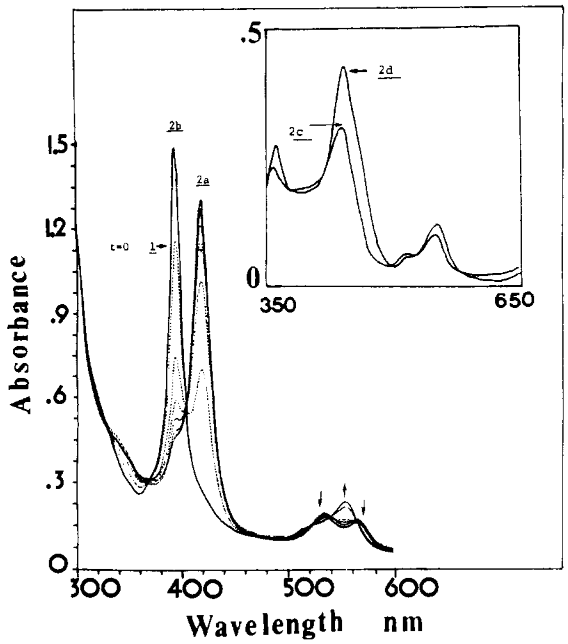

Figure 1. Reaction of 1.0×10^{-5} M CoOEP($CH_2C_6H_5$) with oxygen in toluene at 50 °C. The reaction was monitored every 30 min, starting with complex **1** and then quenching an aliquot from the reaction mixture to room temperature. With time, species **2b** (Co^{II}) appears, followed by the appearance of the (alkylperoxo)cobalt(III) porphyrin, **2a**. Inset: comparison of CoOEP($OOCH_2C_6H_5$)(PPh_3) (8.6×10^{-6} M; **2d**) and CoOEP($CH_2C_6H_5$)(PPh_3) (1.9×10^{-5} M; **2c**).

protons on the coordinated –R or –OOR linkage to high fields.[9] The closer these protons are to the porphyrin ring, the stronger is the effect of shifting the proton resonances to higher field.[10] Thus, in the dioxygen-inserted products, Co^{III}(P)(OOR)(L) (P = porphyrin), because the alkyl protons are now presumably at a greater distance from the porphyrin rings than in the parent Co^{III}(P)(R)(L) complexes, the protons on –OOR are shifted to lower fields.

In contrast, attempts to isolate (alkylperoxo)cobalt(III) porphyrins by additions of alkylhydroperoxides to Co^{III}TPP(Cl), Co^{III}OEP(Cl), or Co^{III}OEP(OH) failed in our hands, as products were detected typical of isoporphyrins, where the alkylhydroperoxide has attacked the porphyrin ring itself analogous to the work of Bruice et al.[11]

In addition to ^{1}H NMR results, further evidence that dioxygen has inserted into the cobalt–carbon bond of these organocobalt porphyrins comes from IR spectra of the isolated (alkylperoxo)cobalt(III) porphyrins. Moderate ν_{O-O} stretching frequencies were found for each (alkylperoxo)cobalt(III) porphyrin isolated in the 835–880-cm^{-1} region, typical of coordinated –OOR complexes.[12]

Previous attempts to isolate and characterize (alkylperoxo)cobalt(III) porphyrins resulted in complexes that were apparently contaminated with starting material.[4] In order to ensure the formation of the six-coordinate Co^{III}(P)(OOR)(L) complexes in high yield, excess L must be present. Recent work has demonstrated the crucial role that L plays in modulation of the Co–C bond strength in Co^{III}(P)(R)(L) complexes.[3] As will be demonstrated below, homolysis of the Co–C bond is an important step in the dioxygen insertion reaction; therefore, modulation of this bond strength is important.

