Bond Reactivities, Acidities, and Basicities within AMo_3X_3 Phases (A = Li, Na, K, In; X = Se, Te)

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In order to explain the varying solubility of AMo_3X_3 phases (A = Li, Na, K, In; X = Se, Te) in polar solvents, we investigate theoretically the chemical character of Mo–Mo, Mo–X, and A–X bonds. The computation of both bond energies as well as the newly defined increments of reactivity, electrophilicity, and nucleophilicity (inspired by a density-functional formalism suggested by Parr and Pearson) reveals that (i) Mo–Mo bonds are chemically inert, (ii) the dissolution of Li- and Na-containing phases is due to the high acidity of A–X bonds, easily attacked by Lewis bases, and (iii) the Mo–X bonds show high basicity throughout the whole series of compounds. The latter finding gives rise to the assumption that strong Lewis acids will seek out Mo–X bonds as "targets" in liquid-state solid-state acid–base reactions.

1. Introduction

The family of compounds AMo_3X_3 (A = K, Rb, and Cs if X = S, A = Li, Na, K, Rb, Cs, Ba, In, and Tl if X = Se, and A = Na, K, Rb, Cs, Ba, In, and Tl if X = Se) that has been synthesized by Potel, Chevrel, and Sergent and their co-workers,[1,2] Hönle et al.,[3] and Huster et al.[4] is remarkable both for structural and physical properties.[5] The structure is of the $TlFe_3Te_3$ type[6] and may be described[7] as a linear condensation of an infinite number of face-sharing Mo_6X_8 octahedra, thereby forming one-dimensional $(Mo_{6/2})^{1}_{\infty}$ metal chains, surrounded by chalcogenide atoms and isolated from each other by electropositive metal atoms of main groups I, II, and III. A view into the structure along two different directions is given in Figure 1.

The lattice dimensions of these materials depend strongly on the method of synthesis. The most reliable parameters have been given by Tarascon et al.,[8] who used low-temperature ion-exchange syntheses, thereby creating the smallest amount of structural defects. Concerning the crystal structure itself, probably the best structural parameters have been measured by Hönle et al.[3]

Great anisotropy is found in all interesting properties of these compounds. This finds its explanation in the highly nonuniform chemical bonding, which obviously results from Mo–Mo covalent bonding and more ionic Mo–X bonding, on one hand, and weak X–X van der Waals contacts, on the other. In short, metallic chains shielded by van der Waals surfaces are held together by electropositive metal ions. As has been proposed earlier,[9,10] the compounds with alkali metal atoms should show a Peierls-like transition from metallic to semiconducting behavior below 100 K,[11] although no *structural* changes have been found so far. Compounds containing main group elements other than from group I remain metallic, probably because of stronger electronic interchain coupling. $TlMo_3Se_3$ even becomes superconducting at around 5.1 K.[11]

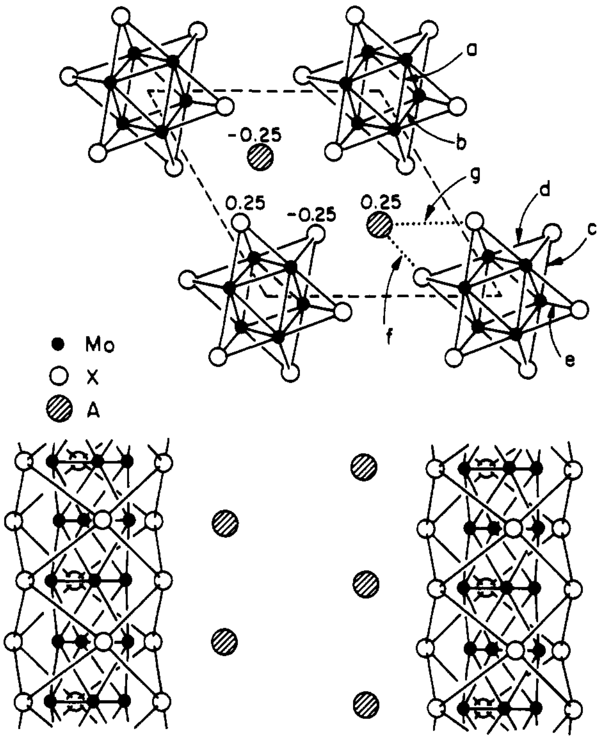

Figure 1. Projection of the crystal structure of AMo_3X_3 phases along the hexagonal axis (top) and approximately along [1120] (bottom). Mo atoms, given as small, filled circles, are bonded to surrounding X atoms, drawn as open, medium-sized circles. Electropositive A atoms, given as large, shaded circles, lie within the central tunnel of the structure. The letters *a*–*g* refer to the labeling of bonds in Tables II and V–VIII.

According to the fragment molecular orbital analysis of Hughbanks and Hoffmann,[9,10] a very wide Mo–Mo bonding band of symmetry a_2 in point group C_{3v} ($3m$) plays the driving role for the metal–semiconductor transition found in alkali phases. It is almost entirely composed from excellently overlapping fragment

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orbitals of symmetry $1a_1''$ in point group D_{3h} ($\bar{6}m2$) belonging to Mo_3Se_3 fragments.

