Coordination Chemistry and the Solid State

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Research into solid-state materials has grown dramatically in the past decade. Motivation for this research includes the search for new materials with interesting new properties. This Account is concerned with solid-state chalcogenides, materials that contain S, Se, or Te as one component. Specific interest in chalcogenides has been fueled by the discovery of their superconducting properties,[1] their application as battery materials,[2,3] and their utility as hydroprocessing catalysts.[4,5] Concomitant with the synthesis of new chalcogenides has been the discovery of new properties (e.g., charge density waves[6]) and new uses (e.g., fast ion conductors[7]).

Despite the increased interest in solid-state materials in the United States, there remains a relatively small community of academic researchers in chemistry involved in the *syntheses* of new materials. It is probable that part of the inertial barrier that prevents synthetic inorganic chemists from entering the solid-state area has been built up by the neglect of solid-state chemistry in the educational process and by the notion that rational routes to solid-state syntheses are lacking. While it remains true that the synthesis of a new ternary material, to take an example, has a distinctly lower chance of success than does the designed synthesis of a new organic or organometallic compound, it is also true that the inorganic chemist can apply knowledge gained outside of solid-state chemistry to increase the chances of successful solid-state syntheses. In the present Account we illustrate how we have applied coordination chemistry as a useful guide to the syntheses of new solid-state materials and to the interrelationships among them. The examples we pick are some of the chalcogenides of the transition metals, especially of Nb and Ta.

Description of Solid-State Structures in Terms of Coordination Polyhedra

To many chemists coordination chemistry and solid-state chemistry would seem to treat diverse subjects. Coordination chemistry is concerned with molecular species; solid-state chemistry is concerned in large measure with extended solid-state structures, many of

which may seem to be rather mysteriously described in terms of closest-packed arrays.[8] Indeed, many extended solid-state compounds are composed of sheets of anions that stack in an ordered manner, most typically in an ABAB... repeat (hexagonal closest packing, hcp) or in an ABCABC... repeat (cubic closest packing, ccp). Cations fill the interstices between adjacent anion layers, which means that in these simple packing schemes the coordination geometry of a centered cation is limited to octahedral or tetrahedral. An example of closest packing is given by solid $SnBr_4$ which crystallizes with an hcp bromine array in which one-eighth of the tetrahedral sites are occupied by Sn^{4+} ions. Of course as a gas, $SnBr_4$ exists as a simple tetrahedral molecule.

For solid compounds such as $SnBr_4$ where coordination polyhedra may be clearly defined, we are led naturally to a bridge between coordination chemistry and solid-state chemistry, a description of solid-state structures in terms of polyhedra that share certain edges, vertices, or faces. Description of structures in this way has been applied previously[9,10] and has been useful in several respects. Pauling's rules[11,12] for the determination of the stability of structures of complex ionic crystals were derived chiefly from such descriptions. Hazen and Finger[13] have used the characteristics of polyhedra in solids to interpret bulk properties, such as thermal expansion, compressibility, and stability. Since the energy levels of simple molecular polyhedra are well-understood, description of solids in a similar way also provides a useful starting point for the characterization of electronic structures.[14] Here we use this description as a guide for the synthesis of new materials.

Let us compare and contrast some pertinent structures and their possible descriptions, starting with TiO_2 and TiS_2. The most common form of TiO_2, rutile, 1, consists of a distorted hcp array of oxide ions with half of the octahedral interstices filled in an ordered way by Ti^{4+} ions.[15] The description may be extended by noting

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Ti ○ O ◯   Ti ○ S ◯   Mo ○ S ◯


