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Correlation of Metal–Metal Bonding in Halides and Chalcides of the Early Transition Elements with That in the Metals

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Values of the average Pauling metal–metal bond order n per metal valence electron (PBO/e) are reported for about 110 metal-rich compounds of transition groups III–VI (including the lanthanides) which are structurally well characterized. The calculations include bond orders over all metal–metal separations with $n > \sim 0.07$ and assume only the presence of closed-shell anions, the Pauling equation $D_n = D_1 - 0.60 \log n$, and D_1 values likewise calculated from the respective metals. Matrix effects—usually anion–anion repulsions that restrict metal–metal bonding—are shown to yield plausible and predictable reductions in PBO/e values, these effects being greater with high nonmetal : metal ratios, large anion or small metallic radii, in M_6X_{12}-type clusters, and in layered and rock-salt-type structures. On the other hand, 32 metal-rich halides and chalcides are found to be relatively free of matrix effects and to be strongly metal–metal bonded relative to their respective metals by the criterion $0.80 \leq$ PBO/$e < 1.05$, these being principally M_6X_8-type clusters and extended (condensed) metal networks. Three special circumstances are considered: reduced metal–metal bonding in the molybdenum chalcides (but not halides), which arises from strong heteroatom bonding and nonmetal repulsions between clusters; a few errant examples with low concentrations of metallic electrons in which core sizes dictate separations (e.g., Ca^{2}N, PBO/e = 22.4); and some clusters of Nb, Mo, and W containing only oxide and fluoride in which nonmetal π contributions evidently give effective bond orders > 1.0.

Introduction

During the past decade a remarkable collection of new structure types has been discovered for reduced halides of the early transition and inner-transition elements (*1*). In general these possess single and double chains of metal octahedra as well as double metal sheets, structural characteristics which are indicative of strong, highly anisotropic metal–metal bonding. The additional discovery of isolated clusters of composition M_6X_{12} for the same elements together with their derivatives not only adds to those known for groups V and VI but also provides conceptual building blocks for the construction of extended structures through cluster condensation. The metal-rich chalcides also provide a thought-provoking collection of unusual stoichiometries and structures (*2*) which, however, show almost nothing in common with the halides in either structure or stoichiometry. The only significant correspondence is a small collection of metal–metal bonded (and usually metallic) diiodides which oc-

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cur in layered disulfide-type structures, among others.

These novel halide structures together with photoelectron spectra and band calculations for some of the phases have been interpreted in terms of a dominance of metal–metal bonding, in the sense that metal–metal bonding takes place as far as possible, subject to the constraint that all exposed vertices and either edges or faces of the metal structure be capped by halide and that all halide be either two or three coordinate to metal. The degree of condensation appears governed more by the halide : metal ratio than by electron count. An important factor appears to be the relatively small amount of mixing of *np* valence orbitals of the halide, chloride especially, into the metal's *nd* valence orbitals, in accord with a 5 to 6-eV separation between the chlorine and metal valence orbitals (*1*). In contradistinction, the very different structures found for the highly reduced chalcides are much less anisotropic in their metal–metal bonding and conduction, and there is both theoretical and experimental evidence for a considerably greater mixing of the metal and nonmetal valence orbitals therein (*2, 3*). These contrasting views of the halides and chalcides are heuristic in character for they serve to emphasize a remarkable difference in the structural chemistries of the two classes of compounds. At the same time, the common features of metal–metal bonding—which may be quite strong when distances in the parent metals are used for comparison—have not been subject to much general systematic interpretation. This is not altogether a matter of neglect; quantitative or even qualitative considerations are often made difficult because the metal bonding features of the many structures provide only a collection of diverse M–M distances and different coordination numbers for different metals which often leave the investigator with only an "apples and oranges" sort of comparison.

The present work was prompted by the unusual characteristics of the extended metal–metal bonding examples noted above, particularly in the halides, and the resulting question as to how the extent of bonding of the metal substructure would compare with that in the metal itself on an equivalent basis, that is, in terms of the number of electrons available. A simple approach to this is provided by the empirical but very useful Pauling bond order equation, viz.,

$$D_n = D_1 - 0.60 \log n, \qquad (1)$$

where D_n is the distance for bond order n and the 0.60 prelog constant is appropriate for $n < 1$ and electron-deficient compounds (*4*).

Earlier applications of Eq. (1) to metal–metal bonding have involved primarily either metals and intermetallics (*4*) or refractory sulfides (*5*). In the latter, the sums of bond orders over all neighbors of each atom, like and unlike, have been found to approximate the bonding orbital count or "valence" of crystallographically different metal or sulfur atoms within a range of about ±15% about the mean valence sum. On the other hand, equations of type (1) have been extensively applied to (insulating) ternary oxides of many elements in fixed oxidation states. Here one employs D_1 and the prelog constant as variables for each element or period and generally achieves classical bond valence sums (±5%) about *all* atoms (*6, 7*). Similarly good results have been obtained for a variety of metal fluorides, D_1 being dependent on oxidation state for the actinides (*8*). In this study the term "bond strength" was used synonymously with "bond order." A recent review of principally the oxide work (*9*) states without clarification that the approach does not work for metallic solids or homonuclear bonds. The present effort, undertaken before this discouraging word was heard, chose to consider in the Pauling sense only the metal–metal portion of the bonding and to test whether its extent was consistent with the electron count. This approach presumes that matrix (steric) effects—metal–metal separations dictated by anion packing or other structural features—can be readily discerned and in some cases shown to be negligible. In fact, the technique works amazingly well even for some chalcides and in any case enables one to compare at once diverse metal–metal bonding for different metallic elements and structures. Though highly useful, the Pauling bond order equation remains an empirical expression of remarkable intuition which lacks substantial theoretical justification.

