4510 (see: Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1980**, 776–785).

Articles

Contribution from the Laboratoire de Chimie Théorique, Université de Paris-Sud, 91405 Orsay, France, and Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

Metallic versus Nonmetallic Properties of Ternary Chalcogenides Ta_2MSe_7 (M = Ni, Pt) and Ta_2NiX_5 (X = S, Se)

Enric Canadell*[1a] and Myung-Hwan Whangbo*[1b]

Received May 11, 1987

The electronic structures of layered chalcogenides Ta_2NiS_5 and Ta_2NiSe_7 were examined by carrying out tight-binding band calculations. In agreement with experiment, Ta_2NiS_5 and Ta_2NiSe_7 are predicted to be semiconducting and metallic, respectively. The calculated band electronic structures of Ta_2NiS_5 and Ta_2NiSe_7 are best described by the oxidation formalisms $(Ta^{5+})_2(Ni^0)(S^{2-})_5$ and $(Ta^{5+})_2(Ni^{2+})(Se^{2-})_5(Se_2^{2-})$, respectively. In Ta_2NiS_5, the Ta^{5+} cations act as good π acceptors of each Ni atom, thereby stabilizing its zero oxidation state. The metallic properties of Ta_2NiSe_7 originate from the fact that the bottom d-block band of the octahedral chains overlaps with the top Se p-block band of the trigonal-prismatic chains. The bottom d-block band of the trigonal-prismatic chains is empty, so that the Ta atoms of the trigonal-prismatic chains are not responsible for the metallic properties of Ta_2NiSe_7.

Recently, Sunshine and Ibers synthesized layered ternary chalcogenides Ta_2NiX_5 (X = S, Se)[2] and Ta_2MSe_7 (M = Ni, Pt).[3] In Ta_2NiX_5 the Ta and Ni atoms have octahedral (OCT) and tetrahedral coordinations, respectively. According to the crystal structure of Ta_2NiX_5 and the oxidation formalism $(Ta^{4+})_2(Ni^{2+})(X^{2-})_5$, it is expected[2] that Ta_2NiX_5 is a one-dimensional metal and hence would exhibit a charge density wave (CDW) phenomenon. However, this Ta_2NiX_5 compound is a diamagnetic semiconductor with the band gaps of 0.13 and 0.36 eV for X = S and Se, respectively,[2] and no evidence for a CDW phenomenon was found.[4] Thus, the oxidation formalism valid for Ta_2NiX_5 is $(Ta^{5+})_2(Ni^0)(X^{2-})_5$, although this formalism was regarded unlikely[2] because it implies the occurrence of highly oxidized metal ions (i.e., Ta^{5+}) in the presence of unoxidized metal atoms (i.e., Ni^0).

In Ta_2MSe_7 (M = Ni, Pt) the M atoms are found in square-pyramidal coordination sites, while the Ta atoms are either in OCT or in bicapped trigonal-prismatic (BTP) coordination sites. The oxidation formalism $(Ta^{5+})_2(M^{2+})(Se^{2-})_5(Se_2^{2-})$ suggests semiconducting properties for Ta_2MSe_7, but it is found to be metallic down at least to 100 K,[3] below which no measurements have been made. By analogy with the metallic properties of $TaSe_3$ and $NbSe_3$,[5] Sunshine and Ibers suggested[3] that the BTP chains are

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(1) (a) Université de Paris-Sud. (b) North Carolina State University.

(2) Sunshine, S. A.; Ibers, J. A. *Inorg. Chem.* **1985**, *24*, 3611.

(3) Sunshine, S. A.; Ibers, J. A. *Inorg. Chem.* **1986**, *25*, 4355.