1

2

4
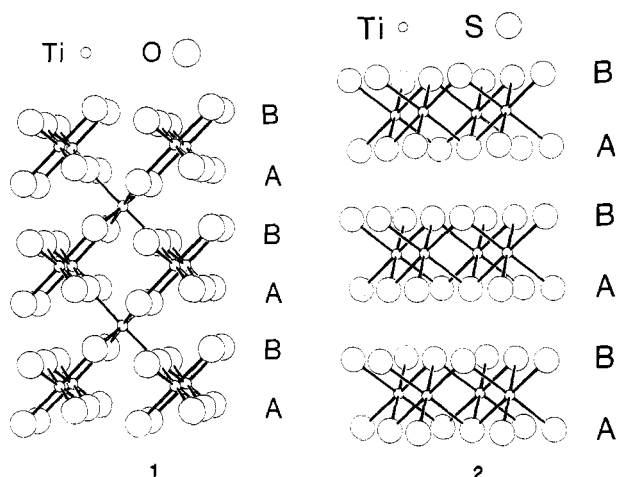
that the octahedra form chains by sharing edges orthogonal to the plane of the paper, 1, with the full three-dimensional structure resulting from an additional association through the sharing of vertices. The structure of TiS$_2$, 2, also consists of an hcp array, now of sulfide ions, with half of the octahedral sites filled, but in a manner that leaves every other layer of interstices either completely empty or completely filled.[16] We have just described a two-dimensional layered structure! Again, a more useful description, one that emphasizes the completely filled layer and the coordination chemistry involved, is in terms of edge-sharing Ti-centered octahedra that extend in two dimensions, 3.


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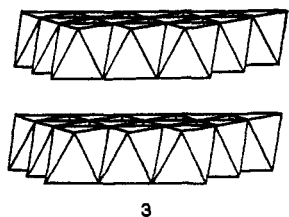
Briefly consider the structure of MoO$_2$[17] and the structures of the isostructural compounds $2H$-MoS$_2$[18] and $2H$-NbSe$_2$, 4. MoO$_2$ exhibits a distorted rutile structure with the Mo atoms forming pairs along the chain direction while $2H$-MoS$_2$ exhibits a layered structure similar to TiS$_2$ except the Mo atoms now center trigonal prisms sharing edges. Such a coordination environment forces a different stacking of the anion layers AABB...; while such a stacking is not closest packed, the stacking of the filled layers is, 4. Trigonal prismatic coordination is infrequently observed in oxide structures. However, it is common in sulfides and is also found in certain coordination compounds, such as Mo(SCHSCS)$_3$[19] and Re(S$_2$C$_2$Ph$_2$)$_3$,[20] where chalcogens surround the metal.

The structures of compounds MQ$_3$ (M = Ti, Zr, Hf, Nb, Ta; Q = S, Se) provide examples where the only useful description is in terms of the coordination polyhedra of the cations. These structures are built from metal-centered trigonal prisms that share faces to
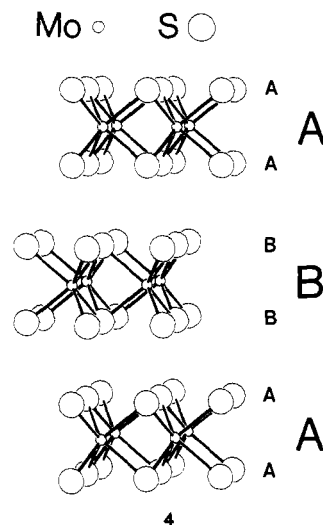
form one-dimensional chains.[21] They are collocated so that the Q atoms from neighboring chains cap the rectangular faces of adjacent chains to give bicapped trigonal-prismatic coordination about each metal atom, 5. In certain chains the trigonal prisms of Q atoms may

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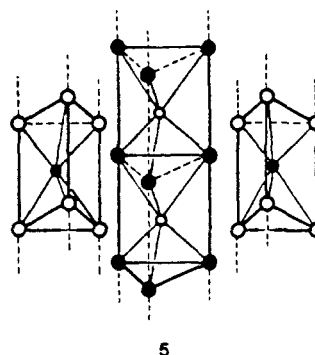
be distorted by the presence of short Q–Q bonds. Because the lengths of these Q–Q bonds vary with the metal atom M, the one-dimensional chains are observed to pack together in dissimilar ways, affording a number of different structures. These structures are difficult, if not impossible, to describe in terms of the anion arrangement because of their low dimensionality and inherent complexity. Moreover, the physical properties of these materials arise from and are best described in terms of the local coordination environments and their extensions as chains.[22-25]

What is to be learned from these brief descriptions that might be useful for anticipating transition-metal chalcogenides with new structural types? There are important differences between transition-metal oxide and chalcogenide structures. As noted above, description of chalcogenide structures in terms of closest packing is not always useful. Thus, for certain chalcogenides we find structures not built from octahedra and tetrahedra. The reduced electrostatic repulsion and increased van der Waals' attraction among chalcogenide ions as compared with oxide ions are commonly given as reasons for the absence of close packing. Probably of more importance, however, at least for sulfides and selenides, are the local metal–anion interactions that

