

Extended Metal-Metal Bonding in Halides of the Early Transition Metals

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Received March 12, 1981

One of the delights of exploratory synthesis is the discovery of new compounds, reactions, structures, etc., which are not only unexpected but also inconceivable on the basis of past experience and intuition. The highly reduced halides of the early transition (and inner transition) elements, with their strongly metal-metal bonded clusters, chains, and sheets in compounds such as $\text{Sc}_7\text{Cl}_{12}$, Sc_5Cl_8 , and ZrCl , provide numerous examples of such unconventional chemistry. And it is all the more remarkable that these highly unusual phases occur in supposedly simple binary metal-halide systems where one might have imagined that all of the interesting compounds had been discovered years ago.

Prior to 1973 the only examples of halides with extended metal-metal bonding of any sort were the metallic diiodides of a few rare earth elements (below) and the unusual and poorly understood Ag_2F , which consists of a layer of fluoride sandwiched between close-packed layers of silver² (anti- CdI_2 type³). This paucity of metal-bonded halides was in striking contrast with the behavior of chalcogenides. There one finds many metallic phases with highly delocalized and fairly isotropic bonding: the cubic TiO , VO , and NbO , complex metal-rich sulfides and selenides (e.g., Ta_6S , Nb_{21}S_8 , Zr_9S_2 , and Hf_9S), and cubic monochalcogenides of many of the rare earth metals.⁴

The results to be described were an outgrowth of studies of reduction of molten rare earth metal trihalides with the respective metals in tantalum containers. These were found to provide a ready route to several new dihalides beyond the classical SmX_2 , EuX_2 , and YbX_2 as well as to many diverse phases with average oxidation states between +2 and +3. (The work has been reviewed.⁵) Three hints of things to come were published in 1973: the Gd_2Cl_3 structure with its infinite metal chains,⁶ the synthesis of the fur-like Sc_2Cl_3 and Sc_2Br_3 of unknown structure,⁷ both originating from these melt studies, and a poorly determined but qualitatively correct structure for the layered ZrCl .⁸

Earlier melt studies had also provided an unusual group of metallic diiodides, the first halides showing extensive electron delocalization. The highly conducting LaI_2 , CeI_2 , PrI_2 , GdI_2 , ThI_2 , and $\text{ScI}_{2.16}$ are obtained directly by reduction of molten MI_3 with M .^{9,10} As an example, the bronze-appearing LaI_2 phase is Pauli paramagnetic (the small paramagnetism associated with conduction electrons), and the polycrystalline material exhibits a room-temperature conductivity very much

like that of lanthanum metal itself. The phase accordingly has been formulated $\text{La}^{3+}(\text{I}^-)_2\text{e}^-$,¹¹ although that representation neglects any La-I covalency. All of these diiodides occur in sulfide- or alloy-type structures, the isostructural LaI_2 , CeI_2 , and PrI_2 in the unusual MoSi_2 (or CuTi_2) layered structure with square-based layers and eight-coordination to adjacent atoms, and the remaining metallic phases in the more usual, layered structure types known for MoS_2 and NbS_2 .^{12,13} Since metallic dihalide phases have not been found with the smaller chloride or bromide, their formation with iodide was interpreted¹¹ in terms of an appreciable metal-iodine covalency and significant nonmetal involvement in the conduction band.

Conventional Halides

A description of metal-metal interactions in the usual reduced halides of the transition metals will serve to contrast them with the remarkable new compounds. The most reduced halides known for the 3d elements from titanium on are the dihalides which occur in layered CdX_2 -type structures.³ The metal ions occupy layers of octahedral (trigonal antiprismatic) interstices between alternate pairs of close-packed halide layers. van der Waals contacts which limit the halide repeat distance possible in these layers to $>3.4 \text{ \AA}$ require the same relatively large period for the metal ions. The metal-metal interactions are accordingly very weak relative to those in the robustly bonded examples to be described and are manifested only by such phenomena as magnetic coupling at low temperatures. Interestingly, scandium is not yet known to form an analogous dihalide. And only the larger Cl, Br, and I anions need to be considered; the fluoride ion affords such large lattice energies for higher oxidation states that even moderately reduced fluorides (e.g., TiF_2 , ZrF_3) are thermodynamically unstable to disproportionation to metal and higher fluoride.

(1) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Energy Research, Office of Basic Energy Sciences, WPAS-KC-02-03.

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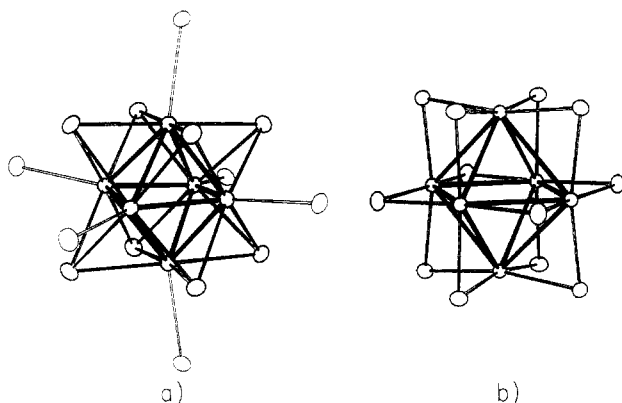


Figure 1. Examples of M_6X_8 and M_6X_{12} clusters. (a) Face-capped Nb_6I_8 cluster in $Cs(Nb_6I_8)I_{6/3}$.¹⁴ The singly bonded iodine atoms which occupy outward directed (exo) positions bridge to other clusters. (b) Edge-bridged Zr_6Cl_{12} cluster in $Zr_6Cl_{12} \cdot K_2ZrCl_6$.¹⁵ Exo positions are occupied by chlorine atoms from $ZrCl_6^{2-}$ anions (not shown) (thermal ellipsoids at the 50% probability level).