Procedure

Pertinent single-bond metallic distances ($2R_1$) are given in Table I. These were in all cases calculated from the R_{12} values of Teatum *et al.* (*10*).[1] Bond order sums for the tabulated structures were carried out for all metal–metal separations about each independent or average atom, including distances with orders down to 0.05–0.08 (D_1 + ~0.7 Å) when sufficient distances were available in the literature source. As a simple example, the metallic and Pauli paramagnetic NbO evidently has three electrons per niobium in a metal-rich valence band. Each niobium has eight neighbors at 2.977 Å ($a/2^{1/2}$) (*11*), giving a bond order per neighbor of $\log^{-1}$ [(2.708−2.977)/0.60] = 0.356. Since second-nearest neighbors at a make a negligible contribution (0.003), the PBO/e value is 8(0.356)/3 = 0.95.

For structures in which the metal atoms are not all equivalent the tabulated data were obtained by dividing the bond order sum per average atom (or for all metal atoms in the independent unit) by the average number of electrons per atom (or the total per independent unit). A sample calculation for a chain compound (Y_2Cl_3) with nonequivalent atoms is given in the Appendix. The number of electrons available was in all cases calculated assuming that nonmetals have more tightly bound valence electrons and are therefore closed shell and that no electrons are localized on a single metal center and are therefore nonbonding (unless indicated otherwise). The last are reasonable assumptions for these materials. (The process of dividing the sum of all bond orders about an average atom or formula unit by the corresponding number of electrons is of course equivalent to using the bond order sum for the unique set of bond distances only, half the above value, and dividing by the number of electron pairs.) No special treatment has been accorded structures in which the metal atoms differ widely in degree of apparent bonding and

TABLE I

SOME SINGLE BOND METALLIC DIAMETERS (Å)[a]

Ca	3.480	Sc	2.921	Ti	2.638	V	2.464			Fe	2.367	Co	2.323
		Y	3.240	Zr	2.918	Nb	2.708	Mo	2.619				
Ba	4.019	La	3.393	Hf	2.874	Ta	2.706	W	2.635				
		Ce	3.297(γ)	Gd	3.243	Ho	3.171	Tm	3.131				
		Pr	3.295	Tb	3.203	Er	3.153	Lu	3.107				
				Th	3.310								

[a] Calculated from the 12-coordinate radii and valences given by Teatum *et al.*, as quoted by Pearson (*10*).

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[1] Newer data for the pure metals are not reflected in some of the R_1 values as well as R_{12} values converted from experimental R_8 data that are listed in Ref. (*4*).

thence in bond order sums, although the method does provide a convenient comparison of these. Additional nonmetal coordination usually compensates for a low M–M bond order about a metal atom.

The compounds considered include nearly all structurally well-known halides and chalcides of the inner transition and transition groups III–VI in which a significant amount of metal–metal bonding seems evident. Examples in which the electron count is sufficiently high that π-type orbitals in simple clusters would also be filled are naturally excluded since the basis of the calculation (the metal) is electron deficient. Filled π molecular orbitals occur with more than one electron per metal atom in dimers and more than two per atom in D_{3h} trimers, e.g., in MoO_2 and Nb_3Cl_8, respectively.

For reference, the structural characteristics of some of the less familiar structure types in which there is a substantial amount of metal–metal bonding are described in Table II.

Results and Discussion

The calculated values of the Pauling bond orders per electron (PBO/e) for the metallic element in a wide range of compounds in which substantial metal–metal bonding can be inferred are listed in Table III. These are organized first by electron count in periodic groups (III–VI) and then arbitrarily into columns for PBO/e values of ≥ 0.80, 0.60–0.79, and <0.60 (high, moderate, and low, respectively). Note that these values refer to the average metal atom in each compound. The following assumptions are implicit and necessary for the bond order results to have significance relative to the metals themselves:

(1) all valence electrons above closed-shell anions are engaged in metal–metal bonding (except when there is magnetic evidence to the contrary);

(2) metal–metal bonding in insulating and metallic compounds does not differ in kind insofar as metal–metal distances are concerned;

(3) nonmetal participation in bonding in the solid is not important in determining metal–metal distances;

(4) the assumed bond-order–distance equation as calibrated by the metal itself applies irrespective of the effective oxidation state, coordination number, and geometry of the metal atom, or the degree of delocalization; and

(5) there are favorable cases involving metal–metal bonding in which metal–metal distances are not governed by nonmetal–nonmetal or metal–nonmetal interactions (matrix effects).

Of course all of these cannot be true in all compounds. We will proceed to evaluate whether the metal–metal bonding in any of the compounds considered can be described (in a distance vs electron count sense) as "just as in the metal." The amazing thing is that a considerable number apparently do so qualify. The first thing to be established is that matrix effect trends appear to be very plausible, pointing the way to compounds where the other conditions may also apply.

Matrix Effects

Examination of the metal–metal bond order per electron with respect to matrix effects gives considerable assurance that the bond lengths and bond orders (strengths) do vary in a sensible way with respect to structure and nonmetal and metallic radii and that the results in the interesting limit of small matrix effects are reasonable. Matrix effects—where metal–metal separations are usually dictated by nonmetal–nonmetal van der Waals contact distances—have long been recognized, particularly in compounds with high nonmetal : metal ratios where nonmetal polyhedra are the structurally organizing

