

NEW MATERIALS FROM HIGH TEMPERATURE SYNTHESIS

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Abstract - Over 40 new and remarkable types of metal-rich compounds have been synthesized since about 1970 by high temperature reactions. These are found in binary and ternary systems of the early (group III-VI) transition and lanthanide elements with the nonmetals Cl, Br, I, O, S, Se or Te. Metal-metal bonding is characteristic of all the structures. These are conveniently organized in terms of the presence of discrete clusters of four to six metal atoms or their condensation products in the form of extended clusters, infinite chains of clusters sharing faces or edges, or double-metal-layered sheets. All the metal structures are well bound by nonmetals in relatively specific ways. Several recent discoveries also involve small nonmetal atoms interstitially bound within the metal units. A range of examples is discussed and illustrated. Some developing concepts and principles involving structural, bonding and electronic regularities and effects and some of the experimental aspects are also considered.

INTRODUCTION

This appears to be a particularly appropriate time to illustrate the value of synthetic studies at high temperatures. The past decade or so has been a period of great excitement as such investigations have led to the discovery of several remarkable groups of totally new and highly unusual compounds that lie along the interface between metals and conventional compounds. These accordingly exhibit extensive and often structurally dominant metal-metal bonding either in clusters of 4 to 12 atoms or in diverse metal-like segments in the form of infinite chains, ribbons or sheets. Appropriate to chemistry along this metal-salt boundary, these "little bits of metal" are in turn well sheathed by the nonmetal component, halide or chalcogenide principally, through what can be viewed as typical salt-like interactions that are often both strong and specific. Included among the new phases are also the beginnings of an interstitial chemistry for small nonmetals within the metal array that is in some ways comparable to that found in the metals themselves. The present development of many of the new areas is very limited, and much remains to be accomplished in establishing not just the identities and limits for the occurrence of such unusual phases but also something of their properties and interrelationships, a theoretical basis for their understanding, and the identification of any new or unusual phenomena that may accompany these unprecedented compositions and structures. Synthetic results of this character are obviously also the first essential step to the development of new and possibly useful materials.

Of course, knowledge of metal-metal bonded compounds is by no means limited to the post-1970 period considered here. High and metal-like conduction has long been known for selected oxides, TiO, VO, NbO, MoO₂, WO₂ and the bronzes, for example, and in a larger group of metal-rich sulfides and selenides (Ref. 1). The latter tend to be structurally complex and fairly isotropic both in their conduction and what can be considered as metal-metal bonding. Many phosphides, nitrides, carbides, etc. may also be so categorized, although Simon (Ref. 2) has described some novel exceptions in older structures such as that of Ti₅Te₄ (chains of metal octahedra sharing vertices) and Nb₂Se (double chains) plus others in what are normally classified as intermetallic phases. In contrast, halides containing metal-metal bonding were long thought to be limited to the unique Ag₂F (anti-CdI₂ type), a few layered metallic diiodides (Ref. 3) and classical halide clusters (which we here restrict to those of four or more atoms) such as (Nb,Ta)₆X₁₂ⁿ⁺ (X = Cl, Br, I), CsNb₄X₁₁ and (Mo,W)₆X₈^{m+} (Ref. 4). Highly anisotropic, extended metal-metal bonding of the sort to be described here has in the past been pretty well limited to the layered chalcogenides such as TiS₂ and NbS₂ and their intercalation derivatives, all of which possess only single metal layers.

The onset of the new era described in this article is fairly well defined by the 1971 report (Ref. 5) of the discovery of what have become known as the Chevrel phases, over 100

molybdenum chalcogenides like $M_xMo_6Ch_8$ ($Ch = S, Se, Te$, $M =$ many metals) which are interesting in their own right for their remarkable structures, rich derivative chemistry and metallic properties but which have become well-known largely because of their high-field superconductivities. The impact that new synthetic discoveries can have is well illustrated by these materials. Parallel and subsequent synthetic efforts have led to the identification of many metal-rich halides and oxides especially that possess a related though unique structural chemistry of considerable novelty. Particular milestones in the latter group have been the discoveries of the first infinite chains of metal clusters in Gd_2Cl_3 reported in 1973 (Ref. 6), Sc_7Cl_{10} in 1977 (Ref. 7) and the oxide analog $NaMo_4O_6$ in 1979 (Ref. 8), the double-metal-layered $ZrCl$ in 1976 (Ref. 9) and the first cluster phase known to be stabilized by an interstitial nonmetal, $Gd_5Cl_9C_2$, in 1982 (Ref. 10).

A significant number of these new compounds occur in what might be thought to be "simple" binary systems. It has become clear that substantial experimental problems and limitations are associated with some syntheses and that these have presumably been responsible for the lack of earlier discovery in systems once thought to have been well investigated. Some of the difficulties will be briefly noted in a later section.

NEW MATERIALS

In this section the recent discoveries in the area of metal-rich chalcogenides and halides will be tabulated and some of their unusual features illustrated. The organization will be in terms of structural relationships while some of the new concepts and generalities that are developing from these findings will be presented later. Many of the discoveries are quite recent, relatively unknown and fragmented, although some subsets have been reviewed (Ref. 2, 11-17). At the same time, the space and time available here require that the more incomplete information on properties and theoretical considerations mainly be left to another place.

The most ready classification for most of these materials is in terms of the degree of the metal-metal interaction, starting with small metal clusters and proceeding through their condensation products in the form of extended clusters and infinite chains to two-dimensional sheets. Considerable diversity still remains in each group. Knowledge of further condensation in the third dimension in these compounds appears to be limited to the unique intercluster interactions found in the Chevrel phases (below) and to the metals themselves although some older examples are found in NbO (Ref. 18) and elsewhere (Ref. 2). The clusters considered will be arbitrarily limited to those containing four or more atoms and among these the great majority will contain six in more or less regular octahedra. The latter readily subdivide into two types, the M_6Y_8 (abbreviated 6-8) type in which eight nonmetal atoms lie outward from (cap) the triangular faces of the metal octahedron and the M_6Y_{12} (6-12) type in which 12 nonmetal atoms lie above (bridge) the edges of the octahedron. The former are found more frequently, but not exclusively, in chalcogenides and the latter, more often with halide. (Relatively few tellurium and iodine examples are known.) An example of each cluster type is illustrated in Fig. 1.

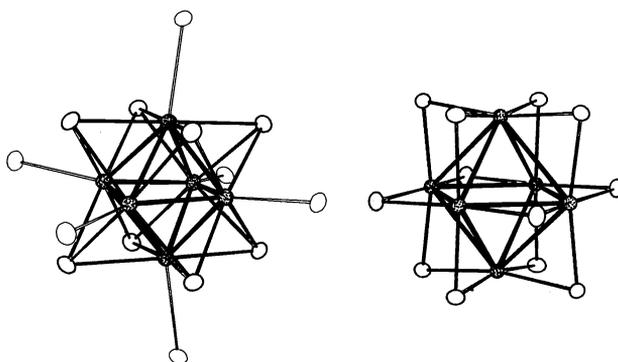


Fig. 1. Examples of M_6Y_8 and M_6Y_{12} clusters with M_6 units in heavy outline: Left - face-capped octahedron, 6-8 type, plus bridging exo atoms ($Cs(Nb_6I_8)I_{6/2}$, Ref. 19); Right - edge-bridged octahedron, 6-12 type (Zr_6Cl_{12} , Ref. 20).