2. Solubility Behavior

The pioneering work of Tarascon, DiSalvo, and co-workers[12] shows that AMo_3X_3 compounds containing Li, Na on the one hand and Se, Te on the other can be dissolved in highly polar solvents. What is found in solution are very long Mo_3Se_3 strings as well as solvated A ions. Interestingly, there are striking differences in solubility behavior from one phase to another. For example, Li compounds are very easily dissolved and Na compounds are only partially (colloidally) soluble, whereas pure K or In compounds are not soluble at all. However, quaternary phases both containing much Li and less In can also be brought into solution. Compounds containing Se do not seem to be more easily dissolved than those containing Te.

As a crude approximation the dielectric constant ϵ of the solvent may serve as a guideline in judging whether the solid will dissolve.[12] Of course, tetrahydrofuran (THF) ($\epsilon \approx 7.32$) is not as good a solvent as *N*-methylformamide (NMF) ($\epsilon \approx 182$), and only the latter actually dissolves AMo_3X_3 phases. However, propylene carbonate PC ($\epsilon \approx 64.4$) is a *worse* solvent compared to dimethyl sulfoxide (DMSO) ($\epsilon \approx 46.7$), in spite of having a higher value of ϵ. These facts can be extracted from the compilation of Tarascon quite easily; an explanation has not been given so far.

A fact that has been overlooked, in our opinion, is that all "good" solvents represent truly strong Lewis bases. One empirical measure of Lewis basicity is the Gutmann donor number DN.[13] Unfortunately, tables of DN's for interesting solvents are far from complete. However, DMSO, which is a better solvent than acetonitrile, actually has a higher DN, 29.8 compared to 14.1. For the best solvent, NMF, no donor number is available, but the "related" compound *N,N*-dimethylformamide (DMF) also has a high DN, namely 26.6. So the "hierarchy" of dissolving power seems to be well correlated with these donor numbers.

It is fairly clear that the dissolution process arises from a competition between lattice energy and solvation energy, the latter being positively influenced by a high dielectric constant. However, it is not clear at the outset which parts of the structure will be disconnected or which parts of the structure will remain intact. One could have imagined further decomposition, breaking Mo–Mo bonds, to Mo_3 or even smaller units. In this paper we are going to propose and prove the hypothesis that besides solvation/lattice energy competition the reactivities, acidities, and basicities of the *bonds* strongly influence the solvation and disconnection behavior.

It appears that a qualitative theory covering the chemical tendencies in solubility is not available. Such a theory has to explain both why (i) the AMo_3X_3 structure is decomposed into "Mo_3Se_3" and "A" species and why (ii) there are such striking differences between compounds containing different electropositive metal atoms. On the basis of the recently proposed concept of atomic or bond reactivities, acidities, and basicities in solid-state structures, we will show that all good solvents (inherently being strong Lewis bases) attack the most *acidic* bonds within the AMo_3X_3 structure type first. [What is meant by the expression "acidic bond" (or "basic bond") will be developed and explained in section 3.] As a result, the structure is physically decomposed at spatial regions of high acidity. Interestingly, there is no a priori theorem stating that these regions automatically coincide with regions of "weak" bonds.

The plain result of the dissolution experiments is that those parts in Figure 1 which are connected with lines ("bonds" between Mo and X atoms) remain attached in solutions while others (no "bonds" between X and A) separate. It is certainly true that Figure 1 is in accordance with an inorganic chemist's intuition. However, one can imagine a quite different representation where the main emphasis is put onto the A–X bonds, for example. How much reality is there in such a representation? In this paper we will also see whether a possible decomposition of the structure into "Mo" and "A–X" fragments could be realized as well.

Table I. Lattice Parameters[8] and Positional Parameters[3] of AMo_3X_3 Phases

compd	*a* (pm)	*c* (pm)
$LiMo_3Se_3$	851.3	448
$NaMo_3Se_3$	862.9	447.9
$NaMo_3Te_3$	923.7	461.3
KMo_3Se_3	902.2	448.1
KMo_3Te_3	959.7	460.0
$InMo_3Se_3$	885.1	449.7
$InMo_3Te_3$	934.2	459.1

atom	Wyckoff posn	*x/a*	*y/b*	*z/c*
A	6*h*	$^2/_3$	$^1/_3$	$^1/_4$
Mo	2*d*	0.1886	0.1540	$^1/_4$ (if X = Se)
Mo	2*d*	0.179	0.141	$^1/_4$ (if X = Te)
Se	2*d*	0.0698	0.3708	$^1/_4$
Te	2*d*	0.071	0.371	$^1/_4$

3. Theory

The work of Parr and Pearson[14,15] offers a possible way to quantify the Lewis acid–base concept by means of an accurate quantum-mechanical description of ground-state properties of finite and infinite molecules. According to density-functional theory[16,17] the so-called *absolute hardness* η is proportional to the second derivative of the ground-state energy E^0 with respect to the particle (electron) number N at the ground-state particle number N_0, namely

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{N^0} \tag{1}$$

If applied to finite molecules, η can be expressed as

$$\eta \approx {}^1/_2(I - A) \tag{2}$$

where I and A stand for ionization potential and electron affinity, respectively.[18] For stable systems, η turns out to be a *positive* energy. The higher the absolute hardness, the more *resistant* the chemical species with respect to electronic perturbations. Therefore, inert molecules have large positive η values whereas reactive ones have small positive values. A molecule with a *negative* hardness will decompose into charged pieces.