TABLE II

SOME LESS WELL-KNOWN STRUCTURE TYPES INVOLVING STRONG M–M BONDING

X/M	Type	Characteristics	Ref.
1.00	ZrCl, ZrBr	Double metal layers between double halogen layers, close packed.	*12, 13*
1.17	Tb_6Br_7	Double chains of metal octahedra sharing *trans* edges, exposed edges bridged by nonmetal (compare Sc_7Cl_{10}).	*14*
1.25	Er_4I_5	Chain of elongated metal octahedra sharing *trans* edges, with halide bridging exposed edges (compare Sc_5Cl_8).	*15*
1.43	Sc_7Cl_{10}	$Sc^{III}Cl_2^+Sc_6Cl_8^-$ or $ScCl_3 \cdot Sc_6Cl_7$. Double chains of metal octahedra sharing *trans* edges, face capped by halide, plus parallel scandium(III) chain.	*16*
1.50	Gd_2Cl_3	Elongated chain of metal octahedra sharing *trans* edges; exposed faces capped by halide.	*17*
1.60	Sc_5Cl_8	$ScCl_2^+Sc_4Cl_6^-$ or $ScCl_3 \cdot Sc_4Cl_5$. Elongated metal octahedra sharing *trans* edges, edge-capped by halide, plus parallel scandium(III) chain (compare Er_4I_5).	*18*
1.71	Sc_7Cl_{12}	$Sc^{3+}Sc_6Cl_{12}^{3-}$. Metal octahedra edge-bridged by halide (Zr_6I_{12} structure) alternating with Sc^{3+} along $\bar{3}$ axis.	*19*
0.80	Ti_5Te_4	Octahedra of metal face-capped by nonmetal (M_6X_8 type); *trans* vertices and capping atoms shared to form columns.	*20*
1.00	$Tl(Fe_3Te_3)$	Chain of trigonal antiprisms of metal sharing opposite faces, shared edges bridged by coplanar nonmetal.	*21*
1.50	$NaMo_4O_6$	Chain of metal octahedra sharing *trans* edges, exposed edges bridged by oxygen (compare Er_4I_5, Sc_5Cl_8).	*22*

unit. In some cases the degree of displacement of the metals from centers of, say, edge- or face-shared nonmetal octahedra toward one another has been taken as a measure of the strength of the metal–metal interactions (*74*). Judging from the bond order results, the degree of restraint provided by the nonmetal array is still quite high in such cases (cf. $NbCl_4$, Ti_7Cl_{16}, Nb_3S_4). In practice few compounds with substantial metal–metal bonding have nonmetal:metal ratios in the metal bonded

TABLE III

AVERAGE PAULING METAL–METAL BONDS ORDERS[a]

	High (>0.8)				Med. (0.6–0.79)				Low (<0.6)			
Electrons/$\bar{M}$	Cmpd.	(Str.)	PBO/*e*	Ref.	Cmpd.	(Str.)	PBO/*e*	Ref.	Cmpd.	(Str.)	PBO/*e*	Ref.
Group III												
2.00	ScCl	(ZrBr)	0.84	(*23*)	LaBr	(ZrCl)	~0.6(1)[b]	(*25*)				
	YCl	(ZrBr)	0.95	(*24*)	TbCl	(ZrCl)	0.77	(*25*)				
					TbCl	(ZrBr)	0.75	(*25*)				
					TbBr	(ZrCl)	0.65	(*25*)				
1.83	Sc_7Cl_{10}		0.93(6)[c]	(*16*)								
	Tb_6Br_7		0.94	(*14*)								
	Er_6I_7	(Tb_6Br_7)	0.90	(*14*)								
1.75	Sc_5Cl_8		1.04	(*18*)					Er_4I_5		0.55	(*15*)
	Tb_5Br_8	(Sc_5Cl_8)	0.96	(*26*)								
1.50	Y_2Cl_3	(Gd_2Cl_3)	0.96	(*27*)	Gd_2Cl_3		0.63[d]	(*28*)				
					Gd_2Br_3		0.61[d]	(*28*)				
	$Sc(Sc_6Cl_{12})$		0.85	(*19*)	$La(La_6I_{12})$	(Sc_7Cl_{12})	0.66*M*	(*29*)				
1.00	$CsScCl_3$	$(CsNiCl_3)$	1.36	(*30*)					LaI_2	$(MoSi_2)$	0.53*M*[b]	(*31*)
									PrI_2	$(MoSi_2)$	0.44*M*	(*31*)
									NdI_2	$(MoSi_2)$	0.45*M*[b]	(*32*)
									PrI_2	$(CdCl_2)$	0.15*M*[b]	(*33*)
									PrI_2	(3*R*-MoS_2)	0.18*M*[b]	(*33*)
									GdI_2	(2H-MoS_2)	0.25*M*[b]	(*31*)
									Pr_4I_8	(MoSBr)	0.32*M*	(*33*)
Group IV												
3.55	Zr_9S_2		1.01	(*34*)								
3.25	Ti_8S_3		0.85	(*35*)	ZrBr		~0.66(2)*M*[b]	(*13*)	Ti_2Se	(Ta_2P)	0.55*M*	(*36*)
3	ZrCl		0.81	(*12*)								
	Ti_2O	$(CdI_2)^{-1}$	1.00	(*37*)	Ti_2S	(Ta_2P)	0.77	(*38*)				
	Hf_2S		0.82	(*39*)	Zr_2Se	(Ta_2P)	0.73	(*40*)				
2.4									Ti_5Te_4		0.50	(*20*)
2.0					Zr_6I_{12}		0.68*M*	(*19*)	$ZrCl_2$	(3*R*-MoS_2)	0.51*M*	(*41*)
					$Zr_6Cl_{12} \cdot K_2ZrCl_6$		0.71	(*42*)				
									$ZrS_{0.99}$	(WC)	0.54*M*	(*3*)
									α-ZrI_2	(β-$MoTe_2$)	0.36*M*	(*43*)
									β-$MoTe_2$		0.34*M*	(*44*)
									WTe_2		0.42*M*	(*44*)
									ThI_2	(4*H*-NbS_2)	0.24*M*	(*45*)
1.71									Ti_7Cl_{16}		0.31*M*	(*46*)
1.5	$Zr_6Cl_{12}Cl_3$	(Ta_6Cl_{15})	0.88	(*17*)								
1.0	$ZrCl_3$[e]		1.13	(*47*)					$Cs_3Zr_2I_9$	$(Cs_3Cr_2Cl_9)$	0.44*M*	(*48*)