The 4d and 5d element halides from group 5 and beyond are well-known for a limited amount of metal-metal bonding in clusters. If, as a point of departure, the relevant examples are limited to those containing six or more well-bonded metal atoms, only the octahedral metal clusters of the $(Mo, W)_6X_8^{m+}$ or $(Nb_6I_8)^{2+,3+}$ type and $(Nb, Ta)_6X_{12}^{n+}$ need be mentioned.³ Views of both types are given in Figure 1. The 6-8 type clusters such as $(Nb_6I_8)I_{6/3}$ ¹⁴ (Figure 1a) can be approximated geometrically as a simple cube of inner halide (heavier outline) with metal on or near the cube faces or, in other words, a metal octahedron that is capped on every face by halide. Additional halide or other ligand always occupies the outward-pointing or exo position on each metal, as shown. In 6-12 type clusters like Zr_6Cl_{12} ¹⁵ (Figure 1b) the metal octahedron is edge bridged by halide atoms. This corresponds to a cube with a metal atom on each face center and a halide on each edge, but the metal atoms are usually found inside the cube faces, evidently because of substantial closed-shell repulsions between halides. The exo (outward-directed) position at each metal atom in these clusters is also occupied, usually by a separate halide (not shown) or one which is integral to another cluster. This feature carries over in the interconnectivity of condensed clusters as well.

First Comes the Synthesis

Containers. The availability of tantalum containers has more than any other single factor made the present sort of research possible. The need for an unconventional material is mandated by the fact that most of the elements of interest react with silica, other ceramics, Au, and Pt to form highly stable compounds. Tantalum (and niobium) is commercially available as seamless tubing and sheet, is readily sealed by arc welding under He or Ar, and is quite inert to metal-halide systems of elements in earlier groups (except perhaps for titanium iodides).

The inertness of tantalum arises particularly because of both its greater nobility (lower ΔH_{form} per equivalent for its halides) and its high melting point (2996 °C) which leads to a reduced (negligible) tendency for alloy

or intermetallic compound formation with the solid elements of interest. Tantalum's strength, ductility, and significant solvent ability for nonmetal impurities (which otherwise would lead to embrittlement) also contribute to making it a superior container material. It is useable well in excess of 1200 °C and, with care in design and sealing, to at least 40-atm internal pressure. This last attribute allows considerably more forcing conditions to be used with the generally more volatile halides than is possible with most other materials.

On the other hand tantalum is expensive and must be kept under vacuum or jacketed in sealed fused silica or stainless steel in order to protect it from air oxidation during heating. Suitable working techniques and container designs for tantalum and niobium have been described recently.¹⁶ Molybdenum is a chemically suitable alternative but is *much* harder to fabricate.

Identification of Products. The use of Guinier powder diffraction¹⁷ provides a considerable gain in both sensitivity and resolution over the more common Debye-Scherrer method utilized earlier.

Synthesis Problems. Although phase diagrams of a number of the molten MCl_3 -M systems of interest have been studied,⁵ the methods used in earlier studies generally do not provide good synthetic routes to or even any evidence for many of the highly reduced phases. The formation of most of the new phases from metal and melt involves very incongruent processes since the compositions of the metal-saturated MX_3 melts usually correspond to only a small amount of reduction. More important are the large electronic and structural changes accompanying the formation of these solids from the melt. The depression of the freezing point of MX_3 by added M corresponds in nearly all cases to the simple reaction



independent of the degree of reduction of the melt and of whether a saltlike or metallic dihalide separates or not.⁵ In contrast, the highly reduced phases desired contain metal-metal bonded aggregates ranging from 6-12 type clusters to infinite chains and sheets. An essential feature of solid-state vis-à-vis molecular chemistry now comes to our attention. These complex structures show a negligible "solubility" in the melt and therefore do not undergo ready crystal growth by recrystallization. This appears to be a major factor in blockage of the metal surface by even thin layers of the new products and their frequent lack of detection in melt studies.

Synthetic efforts thus focus on means whereby equilibrium can be better approached. For example, the best synthesis of the lowest phase in a system may utilize either pressure or, more often, a large excess of metal foil or metal powder (since only the surface is active) in the reduction of a higher halide, relying on a trihalide vaporization or solid diffusion process for reaction. Yields may still only be 5-30% after several weeks at 700-900 °C, and the synthesis of phases of intermediate composition not in equilibrium with the metal may be a particular problem since excess metal cannot be used to aid the attainment of equilibrium. Under such circumstances it is unlikely that one can

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ever safely assert that a particular compound *cannot* be made.

Although some systematics utilizing transport reactions (below) have been developed for the reduced scandium chloride syntheses, many puzzles and inconsistencies remain with others, especially with regard to kinetic factors. For example, the equilibrium phase YCl is seldom formed in long-term reductions of YCl₃ with a large excess of metal in sheet form (only Y₂Cl₃ is formed), but powdered metal readily produces YCl.¹⁸ Clear nucleation effects have been discerned with GdCl₃¹⁹ and are suggested in other systems by poor reproducibility.

Difficulties of these sorts may be compounded by the existence of unprecedented compositions and structures for unknown phases hidden in a system. Under these circumstances the initial synthesis of totally new types of phases sometimes depends a good deal more on art, and luck as well, than on the qualities usually associated with scientific exploration. Advance justification for the research may be equally difficult to provide. An analogy between the synthesizer and an experienced fisherman or gold prospector has been suggested to the author. Although this comparison is apt in that experience, intuition, and serendipity are valuable in all, the latter two efforts differ from innovative synthesis in that the other "professionals" presumably always know what they are looking for!