More generally, the absolute hardness may be calculated using the three-point finite-difference formula

$$\eta \approx {}^1/_2(E^+ + E^-) - E^0 \tag{3}$$

easily applicable to solid-state materials. An accurate partitioning scheme of the absolute hardness into atomic or bond *reactivity increments* ξ has been presented recently,[19] according to

$$\eta \equiv \sum_{R} \xi_R \tag{4}$$

where R stands for the atoms within the primitive unit cell used for the electronic structure calculation.

Using some simplifications that suppress (small) electronic relaxation of deep-lying levels, a simplified gross *atomic reactivity*

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Table II. Nearest Interatomic Distances (pm) in AMo_3X_3 Phases[a]

	$LiMo_3Se_3$	$NaMo_3Se_3$	$NaMo_3Te_3$	KMo_3Se_3	KMo_3Te_3	$InMo_3Se_3$	$InMo_3Te_3$
a(Mo–Mo, 2×)	256	260	261	272	272	267	264
b(Mo–Mo, 4×)	269	270	276	274	278	272	276
c(Mo–X, 1×)	251	254	270	266	280	261	273
d(Mo–X, 1×)	252	256	276	267	286	262	279
e(Mo–X, 2×)	265	266	283	270	287	269	283
f(A–X, 6×)	328	330	347	338	354	335	348
g(A–X, 3×)	328	333	357	348	371	341	361

[a] Due to the fact that above distances have been calculated using the refined positional parameters of $TlMo_3Se_3$ and $TlMo_3Te_3$ according to Hönle et al.[3] and the published lattice constants reported by Tarascon et al.,[8] the standard deviations of the interatomic distances are probably around 3–5 pm.

Table III. EH Energy Parameters for AMo_3X_3 Phases[a]

atom	orbital	H_{ii} (eV)	ζ_1	C_1	ζ_1	C_2
Li	2s	–9.00	0.70			
	2p	–8.00	0.70			
Na	3s	–8.50	0.82			
	3p	–6.25	0.82			
K	4s	–4.34	0.87			
	4p	–2.73	0.87			
In	5s	–12.60	1.90			
	5p	–6.19	1.68			
Mo	5s	–8.34	1.96			
	5p	–5.24	1.90			
	4d	–10.50	4.54	0.6097	1.90	0.6097
Se	4s	–20.50	2.44			
	4p	–14.40	2.07			
Te	5s	–20.80	2.51			
	5p	–14.80	2.16			

[a] The coefficients used in the double-ζ expansion of the d orbitals are designated with *C*. the ζ's are the Slater-type orbital exponents.

increment $\tilde{\xi}_R$ may be written as

$$\tilde{\xi}_R \approx {}^1/_2 \sum_{\mu \in R} \{h_{\mu\mu}\Big(\int_{\epsilon_F^0}^{\epsilon_F^-} P_{\mu\mu}(\epsilon)\,d\epsilon - \int_{\epsilon_F^+}^{\epsilon_F^0} P_{\mu\mu}(\epsilon)\,d\epsilon\Big) + \sum_{R'} \sum_{\nu \in R'} h_{\mu\nu}\Big(\int_{\epsilon_F^0}^{\epsilon_F^-} \mathcal{R}[P_{\mu\nu}(\epsilon)]\,d\epsilon - \int_{\epsilon_F^+}^{\epsilon_F^0} \mathcal{R}[P_{\mu\nu}(\epsilon)]\,d\epsilon\Big)\} \quad (5)$$

while a corresponding *bond increment* reads

$$\tilde{\xi}_{RR',\mathrm{bond}} \approx {}^1/_2 \sum_{\mu \in R} \sum_{\nu \in R'} h_{\mu\nu}\Big(\int_{\epsilon_F^0}^{\epsilon_F^-} \mathcal{R}[P_{\mu\nu}(\epsilon)]\,d\epsilon - \int_{\epsilon_F^+}^{\epsilon_F^0} \mathcal{R}[P_{\mu\nu}(\epsilon)]\,d\epsilon\Big) \quad (6)$$

μ and ν are the atomic orbitals in the LCAO expansion of the crystal orbitals:

$$\phi_j(\vec{k}) = \sum_T e^{i\vec{k}\vec{T}} \sum_R \sum_{\mu \in R} c_{\mu j}(\vec{k})\varphi_\mu \quad (7)$$

h and $P(\epsilon)$ stand for the one-electron Hamiltonian matrix elements and the energy-resolved one-electron density matrix, respectively. If restricted to the non-spin-polarized case and k-averaged over the whole Brillouin zone, the latter can simply be expressed as

$$P_{\mu\nu}(\epsilon) = \sum_j n_j c_{\mu j}^* c_{\nu j} \delta(\epsilon - \epsilon_j) \quad (8)$$

$\mathcal{R}$ stands for the real part of a matrix element that in principle can be complex. The ϵ_F's represent the slightly varying Fermi energies up to which the energy integrations have to be carried out.