We have measured the rate of dioxygen insertion into the Co–C bond[13] for a series of Co^{III}OEP(R)(L) complexes[3] where L = PR_3, or no ligand, and R = $CH_2C_6H_5$ and have found that the observed rate constants for dioxygen insertion correlate with the Co–C bond dissociation energies of such complexes, which have been determined previously[3] (see Figure 2). On the basis of our results described herein and the fact that Co(II) can be detected as an intermediate in the insertion of dioxygen into the Co–C bond of organocobalt porphyrins, we postulate the following mechanism for the overall insertion reaction:

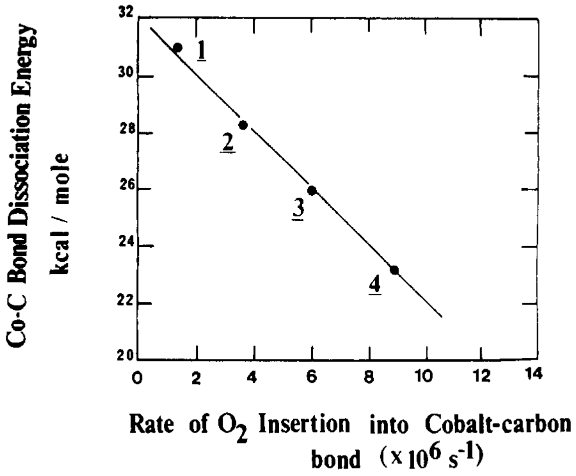

Figure 2. Plot of Co–C bond dissociation energy versus k_{obsd} (50 °C, toluene) for dioxygen insertion into CoOEP(R) and CoOEP(R)(PR_3) complexes; (R = $CH_2C_6H_5$): (1) CoOEP($CH_2C_6H_5$); (2) CoOEP($CH_2C_6H_5$)(P-*n*-Bu_3); (3) CoOEP($CH_2C_6H_5$)($PEtPh_2$); (4) CoOEP($CH_2C_6H_5$)(PPh_3).

$$Co^{III}(P)(R)(L) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co^{II}(P)(L) + R^\bullet \qquad (1)$$

$$R^\bullet + O_2 \xrightarrow{k_2} ROO^\bullet \qquad (2)$$

$$Co^{II}(P)(L) + ROO^\bullet \xrightarrow{k_3} Co^{III}(P)(OOR)(L) \qquad (3)$$

$$\text{net: } Co^{III}(P)(R)(L) + O_2 \rightarrow Co^{III}(P)(OOR)(L)$$

We are currently extending our studies to include kinetic verification of the preceding mechanism as well as to explore the use of these complexes as catalysts for the oxidation of hydrocarbons.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(13) The rate constant for dioxygen insertion into the cobalt–carbon bond was measured spectrophotometrically, by following the increase in absorbance with time of the band absorption with the Co^{III}(P)(OOR) or Co^{III}(P)(OOR)(L) complex. At 50 °C, the following rate constants, (s^{-1}) were measured for dioxygen insertion into Co–R bonds (toluene solvent): Co^{III}OEP($OOCH_2C_6H_5$), 0.000 001 65; Co^{III}OEP($OOCH_2C_6H_5$)(P(*n*-C_4H_9)$_3$), 0.000 003 30; Co^{III}OEP($OOCH_2C_6H_5$)(P(C_2H_5)(C_6H_5)$_2$), 0.000 005 91; s^{-1}; Co^{III}OEP($OOCH_2C_6H_5$)(P(C_6H_5)$_3$), 0.000 009 07.