TABLE III—*Continued*

	High (>0.8)				Med. (0.6–0.79)				Low (<0.6)			
Electrons/$\bar{M}$	Cmpd.	(Str.)	PBO/*e*	Ref.	Cmpd.	(Str.)	PBO/*e*	Ref.	Cmpd.	(Str.)	PBO/*e*	Ref.
Group V												
>4	Ta_4O		0.95	*(49)*	$Nb_{21}S_8$		0.66	*(5)*				
	Ta_6S		0.84	*(50)*								
4	Nb_3P		0.85	*(51)*	Ta_2S		0.78	*(52)*				
					Nb_3Se		0.76	*(53)*				
3.40	Nb_5Se_4	(Ti_5Te_4)	0.8^f	*(54)*	V_5S_4	(Ti_5Te_4)	0.67	*(55)*	Nb_5Te_4	(Ti_5Te_4)	0.5^f	*(54)*
3.33	$CsNb_6I_8I_3$		0.81	*(56)*								
3.17	$Nb_6I_8I_3$		0.80	*(57)*								
3.0	NbO		0.95	*(11)*								
2.67					$K_4Nb_6Cl_{12}Cl_6$		$0.68M$	*(58)*				
					$Nb_6Cl_{12}Cl_2$		$0.66M$	*(59)*				
					$Ta_6I_{12}I_2$		$\sim 0.78(2)^g M$	*(60)*				
2.50	$Nb_6F_{12}F_3$		$\sim 1.12(4)$	*(61)*	$Ta_6Cl_{12}Cl_3$		$0.69M$	*(62)*	$(NMe_4)_3Nb_6Cl_{18}$		$0.59M$	*(63)*
									$CsNb_4Cl_{11}$		$0.56M$	*(64)*
									$CsNb_4Br_{11}$		$0.36M$	*(64)*
2.42									$Tl_{0.5}V_6S_8$		$0.18M$	*(65)*
2.33	$Mg_3Nb_6O_{11}$		1.15^h	*(66)*	Nb_3Se_4	(Nb_3Te_4)	$\sim 0.65M^b$	*(67)*	$(pyH)_2Nb_6Cl_{18}$		$0.47M$	*(68)*
					$H_2Ta_6Cl_{18} \cdot 6H_2O$		0.64	*(69)*	$(NMe_4)_2Nb_6Cl_{18}$		$0.52M$	*(70)*
									$(pyH)_2Nb_6Br_{12}Cl_6$		$0.42M$	*(68)*
									V_3S_4		$0.09M$	*(71)*
									Nb_3S_4	(Nb_3Te_4)	$0.58M$	*(72)*
1.0					NbO_2		0.70	*(73)*	$(NbCl_4)_2$		$0.26M$	*(74)*
									NbS_2Cl_2		0.49	*(75)*
									NbS_2	$(3R)$	0.55	*(76)*
									TaS_2	$(4H)$	0.54	*(77)*
Group VI^i												
4.33	$Tl_2Mo_6Se_6$	$(TlFe_3Te_3)$	1.01	*(79)*								
4.00	$Mo_6Cl_8Cl_4$		1.05	*(80)*								
	$Hg(Mo_6Cl_8)Cl_6$		1.00^b	*(81)*								
	$Mo_6Br_8Br_4 \cdot (OH_2)_2$		0.94	*(82)*								
	$(pyH)_3Mo_6Cl_7SCl_6$		1.04	*(83)*								
	$Mo_6Cl_7SeCl_3$		1.01	*(84)*								
3.80	$(NBu_4)_2Mo_5Cl_8Cl_5$		0.98	*(85)*								
3.75	$(NBu_4)_2Mo_4I_{11}$		0.84	*(86)*								

TABLE III—*Continued*

	High (>0.8)				Med. (0.6–0.79)				Low (<0.6)			
Electrons/$\bar{M}$	Cmpd.	(Str.)	PBO/e	Ref.	Cmpd.	(Str.)	PBO/e	Ref.	Cmpd.	(Str.)	PBO/e	Ref.
Group VI^i (*cont.*)												
3.67	$W_6Br_8Br_6$		1.07	(*87*)								
	$Mo_6S_6Cl_2 \cdot 6\,py$		1.03	(*88*)								
3.33					Mo_6S_8	(Mo_6Se_8)	0.73*M*	(*89*)				
					Mo_6Se_8		0.76*M*	(*90*)				
					Mo_6Te_8	(Mo_6Se_8)	0.65*M*	(*91*)				
3.25	$NaMo_4O_6$		1.03	(*22*)								
3.00									$Mo_4S_4Br_4$		0.50*M*	(*92*)
									$W_6Cl_{12}Cl_6$		0.44*M*	(*93*)
2.75									$GaMo_4S_8$		0.50M^b	(*94*)
2.0	$Zn_2Mo_3O_8$		1.43	(*95, 96*)	$Mo_3(S_2)_3SCl_4$		0.62	(*97*)	MoS_2	(3*R*)	0.38*M*	(*98*)
									WS_2	(2H_6)	0.41*M*	(*98*)
Miscellaneous												
4.33	$TlFe_3Te_3$		0.58(d^2)									
3.33			0.75(d^3)	(*21*)								
3.22	Co_9S_8		1.10(d^6)									
1.22			0.61(d^4)	(*99*)								
3.00	$K_3W_2Cl_9$		0.71^j	(*100*)								
2.67	$Mo_3OCl_3(OAc)_3(OH_2)_3^{2+}$		0.98^j	(*101*)								
2.33	Nb_3Cl_8		0.58M^j	(*102*)								
2.00	MoO_2 (dimer)		0.71^j	(*103*)								
	WO_2 (dimer)		0.79^j	(*103*)								
	$Cs_2Mo_3O_4(C_2O_4)_3(H_2O)_3$		1.67	(*104*)								
	$(NH_4)_5W_3O_4F_9$		1.59	(*105*)								
1.0	$K_3HW_2O_4F_6$		1.06	(*105*)								
	$(NH_4)_2Mo_2O_4F_4(OH_2)_2$		1.23	(*106*)								
0.5	Ca_2N	$(CdCl_2)^{-1}$	22.43	(*107*)								
	Ba_2N	$(CdCl_2)^{-1}$	7.14	(*108*)								
	Ag_2F	$(CdI_2)^{-1}$	1.34	(*109*)								

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[a] *M* = obvious matrix effect, *py* = *pyridine*.