The reader will note that in these increments we have essentially defined an *energy partitioning*, either by atoms or by bonds. The contributions are products of energies (Hamiltonian matrix elements) and density matrix elements. Since the h's are related to overlaps in simplified bonding theories, these decompositions are also related to Mulliken gross and overlap populations, expressed as various sums of $c_\mu c_\nu S_{\mu\nu}$.

Table IV. EH Total Energies, Electrophilic and Nucleophilic Energy Changes, and Absolute Hardnesses of AMo_3X_3 Phases

compd	E (eV)	ΔE^{ele} (eV)	ΔE^{nuc} (eV)	η (eV)
$LiMo_3Se_3$	–549.485	–9.392	10.250	0.429
$NaMo_3Se_3$	–548.483	–9.439	10.255	0.408
$NaMo_3Te_3$	–556.391	–9.543	10.341	0.399
KMo_3Se_3	–545.215	–9.596	10.287	0.345
KMo_3Te_3	–553.291	–9.682	10.367	0.342
$InMo_3Se_3$	–567.550	–9.253	9.532	0.139
$InMo_3Te_3$	–575.773	–9.335	9.533	0.099

To elucidate further acid–base behavior within the solid state a set of atomic and bond *increments for electrophilicity and nucleophilicity* can be set up.[19] For example, a simplified *atomic electrophilicity increment* $\tilde{\xi}_R^{ele}$ may be formulated as

$$\tilde{\xi}_R^{ele} = \sum_{\mu \in R} \{h_{\mu\mu} \int_{\epsilon_F^0}^{\epsilon_F^-} P_{\mu\mu}(\epsilon)\,d\epsilon + \sum_{R'} \sum_{\nu \in R'} h_{\mu\nu} \int_{\epsilon_F^0}^{\epsilon_F^-} \mathcal{R}[P_{\mu\nu}(\epsilon)]\,d\epsilon\} \quad (9)$$

whereas a *bond electrophilicity increment* is given by the formula

$$\tilde{\xi}_{RR',\mathrm{bond}}^{ele} = \sum_{\mu \in R} \sum_{\nu \in R'} h_{\mu\nu} \int_{\epsilon_F^0}^{\epsilon_F^-} \mathcal{R}[P_{\mu\nu}(\epsilon)]\,d\epsilon \quad (10)$$

All atomic electrophilicity increments add up to the *electrophilic energy change* ΔE^{ele}, defined as

$$\Delta E^{ele} \approx E^- - E^0 \equiv \sum_R \xi_R^{ele} \quad (11)$$

while the atomic nucleophilicity increments add up to the *nucleophilic energy change* ΔE^{nuc}:

$$\Delta E^{nuc} \approx E^+ - E^0 \equiv \sum_R \xi_R^{nuc} \quad (12)$$

The definitions for the corresponding nucleophilicity increments are formally identical and can be obtained from the electrophilic ones simply by replacing the varying Fermi energy ϵ_F^- by ϵ_F^+.

It can be shown[19] that there exists a relationship between reactivity increments and increments of electrophilicity and nucleophilicity which reads

$$\xi_R = {}^1/_2(\xi_R^{ele} + \xi_R^{nuc}) \quad (13)$$

for the atoms and, consequently

$$\xi_{RR',\mathrm{bond}} = {}^1/_2(\xi_{RR',\mathrm{bond}}^{ele} + \xi_{RR',\mathrm{bond}}^{nuc}) \quad (14)$$

for the bonds, thereby linking reactivity with acid–base behavior.

With reference back to eqs 10 and 14, how can a chemical bond be "acidic"? After all, it has electrons in it, and does not that make it inherently basic? In general, this is *not* the case. Inspection of eq 10 reveals that a bond increment of electrophilicity, for example, is set up as a product of Hamiltonian matrix elements $h_{\mu\nu}$ and the real part of the difference in *all* "off-site" electron charge densities $\mathcal{R}[P_{\mu\nu}(\epsilon)]$ while moving between two

Table V. Bond Energies (eV) in AMo_3X_3 Phases

	$LiMo_3Se_3$	$NaMo_3Se_3$	$NaMo_3Te_3$	KMo_3Se_3	KMo_3Te_3	$InMo_3Se_3$	$InMo_3Te_3$
a(Mo–Mo, 2×)	-5.722	-5.633	-5.830	-5.298	-5.495	-4.982	-5.255
b(Mo–Mo, 4×)	-3.798	-3.895	-3.794	-4.185	-4.040	-3.827	-3.777
c(Mo–X, 1×)	-8.079	-7.778	-7.050	-7.058	-6.324	-7.489	-6.955
d(Mo–X, 1×)	-7.553	-7.316	-7.755	-6.774	-7.234	-6.627	-7.304
e(Mo–X, 2×)	-5.649	-5.755	-5.956	-6.582	-6.685	-5.745	-6.167
f(A–X, 6×)	-3.449	-3.344	-3.287	-1.401	-1.572	-2.061	-1.950
g(A–X, 3×)	-3.668	-3.530	-4.120	-1.528	-2.003	-2.314	-2.821