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New Monomeric and Binuclear Hydride- and Alkyl-Substituted Platinum(II) Complexes Having Unsubstituted Terminal or Bridging Amide Ligands

Sir:

Despite recent interest in the activation of C–H bonds by low-valent transition-metal complexes,[1] little work has been

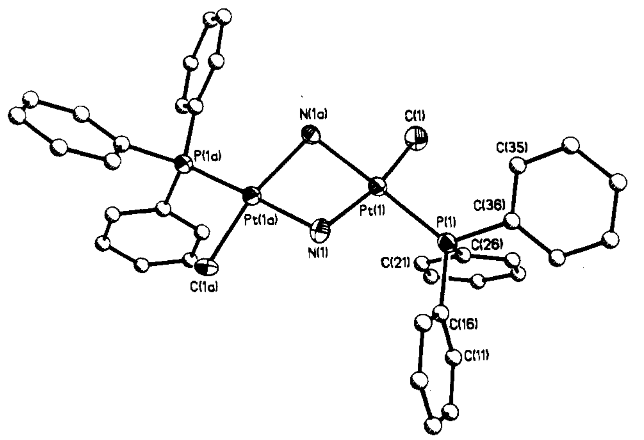


Figure 1. Molecular structure and labeling scheme for one molecule of two crystallographically independent molecules of $[PtCH_3(\mu\text{-}NH_2)PPh_3]_2$ associated by Pt···H interactions. Important distances (Å) and angles (deg) are as follows: Pt(1)-Pt(1a), 3.106 (1); Pt(2)-Pt(2a), 3.117 (1); Pt(1)-P(1), 2.205 (2); Pt(2)-P(2), 2.204 (2); Pt(1)-N(1), 2.13 (1); Pt(2)-N(2), 2.14 (1); Pt(1)-C(1), 2.07 (1); Pt(2)-C(2), 2.08 (1); Pt(1)-N(1a), 2.08 (1); Pt(2)-N(2a), 2.09 (1); Pt(1)-N(1)-Pt(1a), 95.2 (4); Pt(2)-N(2)-Pt(2a), 95.1 (3); N(1)-Pt(1)-N(1a), 77.5 (4); N(2)-Pt(2)-N(2a), 78.2 (3); N(1)-Pt(1)-P(1), 102.9 (2); N(2)- Pt(2)-P(2), 102.5 (2); N(1)-Pt(1)-C(1), 167.7 (3); N(2)-Pt(2)-C(2), 168.5 (3); P(1)-Pt(1)-C(1), 89.1 (3); P(2)-Pt(2)-C(2), 88.9 (3); P(1)-Pt(1)-N(1a), 178.3 (3); P(2)-Pt(2)-N(2a), 177.2 (2); C(1)-Pt(1)-N(1a), 90.4 (4); C(2)-Pt(2)-N(2a), 90.3 (4).

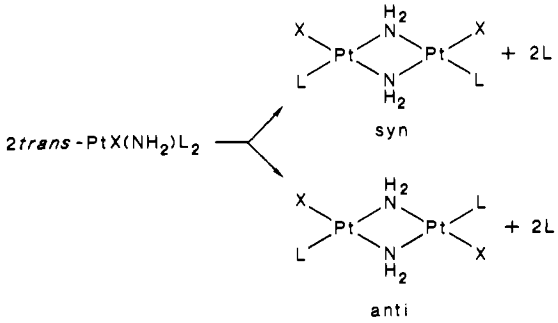
published on the insertion of such complexes into N-H bonds.[2] In developing strategies for the activation of the N-H bonds in ammonia itself, an important aspect is understanding the stability and chemical reactivity of amide hydride and alkyl complexes.[3] In order to investigate the stabilities and reaction chemistry of such compounds, we have now, for the first time, prepared a series of hydride and methyl platinum(II) complexes having also an unsubstituted amide (NH_2^-) ligand.