An additional structural principle apparently always applies to the bonding of either isolated clusters or their condensation products throughout the solid. The empty region that otherwise lies outward (exo, outer or *äusser*) from the metal vertex in each cluster is inevitably occupied by a fifth nonmetal neighbor or other basic group, emphasizing the

availability of an otherwise empty, low energy bonding orbital from the metal in this direction. For example, the additional iodine atoms that serve only to bridge clusters in $\text{CsNb}_6\text{I}_{11}$ into an infinite, three-dimensional solid are shown in the left hand part of Fig. 1, the connectivity then being described as ${}^3[(\text{Nb}_6\text{I}_8)\text{I}_{6/2}^{\text{a}}]$. In some instances the exo atoms may have only a terminal function $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6^{2-}]$ while in other cases some of the inner (i) atoms must also function as outer (a) atoms to vertices in other clusters. Such occurs with $\text{Zr}_6\text{Cl}_{12}$ on the right of Fig. 1 where the detailed connectivity is $\text{Zr}_6\text{Cl}_6^{\text{i}}\text{Cl}_6^{\text{a}}(2/3)\text{Cl}_6^{\text{a-i}}(1/3)$ when the bridging chlorines are subdivided according to whether these are inner or outer to the three zirconium neighbors. These descriptions can become rather complex for an overview and so only the composition of the inner cluster will usually be noted, it being understood that the exo functionality and the overall composition are also satisfied.

The principal examples of the metal-rich chalcogenides and halides that have been reported since 1970 are listed in Table 1 (Ref. 21-72).

TABLE 1. Examples of new metal-metal bonded compounds prepared at high temperatures^a

Composition	Type ^b	Structural Features	Other Examples	Ref.
Clusters				
-isolated				
Mo_3Ch_4	6-8	Mo_6Ch_6 strongly cross-linked ⁻ ; Chevrel phases	$\text{M}_x\text{Mo}_6\text{Ch}_8$ for many M, $\text{Mo}_6\text{Ch}_6\text{X}_2$	11,14, 21
$\text{Cs}_{0.6}\text{Mo}_6\text{S}_7$	6-8	Mo_6S_8 sharing S in cross-linked chains		22
$\text{Re}_3\text{Se}_4\text{Cl}$	6-8	$(\text{Re}_6\text{Se}_8)\text{Cl}_2$ in sheets; Cl on trans-apices	$\text{Na}_4(\text{Re}_6\text{S}_8)\text{S}_4$, $\text{Ba}_2(\text{Re}_6\text{S}_8)\text{S}_3$	23,24
$\text{Mo}_3\text{I}_4\text{Se}$	6-8	$(\text{Mo}_6\text{I}_5\text{Se}_3)$ in Se-bridged chains	$\text{Mo}_6\text{Br}_8\text{S}_2$	25
$\text{Mo}_6\text{Br}_6\text{S}_3$	6-8	$\text{Mo}_6\text{Br}_4\text{S}_4$ sharing S apices, S-bridged into sheets		26
$\text{Mo}_6\text{Cl}_{10}\text{Ch}$	6-8	$(\text{Mo}_6\text{Cl}_7\text{Ch})\text{Cl}_3$		27
ReSeCl	6-8	$(\text{Re}_6\text{Se}_6\text{Cl}_2)\text{Cl}_4$		28
$\text{HgMo}_6\text{Cl}_{14}$	6-8	$(\text{Mo}_6\text{Cl}_8)\text{Cl}_6^{2-}$		29
MoSX	4-4	$(\text{Mo}_4\text{S}_4)\text{X}_4$	GaMo_4S_8 , AlMo_4S_8 , PrI_2	30-33
$\text{Ba}_{0.57}\text{Mo}_4\text{O}_8$		Mo_4 rhomboids (2 types) O-linked into chains	$\text{M}^{\text{I}}_x\text{Ba}_{0.65-x}\text{Mo}_4\text{O}_8$	34,35
$\text{Mg}_3\text{Nb}_6\text{O}_{11}$	6-12			36
$\text{CsNb}_6\text{I}_{11}$	6-8	$(\text{Nb}_6\text{I}_8)\text{I}_{6/2}^-$		19
$\text{Zr}_6\text{Cl}_{12} \cdot \text{M}_2\text{ZrCl}_6$ (M=Cs, K, Na)	6-12	isolated $\text{Zr}_6\text{Cl}_{12}$ with ZrCl_6^{2-} filling exo positions	Zr_6X_{12}	20,37
$\text{Zr}_6\text{X}_{14}\text{C}$	6-12	$(\text{Zr}_6\text{X}_{12})\text{X}_2$, C-centered		38,39
$\text{Zr}_6\text{Cl}_{15}\text{N}$	6-12	$(\text{Zr}_6\text{Cl}_{12})\text{Cl}_3$, N-centered		38
$\text{Sc}_7\text{Cl}_{12}\text{N}$	6-12	$\text{Sc}^{\text{III}}(\text{Sc}_6(\text{N})\text{Cl}_{12})$	$\text{Sc}_7\text{Cl}_{12}\text{B}$, La_7I_{12}	40,41

-continued-

TABLE 1 - continued

-extended clusters				
$\text{In}_2\text{Mo}_{15}\text{Se}_{19}$	6-8	Mo_6Se_8 + confacial octahedra $\text{Mo}_9\text{Se}_{11}\text{C}$	$\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$, $\text{Ag}_{3.6}\text{Mo}_9\text{Se}_{11}$	42-44
$\text{M}_2\text{Mo}_9\text{S}_{11}$, (M=K, Tl)	6-8	Mo_6S_8 + confacial octahedra $\text{Mo}_{12}\text{S}_{14}\text{C}$		45
$\text{Gd}_5\text{Cl}_9\text{C}_2$	6-12	Pairs sharing a Gd_2 edge, C_2 in each	$\text{Gd}_{10}\text{Cl}_{17}(\text{C}_2)_2$ $\text{Gd}_{10}\text{I}_{16}(\text{C}_2)_2$	10
<u>Infinite chains</u>				
-octahedra sharing trans edges				
Gd_2Cl_3	6-8	$[\text{Gd}_4\text{Cl}_4\text{Cl}_{4/2}]$	Cl, Br of Y, Tb, Er, Tm, Lu	6, 46, 47
Sc_5Cl_8	6-12	$[(\text{Sc}^{\text{III}}\text{Cl}_2^+)(\text{Sc}_4\text{Cl}_6^-)]$ double chains	Gd_5Br_8 , Tb_5Br_8	48, 49
Er_4I_5	6-12	Sc_5Cl_8 type without M ^{III} side chain	Gd_4I_5 , Ce_4Br_5	50, 51
$\text{Sc}_4\text{Cl}_6\text{B}$	6-12	B-centered Sc octahedra	$\text{Sc}_4\text{Cl}_6\text{N}$	40
$\text{Sc}_7\text{Cl}_{10}$	6-8	$[(\text{Sc}^{\text{III}}\text{Cl}_2^+)(\text{Sc}_6\text{Cl}_8^-)]$, pairs of Gd_4Cl_6 -type chains sharing edges		7
Er_7I_{10}	6-12	$\text{Sc}_7\text{Cl}_{10}$ type but edge-bridged		50
$\text{Sc}_7\text{Cl}_{10}\text{C}_2$	6-12	Er_7I_{10} type with C-centered Sc octahedra		40
Tb_6Br_7	6-12	Er_7I_{10} type without the M ^{III} side chain	Er_6I_7	52
$\text{Gd}_{12}\text{I}_{17}\text{C}_6$	6-12	zig-zag chains of cis- and trans-edge-shared octahedra, C_2 in each		51
MMo_4O_6 (M=Na, Li, K, In, Sn)	6-12	$[\text{Mo}_4\text{O}_6^-]$ chains	$\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$ $\text{Pb}_x\text{Mo}_4\text{O}_6$	8, 33, 53
$\text{Mn}_{1.4}\text{Mo}_8\text{O}_{11}$	6-12	$[\text{Mo}_4\text{O}_6^-]$ chains with different connectivity		53
$\text{M}_x\text{M}'_{2-x}\text{Mo}_4\text{O}_7$, (M=Sc, Fe, Al, M'=Zn, Fe)	6-12	$[\text{Mo}_4\text{O}_6^-]$ chains in sheets cross-linked by MO_6 and $\text{M}'\text{O}_4$ polyhedra, some mixed metal		16
-other				
$\text{Gd}_2\text{Cl}_3\text{N}$	4-6	N-centered tetrahedra sharing opp. edges		54
$\alpha, \beta\text{-ZrI}_2$		zig-zag chains	$\beta\text{-MoTe}_2$, WTe_2	55
$\text{Na}_{0.85}\text{Mo}_2\text{O}_4$		rhomboids trans-fused to ribbons		53