Transport Reactions. The ScCl₃-Sc system provides a good illustration of the contrast between the variety of reduced halides now known and the limited amount of information obtained earlier via ordinary thermal analysis and powder pattern studies of the MCl₃(l)-M systems. Here only Sc₂Cl₃ was detected. It was later prepared in high yield by the reaction



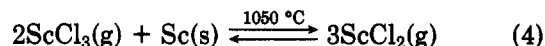
The Sc₂Cl₃ occurs as a dense fur-like material covering the metal where it will persist as a (nonequilibrium) blocking layer for weeks up to ca. 877 °C, its decomposition point.⁷ Notwithstanding, five other reduced scandium chlorides have since been made and characterized by use of chemical (vapor phase) transport reactions.²⁰ This process enhances reactivity and crystal growth, which may account for the apparent prolific cluster chemistry of scandium since such transport reactions have not been reported to occur with the other trivalent elements. The reduced group 5 halides as well as intermediate oxidation state halides of group 4 metals also exhibit transport reactions (or direct sublimation).

Reduced scandium chlorides as best synthesized in sealed tantalum tubing starting with ScCl₃ or a reduced mixture in the cooler end of the tube (850 °C) and strips of Sc metal in the hot (~1050 °C) and central zones. (A 0.9 × 12 cm Ta container, 0.05 × 0.4 × 10 cm Sc strips, a 18-mm (diameter) SiO₂ jacket, and a tube furnace with a 2.5-5 × 46 cm bore are typical.) Equilibrium reduction products are produced, albeit slowly, by a dynamic transport reaction under the temperature

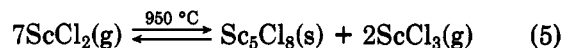
gradient. Gaseous ScCl₂ is thought to be formed by an endothermic reduction of ScCl₃(g) in the hot zone in the sequence



followed by



The ScCl₂ now diffuses to an intermediate temperature zone where it disproportionates to form a lower phase plus ScCl₃(g), such as



and the ScCl₃ recycles in (4).^{21,22} A series of products sometimes forms as well-separated bands of crystals. The process is characteristically slow, and 3-6 weeks may be required to obtain a few tenths of a gram of product. A lower yield of better crystals may be obtained by using a shorter tube (4 cm), a smaller temperature gradient (25 °C), and reduced ScCl_x as a source of ScCl₃(g) at lower activity.

New Clusters

It is useful to describe the metal chain and sheet structures in terms of increasing cluster condensation²³ starting with the isolated 6-8 and 6-12 prototypes. Extension of known 6-12 clusters two groups to the left is a direct benefit of the use of tantalum. The first example with zirconium was Zr₆Cl₁₂Cl_{6/3}, isostructural with Ta₆Cl₁₅, in which the second group of chlorines bridge between all exo positions in separate clusters.²⁴ The compound is formed in relatively oxidized systems by an uncertain transport reaction. More reduced systems at higher temperatures yield Zr₆X₁₂ (X = Cl, Br, I) or Zr₆Cl₁₂·M₂ZrCl₆ (M = Na, K, Cs)^{15,24} (Figure 1b). The most complete calculations^{25,26} on the electronic structure of 6-12 clusters suggest that 12-electron Zr₆X₁₂ clusters with octahedral symmetry should be paramagnetic with four electrons in the highest occupied t_{1u} orbital. Their diamagnetism is thought to arise from the lower symmetry afforded by slight compression of the cluster along its principal 3 axis plus intercluster bridging of the waist halides (in Zr₆X₁₂). (*d*_{Zr-Zr} is 3.195 (1) Å between and 3.204 (2) Å within the metal triangles in Zr₆I₁₂ compared with 3.178 (1) and 3.224 (1) Å, respectively, in the symmetrically bridged Zr₆Cl₁₂·K₂ZrCl₆.)

The analogous Sc₆Cl₁₂, Y₆Cl₁₂, etc., have not been found, perhaps because they would contain only six electrons for bonding within the cluster or, alternatively, because the right reaction conditions have not yet been tried. But a 9-electron example does occur in Sc³⁺-(Sc₆Cl₁₂³⁻) through a clever variation of Zr₆X₁₂ structure.²⁴ The latter has a rhombohedral arrangement of a simple substructure: cubic-close-packed halide layers (A, B, C . . .) between which zirconium triangles are

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Table I
Metal Clusters in Group III Chlorides

Cl/M	representation	structural description	electrons per M ^a	ref
1.714	[Sc(Sc ₆ Cl ₁₂)]	<i>discrete clusters</i> (edge bridged, Zr ₆ I ₁₂ structure) plus Sc(III) in octahedral interstices	1.50	24
1.600	$\frac{1}{2}[(\text{ScCl}_2^+)(\text{Sc}_4\text{Cl}_6^-)]^b$	<i>single chains of metal octahedra</i> (edge bridged by Cl) plus parallel chains of Sc(III)Cl ₆ octahedra, both sharing trans edges	1.75	22
1.50 (3)	unknown (M = Sc)	"mouse fur"		7
1.500	$\frac{1}{2}[\text{Y}_4\text{Cl}_6]$	<i>single chains of metal octahedra sharing trans edges</i> , face capped by Cl (Gd ₂ Cl ₃ type)	1.50	18
1.45 (3)	unknown (M = Sc)			28
1.429	$\frac{1}{2}[\text{ScCl}_2^+](\text{Sc}_6\text{Cl}_6^-)$	<i>double chains of metal octahedra sharing edges</i> (exposed faces capped by Cl) with parallel chain of Sc(III)Cl ₆ octahedra sharing trans edges.	1.50–1.83 ^c	29
1.000	$\frac{2}{3}[\text{M}_{6/3}\text{Cl}_2]$ (M = Sc, Y, La)	<i>double metal layers</i> alternating with double chlorine layers (ZrBr type) or M ₆ Cl ₆ -type clusters sharing six metal edges	2.00	30
				18
				28