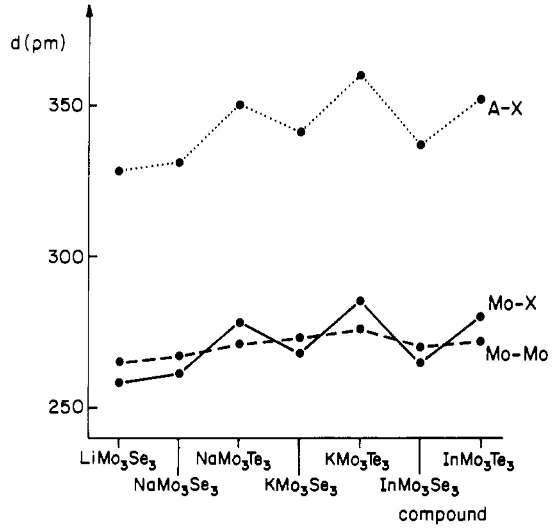


Figure 2. Average Mo–Mo, Mo–X, and A–X internuclear distances (pm) in AMo_3X_3 phases.

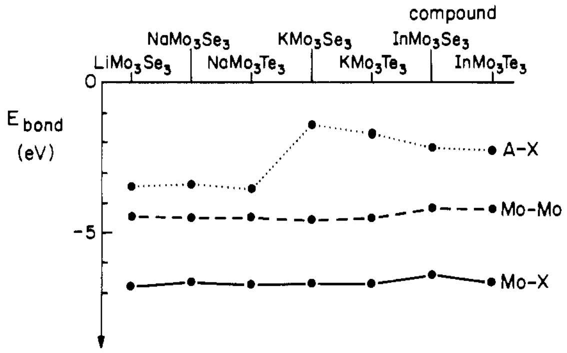
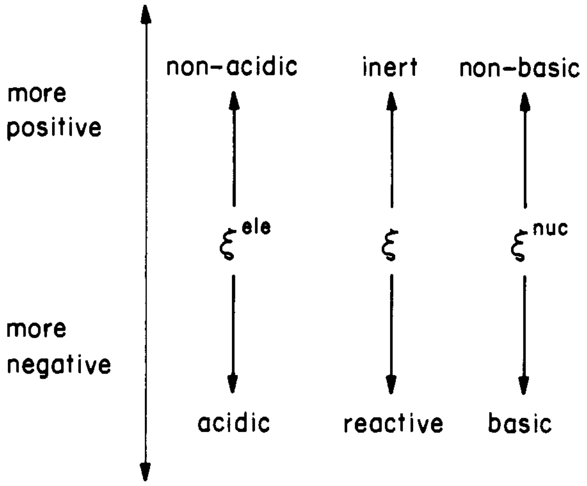


Figure 3. Average Mo–Mo, Mo–X, and A–X bond energies (eV) in AMo_3X_3 phases.

slightly different electron populations. Therefore, while a *single* bonding contribution (s–p, p–p, p–d, etc.) may contain some basic character, the *total electronic interaction* between two atoms (their "connectivity") might be acidic as well as basic.

Indeed, if the connectivity of two atoms involves high-lying, occupied *and* antibonding levels, their bonding will be basic in nature, for the electronic interaction between these atoms will become stronger by *releasing* (donating) *electrons* (partial charge). On the other hand, a highly acidic "bond" will be detected by the electrophilicity increment if there are still some unoccupied levels with bonding character, making this bond a possible *electron acceptor*. Perhaps the best way to avoid reaching a contradiction with our intuition that a bond must be inherently basic is to realize that the sense in which the word bond is used here is a little different from our normal conception. Our use of bond refers to a pairwise partitioning of the total energy of the molecule or what RR′ contributes to the total energy. There is no implication that there is a pair of electrons shared between R and R′. The bonding situation between R and R′ might be electron-poor, or electron-precise, or electron-rich. In a sense our set of increments reveals which type of bonding one has.

In general, due to the fact that all hitherto defined increments are based on total energy calculations, the lower the increments (which are energy values measured in eV), the higher the reactivity, acidity, or basicity. A highly reactive (acidic, basic) atom or bond is easily detected from a large associated *negative* increment of reactivity (electrophilicity, nucleophilicity). On the contrary, an atom or bond showing no sign of reactivity (acidity, basicity) is characterized by a large *positive* increment of reactivity (electrophilicity, nucleophilicity). The following scheme summarizes graphically the trends:



With the help of these increments it is possible, in principle, to characterize local spatial regions within a crystal structure as possible *targets* for electrophilic or nucleophilic attack.

Even using a highly simplified quantum mechanical method of calculation for the solid state such as EH theory, reactive, acidic, or basic regions within extended structures can be visualized quite easily.[19] A generalization to possibly more accurate ab-initio methods has already been derived in a straightforward way.[19]

4. Calculational Results

To compute bond energies and bond increments of reactivity, electrophilicity, and nucleophilicity we undertook three-dimensional tight-binding electronic structure calculations with the help of the extended Hückel approximation.[20-22] The empirical energy parameters, taken from the compilation of Alvarez,[23] may be found in Table III. The lattice parameters were taken from the low-temperature compilation of Tarascon et al.,[8] whereas the refined positional parameters of the A, Mo, and X atoms are based on the structure refinements of Hönle et al.[3] They show the lowest residual factors both for $TlMo_3Se_3$ and $TlMo_3Te_3$. The space group is $P6_3/m$ (C_{6h}^2), No. 176, and the unit cell contains two formula units. As can be seen from Table I, only the Mo and X atoms, both belonging to Wyckoff position 2*d*, vary a little in the positional parameters. The electropositive atoms are fixed on Wyckoff position 6*h*, which is a guess only for the $LiMo_3Se_3$ phase, for which an accurate refinement is missing up to now.