-continued-

TABLE 1 - continued

MMo_2O_4 (M=V,Cr,Fe,Co)	rhomboids linked in ribbons	ReSe ₂	56
TlFe ₃ Te ₃	~6-8 confacial octahedra, planar M ₃ Ch ₃ ⁻ units	M ^I Mo ₃ Ch ₃ , M=Li-Cs,In,Tl,Ag	57-61
Double-metal sheets^d			
ZrX	close-packed layers X-Zr-Zr-X	Cl and/or Br of Hf, Sc, Y and 10 lanthanides	9,47, 62-67
M ₂ Cl ₂ C (M=Sc,Y,Zr)	ZrX structure with C in all M ₆ octahedra	Zr ₂ X ₂ B, Zr ₂ X ₂ N, Ta ₂ S ₂ C	38,68,69
ZrXH	ZrX with H in Zr ₄ tetrahedra	ZrXO _{0.3} , ZrClN _{1-x} , ScClH	70,71, 38,40
Zr ₂ X ₂ H	distorted ZrX with H in half of Zr ₄ tetrahedra		70
Li _{0.2} YCl	40% intercalation of YCl	Li _{0.5} GdCl	68,72
M _{0.2} YClO (M=Li-Cs)	intercalated YCl with O in all Y ₄ tetrahedra		68
M _{0.4} Y ₂ Cl ₂ C (M=Li-Cs)	intercalated YCl with C in all Y ₆ octahedra		68

^a X = Cl, Br, I; Ch = S, Se, Te. ^b 6-12 type is M₆Y₁₂, edge-bridged by Y; 6-8 type is M₆Y₈, face-capped; 4-4 is cubane-like. ^c See text. ^d All 6-8 type; X = Cl, Br only.

The frequency with which nominal octahedral metal groups appear allows a useful 6-8 or 6-12 classification to be applied, not only to isolated clusters but also for extended and infinite metal arrays where these may be imagined to originate by condensation through shared apices, faces or, most frequently, edges of the metal octahedra (Ref. 2, 12, 73). The collection of new compounds as a whole provides very good definition of the novelty, significance, and opportunities in this area of high temperature, solid state chemistry.

The Chevrel phases M_xMo₆Ch₈ plus some of the newer variants listed illustrate the beautiful versatility in structures (and properties) that can be achieved synthetically. The extent to which the exo bonding can be exceedingly important in determining the structure and the properties of the material is also seen (Ref. 74). The Mo₆Ch₈ and M_xMo₆Ch₈ phases and many of their derivatives are metallic (and often super-) conductors because of this function. The parent cluster, lacking any additional anions to occupy the outer sites, achieves a significant gain in stability (Ref. 75) by filling exo positions with 6 of 8 of the inner chalcogenides from other clusters. The strength of these bridges is indicated by the fact that the Mo-Ch^a distances are substantially the same as the Mo-Chⁱ separations. This coordination of six chalcogenide atoms from other clusters into empty orbitals at molybdenum plus the complementary use of six of the inner atoms to fill exo positions in adjoining clusters leads to a particularly remarkable rhombohedral structure in which Ch-Mo-Ch-Mo rhomboids hinge each cluster to six others and, most importantly, generate six longer intercluster Mo-Mo bonds as diagonals of these rhomboids. This is illustrated in a portion of the structure shown in Fig. 2. (Vertical three-fold axes and an inversion center at each cluster generate the entire structure.) The intercluster bonding shown, which is essential for the metallic properties, is naturally not evident when only a 6-8 classification is used (Table 1). The relatively open structure generated by this bridging also leaves room for added heterometals that reduce the clusters and form the important M_xMo₆Ch₈ derivatives (which were actually discovered first). The intercluster Mo-Mo bonding persists, though often at longer distances, on reduction to the ternary phases and in the extended cluster structures (below) while it becomes limited to one or two directions in some of the diverse derivatives such as Mo₆Br₆S₃ and Mo₆I₈Se₂. The intercluster Mo-Mo bonds always appear to arise through the medium of intercluster Ch^{i-a} bonds. This characteristic for Re₆Se₈Cl₂ is shown in Fig. 3, where the two additional chlorines cap apices

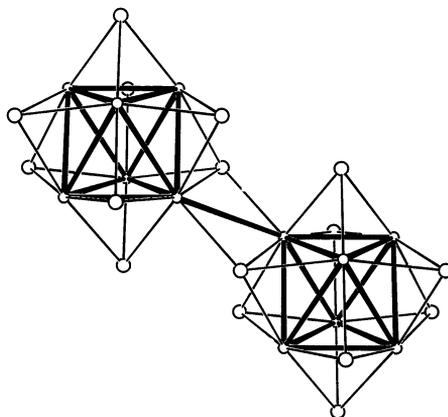


Fig. 2. Two Mo_6S_8 clusters plus the important intercluster Mo-S and Mo-Mo bonding. Nearest neighbor Mo-Mo separations ("bonds") are in heavy outline.

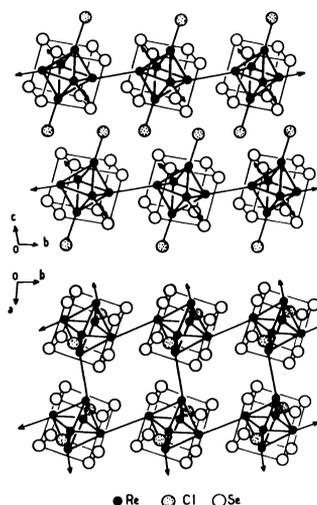


Fig. 3. Two views of the $\text{Re}_6\text{S}_8\text{Cl}_2$ structure showing (top) sheets generated by non-bridging chlorine atoms (dotted) and (bottom) Re-Re bonding between clusters in sheets. (Intercluster Re-Se bonding is not shown.) (Reproduced from Ref. 23.)

and do not bridge, giving intercluster Re-Se bridging and therefore Re-Re bonding only in sheets. A further increase in nonmetal:metal ratio will eventually lead to the formation of isolated clusters as in the well-known $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4$ (Ref. 4). A considerable variety of interesting rhenium examples of this sort have recently been described, e.g., $\text{Cs}_2(\text{Re}_6\text{Se}_6\text{Cl}_2)\text{Cl}_6$ and $(\text{Re}_6\text{Se}_4\text{Cl}_4)\text{Cl}_6$ (Ref. 28).

On the other hand, it seems natural that a nonmetal:metal ratio below 8:6 should lead to cluster condensation if the above precepts regarding face-capping and exo bonding are maintained. Fortunately, the bonding is favorable, and small extended clusters are formed by face-sharing of 6-8 groups, namely the $\text{Mo}_9\text{Se}_{11}$ (Ref. 42) and $\text{Mo}_{12}\text{S}_{14}$ (Ref. 45) shown in Fig. 4 along with the Mo_6Ch_8 cluster described earlier. These two polyclusters were first found in compounds in which they alternated with Mo_6Ch_8 clusters, but the former has recently been found alone in $\text{Ag}_{3.6}\text{Mo}_9\text{Se}_{11}$. The central units in the condensed clusters are now planar Mo_3Ch_3 groups, while exo bridging atoms (dotted) are retained and necessary only at the ends of the extended clusters where pairs of Mo-Ch bonds again generate intercluster Mo-Mo bonding, metallic conduction and sometimes superconductivity.