^a In metal-metal bonded unit only. ^b Infinite one-dimensional chain in Niggli notation. ^c Value depends on interpretation of magnetic properties.

centered around well-separated chloride vacancies in the central (B) layer to generate Zr₆ trigonal antiprisms. The vacant antiprismatic interstices which remain between halide layers A and C along the $\bar{3}$ axis of the Zr₆ antiprism are occupied by the isolated scandium atoms in Sc(Sc₆Cl₁₂). (La₇I₁₂, etc., has been found in the same structure.²⁷)

Extended Metal-Bonded Structures

All of the remaining binary structures can be described in terms of cluster condensation and are known only for group 3 elements except for the ZrX and HfX end members. As a guide, the reduced scandium, yttrium, and lanthanum chlorides now identified at least stoichiometrically are catalogued in Table I.^{28–30} Additional halides of some heavier rare earth metals^{18,31,32} provide not only additional examples of these structures but also new compositions with related structures.

Single Chains. The first known stage conceptually involves condensation of Sc₆Cl₁₂ units to form Sc₅Cl₈,²² with infinite chains of scandium octahedra sharing trans edges, by elimination of the shared elements Sc₂Cl₄ plus chlorine bridging what becomes the shared Sc₂ edge (i.e., the closest atoms in Figure 1b). Actually the phase again contains isolated scandium(III) atoms, this time in a chain of parallel chloride octahedra also sharing trans edges, as shown at the top in Figure 2. Chlorine atoms in the shared edges also occupy apex positions on two neighboring metal chains, bridging the chain pairs into sheets. Finally, the seemingly singly bonded, apex chlorine atoms in chloroscandium(III) chains are the same as those which bridge the side edges of the metal octahedra in another sheet, thus linking the sheets together. All chlorine atoms are three-coordinate to metal. $\frac{1}{2}[(\text{ScCl}_2^+)(\text{Sc}_4\text{Cl}_6^-)]$ is an apt and simple representation after some minor assumptions regarding assignment of shared chlorides. (The description $\frac{1}{2}[\text{ScCl}_3\text{Sc}_4\text{Cl}_5]$ also has some merit, as the structurally related Er₄I₅ is known.³¹)

All scandium-chlorine distances on both chains, 2.53–2.58 Å, are close to the 2.58 Å value in ScCl₃. In

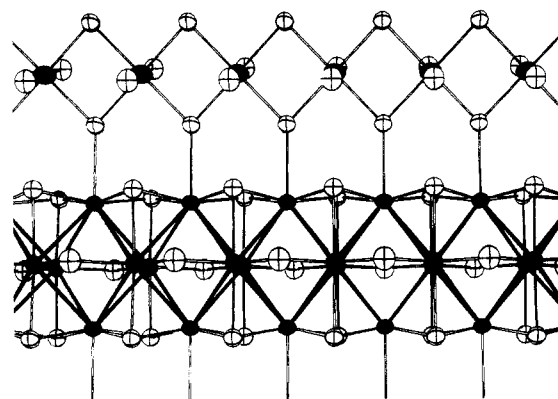


Figure 2. The infinite parallel chains in $[(\text{ScCl}_2)(\text{Sc}_4\text{Cl}_6)]$, consisting of chlorine octahedra containing scandium(III) (top) and edge-bridged, elongated metal octahedra (heavy outline), both sharing trans edges.²² Dangling bonds shown at the bottom go to chlorine atoms at the top in other chains (90% probability thermal ellipsoids).

fact, metal-halogen distances in all of the reduced structures considered are quite close to those observed in normal-valent halides of the respective elements. This evident absence of substantial screening of the metal by the reduction electrons emphasizes the distribution of these electrons *within* the metal clusters, chains, or sheets. The scandium-scandium distances in Sc₅Cl₈ are indicative of strong bonding. The shortest is the shared edge, 3.02 Å, followed by 3.21–3.22 Å between atoms in that edge and the apices, while the 3.52 Å repeat distance along both chains seems relatively unimportant. The shorter distances imply significant Sc-Sc bonding when compared with 3.26–3.31 Å in the hexagonal close packed (hcp) metal and 2.91 Å for the calculated single-bond metallic diameter. This aspect is typical for all of the structures considered here, although I will in general not discuss it in detail. Strong bonding is also implicit in the bond order calculations to be cited later.

Certainly not even a very well informed and imaginative chemist could ever be expected to predict that a close structural relationship would exist between a reduced scandium chloride, terbium bromide, and sodium molybdenum oxide, but in fact all contain infinite one-dimensional M₄X₆ chains with the structure and connectivity shown in Figure 2. All three—Sc₅Cl₈, β-

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(30) Poeppelmeier, K. R.; Corbett, J. D. *Inorg. Chem.* 1977, 16, 294.

(31) Berroth, K.; Simon, A. *J. Less-Common Metals* 1980, 76, 41.