[b] Structure refined from powder data.

[c] Depends on assumptions regarding paramagnetism (see Reference).

[d] Questionable single-bond radius (Ref. (*27*)).

[e] Localized state, *calculation not meaningful*.

[f] Atom positions not refined.

[g] Sizeable distortions.

[h] Profile analysis of powder data.

[i] Chevrel phases elsewhere (*78*).

[j] Occupied π state.

unit above 2.0 if "substantial" is taken to mean a PBO/*e* value above about 0.6.

Structures derived by what can be conceptually viewed as cluster condensation will provide some of the most interesting results in the present examination, and both the structural parentage and the source of the matrix effect in these can be seen from the M_6X_{12}- and M_6X_8-type clusters shown in Fig. 1, where X atoms edge- and face-bridge the metal octahedra, respectively. The ideal geometry places each metal vertex nearly coplanar with the four neighboring nonmetals so that both elements lie on the same cube. The smaller crowding inherent in the M_6X_8 type is represented by the ideal values of 1 and $2^{1/2}$ for d_{X-X}/d_{M-M} in M_6X_{12} and M_6X_8, respectively, when X atoms are in contact. However, strong metal–metal bonding together with the larger matrix effect (anion–anion repulsion) in real M_6X_{12} examples results in a configuration in which the metals are drawn inside the cube on which the nonmetal atoms lie, as shown; in other words, the distortion is probably always a manifestation of nonmetal crowding.[2]

On the other hand, weak M–M bonding in M_6X_8 clusters places the metal atoms slightly outside of the faces of the nonmetal cube and only with strong bonding are they nearly coplanar. Diminished crowding in M_6X_8 is manifest in molybdenum chalcide and halide chemistry, where a smaller D_1 relative to that in niobium requires a smaller octahedron to achieve the same bond order. Consequently the only M_6X_{12}-type species for group VI (that is structurally well characterized) is $W_6Cl_{12}^{6+}$, where the higher oxidation state (lower electron count) allows for longer W–W bonds and additional (and stronger) W–Cl interactions contribute more binding to the stability. The stability of the Nb_6I_8 cluster unit in Nb_6I_{11} is unique relative to the many M_6X_{12} clusters found with the other group V halides. This result must again represent the results of a steric or matrix effect, in this case arising from the large size of the iodide ion. The magnitude of difference between $Mo_6Cl_8^{4+}$ (24*e*, PBO/*e* = 1.05) and Mo_6S_8 (20*e*, 0.73) will receive later consideration in terms of matrix and electronic effects in the latter.

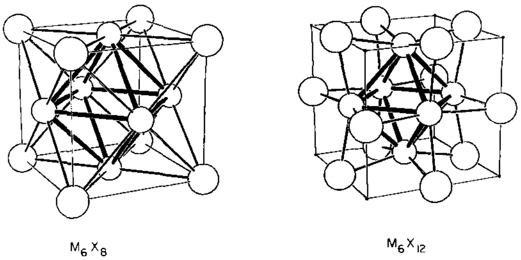

FIG. 1. M_6X_8 and M_6X_{12} cluster types viewed as metal octahedra face-capped and edge-bridged by nonmetal atoms, respectively.

Table IV lists pairs of compounds with their respective PBO/*e* values that reflect clear matrix effects, the metal–metal bond order decreasing, often substantially, with either an increase in the size of the nonmetal or a decrease in (metallic) size of the metal for fixed anion and structure. There appear to be *no* exceptions to the plausibility of such bond order comparisons.[3]

Before discussing the most interesting collection of compounds for which PBO/*e* approaches 1.0, two other obvious cases of matrix effects must be noted—layered and rock salt structures. Clearly the closest possible approach of the metal ions in layered structures sequenced X–M–X is severely constrained if nonmetal radii are appreciably larger than the metallic radii, as is usually the case. This is reflected in PBO/*e* values of ~0.53 for $ZrCl_2$ and NbS_2

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[2] In NbO the 6–12-type clusters share faces ($Nb_{6/2}O_{12/4}$), thereby requiring coplanarity of atoms on the cube faces (*74*). The structure is naturally limited to small nonmetals.

[3] The apparent contradiction provided by Mo_6S_8 (0.73) and Mo_6Se_8 (0.76) is not significant but a logical consequence of the character of the bonding in this unusual structure, as discussed later.

TABLE IV

BOND ORDERS REFLECTING PLAUSIBLE MATRIX EFFECTS[a]

ZrCl	0.81	vs	ZrBr	~0.66
TbCl	0.77	vs	TbBr	0.65
PrI_2 ($MoSi_2$)	0.44	vs	PrI_2 ($CdCl_2$, MoS_2)	0.15
$Zr_6Cl_{12}^{3+}$	0.88	vs	$Zr_6Cl_{12} \cdot K_2ZrCl_6$	0.71
Zr_6I_{12}	0.68	vs	ZrI_2 (β-$MoTe_2$)	0.36
$Nb_6F_{12}F_3$	~1.1	vs	$Ta_6Cl_{12}Cl_3$	0.69
Nb_6I_{11}	0.80	vs	$Nb_6Cl_{12}Cl_2$	0.66
$W_6Br_8^{6+}$	1.07	vs	$W_6Cl_{12}^{6+}$	0.44
$Mo_6Cl_8^{4+}$	1.05	vs	$Mo_6Br_8^{4+}$	0.94
Ti_2S	0.77	vs	Ti_2Se	0.55
Zr_2Se	0.73			
Nb_5Se_4	.0.8	vs	Nb_5Te_4	0.5
Nb_3S_4	0.58	vs	V_3S_4	0.14
$Mo_6Cl_8^{4+}$	1.05	vs	Mo_6S_8	0.73
$ZrCl_2$ (3*R*-MoS_2)	0.51	vs	MoS_2	0.38
$Nb_8I_8^{3+}$	0.80	vs	Mo_6Te_8	0.65