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Table I.
Coordination Geometries in Some Chalcogenides

compound	metal coordination[a]	ref
NbS	trig prism.	27
NbS_2, $NbSe_2$	oct, trig prism.	28–30
$NbTe_2$, $TaTe_2$	oct	31
TaS_2, $TaSe_2$	oct, trig prism.	32–34
Nb_2Se_3, Ta_2Se_3	oct	35
NbS_3, $NbSe_3$	bicapped trig prism.	35–37
$NbTe_4$, $TaTe_4$	sq antiprism.	38, 39
TaS_3, $TaSe_3$	bicapped trig prism.	40, 41
Nb_3S_4, Nb_3Te_4	oct	42, 43
NiS	oct, sq pyr	44
NiS_2, $NiTe_2$	oct	45, 46
Ni_6Se_5	sq pyr, oct, tetr	47
Ni_3S_2	tetr	48
Ni_3S_4	tetr, oct	49
Ni_7S_6	tetr, sq pyr	50
PdS, PdS_2	sq planar	51, 52
$PdTe_2$	oct	53
PdTe	oct	54
PtS, PtS_2	sq planar	55
$PtTe_2$	oct	53
PtTe, Pt_2Te_3, Pt_3Te_4	oct	56
$K_2Ni_3S_4$, $Cs_2Pd_3S_4$	sq planar	57
$Cs_2Pt_3S_4$, K_2PtS_2	sq planar	58, 59
$K_2Pt_4S_6$	oct, sq planar	60
$LaPd_3S_4$	sq planar	61
$CoNi_2S_4$, $NiCo_2S_4$	tetr, oct	62, 63
Nb_3FeSe_{10}	bicapped trig prism.	64

[a] sq = square; oct = octahedral, trig prism. = trigonal prismatic; pyr = pyramidal; tetra = tetrahedral.

allow a specific hybridization on the anion that is consistent with the coordination demands of the cation.[26] Such interactions result in the common occurrence of layered structures for the transition-metal chalcogenides and the peculiar trigonal-prismatic coordination behavior of the lighter cogeners of the second- and third-row transition metals. The other important feature of chalcogenides is the presence of Q–Q bonds. Except in the trivial case of peroxides, O–O bonds are not found in oxides.

Common Coordination Geometries in Solid-State Chalcogenides

To proceed with our goal of achieving a new entry point into Nb and Ta chalcogenide chemistry, a knowledge of the preferred coordination geometries of the metal atoms of interest is useful; such information is also useful for an understanding of interrelationships among their structures. In Table I are listed the coordination geometries found in the Nb–Ta/Q (Q = S, Se, Te) binaries, the Pd–Ni–Pt/Q binaries, and some metal/Ni–Pd–Pt/Q ternaries that were known prior to our investigations.[27–64] As we are interested in regular

coordination geometries of chalcogens about a metal atom, we have not included the metal-rich chalcogens of Nb, Ta, Pd, and Pt in Table I.

From the binaries we see that Ta and Nb display both octahedral and trigonal-prismatic coordination; trigonal-prismatic coordination is more common in those compounds with higher valent Nb or Ta ions that were prepared at intermediate temperatures, the preparative conditions often used in this laboratory. The stereochemistry of Ni in these solid-state materials is less regular. But we see from Table I that Pd and Pt prefer square-planar coordination in sulfides and selenides and octahedral coordination in tellurides. The same environment is present in the ternaries, with the exception of the occurrence of an octahedral environment for one Pt atom in the compound $K_2Pt_4S_6$. Of course, we must augment our structural approach with a consideration of oxidation states and electron configurations. If the formal oxidation states $2K^+$, $1Pt^{4+}$, $3Pt^{2+}$, and $6S^{2-}$ are assigned to the ions in $K_2Pt_4S_6$, then one is not surprised that the d^6 Pt^{4+} ion is octahedral and that the d^8 Pt^{2+} ions are square-planar.

Note that the preferred geometries in Table I are not necessarily those found most commonly for a given metal in its coordination compounds.