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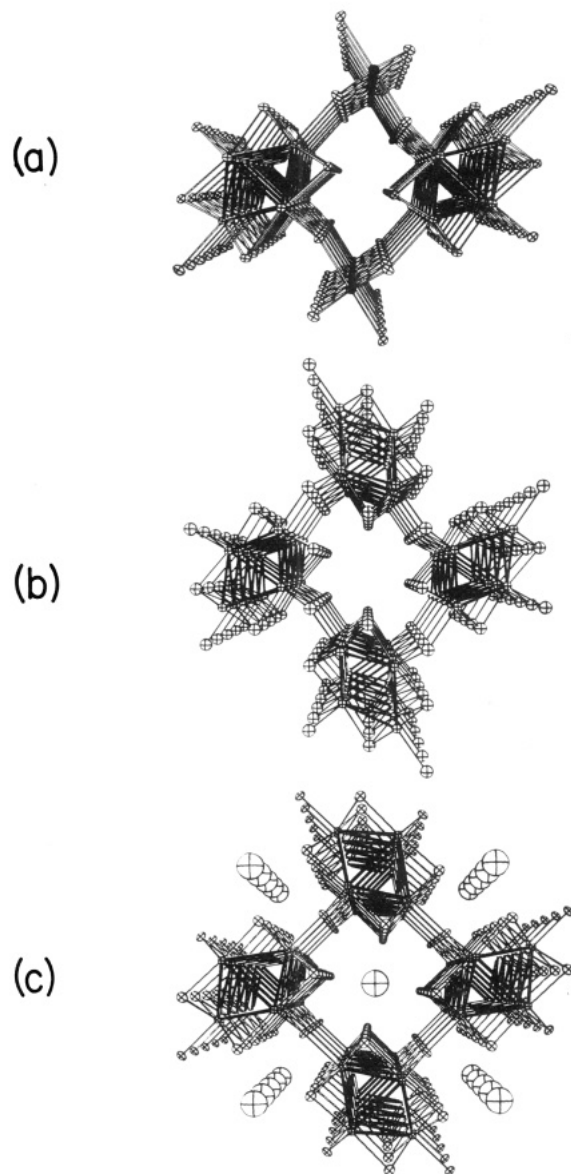


Figure 3. Projections along the short axes of three phases containing M_4X_6 metal-bonded chains: (a) two sheets of $Sc_5Cl_8 = (ScCl_2)(Sc_4Cl_6)^{22}$ (Figure 2 viewed from the side); (b) β - Tb_2Br_3 ; (c) $NaMo_4O_6$.³³ Three-coordinate bridging atoms exhibit the same connectivity in all three structures.

Tb_2Br_3 , and $NaMo_4O_6$ —were independently discovered and structurally characterized over a period of only about 2 years.

Figure 3a shows two of the chain pairs in Sc_5Cl_8 , each of which is derived from Figure 2 by a 90° rotation about a vertical axis in the plane of the paper. The scandium(III) atoms are seen as a string of darkened ellipsoids. In Figure 3b is a similar view of "Heissluft" Tb_2Br_3 discovered in Simon's group.³² Comparison of this with Sc_5Cl_8 at the top shows that ${}^1[M_4X_6]$ chains are retained while the ${}^1[Sc^{III}Cl_2]$ chains are neatly replaced by two more ${}^1[M_4X_6]$ strings rotated by about 75° . The connectivities of the three-coordinate inter-chain atoms are the same through the series, bridging between metal atoms on one side and exo to a single metal atom on the other. And the bottom of Figure 3 is the equivalent projection of the phase ${}^1[Na^+(Mo_4O_6^-)]$ from Torardi and McCarley.³³ The ar-

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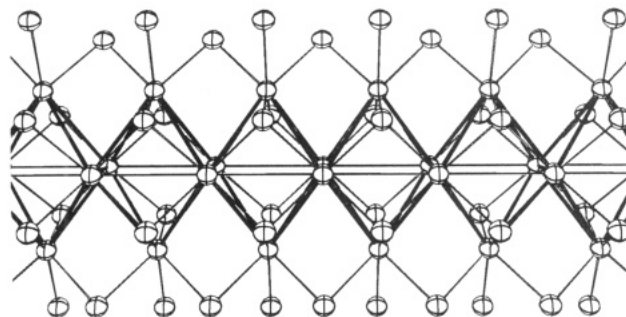
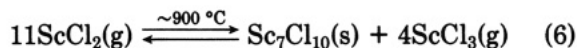


Figure 4. The infinite chain in Y_2Cl_3 ¹⁸ with the metal-bonded octahedra in heavy outline. Duplicate atoms at the top and bottom bridge to other identical chains (90% thermal ellipsoids).

angement now appears "squared up" in a tetragonal cell with planar bridging oxygen atoms and interstitial sodium cations. The electron counts per M_4X_6 unit in the three are 7, 6, and 13, respectively, which is reflected in all M-M distances, most strikingly in the chain repeats of 3.52, 4.02, and 2.86 Å, respectively. Anion size goes hand in hand with this trend and is doubtlessly important in determining which phases are possible at a given electron concentration. Such ${}^1[M_4X_6]$ chains would appear to be important building blocks in the solid state, and more examples are to be expected.

An infinite chain with the same M_4X_6 composition but with quite different capping and connectivity occurs in Gd_2Cl_3 , the first extended halide structure discovered,⁶ as well as in Y_2Cl_3 ,¹⁸ Tb_2Cl_3 , Er_2Cl_3 , Lu_2Cl_3 , and a number of bromides.^{32,34} As shown in Figure 4 for Y_2Cl_3 , metal octahedra of the face-capped M_6X_8 type (which are not known for these elements) share very short (3.27 Å) edges. Double chains of chloride, one forward, one in back, bridge to apices of identical chains above and below, giving ${}^1[(Y_{4/2}Y_2Cl_4)Cl_2]$. The packing of the sheets allows half of the face-capping chlorine atoms on one chain to fill exo positions on yttrium atoms in the shared edge in another. X-ray photoelectron spectra³⁵ (XPS) and band calculations³⁶ indicate the band is split and the phase is a semiconductor.