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Table I. Exponents and Parameters Used in the Calculations[a]

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	c_1[b]	c_2[b]
Ta	6s	-10.10	2.28			
	6p	-6.86	2.24			
	5d	-12.10	4.76	1.94	0.6597	0.5589
Ni	4s	-9.70	2.10			
	4p	-5.15	2.10			
	3d	-13.49	5.75	2.30	0.5798	0.5782
Se	4s	-20.50	2.44			
	4p	-13.20	2.07			
S	3s	-20.00	1.817			
	3p	-13.30	1.817			

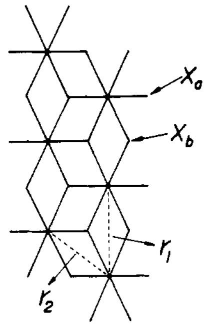
[a] A modified Wolfsberg–Helmholz formula[10] was used to calculate the off-diagonal H_{ij} values. [b] Contraction coefficients used in the double-ζ expansion.

responsible for the metallic properties of Ta_2MSe_7, which was proposed to occur via charge transfer from the Se atoms to the Ta atoms of BTP chains, thereby creating Ta^{4+} cations.

In the present study, we perform tight-binding band calculations[6] on Ta_2NiS_5 and Ta_2NiSe_7 to gain some insight into the origin of their apparently puzzling electrical properties. The atomic parameters employed in our band calculations based upon the extended Hückel method[7] are summarized in Table I.

Results and Discussion

A. Ta_2NiX_5 (X = S, Se). The Ta_2NiX_5 phase contains layers of composition Ta_2NiX_5. It is convenient to consider each Ta_2NiX_5 layer in terms of the double OCT chain, Ta_2X_6 depicted in **1**. These Ta_2X_6 chains can be condensed to form a Ta_2X_5 net by sharing their apical X atoms (X_a). When the Ta–X_a–Ta linkages are bent, every two adjacent apical X atoms form a tetrahedral hole with every two adjacent basal X atoms (X_b). Then the Ta_2NiX_5 layer is obtained by filling all the tetrahedral holes with Ni atoms (see **2**). In the Ta_2X_6 double OCT chains **1**, the Ta···Ta distances r_1 and r_2 are fairly long (i.e., greater than 3.40 and 3.49 Å for X = S and Se, respectively[2]) so that there is no significant Ta···Ta bonding. Around each Ni atom, however, there are four Ta atoms in a square-planar arrangement with a very short Ta···Ni distance (i.e., 2.747 and 2.813 Å for X = S and Se, respectively[2]).



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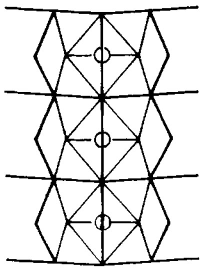

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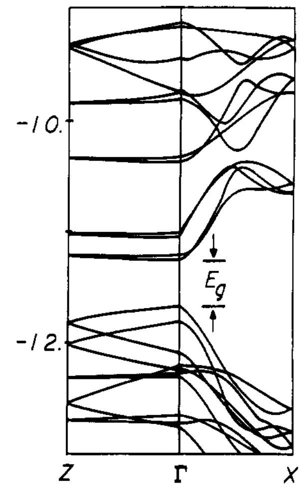

Figure 1. Dispersion relations of the bands calculated for a Ta_2NiS_5 layer, where E_g refers to a band gap. In units of the reciprocal vectors a^* and c^*, the vector points Γ, X, and Z are defined as Γ = (0, 0), X = (a^*/2, 0), and Z = (0, c^*/2).

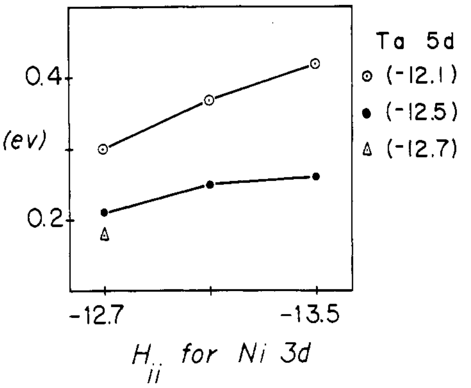

Figure 2. Calculated band gap as a function of the valence-shell ionization potentials of the Ni 3d and Ta 5d orbitals.