Linking of Polyhedra To Form New Solid-State Compounds

It would be naive to believe that solely from a knowledge of preferred coordination numbers can we predict compositions and structures of unknown ternary chalcogenides and then successfully synthesize them. But a knowledge of these geometries enables us to think about combinations of metals that will potentially yield new structures, especially structures that are free from

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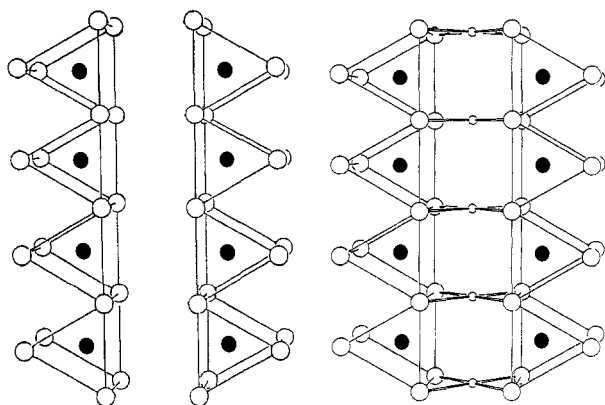
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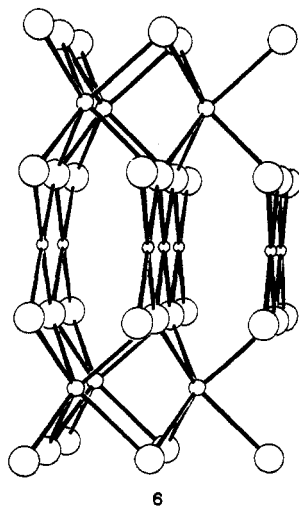(63) Huang, C.; Knop, O. *Can. J. Chem.* **1971**, *49*, 598.

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Figure 1. (a, left) Two columns of edge-shared trigonal prisms. (b, right) Linking of trigonal prisms with square planes. Nb atoms are filled circles, Se atoms are large open circles, and Pd atoms are small open circles here and in Figures 2 and 3.

Figure 2. An individual chain in $Nb_2Pd_3Se_8$.

Figure 3. Structure of one slab of Nb_2PdSe_6 showing trigonal prisms and square planes.

substitutional disorder. For example, the trigonal prism dominates Nb and Ta chalcogenide chemistry, the square plane dominates Pd and Pt chalcogenide chemistry, and the layer structure is common in the former system. In thinking about yet to be discovered ternary compounds in the Nb–Ta/Ni–Pd–Pt/Si–Se–Te systems, we may thus usefully consider various ways of combining trigonal prisms and square planes to form new structures.
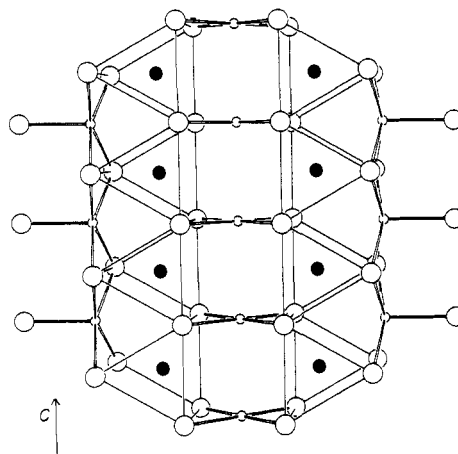
We initially proposed to modify an existing material, the layered dichalcogenide $2H$-NbS$_2$, by inserting Pd atoms between the layers. After all, a large number of atoms and molecules have been intercalated into the layers of NbS$_2$.[2,65] The Nb atoms already have trigonal-prismatic coordination; all we wished to do was insert Pd atoms into square-planar sites. One possible structure would follow from change of the AABB... packing of S atoms in NbS$_2$, **4**, to a simple hexagonal packing AAAA... of the NbS structure with subsequent insertion of Pd atoms in a square-planar environment to afford **6** of stoichiometry NbPdS$_2$. The structure is
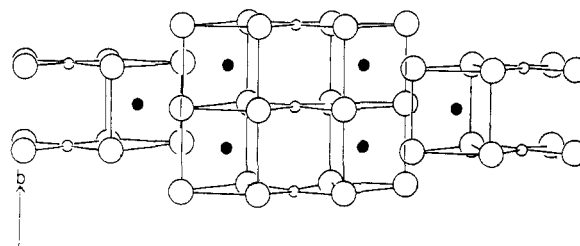

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simple, but perhaps the thought is too simple as we have yet to synthesize the material. We also considered the ordered placement of Nb or Ta atoms with square planes into the packing of rhombic prisms, described by Nyman.[66] This too led us nowhere.