[a] Data selected from Table III. Structure types in parentheses.

and 0.38 for MoS_2, all of which occur in various layered polytypes in which there is trigonal prismatic coordination of nonmetal about metal and significant *M–M* interactions. The metallic radii for the 3*d* elements are naturally smaller than for 4*d* and 5*d* elements discussed above, so that repeat distances in the CdX_2-type dichlorides are larger (~3.6 Å), and apparent metal–metal bond orders and the strength of the metal interactions by other measures (*110*) are both very low. Bond orders for the double-metal-layered Zr*X*-type phases (Table II) appear to reflect some of the same problems; each metal layer must maintain the period of the halide layer but interpenetration of the two metal layers is not as restricted, and strong metal–metal bonding can still result (*12, 13*). Unscreened metal core repulsions may still limit the approach of the metal layers, especially with the more strongly bound zirconium phases.

Metal–metal bonding in all phases with a NaCl-type structure may be governed by a substantial matrix effect, and the same will apply to some extent to NiAs-type structures. The diminished metal–metal bonding achieved in rock salt structures was perceived some years ago by Rundle (*111*) in a consideration of the so-called interstitial phases of composition *MX*. For substantially all of the compounds considered here the observed *M–X* separations approach the sums of the crystal or "ionic" radii (*112*) for the nonmetal and for the metal core in its normal oxidation state. Thus, the electrons involved in metal–metal bonding, metallic or not, are often not significantly screening to the nonmetal; otherwise a considerable increase in the metal–nonmetal separations would be expected, ~0.15–0.23 Å/unit oxidation state based on crystal radii. This circumstance means that the *M–M* separation in a NaCl-type structure is substantially fixed at about $2^{1/2}d_{M-X}$, a distance which has nothing to do with the strength of the metal–metal binding. Accordingly, PBO/*e* values calculated for the metallic monosulfides of the rare earths in the rock salt structure (ScS: 0.68, YS: 1.01, LaS: 0.69 (*2*) and GdS: 0.82 (*113*)) reflect principally only the relationship between crystal and metallic radii. Peripheral examples in which the number of electrons engaged in metal–metal bonding tends to zero will be noted later.

Examples in Table III marked *M* are those in which a matrix effect of some sort is probably operable according to the above discussion.

Metal-like Examples

Compounds in which the degree of metal–metal bonding approaches that of the metal itself do clearly exist, and these logically and properly occur in instances where matrix effects should be minimal. Although this conclusion could in a few cases be simply deduced from distances alone most would be obscure because of the difficulty of handling a collection of different distances and different metals.

About 35% of the phases listed in Table III exhibit strong metal–metal bonding

(PBO/e $\geq$ 0.80). These fall mainly in the following categories.

1. For M_6X_{12}-type clusters only those of the group V metals with small nonmetals, $Nb_6F_{12}F_3$ and $Mg_3Nb_6O_{11}$, are well bonded. Chlorides qualify for metals with larger metallic radii, viz., $Zr_6Cl_{12}^{3+}$ ($>Zr_6Cl_{12}$) and $Sc_6Cl_{12}^{3-}$.

2. The lower nonmetal repulsions inherent in M_6X_8-type clusters allow "good" bonding in $(Nb_6I_8)I_3$ and for a good fraction of the group VI examples, in spite of the smaller single-bond metallic radii of the latter. These include $Mo_6X_8^{4+}$ (X = Cl, Br) and $Mo_6Cl_7Y^{3+}$ (Y = S, Se) as well as the less reduced and therefore larger $W_6Br_8^{6+}$ and $Mo_6S_6Cl_2 \cdot 6$ py.

3. Condensation of both 6–8 and 6–12-type clusters is found frequently in halides of group III elements (rare earth metals included), giving a remarkable collection of metal-rich single- and double-chain halides such as Sc_5Cl_8, Sc_7Cl_{10}, Tb_6Br_7, and Y_2Cl_3, and most exhibit high bond orders. (Gd_2Cl_3 would probably also qualify but the reference D_{12} for the metal appears to be anomalously low (*27*); lanthanum also shows a volume anomaly (*114*) and calculations for its compounds may be similarly affected.) The larger metallic radii for the group III elements mean halide repulsions in the presence of "good" metal–metal bonds are less than those for later groups.[4] The degree of condensation in these extended clusters appears to be determined principally by the X:M ratio (*1*), but reasons for the choice between face capping or edge capping by halide in extended chains are more subtle. Most of the metal octahedra that formally comprise the chains are substantially elongated along the chain, thereby reducing nonmetal repulsions along that direction. More important nonbonding interactions appear to take place between sheathing nonmetals around the circumference of the chain and between these and the nonmetal atoms (ignored until now) that fill *exo* positions and bridge between chains.