Figure 1 shows the dispersion relations for some of the bands calculated for a Ta_2NiS_5 layer. In general, these bands are dispersive along the chain axis (i.e., the *a* axis) but relatively flat along the direction perpendicular to the chain axis. Our calculations show that Ta_2NiS_5 has a direct band gap at Γ. As summarized in Figure 2, Ta_2NiS_5 is calculated to have a direct band gap at Γ for any reasonable choice of the valence-shell ionization potentials (VSIP's) of the Ni 3d and the Ta 5d orbitals. It should be noted that the direct band gap at Γ persists even when the VSIP value of the Ni 3d orbital is raised to as high as that of the Ta 5d orbital. This phenomenon basically occurs since the symmetry of the Ta_2NiX_5 layer is low. For any linear combination of Ta d orbitals, therefore, there exists a corresponding linear combination of Se p orbitals with the same symmetry. The interaction between such levels would widen their energy difference, thereby leading to a band gap. Consequently, Ta_2NiX_5 is predicted to be a semiconductor, and the oxidation formalism $(Ta^{5+})_2(Ni^0)(X^{2-})_5$ is appropriate for Ta_2NiX_5. In organometallic compounds, the Ni^0 oxidation state is found with strong π acceptors.[8] By analogy, it is reasonable to suggest that the empty t_{2g} levels of each Ta^{5+} cation act as good π-acceptor levels for the Ni^0 atoms. This interpretation is consistent with the observation that the Ta···Ni distances are quite short and also with our computational result that the overlap population for the Ta···Ni contact is considerably larger than that for the Ta···Ta contact (e.g., 0.09 vs 0.02 in Ta_2NiS_5). Our calculations show that the Ta d-block bands

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(5) (a) Meerschaut, A.; Rouxel, J. In *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures*; Rouxel, J., Ed.; Reidel: Dordrecht, The Netherlands, 1986; p 205. (b) Whangbo, M.-H. *Ibid.*, p 27.

(6) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.

(7) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1399.

(8) (a) Malatesta, L.; Cenini, S. *Zerovalent Compounds of Metals*; Academic: New York, 1974. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 797.

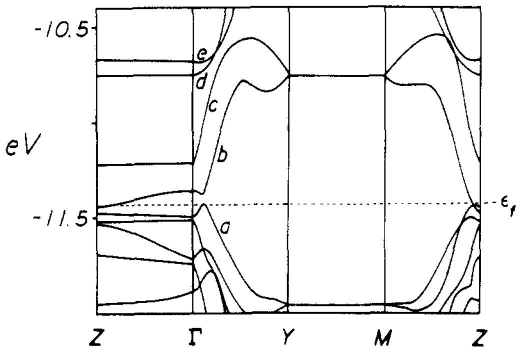
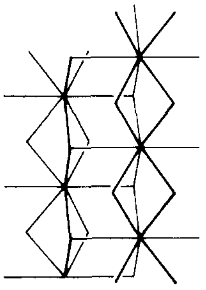


Figure 3. Dispersion relations of the bands calculated for a Ta_2NiSe_7 layer, where the dashed line refers to the Fermi level. In units of the reciprocal vectors b^* and c^*, the vector points Γ, Y, and Z are defined as $\Gamma = (0, 0)$, $Y = (b^*/2, 0)$, $Z = (0, c^*/2)$, and $M = (b^*/2, c^*/2)$.

of Ta_2NiX_5 (i.e., the upper part of Figure 1) along the $\Gamma \rightarrow X$ line are practically the same as those of the isolated double OCT chain Ta_2X_6 (**1**)[9] and the latter lie slightly lower in energy (~0.1 eV). This supports our suggestion that the t_{2g} levels of Ta^{5+} act as π-acceptor levels for Ni^0 in Ta_2NiX_5.

B. Ta_2MSe_7 (M = Ni, Pt). The Ta_2MSe_7 phase consists of layers of composition Ta_2MSe_7. Convenient building blocks for a Ta_2MSe_7 layer are the Ta_2Se_6 double OCT chains (**1**) and the double BTP chains **3**. Chains **1** and **3** can be brought together to form a layer of composition Ta_2Se_7 in such a way that every three Se atoms of **1** (i.e., two apical and one basal Se atoms) form a square pyramid with every two adjacent capping Se atoms of **3**. When such square-pyramidal sites are occupied by the metal atoms M (see **4**), we obtain the Ta_2MSe_7 layer.