The new amide complexes have been prepared by reacting the cationic ammine complexes *trans*-$[PtX(NH_3)L_2]ClO_4$ (X = H, L = PPh_3, PEt_3, PCy_3; X = Me, L = PPh_3, PEt_3, $PMePh_2$, PCy_3) with amide ion or other bases (eq 1).[4,5] The reaction sequence

$$trans\text{-}[PtX(NH_3)L_2]ClO_4 + B^- \rightarrow trans\text{-}PtX(NH_2)L_2 + BH + ClO_4^- \quad (1)$$

$$B^- = NH_2^-,\ 4\text{-}Me(2,6\text{-}t\text{-}Bu)_2C_6H_2O^-;\ X = H$$

involves an initial deprotonation to give the neutral monomeric complex *trans*-$PtX(NH_2)L_2$, which can then subsequently dimerize to an equilibrium mixture of the syn and anti isomers of $[PtX(\mu\text{-}NH_2)L]_2$ (X = H, L = PPh_3, PEt_3; X = Me, L = PPh_3, PEt_3, $PMePh_2$; **1-5**) (eq 2).[6] The $^{31}P\{^1H\}$ NMR spectra of these



(2)

X, L: H, PPh_3 (**1**), H, PEt_3 (**2**), Me, PPh_3 (**3**), Me, PEt_3 (**4**), Me, $PMePh_2$ (**5**)

binuclear complexes show a composite A_2, $[A]_2X$, $[A]_2[X]_2$ pattern (X = ^{195}Pt, $I = {}^1/_2$, 33.7% abundance). The anti isomers have the larger $^4J(PP)$ couplings. The equilibrium percentage of the anti isomer in $[PtMe(\mu\text{-}NH_2)L]_2$ formed by reaction 2, as determined by $^{31}P\{^1H\}$ NMR spectroscopy, are 100% (**3**), 50% (**4**), and 75% (**5**). The fraction of the syn isomer is therefore the greatest for ligands L that are strong donors and that have small cone angles. This result correlates with the expected lower steric constraints in the anti isomer.

The X-ray crystal structure of $[PtMe(\mu\text{-}NH_2)PPh_3]_2$ (**3**) shows the compound to be binuclear with an anti stereochemistry. The crystal has a 45° dihedral angle between coordination planes[7] and a large-range intermolecular "agostic" interaction between the μ-NH_2 hydrogens and the platinum(II) centers of an adjacent molecule.[8] The long (>3.1-Å) intramolecular distance between platinums shows that there is no intermetallic bonding in the complex. The distorted Pt_2N_2 ring has acute N-Pt-N and obtuse Pt-N-Pt angles. The Pt-N and Pt-C distances are normal, and the *cis*-C-Pt-N and *cis*-C-Pt-P angles are close to 90°.

Addition of excess tertiary phosphine L to the syn or anti isomer of $[PtMe(\mu\text{-}NH_2)L]_2$ (**3-5**) in C_6D_6 solvent causes slow bridge cleavage to give a solution containing the bridge-cleaved monomeric complex *cis*-$PtMe(NH_2)L_2$ (eq 3). This substitution

$$[PtMe(\mu\text{-}NH_2)L]_2 + 2L \rightarrow 2cis\text{-}PtMe(NH_2)L_2 \quad (3)$$

cleavage reaction occurs more rapidly with the syn than with the anti isomer. The cis stereochemistry of the resulting monomeric product correlates with the relative trans effect Me > PPh_3.

As expected, the hydride analogue complexes are less stable than the methyl congeners.[9] Treating *trans*-$[PtH(NH_3)L_2]ClO_4$ (L = PPh_3, PEt_3) with either NH_2^- or $4\text{-}Me(2,6\text{-}t\text{-}Bu)_2C_6H_2O^-$ gives $[PtH(\mu\text{-}NH_2)L]_2$, but solutions of either complex are thermally unstable at 25 °C. For $[PtH(\mu\text{-}NH_2)PPh_3]_2$ in $CDCl_3$, the complex reacts with the solvent to give *cis*-$PtCl_2(PPh_3)_2$ within 30 min (eq 4). For $[PtH(\mu\text{-}NH_2)(PEt_3)]_2$ in C_6D_6 solvent,

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(5) We have not determined whether NH_2^- reacts as a base toward the complexed ammine or as a ligand to platinum(II).