4. A number of metal-rich chalcides, Hf_2S, Zr_9S_2, Ta_6S, and NbO, for example, exhibit strong metal–metal bonding in the bond order sense. The chain structure of Ti_5Te_4, in which M_6Ch_8 clusters share opposite faces (Table II), provides an analogy to extended halide structures. But the size combination of elements in the two examples for which refined positional data are available, Ti_5Te_4 and V_5S_4, would not be considered optimal for strong metal–metal bonding. Reasons why some other chalcides do not bond as well (Table III) are more difficult to perceive since most of the structures are quite complex; however, a matrix-type restriction on metal–metal bonding in one direction in many sulfide structures is immediately suggested by short unit cell axes of 3.32–3.36 Å (*2*), about the lower limit for S–S distances in many metal sulfide structures. In fact, all of the group V and VI sulfides together with several of the group IV examples that exhibit d_{S-S} values $\leq$3.37 Å have PBO/e $<$ 0.8, and those two with all $d_{S-S} > 3.9$ Å have PBO/e $\sim$ 1.0 (Ta_6S and Zr_9S_2). Although the van der Waals radius for the sulfide *ion* is slightly greater than that for chloride the sizes of both will be reduced in magnitude and perhaps reversed in proportion by M–X covalency, which should be somewhat greater for the sulfide. Again, the metal–metal bonding electrons in these solids evidently do not screen the anion very well, meaning that metal–nonmetal distances and covalency as well as the effective nonmetal radii are found to approach those found in the higher-valent MX_n compounds even though the formal oxidation states in the phases of interest are quite low.

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[4] It is not obvious from these considerations alone why cluster condensation should not also occur in zirconium chlorides with 1.0<Cl : Zr<2.0 unless this requires that the electron count in the chain exceed some critical value.

The Molybdenum Chalcides

The low effective bonding in Mo_6S_8 in particular (PBO/*e* = 0.73) at first sight presents somewhat of a puzzle. The 20-electron cluster is in effect disproportionately large even when the intercluster Mo–Mo distance and lower electron count are taken into account. This result is particularly striking when compared with bond orders per electron near 1.0 for the 24-electron $Mo_6Cl_{12}^{4+}$ and its derivatives and for $Mo_6Br_8^{4+}$ and $Mo_6Cl_7Y^{3+}$ (Y = S, Se) (Table III). The PBO/*e* value of 1.03 for the 22-electron $Mo_6S_6Cl_2 \cdot 6$ pyridine is especially noteworthy, demonstrating that intracluster sulfur–sulfur repulsion clearly cannot be a major factor in the greater size of the cluster in Mo_6S_8.

The distinction certainly must originate with the very different intercluster bonding required in the Mo_6Ch_8 phases because of the very low ratio of nonmetal to metal and the absence of cluster condensation. A maxim of cluster chemistry is that the *exo* (apical or outward pointing) position of each cluster metal atom is always filled (*74*). Although the other Mo_6X_8-type clusters cited in this comparison all contain either additional basic ligands (py, H_2O) or extra halide anions for this purpose (sometimes bridging between clusters as in $Nb_6I_8I_{6/3}$), Mo_6S_8 and Mo_6Se_8 are in effect much more acidic and must provide this function from within. Thus six out of eight chalcide groups therein both cap triangular faces of the metal cluster and occupy *exo* positions at molybdenum atoms in other clusters. A systematic means of accomplishing this is readily achieved in the $R\bar{3}$ space group but the Mo antiprism is clearly elongated by packing problems arising from the additional coordination of an inner sulfur atom to a fourth, *exo* position. The strength of this *exo* Mo–S bond judged by distances is impressive—the intercluster Mo–S bonds are the same length (3.425 Å) as the shortest of the intracluster bonds (3.426–3.460 Å) (*89*). The tight bonding thus achieved in the Mo_6S_8 array is illustrated by the short 3.34-Å separation of sulfurs between clusters. The packing problems are a little less severe in Mo_6Se_8 because of the intrinsically larger intercluster Mo–Se bonds, although short intercluster Se–Se contacts occur (3.38 Å) and the cluster is still elongated. For comparison, the *exo* positions Zr_6X_{12} and $Sc(Sc_6Cl_{12})$ are similarly occupied by edge-bridging chloride in other clusters but the *exo* M–X distances are about 0.2 Å longer than those within the cluster.

Within the bridged structure of Mo_6Ch_8 the effect on bond orders of the further reduction to form the so-called Chevrel phase $M_xMo_6Y_8$ is sensible as the PBO/*e* values smoothly increase to ~0.85. A more detailed analysis of these factors will appear elsewhere (*78*).

The reduction in nonmetal repulsive interactions which are achieved during cluster condensation to a product with a lower nonmetal : metal ratio is strikingly shown by the results for the infinite chains $(Mo_6Se_6^{2-})_\infty$ in the thallium salt, where the shortest selenium–selenium distances are now nearly 3.8 Å and PBO/*e* = 1.01. Comparable differences can be expected for products with intermediate degrees of condensation (*115*). Of course it might be argued that the low values of PBO/*e* found for the chalcides only reflect the failure of the simplistic approach utilized in this study so that, for example, covalency and mixing of sulfur orbitals into the nominal metal valence band do contribute to the Mo–Mo binding. However, although covalency must be substantial the very good adherence of the $MoS_6Cl_2 \cdot 6$ py, $(Mo_6Se_6^{2-})_\infty$, and Mo_6Cl_8-type examples to this simple bond order picture encourages the view that the chalcide contribution to metal–metal bonding is not very significant insofar as metal–metal distances are concerned. Covalency has been invoked to explain the metallic properties of some layered diiodides (*116*) but there a substantial matrix effect (iodine packing in layers) appears to obscure any effect on intrinsic metal–metal bonding.