Taking a more local view of certain fragments, we considered Figure 1a in which we show two columns of edge-shared trigonal prisms, each prism being occupied by a Nb or Ta atom. We have stacked these columns so as to emphasize the square-planar hole left between them. Figure 1b shows the insertion of a Pd atom into that hole to bond these columns together. This is one way we might envision the combination of square planes and trigonal prisms; indeed, we synthesized the compound $Nb_2Pd_3Se_8$[67] in which this combination occurs. Figure 2 shows one chain of this structure; the figure stresses the linking of the metal-centered polyhedra. These chains are interconnected so as to produce a structure with one-dimensional channels. That we obtained a channel structure rather than a layer structure was a surprise; that the structure contains in addition to the anticipated square-planar Pd atoms the first example of square-pyramidal Pd atoms in a solid-state structure was also a surprise. Thus, this structure illustrates certain limitations of applying the idea of preferred coordination geometries to solid-state syntheses.

Nevertheless, this approach has led to the synthesis of a number of new ternary chalcogenides, all with unprecedented structural types; these include the homologous series of compounds Nb_2PdSe_6, $Nb_2Pd_{0.71}Se_5$, and $Nb_3Pd_{0.72}Se_7$.[68-70] Each of these compounds contains Nb-centered, simple or capped, trigonal prisms of Se atoms that are linked by Pd atoms in a square-planar site. This linking of metal polyhedra is represented pictorially for Nb_2PdSe_6 in Figure 3. This set of trigonal prisms and square planes forms a two-dimensional

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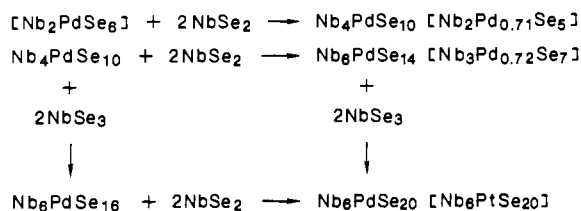(69) Keszler, D. A.; Ibers, J. A.; Shang, M.; Lu, J. *J. Solid State Chem.* **1985**, *57*, 68.
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slab. As in the MQ_2 structures, these layers stack in an ABAB... sequence with only van der Waals' forces holding adjacent layers together. How are the compounds $Nb_2Pd_{0.71}Se_5$ and $Nb_3Pd_{0.72}Se_7$ of such odd stoichiometry structurally related to the simple material Nb_2PdSe_6? They are layered like Nb_2PdSe_6, but the van der Waals' gap is no longer empty. Additional Pd atoms are now disordered on a single crystallographic site between the layers, affording the peculiar stoichiometries. The structures of the layers themselves differ from that of Nb_2PdSe_6 only in the number of prismatic chains and their disposition relative to the Pd-centered square planes. It also follows that as the stoichiometry and structure of the layers change so also do their stacking and the detailed nature of the gap between them. We have discussed with the aid of several illustrations the details of these structural results elsewhere.[70]

We believed that the simple principle of linking trigonal prisms could be extended to phases richer in chalcogen since the MQ_3 compounds also contain M atoms in a trigonal-prismatic environment. An example of a chalcogen-rich phase is Nb_8PtSe_{20}, which contains Nb atoms in trigonal-prismatic, monocapped trigonal-prismatic, and bicapped trigonal-prismatic environments.[71] Its structure is analogous to those in the Nb–Pd–Se system mentioned above as it is composed of chains of Nb-centered trigonal prisms linked by square-planar Pt atoms. In fact, the structure is comprised of the layer found in $Nb_3Pd_{0.72}Se_7$ with the addition of two chains of Nb atoms in bicapped trigonal prisms. With no Pd atoms present in the gap it is a true layered compound.