Double Chains. The next stage of condensation known and the second extended chain discovered,²¹ Sc_7Cl_{10} , is obtained from the presumed transport reaction



in a lower temperature region than for Sc_5Cl_8 (cf. eq 4 and 5). The structure involves further edge sharing of two chains of metal octahedra displaced by half their repeat. The side view is difficult to visualize, but a projection along one chain pair (Figure 5) illustrates the important concepts. Features of both of the foregoing chain types are retained; exposed metal triangles are face capped, and a parallel ${}^1[ScCl_2^+]$ chain bridges between apices on the metal chain. The result has the approximate formulation ${}^1[(ScCl_2^+)(Sc_6Cl_8^-)]$. The further interconnection of these is of same character as shown in Figure 3a, although distances to the dangling chlorine bridges in Figure 5 are 0.4 Å longer than to the ${}^1[ScCl_2^+]$ chain. This is the only phase discussed which is paramagnetic (other than from obvious core states,

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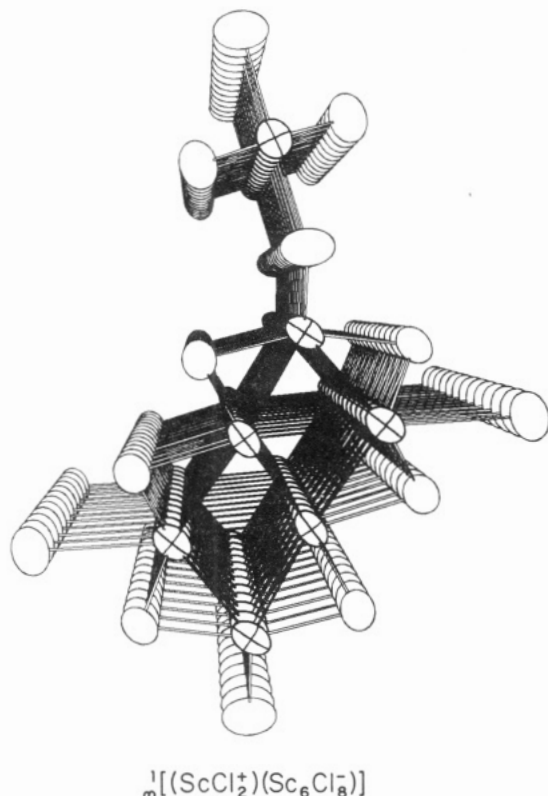


Figure 5. $[(\text{ScCl}_2)(\text{Sc}_6\text{Cl}_8)]^{21}$ showing chain of Sc(III)Cl_6 octahedra (top) and a double chain of distorted scandium octahedra (bottom). Both chains are formed by sharing edges. Scandium is shown as crossed ellipsoids (90%).

e.g., $4f^7$ in Gd_2Cl_3). This may result from either itinerant paramagnetism or localization of two (of 11) of the reduction electrons on, say, the outer apices of the chain. The scandium(III) and reduced metal states in $\text{Sc}_7\text{Cl}_{10}$ can be readily distinguished in the XPS data for $\text{Sc}(2p)$ levels, while data for the valence region strongly suggest metallic behavior.²⁹

Continued condensation of this sort leads directly to the double metal sheet structure of the monohalides (below), and its continuation in the third dimension would produce the close-packed metal. Materials exhibiting intermediate stages of condensation in either the two or three dimensional regime are likely, analogous to the short chains which derive from Mo_6Se_8 .³⁷ There is evidence for other structure types: a phase of analytical composition $\text{ScCl}_{1.45 \pm 0.03}$ gives XPS core and valence data very different from those found for $\text{Sc}_7\text{Cl}_{10}$ even though the latter corresponds to the very similar composition $\text{ScCl}_{1.429}$.²⁹

The Monohalides. The ultimate result of cluster condensation in two dimensions is the ZrCl -^{8,38} (or ZrBr -³⁹) type structure, in which M_6X_8 -type clusters are condensed by sharing all edges around the waist ($\bar{3}$ axis) to generate infinite, double metal layers with exposed faces capped by halide, ${}_{\infty}^2[\text{M}_{6/3}\text{X}_2]$, as shown in Figure 6. This may also be described as close-packed layers sequenced Cl-Zr-Zr-Cl with three four-layer slabs in the unit cell. Each metal in ZrCl has six like neighbors in the same layer at 3.42 Å and three more in the adjoining layer at 3.09 Å, which distances compare with 3.19 Å in the hcp metal. The compound has the ap-

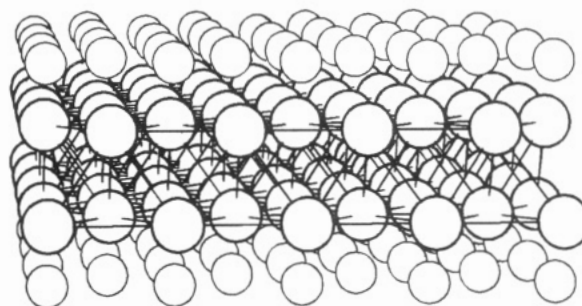
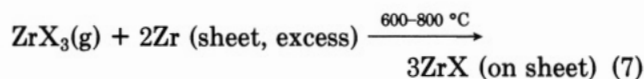


Figure 6. The ZrCl structure³⁸ with zirconium represented by the larger, interconnected spheres.

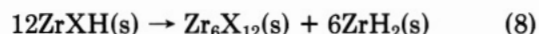
pearance of graphite as well as a similar susceptibility to cleavage and grinding damage. The polytypic ZrBr is obtained by interchange of two adjacent slabs. The black phases are Pauli paramagnetic and metallic by XPS,^{39,40} conductance,⁸ and theoretical⁴¹ criteria and appear to be good approximations to two-dimensional metals.

The zirconium monohalide crystals appear to grow epitaxially on the metal from a direct reaction of gaseous ZrX_3 (or ZrX_4), viz.



which is perhaps a common process in metal-halide reactions where transport or vaporization of the product does not occur. The ZrX phases are more reactive than the metal and are therefore useful reductants in the preparation of intermediate halides.