(6) For *trans*-$[PtMe(NH_3)(PEt_3)_2]^+$ we observe this first intermediate *trans*-$PtMe(NH_2)(PEt_3)_2$ (^1H NMR δ 0.26 (Me, $^2J(PtH)$ = 62.8 Hz, $^3J(PH)$ = 6.1 Hz), -0.16 (NH_2); ^{31}P NMR δ 15.0 ($^1J(PtP)$ = 2937 Hz)) in the initial stages of the reaction.

(7) For $C_{38}H_{40}N_2P_2Pt_2$: monoclinic, $C2/c$, a = 22.592 (5) Å, b = 11.844 (3) Å, c = 29.403 (6) Å, β = 116.43 (2)°, V = 7046 Å^3, Z = 8, D(calcd) = 1.841 g cm^{-3}, temperature 295 K, μ(Mo Kα) = 84.7 cm^{-1}, T(max)/T(min) = 1.28. Of 6660 data collected (Nicolet R3m/μ, 2θ(max) = 50°), 6198 were independent and systematically present (R_{int} = 0.035) and 4433 with $F_o \geq 3\sigma(F_o)$ were considered observed. E statistics suggested centrosymmetry, and the successful refinement in $C2/c$ proved the choice correct. The structure was solved by heavy-atom methods. All hydrogen atoms were treated as idealized contributions except for those of N(1) and N(2), which were found and isotropically refined. All non-hydrogen atoms were refined anisotropically. At convergence $R(F)$ = 4.04%, $R(wF)$ = 4.86% [all data, $R(F)$ = 6.50%, $R(wF)$ = 5.71%], GOF = 1.051, Δ/σ = 0.08, $\Delta(\rho)$ = 1.2 e Å^{-3} (0.92 Å from Pt(1)), N_o/N_v = 13.0. The asymmetric unit consists of two independent, but chemically identical, half-molecules on sites with a common twofold rotational axis. All computations were done in SHELXTL (5.1), Nicolet Corp., Madison, WI.

(8) Pt···H is 2.65 Å.

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

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

however, the observed product is $\mathrm{Pt(PEt_3)_3}$ (eq 5), the reductive elimination product.[10] The elimination of $\mathrm{NH_3}$ from the anti isomer of $[\mathrm{PtH}(\mu\text{-}\mathrm{NH_2})(\mathrm{PEt_3})]_2$ 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*-$[\mathrm{PtX(NH_3)L_2}]\mathrm{ClO_4}$ with strong bases was monomeric with a trans stereochemistry. We now find that such monomeric complexes *trans*-$\mathrm{PtX(NH_2)L_2}$ (X = H, Me) can be readily prepared with a bulky ligand L, such as $\mathrm{PCy_3}$ (eq 6).

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

$$\mathrm{X = H, Me}$$

Indeed, solutions of these sterically stabilized compounds *trans*-$\mathrm{PtX(NH_2)(PCy_3)_2}$ *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*-$[\mathrm{PtH(NH_3)(PPh_3)_2}]\mathrm{ClO_4}$, 32109-33-4; *trans*-$[\mathrm{PtH(NH_3)(PEt_3)_2}]\mathrm{ClO_4}$, 110719-69-2; *trans*-$[\mathrm{PtMe(NH_3)(PPh_3)_2}]\mathrm{ClO_4}$, 110719-71-6; *trans*-$[\mathrm{PtMe(NH_3)(PEt_3)_2}]\mathrm{ClO_4}$, 110719-73-8; *trans*-$[\mathrm{PtMe(NH_3)(PMePh_2)_2}]\mathrm{ClO_4}$, 110719-75-0; *cis*-$\mathrm{PtMe(NH_2)(PPh_3)_2}$, 110719-76-1; *cis*-$\mathrm{PtMe(NH_2)(PEt_3)_2}$, 110719-77-2; *cis*-$\mathrm{PtMe(NH_2)(PMePh_2)_2}$, 110719-78-3; *cis*-$\mathrm{PtCl_2(PPh_3)_2}$, 15604-36-1; $\mathrm{Pt(PEt_3)_2}$, 66916-63-0; *trans*-$[\mathrm{PtH(NH_3)(PCy_3)_2}]\mathrm{ClO_4}$, 110719-80-7; *trans*-$\mathrm{PtH(NH_2)(PCy_3)_2}$, 110719-81-8; *trans*-$[\mathrm{PtMe(NH_3)(PCy_3)_2}]\mathrm{ClO_4}$, 110719-83-0; *trans*-$\mathrm{PtMe(NH_2)(PCy_3)_2}$, 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.