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Table VI. Simplified Bond Reactivity Increments $\tilde{\xi}_{RR',\mathrm{bond}}$ (meV) in AMo_3X_3 Phases

	$LiMo_3Se_3$	$NaMo_3Se_3$	$NaMo_3Te_3$	KMo_3Se_3	KMo_3Te_3	$InMo_3Se_3$	$InMo_3Te_3$
a(Mo–Mo, 2×)	122	116	109	102	98	–65	–140
b(Mo–Mo, 4×)	102	101	116	97	113	75	116
c(Mo–X, 1×)	51	45	60	40	54	3	15
d(Mo–X, 1×)	27	33	19	38	24	51	10
e(Mo–X, 2×)	–15	–26	–42	–52	–59	–87	–52
f(A–X, 6×)	7	7	9	9	12	116	118
g(A–X, 3×)	–8	–9	–14	–11	–15	42	–40

Using above-mentioned geometrical parameters, all important internuclear distances could be calculated.[24] These are shown in Table II.

With reference to Figure 1, there are seven important internuclear distance types which we will call *a–g*. Types *a* and *b* are Mo–Mo contacts, types *c–e* are Mo–X contacts, and types *f* and *g* are A–X contacts. To simplify the discussion we will from now on *average* these bond distances to yield *characteristic* Mo–Mo, Mo–X, and A–X bond distances. On the basis of the multiplicity of the bonds, a characteristic Mo–Mo bond length is given as $^1/_6(2a + 4b)$, whereas for the case of the characteristic Mo–X bond it is $^1/_4(1c + 1d + 2e)$. Trivially, for the characteristic A–X bond we have $^1/_9(6f + 3g)$. Since we want to treat the Mo–Mo, Mo–X, and A–X bonding substructures as separate entities, this averaging procedure will be continued in the electronic structure part, too.

In order to make the trends in bond lengths as clear as possible, Figure 2 shows the course of the average Mo–Mo, Mo–X, and A–X bond distances while going through the series of the AMo_3X_3 compounds. Remember that the computed values are based on the specific bond lengths in Table 2.

From Figure 2 several different conclusions can be drawn. First, the characteristic Mo–Mo bond length increases smoothly from 265 to 276 pm in order from the Li compound to the K compounds and decreases a little to 272 pm at the In compounds. Obviously, Mo–Mo bonding is not very strongly influenced by changes in the A and X composition. The Mo–X bond lengths, however, show a characteristic zigzag pattern around 271 pm between the Se and Te compounds. While the average Mo–X bond lengths have the same trend as the Mo–Mo bond lengths in going through the series, Mo–Se bonds are about 16 pm shorter than Mo–Te bonds, in good agreement with the difference in Pauling covalent radii, which is 20 pm.[25] The zigzag pattern is even easier to recognize for the A–X bonds which lie around 343 pm, and the difference between A–Se and A–Te bonds is approximately 18 pm.

We come to the electronic structure calculations. A total number of 28 *k*-points within the irreducible wedge of the Brillouin zone was used to calculate average properties. The resulting total energies and electrophilic and nucleophilic energy changes as well as the absolute hardnesses can be found in Table IV. Despite the fact that no clear trend can be recognized for the total energies, the absolute hardness values give a clear hint of "softening" of the compounds' electronic *resistance* (see section 3). In the order from $LiMo_3Se_3$ to $InMo_3Te_3$, the absolute hardness η decreases continuously from about 0.43–0.10 eV. Although all the compounds are metallic (at least at room temperature), the softening can be explained by the intensification of covalent bonding along the series Li, Na, K, and In. Consequently, the Te compounds are always less "hard" than the Se compound. This argument can be strengthened by keeping in mind that, for insulators, the hardness is half the band gap,[18,19] and the latter is widened by greater ionicity.

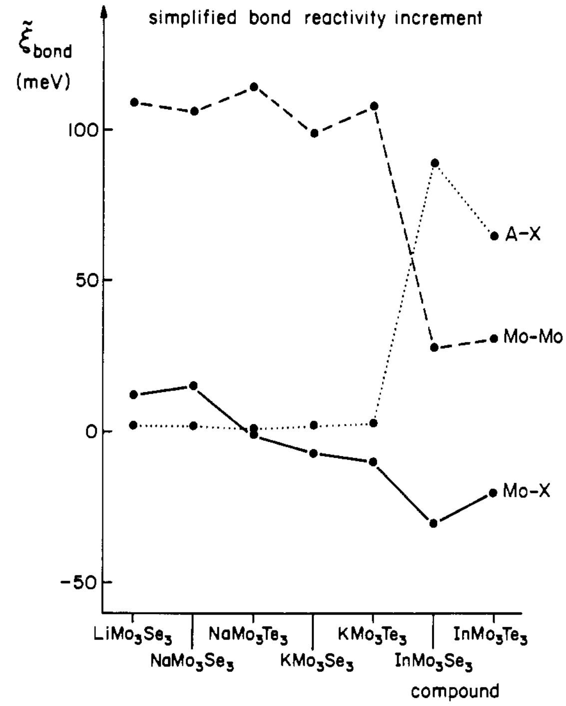

Figure 4. Average Mo–Mo, Mo–X, and A–X simplified bond reactivity increments (meV) in AMo_3X_3 phases.