Some Negative Results in Polar Compounds

General application of these bond order ideas occasionally requires some further consideration as to whether observed *M–M* distances may in special cases be determined by other than metal–metal bonding. An example was noted earlier with rock salt structures, where attractive (coulombic) forces and crystal radii appear to the principal factors in determining the separations of the metal cores. A related problem arises with a few other compounds in which the number of metallic electrons is relatively small. Obviously, metal–metal bond orders of 1.36 and 0.23 calculated from the separation of calcium ions in CaO and CaF_2, respectively, are meaningless because of the absence of any electrons above the tightly bound $2p^6$ anion levels that could contribute to Ca–Ca bonding. A related situation must apply to Ca_2N (PBO/*e* = 22.4), Ba_2N (7.14) and Ag_2F (1.34). The first two have an anti-$CdCl_2$-type structure and the last, anti CdI_2, so that the three-layer slabs all contain a layer of small nonmetal atoms or ions sandwiched between two close-packed layers of metal. The metal–metal separations in Ca_2N within each metal layer, between the two layers separated by nonmetal and between the slabs are, respectively, 3.64 (×6), 3.23 (×3) and 4.35 (×3) Å and in Ag_2F, a contrasting 3.00, 3.87, and 2.81 Å, respectively. The Ca–N separation in the former is close to that in Ca_3N_2. Clearly the short 3.23-Å separation between calcium atoms in different layers about the nitrogen layer is determined principally by the size of these "ions" and not by significant metal–metal bonding across the slab (bond order = 2.61) when there are only 0.5 electrons per calcium. The large 4.35-Å separation between calcium atoms in different slabs speaks for a relatively polar charge distribution. The polarity in Ag_2F appears to be markedly less since the relative magnitudes of the separations between silver layers in the same and different slabs are reversed, and the Ag–Ag bond order contributions are about equally distributed between intralayer and intraslab interactions.

There is a recognizable group of generally small clusters listed in Table III for which PBO/*e* values are appreciably above 1.0 and which might conceivably involve a common exception. These are $Mg_3Nb_6O_{11}$ (PBO/*e* ~ 1.15), perhaps Nb_6F_{15} (1.12 ± 0.04), $Zn_2Mo_3O_8$ (1.43), and four discrete anions (Table III—Miscellaneous): $Mo_3O_4\ (\text{oxalate})_3^{2-}$ (1.67); $W_3O_4F_9^{5-}$ (1.59); $Mo_2\ O_4F_4(OH_2)_2^{2-}$ (1.23); and, perhaps, $HW_2O_4F_6^{3-}$ (1.06). All involve fluoride or oxide and group V or VI metals and the last five contain a group VI element with a formal oxidation state of +4 or +5. A polar matrix interpretation might be imagined, such that a strong interaction of the highly charged metal cores with the small anions is more important in determining the interstice, and hence the metal–metal separations, than is the number of electrons available. However, the metal atoms in some are clearly drawn together. A better approach is to attribute these short metal–metal bonds to nonmetal π interactions which accompany the observably shorted metal–nonmetal σ bonds, this effect contributing additional electrons and bonding to the metal framework (*117*).

An assumption throughout the present study has been the invariance of the metallic radii to formal oxidation state. This is not reasonable in detail since an orbital's radial extension must depend on electron count because of interelectronic coulomb repulsion. Matrix effects usually dominate with higher oxidation states because of the higher $X:M$ ratios, though perhaps some of the low results simply attributed to these effects have a broader origin. Only $ZrCl_3$ among the compounds listed is known to have a localized magnetic state (*118*), so that the bond order calculation (1.13) is not meaningful. The more reduced $ZrCl_2(3R)$, Zr_6Cl_{12}, and Zr_6Cl_{15} are all collective in bonding and electronic properties (*119* and references therein). The situation with the diamagnetic $CsScCl_3$ (PBO/e = 1.36) is not yet understood.

Finally, it should be noted that a serious attempt has not been made to apply the bond order approach to the metal-rich pnictides. A few calculations on phosphides seemed to give erratic results. The ideas applied here should also be applicable to the metal–metal bonding in the so-called interstitial metal compounds as long as the valence state ("charge") on the interstitial species can be inferred with some probability, e.g., O^{2-} and H^-, and high-symmetry structures with clear matrix effects are avoided.

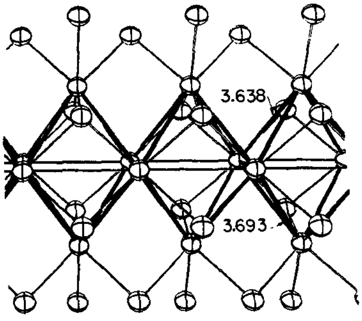
In principle the above calculations could be extended to include valence sums for all bonds about all atoms, as has already been successfully done for many insulating oxides (*5*). The isolated scandium(III) atoms in Sc_5Cl_8 provide a good starting point but it is quickly discovered that the chlorine bonds to metal in the chain require a different equation. Still, with two adjustable parameters the bond order (valence) sums over all seven independent atoms in Sc_5Cl_8 range between 2.96 and 3.15 for scandium, and 0.88 and 1.13 for chlorine, with the significant fraction of the former coming from metal–metal bonding. However, applicability of these equations to other scandium halide phases is not very satisfactory. The difficulty can be foreseen by the fact that different types of chlorine atoms of equal coordination number may exhibit distances differing by ≥0.07 Å (e.g., in Y_2Cl_3 and Zr_6Cl_{15}). In effect, every oxidation state in these delocalized examples may still require somewhat different parameters to describe the M–Cl bonds (as in some fluorides (*8*)) but a separate equation for the generally longer *exo* bonds will also be necessary. These problems are evidently avoided when only fixed oxidation states are considered.

Appendix: Sample Calculation for Y_2Cl_3

For Y metal: $D_1 = 3.601 + 0.6 \log (3/12) = 3.240$ Å where 3.601 Å is the average D_{12}

Distances (Å) in Y_2Cl_3 (the center of the cluster has $\bar{2}$ symmetry) are (*27*)

Shared edge	$3.264 \times \frac{1}{2}$ Å
Edge to apex	3.638×2
	3.693×2
Repeat[5]	3.825×2



For average Y in Y_2Cl_3, with 1.5 electrons

D (Å)	n
$3.264 \times \frac{1}{2}$	0.452
3.638×2	0.431
3.693×2	0.349
3.825×2	0.210[5]
	1.442

1.442/1.5 = 0.961

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[5] One might choose to exclude the more isolated apex–apex repeat, which would lower the result to 0.891.

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