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(10) ^{195}Pt NMR shows a quartet (^{1}J(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 $\mathrm{Ta_2MSe_7}$ (M = Ni, Pt) and $\mathrm{Ta_2NiX_5}$ (X = S, Se)

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Received May 11, 1987

The electronic structures of layered chalcogenides $\mathrm{Ta_2NiS_5}$ and $\mathrm{Ta_2NiSe_7}$ were examined by carrying out tight-binding band calculations. In agreement with experiment, $\mathrm{Ta_2NiS_5}$ and $\mathrm{Ta_2NiSe_7}$ are predicted to be semiconducting and metallic, respectively. The calculated band electronic structures of $\mathrm{Ta_2NiS_5}$ and $\mathrm{Ta_2NiSe_7}$ are best described by the oxidation formalisms $(\mathrm{Ta^{5+}})_2(\mathrm{Ni^0})(\mathrm{S^{2-}})_5$ and $(\mathrm{Ta^{5+}})_2(\mathrm{Ni^{2+}})(\mathrm{Se^{2-}})_5(\mathrm{Se_2}^{2-})$, respectively. In $\mathrm{Ta_2NiS_5}$, the $\mathrm{Ta^{5+}}$ cations act as good π acceptors of each Ni atom, thereby stabilizing its zero oxidation state. The metallic properties of $\mathrm{Ta_2NiSe_7}$ 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 $\mathrm{Ta_2NiSe_7}$.

Recently, Sunshine and Ibers synthesized layered ternary chalcogenides $\mathrm{Ta_2NiX_5}$ (X = S, Se)[2] and $\mathrm{Ta_2MSe_7}$ (M = Ni, Pt).[3] In $\mathrm{Ta_2NiX_5}$ the Ta and Ni atoms have octahedral (OCT) and tetrahedral coordinations, respectively. According to the crystal structure of $\mathrm{Ta_2NiX_5}$ and the oxidation formalism $(\mathrm{Ta^{4+}})_2(\mathrm{Ni^{2+}})(\mathrm{X^{2-}})_5$, it is expected[2] that $\mathrm{Ta_2NiX_5}$ is a one-dimensional metal and hence would exhibit a charge density wave (CDW) phenomenon. However, this $\mathrm{Ta_2NiX_5}$ 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 $\mathrm{Ta_2NiX_5}$ is $(\mathrm{Ta^{5+}})_2(\mathrm{Ni^0})(\mathrm{X^{2-}})_5$, although this formalism was regarded unlikely[2] because it implies the occurrence of highly oxidized metal ions (i.e., $\mathrm{Ta^{5+}}$) in the presence of unoxidized metal atoms (i.e., $\mathrm{Ni^0}$).

In $\mathrm{Ta_2MSe_7}$ (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 $(\mathrm{Ta^{5+}})_2(\mathrm{M^{2+}})(\mathrm{Se^{2-}})_5(\mathrm{Se_2}^{2-})$ suggests semiconducting properties for $\mathrm{Ta_2MSe_7}$, 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 $\mathrm{TaSe_3}$ and $\mathrm{NbSe_3}$,[5] Sunshine and Ibers suggested[3] that the BTP chains are

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