The chemistry of these planes and prisms can be summarized in the following equations

$[Nb_2PdSe_6]\ +\ 2\,NbSe_2\ \longrightarrow\ Nb_4PdSe_{10}\ [Nb_2Pd_{0.71}Se_5]$

$Nb_4PdSe_{10}\ +\ 2\,NbSe_2\ \longrightarrow\ Nb_6PdSe_{14}\ [Nb_3Pd_{0.72}Se_7]$

$\qquad\qquad +\qquad\qquad\qquad\qquad\qquad +$

$\qquad 2\,NbSe_3\qquad\qquad\qquad\qquad\quad 2\,NbSe_3$

$\qquad\quad \downarrow\qquad\qquad\qquad\qquad\qquad\qquad \downarrow$

$Nb_6PdSe_{16}\ +\ 2\,NbSe_2\ \longrightarrow\ Nb_8PdSe_{20}\ [Nb_8PtSe_{20}]$

where the compounds in square brackets are those that have been isolated. The interrelationships among the various structures are emphasized in terms of the addition of infinite, one-dimensional chains of $NbSe_2$ or $NbSe_3$. All of these compounds obey the simple rules of coordination preference that were outlined above. Describing these structures in terms of the metal coordination makes the interrelationships easy to understand.

To learn more about the solid-state coordination geometries of the metal atoms of the Ni triad in chalcogenides, we investigated the substitutional chemistry of the phase $Nb_2Pd_3Se_8$. The structural analysis of $Ta_2Pt_3Se_8$ and $Ta_2Ni_3S_8$[72] revealed that they are isostructural with $Nb_2Pd_3Se_8$ with Pt and Ni atoms occupying both the square-planar and square-pyramidal coordination sites. The partial replacement of Pd atoms by Ni atoms ($Nb_2Pd_{3-x}Ni_xSe_8$, $x \leq 1$) revealed that Ni preferentially occupies the square-pyramidal site instead of the square-planar site.[73] This behavior is
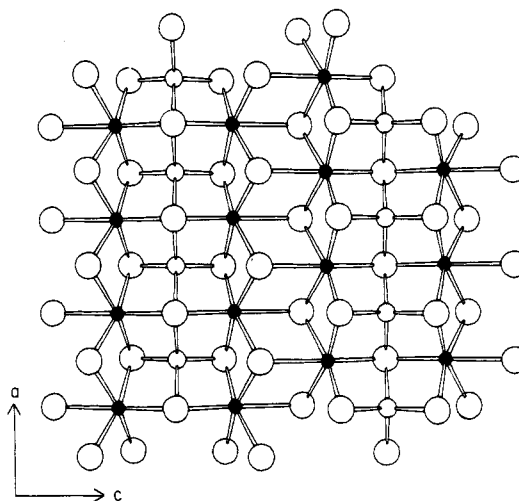

Figure 4. View of the Ta_2NiSe_5 structure. Here and in Figure 5 small empty circles are Ni atoms, filled circles are Ta atoms, and large open circles are Se atoms.

consistent with expectations derived from a strictly local viewpoint of electronic structure. The formal oxidation states and electron configurations Nb^{5+}, d^0 and Pd^{2+}, d^8 may be assigned to the compound $Nb_2Pd_3Se_8$. Clearly, the highest occupied energy levels in the solid will be largely of Pd d-orbital character. Focusing on the local coordination environments only, we expect the highest occupied energy level to be composed mostly of the d orbital of Pd^{2+} that is directed at and is antibonding with the Se apex of the square pyramid.[74] Because of the smaller radial extension of the 3d orbital of Ni as compared with the 4d orbital of Pd, substitution of Ni on the square-pyramidal site will lower the energy of the highest occupied level and thus the total energy of the structure.

Further examination of the Ta/Ni–Pt/Se systems has provided additional insight into the coordination preferences of Ni and Pt atoms in these types of compounds. The synthesis and study of the compound Ta_2NiSe_5[75] gave the first indications of the diversity of Ni coordination that can be expected. In this structure the Ni atoms reside in tetrahedral sites between double chains of corner-shared Ta-centered octahedra (Figure 4). Tetrahedral coordination around Ni atoms has previously been observed in thiospinels.[62] This compound and $Co_2Ta_4PdSe_{12}$[69] represented our first examples of Ta atoms in an octahedral environment although this geometry was anticipated from the ternary Ta/S–Se systems (e.g., $1T$-TaQ_2).[32–34] The analogous compounds Ta_2PdSe_5 and Ta_2PtSe_5 do not form, consistent with the unlikelihood of Pd or Pt in tetrahedral sites.