A detailed analysis of the bond energies within the one-electron approximation, namely the expression

$$E_{RR'} = \sum_{\mu \in R} \sum_{\nu \in R'} \int^{\epsilon_F^0} h_{\mu\nu} \mathcal{R}[P_{\mu\nu}(\epsilon)]\, d\epsilon \qquad (15)$$

is given in Table V for all seven interatomic distances in the different compounds. A graphical representation can be seen in Figure 3, where characteristic *average* bond energies for the Mo–Mo, Mo–X, and A–X combinations are depicted, calculated according to the recipe for the average bond lengths presented before. Interestingly, we find very smooth curves both for the Mo–Mo bonds (–4.42 ± 0.21 eV) and for the Mo–X bonds (–6.66 ± 0.26 eV). So the metal–nonmetal bonds are about 1.5 times "stronger" than the metal–metal bonds. However, no zigzag pattern is visible. On the contrary, the zigzag pattern in the bond lengths leads to a remarkable constancy in the bond energies. The comparatively "weak" A–X "bonds" (–2.58 ± 1.13 eV), on the other hand, show a sharp decrease in bond energy for the K compounds (reduced by ≈2.1 eV), becoming smaller again for the In phases. This is an unexpected finding, showing that the local geometry (which is mainly dominated by the global X–X van der Waals contacts) is most unfavorable for the case of the relatively large K cations. We stress that the relative strength of the A–X bonds *cannot* be well correlated with the solubility behavior. The *stronger* A–X bonds (Li–Se, Na–Se, Na–Te) are broken whereas the *weaker* (K–Se, K–Te) remain intact. Therefore, differences in bond energies are not responsible for the solubility order! There is another underlying reason responsible for the differences in "chemistry", which we will touch on in a moment.

A point that might be made here (noted by a perceptive reviewer) is that in the construction of usual bonding arguments,

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(24) Busing, W. R.; Masten, K. D.; Levy, J. A. ORFFE-3. ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, TN, 1971.

(25) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

Table VII. Simplified Bond Electrophilicity Increments $\tilde{\xi}^{\mathrm{ele}}_{\mathrm{RR',bond}}$ (meV) in AMo_3X_3 Phases

	$LiMo_3Se_3$	$NaMo_3Se_3$	$NaMo_3Te_3$	KMo_3Se_3	KMo_3Te_3	$InMo_3Se_3$	$InMo_3Te_3$
a(Mo–Mo, 2×)	325	309	300	266	263	132	23
b(Mo–Mo, 4×)	126	120	119	93	94	242	254
c(Mo–X, 1×)	6	1	13	11	29	−10	−13
d(Mo–X, 1×)	8	16	38	28	34	115	29
e(Mo–X, 2×)	211	190	121	137	87	−20	2
f(A–X, 6×)	−10	−8	−8	0	1	224	132
g(A–X, 3×)	−7	−12	−13	−15	−17	117	55

using overlap populations, one is best advised to compare the different systems at one and the same bond length. Here we compare the various structures at their real bond lengths, which differ. The justification for this is that our increments contribute to an energy partitioning, and it is appropriate to compare contributions to the total energy, which are made up of overlap population-like terms *multiplied* by Hamiltonian matrix elements.

In Table VI, the simplified bond reactivity increments $\xi_{\mathrm{RR',bond}}$ according to eq 6 are given. From these distinct values, *average* increments for Mo–Mo, Mo–X, and A–X bonds are shown in Figure 4. The scheme presented before might help the reader to follow the qualitative course of the three different increments defined so far. In becoming more *negative*, ξ, ξ^{ele}, and ξ^{nuc} indicate local reactive, acidic, and basic tendencies within a crystal. More *positive* values, however, show the tendency for inert, nonacidic, and nonbasic behavior.

The reader will note that values of the increments are small, and the differences between them are smaller. Nevertheless, in the spirit of a perturbation theoretic analysis, we believe that one can draw from these small numbers indications of real, chemically important differences.

A reactivity increment itself is the average over increments of electrophilicity and nucleophilicity (see eqs 13 and 14). Therefore, Figure 4 provides us with a kind of "amphoteric" increment. It is fairly clear that the Mo–Mo bonds are the least reactive bonds within the structure, as they, except for the case of the In phases, possess the largest positive reactivity increments. We do not expect the Mo–Mo bonds to be sensitive to slightly varying electronic conditions. One may well take the view that this fact is of major importance for the "survival" of the infinite Mo string, wrapped in an X cover, during its reaction with the highly polar solvents.

On the contrary, both Mo–X as well as A–X bonds (except the case of the In phases) show small positive or even negative reactivity increments. So indeed these bond types form the reactive internal regions of the structure. Moreover, it is noteworthy that the reactivity increments give a totally different description of the structure than the bond energies, as one can easily understand by comparing Figure 3 with Figure 4.