The two monohalides are remarkable in their reversible reaction with hydrogen at $\geq 100^\circ\text{C}$ to form $\text{ZrXH}_{0.5}$ and $\text{ZrXH}_{1.0}$ phases.⁴² According to NMR studies,⁴³ both involve distribution of the hydrogen over principally the tetrahedral holes between the double metal sheets. The ZrXH phases appear metastable and disproportionate at 600°C or above¹⁵ as



In addition to the formal d^3 examples ZrCl , ZrBr , and HfCl , comparable d^2 compounds in the same structure types occur for many trivalent elements, e.g., ScCl ,³⁰ YCl ,¹⁸ LaCl ,²⁸ and LaBr as well as for Pr , Gd , Tb , Ho , Er , and Lu .¹⁹ With one-third fewer electrons binding the layers, the metal-metal distances are naturally larger, e.g., 3.75 and 3.51 Å in YCl ⁴⁴ vs. 3.42 and 3.09 Å in ZrCl . Some of the same rare earth elements exhibit not only further examples of the structures already described, such as Tb_5Br_8 ,³² but also new structures of the same genre, i.e., Er_4I_5 ³¹ corresponding to Sc_5Cl_8 minus ScCl_3 and therefore the side chain (Figure 2), and Tb_6Br_7 ⁴⁵ which is analogously related to $\text{Sc}_7\text{Cl}_{10}$ (Figure 5) but edge bridged by halide.

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Structural and Bonding Generalities

Bonding in these approximations to low-dimensional metals is doubtlessly best represented with highly delocalized band models. Electron counting rules do not seem particularly applicable. In traditional clusters $\text{Mo}_6\text{X}_8^{4+}$, $\text{Nb}_6\text{I}_8^{2+,3+}$, and $(\text{Nb}, \text{Ta})_6\text{X}_{12}^{n+}$ ($n = 2, 3, 4$) 4.0, 3.17–3.33, and 2.33–2.67 electrons per metal atom, respectively, are conventionally assigned to metal bonding orbitals. Clearly there is nothing special about that value for 6–12 clusters when elements with lower atomic numbers are utilized, giving 2.0 in Zr_6X_{12} and 1.75 in $\text{Sc}_6\text{Cl}_{12}^{3-}$ and $\text{Zr}_6\text{Cl}_{12}^{3+}$. But as noted before,⁴⁶ the near constancy of these electron concentrations during cluster condensation of the group 3 metals is especially remarkable. As shown in the next to the last column in Table I, condensation of discrete clusters through chains to double metal sheets is found to take place within the fairly narrow range of 1.5–2.0 electrons per metal atom. A logical conclusion, considering also the character of the structures, is that the degree of condensation is governed more by the X:M ratio and that condensation proceeds insofar as possible to maximize electron-deficient M–M bonding as long as all edges or faces of the metal chain or sheet are capped by halide and exposed exo positions are also occupied by secondary interactions with otherwise bound halide. Isolated anionic or low coordination halide is not found.

Bond Orders. The degree of metal–metal bonding in these phases can be shown to be metal-like in a distance–electron count sense.⁴⁷ For this purpose Pauling bond orders n ($D_n = D_1 - 0.6 \log n$) are summed over all independent metal–metal separations ($n \geq 0.05$) and divided by the number of electron pairs available. The resulting quantity (PBO/e) is in the range 0.81–1.05 for all of the scandium and yttrium phases considered here as well as for Tb_6Br_7 , Tb_5Br_8 , Er_6I_7 , ZrCl (borderline), $\text{Zr}_6\text{Cl}_{15}$, most discrete M_6X_8 type clusters with other elements, and a number of metal-rich chalcogenides. Since distances in and valences of the individual metals themselves serve as the calibration for D_1 (PBO/e \equiv 1.0), the aggregate of metal–metal interactions even in these low symmetry structures is thus *metal-like* when considered in terms of the electron count. On the other hand, matrix effects—metal–metal separations dictated or restricted by close nonmetal–nonmetal contacts—produce characteristically low PBO/e values, for example, in Zr_6I_{12} and nearly all 6–12 clusters of niobium and tantalum.

These observations and the character of the structures shown in Figures 2–6 support the idea that these compounds are dominated by metal–metal bonding. Metallic radii provide some rationale for their occurrence in this portion of the periodic table.⁴⁷ The lower limit for the repeat dimension in these extended structures is dictated by the minimum period possible in the accompanying nonmetal sheath, about 3.4 Å for chloride. If metal–metal bond orders paralleling the nonmetal–nonmetal contacts in a chain are required to be ≥ 0.10 for stability,⁴⁸ then $D_n = D_1 + 0.6$, and the minimum single-bond metallic diameter for a chloride is $3.4 - 0.6 = 2.8$ Å. All of the trivalent elements in the

scandium family plus the rare earth elements Zr and Hf ($D_1 = 2.92$ Å) meet this requirement, but not Ti. Bromide contacts are characteristically 0.1–0.2 Å larger, so ZrBr might be judged to be borderline by this criterion; however, the sheet structure is somewhat more strongly bound than a chain since each metal has *six* neighbors in the same layer with $n = 0.11$.

Niobium and tantalum, with $D_1 = 2.71$ Å, fall short by this measure. Furthermore, their analogues would contain one or two more electrons per metal atom than found in the prolific trivalent examples (Table I) or ZrX. Admittedly, this could mean only that different structures would be formed which are presently inconceivable. Notwithstanding, stoichiometries with X:M $\leq 1.5:1$ appear to be necessary for strong, extended bonding, and their absence for niobium or tantalum halides is either a restatement of the above or an observation on the inadequacies of all synthetic attempts to data.

Chalcogenide Contrasts. The chalcogenides constitute the best studied group for comparison. In addition, utilization of chalcogenide in place of halide could be imagined to relieve matrix effects or to allow isoelectronic variants of the novel halide structures to form further into the transition series. But in fact the structural principles change sufficiently that the metal-rich chalcogenide phases are generally not at all comparable to halides.⁴⁶ The former are generally more nearly isotropic in both structure and properties. The only similarity occurs with Hf_2S_4 where double metal layers are separated by a single layer of nonmetal (compare ZrCl).