The end limit for this type of condensation is found in the remarkable phases $\text{M}^{\text{I}}\text{Mo}_3\text{Ch}_3$. Here the infinite chains $\frac{1}{2}[\text{Mo}_3\text{Ch}_3^-]$ have the same appearance as the central portion of the $\text{Mo}_{12}\text{S}_{14}$ unit shown but without any interchain bonding except that provided by the

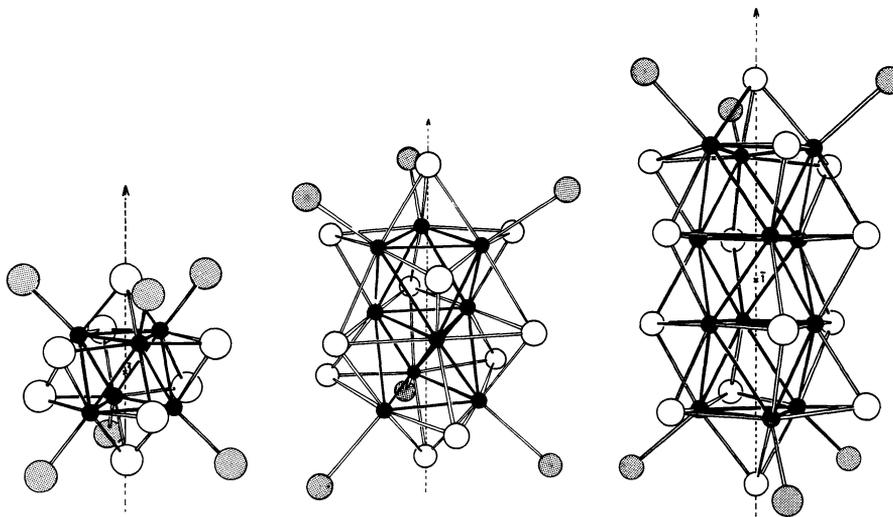


Fig. 4. The Mo_6Ch_8 , $\text{Mo}_9\text{Se}_{11}$ and $\text{Mo}_{12}\text{S}_{14}$ clusters: Mo - solid, Ch - open, intercluster bridging Ch from other clusters - dotted. (Vertical three-fold axes and inversion centers are marked.)

cation. An interesting product would be the oxidized and cation-free material with regular and presumably weak interchain interactions.

One of the more remarkable features of this new chemistry is the considerable number of infinite chain compounds now known that are based on 6-8 or 6-12 metal octahedra condensed by sharing opposite edges. Eight distinct structural arrangements with respect to cluster type or interchain features are now known with the trivalent elements, the compounds having average oxidation states for the metals that range from 1.17 to 1.60 (Table I). Condensation of 6-12 type clusters via a common metal edge can be readily imagined - Fig. 5 -

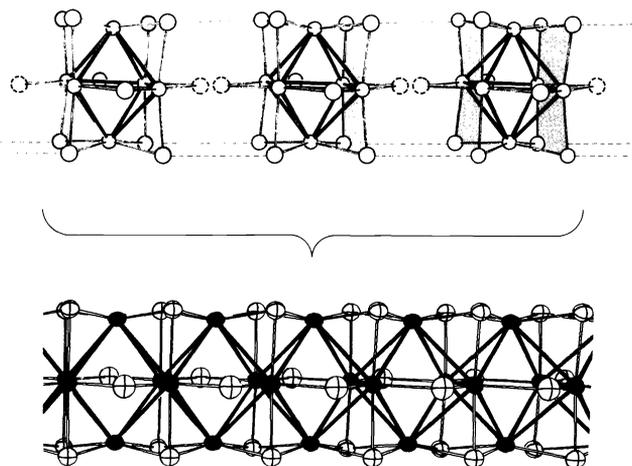


Fig. 5. The condensation concept applied to conversion of M_6Y_{12} -type clusters to an infinite M_4Y_6 chain. The shared elements are shaded.

through joining of opposite faces of the square prism defined by the top and bottom four halides in the isolated cluster, the halide that bridges what becomes the shared metal edge also being eliminated. The resulting composition is $\text{M}_2\text{M}_{4/2}\text{Y}_{8/2}\text{Y}'_2 = \text{M}_4\text{Y}_6$, Y' being the halide bridging the side edges.

The first infinite chain halide discovered, Gd_2Cl_3 , is derived by the alternative process, condensation of 6-8 clusters. The result is shown in Fig. 6. Chlorine atoms cap all exposed faces while zig-zag rows of chlorine atoms bridge between the apices of separate

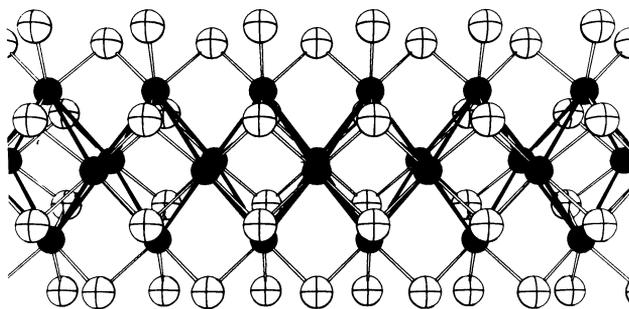


Fig. 6. A portion of the infinite chain structure found of Gd_2Cl_3 (Gd - solid, Cl - open spheres).

chains to generate sheets (a duplicate set of the bridging atoms is shown in the Fig.). Thus a 6-8 cluster has condensed to $M_2M_{4/2}X_4X'_{4/2}$, X' being the halide between the chains. (Additional chlorine atoms from other sheets occupy the exo positions on the shared Gd_2 edges.) It should be noted that the octahedra in nearly all of these condensed halides are distorted, the chain repeat in the present case, 3.82 Å, being one extreme with the shared edge at 3.27 Å the other. Chlorine appears to be relatively tightly packed around these chains with typical van der Waals separations; this factor may be responsible for some lengthening of the metal octahedra since these must have the same period as chlorine.

Other structures with infinite chains are based mainly on 6-12 type building blocks and exhibit both different ways of accommodating counteractions and double chains. Figure 7 (opposite) illustrates three other ways in which metal octahedra chains occur in compounds, all views now being down the chain axes. At the top $Sc_5Cl_8 = \frac{1}{2}[(ScCl_2^+)(Sc_4Cl_6^-)]$ achieves a higher electron count within the cluster chains through inclusion of an exactly commensurate chain of $Sc^{III}Cl_6$ groups also sharing trans edges, the halides in this also occupying all exo positions of the Sc_4Cl_6 chain via three-coordinate bridging halides. The same cation and bridging functions appear in $\frac{1}{2}[(ScCl_2^+)(Sc_6Cl_8^-)]$ in Fig. 7(b) where pairs of metal chains are now fused via side edge to give double chains. (The chains are actually now face-capped, which is of no matter in this projection, but the edge-bridged equivalent is found in Er_7I_{10} and $Sc_7Cl_{10}C_2$ and the cation-free chain, in Tb_7Br_7 .) Finally, 4-6 chains bridged in exactly the same way as in Sc_5Cl_8 are found in $\frac{1}{2}[Na^+(Mo_4O_6^-)]$ (Fig. 7(c)) with the counteractions in channels. The same connectivity without the cation is found in Sc_4Cl_6B , while Er_4I_5 achieves the lowest oxidation state in the series by having the side-bridging halides (Fig. 5) fulfill this function in two parallel chains to produce sheets.

The metal array in $NaMo_4O_6$ is considerably more tightly bound than is the scandium analog, befitting its higher electron count. This condition is made possible by the presence of the smaller oxide since the anions on these chains of course have the same period as the octahedra (2.86 Å). Subsequent research in McCarley's group (Ref. 16, 34, 35, 53) has revealed that a prolific chemistry of this sort exists for ternary and quaternary molybdenum oxides. Figure 8 shows another version of Mo_4O_6 chains in $Sc_{0.75}Zn_{1.25}Mo_4O_7$ where sheets of these are held together by ZnO_4 , ZnO_6 and ScO_6 polyhedra. A considerable variety of other atoms may be used in the latter functions (see Table). The apex but not the waist separations in the Mo octahedra now also show a long-short alternation. It is amazing that no molybdenum oxides with oxidation states less than +4 were known before these discoveries. Synthesis temperatures and therefore the thermal stabilities of these products are among the highest for the compounds considered here, 1100-1600°C.