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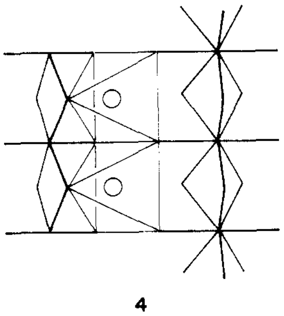

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Figure 3 shows the dispersion relations for some of the bands calculated for a Ta_2NiSe_7 layer. In general, these bands are dispersive along the chain axis (i.e., the b axis) but relatively flat along the direction perpendicular to the chain axis. There are two bands, a and b, that are partially filled. Bands a and b are primarily represented by the Se p orbitals of the BTP chains and by the Ta d orbitals of the OCT chains, respectively. The two bands switch their orbital character near Γ along the $\Gamma \rightarrow Y$ line. In short, the top of the highest lying Se p-orbital band overlaps slightly with the bottom of the lowest lying Ta d-block band, so that Ta_2NiSe_7 is a semimetal. In Ta_2NiSe_7, the bottom d-block and the top Se p-block bands overlap essentially because these bands arise from the orbitals of different chains. In Ta_2NiX_5, however, the corresponding two bands arise from the orbitals of the same chain, which leads to a strong mixing between the two and hence to a band gap.

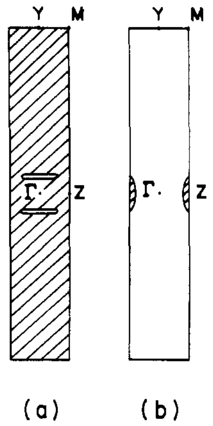

Figure 4. Fermi surfaces calculated for a Ta_2NiSe_7 layer: (a) hole pockets of the top selenium p-block band; (b) the electron pocket of the bottom d-block band.

Bands b and c are derived primarily from the d orbitals of the double OCT chains and are lower lying in energy than bands d and e derived mainly from the d orbitals of the double BTP chains. Consequently, this study shows that the d-block bands of the BTP chains are not responsible for the metallic properties of Ta_2NiSe_7, unlike the case of $TaSe_3$ and $NbSe_3$. It is the bottom d-block band of the double OCT chains and the top p-block band of the BTP chain Se atoms that are largely responsible for electrical conduction in Ta_2NiSe_7.

The Fermi surfaces associated with bands a and b are shown in parts a and b, respectively, of Figure 4. Band a provides two hole pockets of a cigar shape centered at $(\pm 0.055b^*, 0)$. Each hole pocket, elongated along the c^* axis, has the dimension of roughly $0.01b^* \times 0.7c^*$. Note that the two hole pockets are nested by the wave vector $\mathbf{q} \cong (0.1b^*, 0)$. Band b leads to an electron pocket of an ellipse shape, elongated along the b^* axis, which has the dimension of roughly $0.08b^* \times 0.15c^*$. Therefore, the Ta_2MSe_7 phase is expected to be a two-dimensional metal, although it is made up of the OCT and BTP chains.

Concluding Remarks

This band electronic structure study predicts the layered chalcogenides Ta_2NiX_5 and Ta_2MSe_7 to be semiconducting and metallic, respectively, which is in agreement with experiment. The oxidation formalism appropriate for Ta_2NiX_5 is $(Ta^{5+})_2(Ni^0)(X^{2-})_5$, and the Ta^{5+} cations act as good π acceptors, thereby stabilizing the Ni^0 atoms. The oxidation formalism appropriate for Ta_2MSe_7 is $(Ta^{5+})_2(Ni^{2+})(Se^{2-})_5(Se_2{}^{2-})$, and its metallic properties originate from the fact that the lowest lying tantalum d-block band overlaps slightly with the highest lying selenium p-block band. Therefore, Ta_2MSe_7 is a semimetal. The partially filled d-block band does not originate from the BTP but from the OCT chains. The two partially filled bands give rise to closed Fermi surfaces, so that Ta_2MSe_7 is a two-dimensional metal. Nevertheless, the two hole pockets arising from the selenium p-block band are nested by the vector $\mathbf{q} \cong (0.1b^*, 0)$, and therefore an interesting CDW phenomenon is expected.

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Registry No. $NiTa_2S_5$, 98104-46-2; $NiTa_2Se_7$, 104548-68-7.

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(9) For an analysis of the band structure of a double OCT chain, see: Canadell, E.; Whangbo, M.-H. *Inorg. Chem.* **1986**, *25*, 1488.

(10) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.