In the chemist's idiom these substantial differences arise because the lower charged chloride (or bromide) bonds to metal less covalently than sulfide (or selenide) owing to the former's lower polarizability and higher ionization energy, an effect which also contracts metal-based d orbitals in the halide. In the solids this means the nonmetal valence band, np^6 , is further removed in energy from the metal valence (conduction) band in halide than in chalcogenide so that halide contributes less to the metal-rich conduction or valence band and to metal–metal bonding. This is in accord with the observations that metal-bonded halides appear in metal-dominated structures significantly further to the left in the transition elements than with the metallic chalcogenides where the nonmetal appears to have an homogenizing effect on the structure. It will be recalled that only the metallic diiodides show structural similarities to chalcogenides, a reasonable consequence of greater iodide covalence and participation in the formation of a conduction band.

Differences of the above sort are easily recognized in a photoelectron spectra of the valence region. For example, the chlorine $3p^6$ levels in ZrCl and ZrCl_2 (3R-MoS₂ type³) are well separated and resolved from the metal "4d" levels⁴⁰ while metal and nonmetal valence levels in ZrS and MoS₂ are broader and overlap considerably in energy. This is not to suggest that the ZrCl and ZrCl_2 are ionic; only a modest charge transfer from metal to chlorine is reasonable in structures which contain adjacent chlorine layers.

Outlook

Any prognostication about what is to follow seems a bit hazardous in view of the remarkable array of totally

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(48) That this is too simple a generalization is seen in the additional zig-zag bonding achieved in chains (Figures 2, 4), but the conclusion still appears correct and useful.

new compositions and structures that have been found in the last few years in halide systems of the earlier transition elements, in spite of both considerable synthetic difficulties and earlier evidence that none existed. Additional extended structure types certainly exist and, likely as not, unprecedented configurations as well. Microcrystalline products have been discovered in MCl_3 -M systems with powder patterns which cannot be reconciled with those calculated for known structure types. And attention should be called once again to the fact that these wonderful materials occur in what are often considered "simple" binary metal-halogen sys-

tems. The likelihood that all stable bonding arrangements can be achieved electron precise in binary systems seems remote. Ternary systems involving low-field cations or other metals or anions with different oxidation states would also appear to provide bright prospects for the solid-state chemists' future.

The research described from my laboratory has been made possible only through both the enthusiasm and persistence of the excellent group of co-workers listed in the references and the continued support of the U.S. Department of Energy, Basic Energy Sciences (and its predecessor agencies), through the Ames Laboratory.

Bond Dissociation Energy Values in Silicon-Containing Compounds and Some of Their Implications

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Received February 6, 1981

Silicon occupies a special position in the hierarchy of elements. On the one hand the tetravalency of many of its compounds, which show remarkable stability, resembles that of saturated carbon compounds. On the other hand, its lack of ability to form obviously stable multiple-bonded compounds, its poor ability to catenate, its many crystalline compounds, and its ability to expand its coordination sphere are all more characteristic of other elements. Its chemistry may also be said to lie between that of organic and inorganic chemistry. Moreover, silicon is the second most abundant element of earth's crust and is today the vital component of the microchip technological revolution. Thus it need be no surprise that there is currently an expanding interest in silicon chemistry.

In the field of reaction mechanisms there has been an explosion of research on chemical intermediates in the last two decades, and silicon chemistry is no exception to this. There is active work now going on into silicon-containing free radicals, the π -bonded silicoolefins, the divalent silylenes, and unstable silicon-containing ring compounds such as silacyclopropane and silabenzene as well as much else. One of the more powerful ways to bring coherence to this field is through the establishment of reliable thermochemistry. With this objective in mind we embarked, some 7 years ago, on a program of bond dissociation energy¹ measurements in silanes.

Bond dissociation measurements are of assistance to this endeavour in two ways. First of all they provide the fundamental information on the strengths of bonds in important key molecules. Consequent upon this, much other information becomes available, for example,

the magnitudes of substituent effects and specific stabilizing influences in free radicals. There is the inevitable, yet fruitful, comparison of bonds strengths in silanes with their counterpart organic compounds. The second way in which such measurements are valuable is in providing a framework of free-radical heats of formation. This information has always been of immense use in mechanistic chemistry. Put simply, knowing the enthalpy change of reaction is the essential first stage in deciding whether such-and-such a proposed process is likely to go or not. It is sometimes surprising to this author how much time and effort has been devoted to the *theoretical* calculation of these quantities when measurement (or even crude estimation) of a few heats of formation will provide the answers desired. In this Account results obtained for silicon compounds are reviewed and discussed both for their intrinsic interest and for their bearing on questions of stability and reactivity of intermediates.

Our method of approach has been to study the gas-phase kinetics of the reaction of iodine with a series of silanes. This technique was pioneered by Sidney Benson in 1961 and has been reviewed by Benson and Golden.² It is not our purpose to review the possible methods by which bond dissociation energies may be determined or to discuss their applicability or relative merits.³ However, it is worth recalling that our method has been applied extensively to organic molecules to give values for C-H bonds which are generally agreed⁴⁻⁶

(1) A bond dissociation energy $D(A-B)$ is defined as the standard enthalpy change for process $A-B(g) \rightarrow A\cdot(g) + B\cdot(g)$. Despite the illogicality of the use of the word energy to describe enthalpy, we stick to tradition in the name. We also retain D as the symbol although others have preferred DH .^{2,3}

(2) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

(3) For general information the reader is referred to S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965), and references cited therein.

(4) Tabulations are given by (a) K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, **56**, 1516, 1537 (1973); (b) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976. Where slight disagreements occur, (b) is preferred as being more up to date.

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