The next stage known for cluster condensation is infinite double-metal sheets, which can be viewed as the end member of the interchain condensation shown in its first stage for Sc_7Cl_{10} in Fig. 7(b). The result is close-packed layers sequenced X-M-M-X, as depicted in Fig. 9. This turns out to be a rather common structure now known not only for chlorides and/or bromides of zirconium and hafnium, where the formal electron count binding the double-metal-layers is d^3 , but also in a dozen rare-earth metal monohalides where the configuration is d^2 . This decrease in electron count results in weaker bonding between metals in different layers, e.g., 3.09 Å in $ZrCl$ increasing to 3.51 Å in YCl , together with a somewhat smaller increase within the layers as well. Such phases appear to be metallic, Pauli paramagnetic (except for lanthanide f^n cores) and graphitic, with a decomposition point for $ZrCl$ above 1100°C. The analogous iodides are not known.

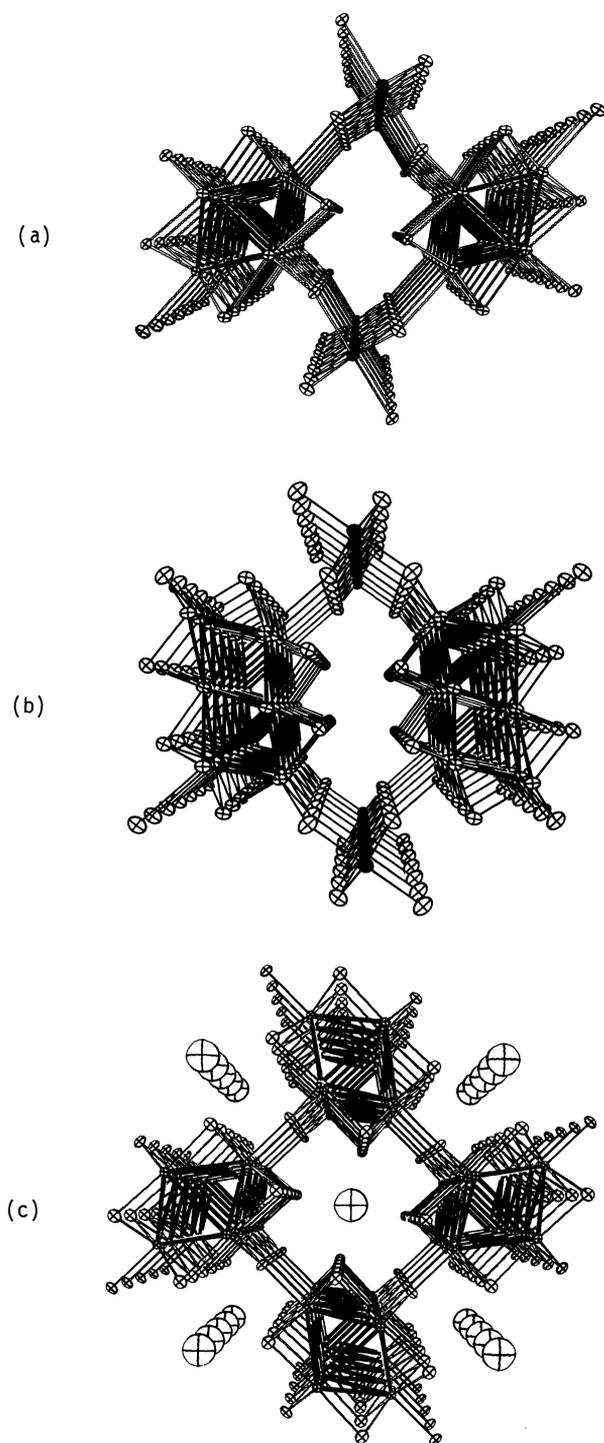


Fig. 7. Representative examples of infinite chains of metal octahedra viewed approximately along the metal chains: (a) $(\text{Sc}^{\text{III}}\text{Cl}_2^+)(\text{Sc}_4\text{Cl}_6^-)$ with solid ellipsoids for isolated scandium atoms; (b) the double metal chain structure $(\text{Sc}^{\text{III}}\text{Cl}_2^+)(\text{Sc}_6\text{Cl}_8^-)$; (c) $\text{Na}^+(\text{Mo}_4\text{O}_6^-)$ chains. (The same interconnection of chains continues in the plane of the paper as well.)

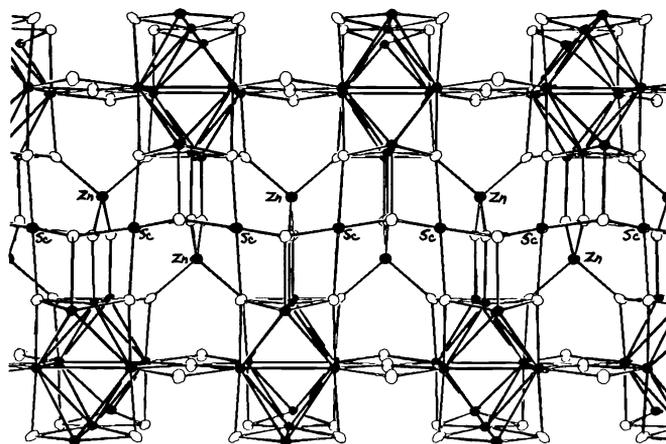


Fig. 8. A view along the chains in $\text{Sc}_{0.75}\text{Zn}_{1.25}\text{Mo}_4\text{O}_7$, with metal atoms as solid ellipsoids. The same connectivity also extends vertically in the Fig.

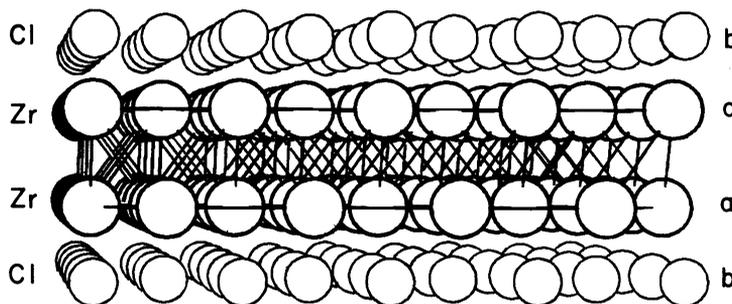


Fig. 9. A section of the four-layer structure of ZrCl , with the shorter Zr-Zr separations drawn in.

These compounds exhibit a novel interstitial chemistry in the metal-like region between the double-metal layers, the same basic four-layer structure being retained when the nonmetals are bound therein, usually with some expansion or contraction of the metal array. The nominally octahedral metal interstices may all be filled with B, C or N atoms (Z) to give stoichiometric compositions $\text{M}_2\text{X}_2\text{Z}$, while the smaller tetrahedral holes are fully occupied in ScClH and ZrXH and partially in $\text{ZrClO}_{0.4}$ and ZrXN_{1-x} . Intercalation with and without simultaneous interstitial atom incorporation may also be accomplished with the trivalent element derivatives (Table 1) although metal oxidation states in these are now fairly high and metal-metal bonding is probably not very significant.

A striking number of interstitial derivatives of other metal cluster and chain structures have also been found recently. The $\text{Gd}_{10}\text{Cl}_{18}\text{C}_4$ shown in Fig. 10 and the closely related $\text{Gd}_{10}\text{Cl}_{17}\text{C}_4$ are the only published examples that involve short segments of the infinite chains of edge-sharing clusters, in this case dimers. Again, the exo positions of the gadolinium atoms in the double cluster shown (except for those in the shared edge) are occupied by chlorine atoms from other like units. These phases together with the similar infinite chain $\text{Gd}_{12}\text{I}_{17}\text{C}_6$ are particularly remarkable in that incompletely reduced carbon in C_2 units is found oriented diagonally across all clusters, with the C-C distances corresponding to a Pauling bond order of about 1.3. This can be imagined to arise from covalent bonding of a C_2^{n-} group, $n \sim 5.7$, to the gadolinium atoms of the cluster, primarily through filled π^* orbitals (Ref. 17, 51), the number of electrons available precluding the formation of single carbide-like interstitials. However, the latter are found in the more electron-rich $\text{Gd}_3\text{Cl}_3\text{C}$ in which 6-12-like clusters share three non-adjacent edges (Ref. 76). The N-centered $\text{Gd}_2\text{Cl}_3\text{N}$ appears to be the only example of tetrahedral clusters forming an infinite chain.