The chalcogen-rich isostructural compounds Ta_2MSe_7 (M = Ni or Pt) have also been prepared.[76] This structure contains Ta-centered bicapped trigonal prisms of Se atoms that contain an Se–Se bond analogous to $TaSe_3$.[40] In addition to these chains of trigonal prisms the structure also contains chains of Ta-centered octahedra and Pt- or Ni-centered square pyramids (Figure 5). All of the coordination geometries, except the bicapped trigonal prism, had been observed in other

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(74) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 310.
(75) Sunshine, S. A.; Ibers, J. A. *Inorg. Chem.* **1985**, *24*, 3611.
(76) Sunshine, S. A.; Ibers, J. A. *Inorg. Chem.* **1986**, *25*, 4355.

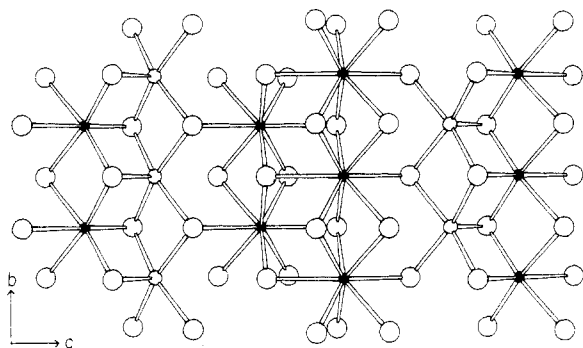**Figure 5.** View of the Ta_2NiSe_7 structure.

ternary compounds already mentioned. This structure is closely related to another ternary structure, Nb_3Fe-Se_{10}, where Nb atoms possess both octahedral and bicapped trigonal-prismatic coordination.[64]

Although we are describing structures as being built from simple coordination polyhedra, we have as yet offered few comparisons of metrical details and physical properties between these extended arrays and molecular systems. Instead, we wished deliberately to highlight in simple terms the remarkable structural aspects of this group of materials that were completely unknown prior to our investigations. Nevertheless, some comments on metrical details are informative; some Ni-S distances are used as examples.

In Ta_2NiS_5 the Ni-S distance in the tetrahedron (2.243 (5) Å) is longer than that of the distance (2.218 (6) Å) in the square plane in $Ta_2Ni_3S_8$. Such a lengthening of the bonding distance in changing from a square plane to a tetrahedron is well-known in molecular chemistry, and its origins have been described.[77] That a similar behavior is observed in the solid state comes as no surprise; there is no change in the physics of bonding in going from a molecule to a solid. Indeed, it has been common for some time for tables of crystal radii[78] to be derived from a combination of data from molecules and from solids. There are, however, certain

metrical differences between solids and molecules. As an example, the Ni-S distance to the apex of a square pyramid in $Ta_2Ni_3S_8$ is 2.321 (5) Å, whereas in the molecule diiodo[bis(o-methylthiophenyl)phenyl-phosphine]nickel(II)[79] it is much longer (2.79 (1) Å). Presumably, this rather weak molecular interaction shortens in the solid because of the more stringent packing requirements of the chalcogen.

Our desire to study further the concept of coordination chemistry in the solid state has led to the investigation of the tellurides. The binary Nb-Ta/Te systems include the compounds $NbTe_4$ and $TaTe_4$ where the metals are in a square antiprism of Te atoms. In the compounds $NbTe_2$ and $TaTe_2$ the metals occupy octahedral sites. Interestingly, our first attempt to synthesize a ternary telluride produced $NbNiTe_5$ with Nb in a bicapped trigonal prism of Te atoms and Ni octahedrally coordinated.[80] This Nb coordination is observed in sulfides and selenides but not in tellurides although this may be related to the scarcity of known Te compounds.

Concluding Remarks

In this Account we have sketched how the concept of preferred coordination geometries of metal atoms, a concept taken from coordination chemistry, is useful not only in understanding the interrelationships among solid-state structures but also as an aid to the synthesis of new compounds. We have used ternary chalcogenides as illustrations. As for all concepts there are limitations to its use, but it has the advantage of being conceptually simple and readily applied to solid-state problems by those not steeped in the culture of the subject.

(77) Reference 74, p 304.
(78) (a) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751. (b) See: Shannon, R. D. In *Structure and Bonding in Crystals*; O'Keeffe, M., Navrotsky, A., Eds.; Academic: New York, 1981; Vol. II, p 53.
(79) Meek, D. W.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1915.
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