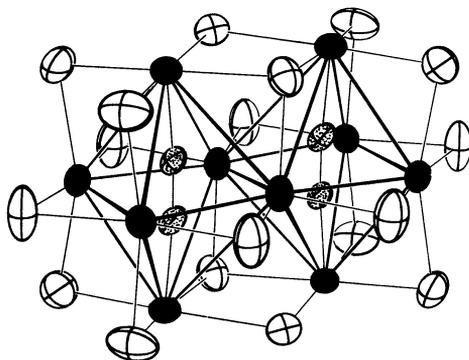


Fig. 10. The dimeric cluster $Gd_{10}Cl_{18}(C_2)_2$, with metal and carbon atoms as solid and dotted ellipsoids, respectively. (Reproduced from Ref. 10.)

The intrinsically smaller cavities in zirconium and scandium cluster phases appear to accommodate single second-period nonmetals better. In addition to the layered monohalide derivatives noted above, several isolated clusters and chain derivatives have been found recently. The previously reported $(Zr_6Cl_{12})Cl_3$ (Ref. 77) is now known to be the nitride and the same is true of $Sc(Sc_6Cl_{12})$ (Ref. 40), these now being 14-electron clusters as is $Zr_6I_{12}(C)I_2$. Many other examples, not all 14-electron in count, appear likely. The infinite chain Sc_4Cl_6Z , $Z = B, N$, and $Sc_7Cl_{10}C_2$ (single carbon) have already been noted. Fortunately, there are also a substantial number of compounds in which the clusters, chains or sheets appear quite free of nonmetal interstitials as judged both by careful X-ray studies and by the synthesis of these phases in high yields in "clean" systems without the purposeful addition of one of these nonmetals.

DEVELOPING PRINCIPLES AND CONCEPTS

Many of the compounds described here are relatively new, and so many opportunities remain regarding the measurement and understanding of their properties. At the present time the compositions and structures known for many phases are sufficient to allow some generalizations to be achieved, especially regarding structures, bonding and some electronic regularities and effects.

Structural generalities

Some developing concepts have already been utilized in the previous section in organizing the results in terms of cluster building blocks and their condensation products in polyclusters, infinite chains and sheets formed via corner, edge or face-sharing of metal cluster atoms. Some further observations regarding cluster types and coordination characteristics are useful. The frequency with which the six-metal "octahedral" cluster appears is impressive. As far as can be perceived, the choice between 6-8 and 6-12 cluster types is largely a matrix effect, the 6-8 arrangement being favored with the smaller clusters (shorter M-M bonds) that are formed with the later transition elements or the larger nonmetals because of the greater nonmetal separations and fewer repulsions therein (Ref. 78). The cross-over point with halide appears to be at niobium where the 6-8 type occurs with iodide in Nb_6I_{11} but only the Nb_6X_{12} cluster is found for $X = F, Cl, Br$. That these repulsions in 6-12 clusters are real is suggested by the observation that the nonmetal atoms usually lie on a larger cube than do the face-centered metals - see the right side of Fig. 1. However, obvious repulsions do not always seem sufficient to explain the configurations of some infinite chain compounds listed in Table 1. Matrix effects are presumably responsible for the absence of $TiCl$, ZrI , and $Mo_6Ch_{12}^{4-}$ examples and of condensed niobium halide clusters, at least with a 6-12 configuration. We have already noted that a high metal: nonmetal ratio also favors, or provides the driving force for, cluster condensation since the stable products always have all exposed cluster edges or faces bonded by nonmetal and exo positions occupied, even if some nonmetal atoms have to do double duty. Cluster condensation thus appears to be a defense mechanism to loss of nonmetal bonding.

Consideration of the relative metal-nonmetal coordination relationships in more normal-valent compounds is instructive. As discussed by McCarley (Ref. 16), MO_6 octahedral arrangements tend to be quite pervasive in oxides. Compounds with somewhat low oxidation states and therefore low O:M ratios are well known to retain this feature through extensive sharing of nonmetal atoms between coordination polyhedra. In some cases this also leads to

supplemental metal-metal bond formation through shared edges or faces of the MO_6 polyhedra. Serious matrix restrictions may exist on the metal-metal separations that can be tolerated in such cases (Ref. 18), although the small size of oxygen is usually favorable. Metal-metal bonding in such MO_6 aggregates evidently leads only to relatively small metal clusters, e.g., dimers in NbO_2 (d^1) and VO_2 (d^2) and trimers in $Zn_2Mo_3O_8$ (d^2) and $Zn_3Mo_3O_8$ (d^{2-67}) where close-packed oxygen arrangements can still be perceived. More reduction and/or a lower oxygen content then leads to loss of the MO_6 construction and further aggregation, for example in $Ba_{0.57}Mo_4O_8$ (d^{2-28} , rhomboids) or $NaMo_4O_6$ (d^{2-67} , infinite chains). The molybdenum atoms in the latter phase still retain four or five oxygen neighbors but have gained five or four molybdenum neighbors, respectively. (This counting of Mo-Mo "bonds" ignores their lengths although these are usually 0.12 Å or more greater than the single bond radius.) Likewise, in the zirconium chlorides the environment about zirconium goes from six Cl in $ZrCl_4$ to five Cl plus four Zr in Zr_6Cl_{12} (d^2) and three Cl and nine (three plus six) Zr in $ZrCl$ (d^3), the total coordination number increasing sizably even though the Zr-Cl distances remain virtually constant. (In general the differentiating electrons in these compounds are not screening to metal-nonmetal separations (Ref. 13) so the matrix problem does not diminish on reduction.) Most of the metal clusters, chains or sheets appear to be well sheathed by nonmetals with separations between the latter that are not far from the van der Waals sums, i.e., with high packing efficiencies. This serves to insulate the low-dimensional metal arrays, in effect driving the electrons into the metal-rich regions and retaining the maximum number of obviously favorable nonmetal-metal bonds.

The delocalization of metal-bonding electrons would appear to be a significant factor in these discrete and extended clusters relative to that in dimers or trimers in systems in which nonmetal coordination number is retained. The development of certain metal-like characteristics in the former is striking, namely, the attainment of especially high coordination to other metal atoms at longer distances (lower metal-metal bond orders) and the presence of low electron counts relative to the number of orbitals available (occupation of the more bonding states). We are less well equipped to deal with the obvious thermochemical advantages of making metal-metal bonds in compensation for loss of metal-nonmetal bonds although the former must be comparable in strength to those in the respective elements in order to preclude disproportionation of these low-valent compounds, a circumstance that was pointed out some time ago by Schäfer and Schnering (Ref. 18).

At the present time, two particular types of new phases formally derived by cluster condensation appear to have a wide spread occurrence and significant stability in their own right, the diverse monohalides and the 6-12-derived infinite chains of the composition M_4Y_6 . Both are remarkable for the variety of the elements involved and in the range of electron counts possible. The 4-6 chains are now known to occur in $[(ScCl_2)(Sc_4Cl_6)]$, Er_4I_5 , Sc_4Cl_6Z and in $M^I Mo_4O_6$, $(M, M^I)_2 Mo_4O_7$ and $Mn_{1-4} Mo_6O_{11}$, the group subdividing into two rather distinct classes depending on the anion matching the repeat distance in the chain and the number of electrons available for metal-metal bonding. A search for examples containing group IV or V elements that would have appropriate repeat distances and electron count, for example, in the ternary niobium sulfides, has to date been unsuccessful (Ref. 79).

Bonding comparisons

The unusual compounds found in the metal-rich area naturally raise questions regarding reasons for these remarkable differences from other compounds as well as their resemblances to metals (Ref. 12, 13, 78). In general, the chlorides and bromides reported here for group III-V elements are structurally quite distinctive relative to the sulfides and selenides of the same elements. For example, the halides tend to be much more anisotropic in structure, bonding and conduction properties (where known). In fact, the only similarities between the halides and chalcogenides occur either with the metallic diiodides or in the molybdenum and rhenium clusters, while molybdenum oxides seem to be a case apart again. Much of this distinction appears to arise because of the considerably smaller mixing of chlorine or oxygen valence orbitals into the metal-metal bonding orbitals or band relative to that which occurs with the heavier nonmetals. This is particularly evident in valence photoelectron spectra of the reduced halides where the nonmetal valence band is notably narrower and better separated or resolved from that of the metal conduction (or valence) band, for example, for $ZrCl$ (Ref. 80) relative to that observed with ZrS or NbS (Ref. 81). A lower polarizability and effective charge and more tightly bound valence electrons with the lighter halides would all tend to lessen the covalency and mixing between the indicated bands, as observed. Greater structural dominance of the metal array in halides is certainly conceivable under these circumstances. It will be noted that at the same nonmetal:metal ratio the halides also have the greater electron count for metal-metal bonding while at the same oxidation state the number of chalcogens is half as great and the opportunity for more extensive metal-metal bonding that much greater, consistent with the structures found. The contrast between the equally remarkable reduced molybdenum oxides and the sulfides and selenides likely involves similar or related effects that favor the lower symmetry oxide structures.

Nearly all of the new chain and sheet structures found for halides and oxides (Figs. 6-9) require that the nonmetals have the same period as the metal array. It is easy to understand why these are found in chlorides and bromides only for metals earlier in the periodic table which have the larger metallic radii while the shorter metal-metal bonds with molybdenum require the smaller oxygen counterion. Some structures avoid parallel nonmetal and metal repeats and thereby accommodate larger anions, for example, the zig-zag chains in ZrI_2 and confacial octahedra (alternating Mo_3Ch_3 units) in the extended and infinite molybdenum sulfides and selenides, Fig. 4. On the other hand, isolated clusters become predominant going to the right in the periodic table because the short metal-metal bonds relative to nonmetal sizes preclude further condensation (although the intercluster bonding in the Chevrel phases is an interesting alternative). The small nonmetal size is obviously an advantage in the noteworthy molybdenum oxides as it is in the binary and ternary oxides of the 3d elements that provide the principal examples of metallic behavior with these elements.

The paucity of oxides in Table 1 is noteworthy, there being only the new molybdenum phases and a single cluster structure $Mg_3Nb_6O_{11}$ plus a few layered materials like $LiNbO_2$ (intercalated MoS_2 -type, Ref. 82). The situation with fluorides is even sparser, the prime example being $(Nb_6F_{12})F_3$ (Ref. 18). The absence of more oxides or fluorides is usually attributed to the unusually high lattice energies of higher oxidation state compounds with the small oxide or fluoride that lead to disproportionation of the more reduced phases. In this sense the condensed molybdenum oxides seem even more exceptional.

Although the metal-metal bonding in the phases under discussion occurs in widely diverse structures, some significant regularities can still be found in the aggregate amount of metal-metal bonding achieved in many of these relative to the bonding in the metals themselves when just the smaller number of bonding electrons available in the former are taken into account (Ref. 78). A useful basis for this comparison is the Pauling bond order \bar{n} defined as $\log \bar{n} = (d_1 - d_n)/0.6$ where d_1 is the calibration obtained from the pure metal. In this sense a compound that bonds "just like the metal" will have unity for the ratio of the Pauling bond order summed over all unique metal-metal separations to the average number of valence electrons available. (The anion valence bands are conventionally assumed to lie below the metal valence or conduction band and therefore to be fully occupied.) In fact, about two dozen of the compounds known in 1980 come within 10% of this figure and over a third are in the range of 1.0 ± 0.2 . The first group includes YCl , Tb_6Br_7 , Sc_5Cl_8 , Y_2Cl_3 , Nb_6F_{15} , $Tl_2Mo_6Se_6$, Mo_6Cl_{12} and $NaMo_4O_6$ among the compounds considered here. Compounds achieving less metal-metal bonding in this sense all plausibly fall into the category of "matrix effects", namely, cases in which nonmetal-nonmetal contacts limit the metal-metal approach to some degree. The matrix effect naturally increases with nonmetal:metal ratio and with anion size and thereby limits the metal-metal bonding achieved in many layered compounds, 6-12 clusters and the strongly cross-linked 6-8 Chevrel phases. On the other hand, the molybdenum 6-8 clusters with independent exo components are evidently unaffected (Ref. 74).

Electronic considerations

The least clear aspects of this new chemistry are the electronic properties and the electronic "rules" that govern the formation of these materials. The exceptions are the relatively well-studied Chevrel phases. Rather than elaborate on this category, the discussion will be limited to what can be perceived or understood about electronic effects in the many diverse materials that make up all but the first entry in Table 1. In many cases even obvious properties are not known. On the other hand, a great majority of these phases appear to involve highly delocalized bonding and therefore exhibit only diamagnetic or Pauli paramagnetic properties unless the obvious odd-electron clusters or lanthanide elements with f^n cores are involved.

One characteristic of some of these condensed solids is the relatively small dependence of the degree of condensation on electron count (Ref. 12). Thus all of the metal-metal bonded phases for group III elements have electron counts between 1.5 and 2 electrons per metal in the metal bonded portion. (The status of the isolated clusters here that are certainly free of centered nonmetals is not clear.) Similarly, all phases between Mo_6Ch_8 and the infinite $M_{12}Mo_6Ch_6$ plus the Mo_4O_6 examples occur with between 3.25 and 4.3 electrons per molybdenum atom versus six in the metal. In both series differences in counterions and in the mode of nonmetal sharing serve to minimize these ranges to some degree. The fact that the nonmetal:metal ratio in many respects appears to be more important than the electron count in determining degree of condensation is of course consistent with rather specific and evidently important bonding modes that the nonmetals exhibit in these structures. It is noteworthy that there are sizable gaps in both structure and electron count between the lowest known compounds in these series and the metals.

Electronically, the isolated clusters are easiest to understand. It is well-known that the Chevrel (6-8 type) clusters achieve a full band and semiconduction with 24 metal-based

electrons, and clusters containing a greater number do not seem to be well documented. Compositions 3 to 8 in Table 1 all involve this limit. Accordingly, rhenium clusters or mixed molybdenum chalcogenide halides beyond $\text{Mo}_6\text{Ch}_6\text{X}_2$ contain more anions and exhibit less intercluster metal-metal bonding. The niobium analogs of the Chevrel phases would, if stable, involve either lower electron counts or a lower oxidation state together with more condensation. Clear evidence for either is lacking, and alternative and apparently unrelated chalcogenides are stable instead. In the case of niobium or tantalum halides, there seems to be a considerable preference for the more tightly-packed 6-12 clusters (except with iodide) although a greater cluster electron count would pertain for a 6-8 stoichiometry.

The electron count in the diverse M_4Y_6 chains appears to be directly reflected in the aggregate amount of metal-metal bonding found. The lower limit is six electrons per chain unit in Gd_4Cl_6 and seven in Sc_5Cl_8 and Er_4I_5 , and this count jumps to 13 in NaMo_4O_6 and 14.75 in $\text{Sc}_{0.75}\text{Zn}_{1.25}\text{Mo}_4\text{O}_7$, the proportionate contraction in bond distances along this series, especially along the chain length, indicating that the electrons are being fed into bonding states (Ref. 15). The principal effect of the added electrons in the last step in this sequence is to cause tilting of the shared octahedra and the generation of short-long distances involving only the apex atoms.

Very useful to the understanding of the last two compounds in this series are the extended Hückel band calculations for the one-dimensional models (Ref. 83). The NaMo_4O_6 phase is clearly metallic by these approximations, with a substantial density of occupied Mo-Mo states (with very little oxygen contribution) peaking at ~ 1.2 eV below E_F , features that are in semiquantitative agreement with the UPS spectrum (Ref. 53). Reasons for the observed distortion that occurs with more than ~ 14 electrons per formula unit were also established. The same theoretical approach (Ref. 75) has also provided an illuminating consideration of the bonding in the Mo_6Ch_8 , $\text{Mo}_9\text{Ch}_{11}$, $\text{Mo}_{12}\text{Ch}_{14}$ and $\infty[\text{Mo}_3\text{Ch}_3^-]$ examples. An orbital interpretation for the stabilizing intercluster Mo-Ch bonding was also given, an interaction of the sort that appears quite general for clusters and their condensation products. A good separation of bonding and antibonding states is found for the Mo_3Ch_3^- chains, these being spanned by a single wide band and a low density of states at the Fermi level for the indicated composition. A more detailed calculation has provided somewhat similar results for TlMo_3Se_3 (Ref. 84). It would appear that the oxidation of Mo_3Ch_3^- to the neutral chain with 12 electrons per unit that was suggested earlier may proceed only with distortion and loss of linearity or periodicity.

Judging from PES data and a few band calculations, strong metal-metal interactions in many if not most of the infinite structures cause a sizable splitting of the d orbital manifold. In ZrCl the bonding nearly produces a gap in the d states, leaving only a low density of states at E_F (Ref. 80, 85, 86), while in Gd_2Cl_3 the d states are split to yield a gap of about 1 eV judging from both theory and experiment (Ref. 86, 87). The same two measures indicate that introduction of carbon into octahedral interstices in ZrCl to give $\text{Zr}_2\text{Cl}_2\text{C}$ leads to a new band derived from carbon 2p (and zirconium 4d) at ~ 4 eV but leaves a significant density of occupied states at E_F (Ref. 38).

Electron counts in isolated 6-12 clusters evidently may range from 12 to at least 16 although 14 appears to be a point of some stability for zirconium according to both experiment and calculation (Ref. 38). The insertion of small nonmetals in the octahedral clusters generates low lying a_{1g} and t_{1u} levels from a combination of nonmetal s and p valence levels and otherwise occupied and bonding cluster orbitals of like symmetry. Since the antibonding levels obtained lie fairly high, the nonmetal has in effect added its particular number of valence electrons to the cluster with an apparently sizable gain in overall stability. This interstitial derivatization then allows access to otherwise electron-poor clusters lying further to the left in the periodic table, $\text{Zr}_6\text{Cl}_{12}(\text{C})\text{Cl}_2$, and $\text{Zr}_6\text{Cl}_{12}(\text{N})\text{Cl}_3$ being isoelectronic with the known $\text{Nb}_6\text{Cl}_{12}^{4+}$. Interstices of about the dimensions found in the zirconium and scandium chain and sheet structures appear to accommodate second-period elements fairly readily, the larger occurring in the octahedral surroundings and the smaller, in the tetrahedral sites, e.g., in $\text{Zr}_2\text{Cl}_2\text{C}$ and $\text{ZrClO}_{0.4}$, respectively. On the other hand, larger nonmetal units such as dicarbon appear to be well bound in the larger interstices formed by less strongly bound and larger lanthanide elements, e.g., in $\text{Gd}_5\text{Cl}_9\text{C}_2$ (Fig. 10).

EXPERIMENTAL ASPECTS

Although a synthetic discovery is obviously the first essential step to a new material, it is not within the intent of this article to consider the experimental techniques and problems associated with the preparation of the diverse group of compounds listed in Table 1. General introductions to solid state synthesis have been given elsewhere (Ref. 88, 89). It is still worthwhile to note some of the special techniques required for these discoveries and some of the more serious problems that limit either the production of better or larger amounts of these products or the realization of as yet unknown phases. By far the most

important requirement for the successful high temperature synthesis of the new group III and IV halides is the container. Although silica, conventional refractories and the platinum metals all fail, welded tantalum (or niobium) containers appear to be highly suitable (Ref. 90). (This may not apply to some sulfides, however.) The molybdenum and rhenium chalcogenide reactions may be synthesized in fused silica, especially with internal Al_2O_3 or BN crucibles for further protection, while sealed molybdenum itself is very suitable for the lower molybdenum oxide compounds. Molybdenum would be suitable for halide systems of earlier elements as well but it is generally not used unless necessary because of greater difficulty in its fabrication. Most of the reduced halides considered are not stable to a moist atmosphere.

Discovery of a new material nearly always involves a fair measure of serendipity in a somewhat intuitive or random search of reactant, temperature and time space. The easiest materials to find are those for which kinetic problems involved in their formation are minimal at some elevated temperature. Although purification and separation of a product by a chemical transport reaction is traditional and very useful, most conventional transporting agents are not stable in these highly reduced systems, and any transport or volatilization appears to take place through autogenous species. In fact, the general problem with a number of these highly reduced and condensed systems is the absence of good nucleation and crystal growth or of simple volatilization or solution processes to aid product formation and isolation. In these cases yields below 10-15% in systems that are obviously far from equilibrium after several weeks at temperature are not uncommon. Furthermore, the phase forming the best crystals is usually preferentially sampled first. Several instances of surface blockage are known as well as evidence for nucleation and growth problems from observations of limited epitaxial growth of a new phase on either a metal reductant or another phase (e.g., Ref. 13, 37, 48, 65-67, 77). As a result of these and other factors, reaction periods of several weeks are often employed, even with supposedly volatile or mobile halides, and use of a higher temperature is frequently the only other useful variable although not without some unfortunate consequences (below). The preparation of the lowest phase can sometimes be forced by the use of a large excess of metal, but the synthesis of intermediate phases may provide significantly greater problems in these cases. In view of these many factors, it is dangerous to assert that all phases have been found in a given system or that an anticipated compound does not exist. Furthermore, yields to the 5-10% range or so are within the range that may be achieved for compounds stabilized by small interstitial nonmetals in the metal framework when adventitious impurities are the source of the nonmetal atoms. Several phases have in fact been discovered under just these circumstances, whereafter the purposeful introduction of a good source of that element often gave the phase in a substantially quantitative yield (Ref. 10, 38-40, 68).

Another problem in solid state synthesis is the general use of high and higher temperatures as the most direct way to overcome kinetic problems. In so doing the investigator preferentially samples only the thermodynamically more stable products. Thus a very large fraction of the compounds listed in Table 1 are stable above 700°C. Many more interesting phases must have upper temperature limits of stability, above which they incongruently decompose into other phases, sufficiently low that their rates of formation using straightforward (brute force) techniques are negligible. A long term and continuing challenge to the synthesizer is the development of routes whereby reasonable reaction rates are obtained at more moderate temperatures, say 500°C. The application of pressure and the introduction of fluxes are two obvious means for this. However, fluxes may not be very useful in some instances since solution of an infinite condensed product or intermediate will require its conversion to a small solute, making the solution process very incongruent and therefore of lower utility. Many challenges remain.

OUTLOOK

It is clear that the study of metal-rich phases that mimic both metals and salts is young and burgeoning and that opportunities abound for creative efforts both in synthesis and on theoretical, structural and property studies of these materials. Many of these new compounds occur in simple binary systems, and large areas of ternary and quaternary system space remain unexplored. Furthermore, some systems studied are apt to be incompletely known, the phases cited being the more crystalline and more stable that could be studied by single crystal X-ray diffraction. And what is difficult to convey regarding exploratory synthesis is the certain "touch", insight, cleverness, new approach or luck that may be necessary in order to ferret out what are often unanticipated and even inconceivable compounds.

Finally, the need for new materials in science and technology has been well documented (Ref. 91). Although derivative-type synthesis plays an important role in developmental work, history also shows that synthetic discoveries that have led to landmark advances in solid state science have nearly always been made through exploratory synthesis rather than by design. The research leading to the identification of somewhat more than 90% of the new types of phases listed in Table 1 has been of this character.

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