Finally, to elucidate the solubility behavior, we break the amphoteric reactivity increments down into increments of electrophilicity and nucleophilicity. In Table VII we give the simplified bond electrophilicity increments $\tilde{\xi}^{\mathrm{ele}}_{\mathrm{RR',bond}}$, calculated according to eq 10, for the seven bond types *a*–*g*. For convenience, *averaged* values have been drawn in Figure 5. The heterogeneity in the bonds' acidic character is astonishing. First, the Mo–Mo bonds are not acidic at all since they always have highly positive increments. Second, the Mo–X bonds display a nearly continuous increase in acidity in going from the Li phase to the In phases. With the exception of the In phases, however, the Mo–X bonds do not represent the most acidic bonds. These are, indeed, the A–X bonds that incorporate Li, Na, K on the one side and Se, Te, on the other. Of course, such local "islands of acidity" have a strong tendency to react with Lewis bases—in perfect agreement with the solution experiments! As already mentioned in section 2, "good" solvents for the AMo_3X_3 family are equally strong Lewis bases, having high donor numbers. *So the event of solvation appears to be started by a solid-state liquid-state donor–acceptor acid–base reaction, and the A–X bonds represent the "targets" for the nucleophilic solvents.*

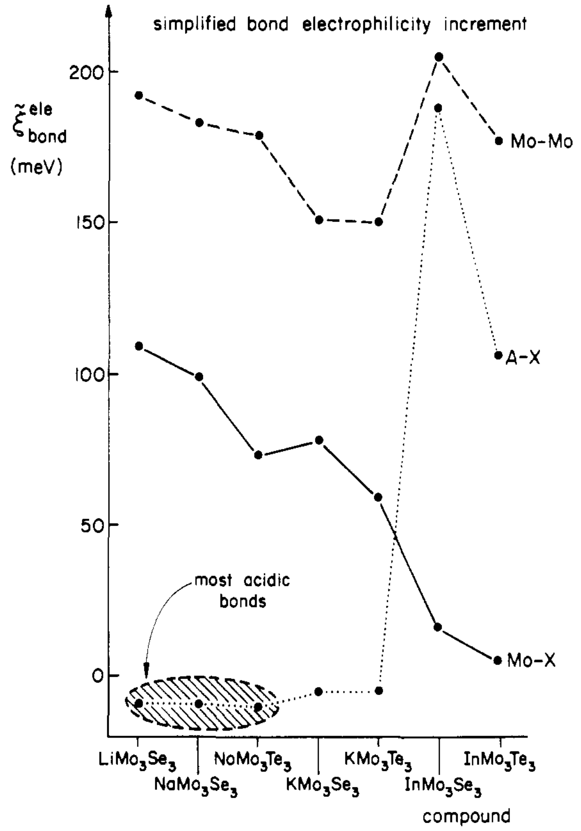

Figure 5. Average Mo–Mo, Mo–X, and A–X simplified bond electrophilicity increments (meV) in AMo_3X_3 phases.

Moreover, the compounds $LiMo_3Se_3$, $NaMo_3Se_3$, and $NaMo_3Te_3$, easily dissolved by Lewis bases, have the largest negative A–X bond electrophilicity increments, as expected. The values of the K compounds, although already more positive (less acidic), seem to appear too negative. Yet KMo_3Se_3 and KMo_3Te_3 *cannot* be brought into solution. Perhaps this is a sign that the extended Hückel parameters for K need further modification. In general the extended Hückel method has difficulties with the alkali metals. There is great difference between the wave functions and ionization potentials of s and p electrons in M or M^+ and some arbitrariness in the choice of the extended Hückel parameters. For the In compounds, however, no acidic bonds are detected, in accordance with experiment.

Is there an alternative solubility behavior? We think so. Table VIII gives the simplified bond nucleophilicity increments of all the bonds. These have been *averaged* and sketched in Figure 6. The basic character of the Mo–Mo bonds (except those within In phases) is still the weakest of all. Likewise, the A–X bonds appear to be hardly basic—of course they *cannot* be so, as they proved to be the most acidic! On the contrary, all Mo–X bond nucleophilicity increments are strongly negative, indicating these bonds are highly basic. We propose that these "islands of basicity" should be easily attacked by a strong Lewis acid. Keeping in mind that such a solvent should both have a high Gutmann acceptor number AN[13] (strong acidity) and a high dielectric constant (giving rise to a high solvation energy), we believe that trifluoromethanesulfonic acid CF_3SO_3H (AN ≈ 129.1) or antimony pentachloride in 1,2-dichloroethane (AN ≈ 100.0),[13]

Table VIII. Simplified Bond Nucleophilicity Increments $\tilde{\xi}^{nuc}_{RR',bond}$ (meV) in AMo_3X_3 Phases

	$LiMo_3Se_3$	$NaMo_3Se_3$	$NaMo_3Te_3$	KMo_3Se_3	KMo_3Te_3	$InMo_3Se_3$	$InMo_3Te_3$
a(Mo–Mo, 2×)	−82	−77	−81	−62	−66	−263	−302
b(Mo–Mo, 4×)	78	82	113	101	132	−92	−21
c(Mo–X, 1×)	96	89	108	68	80	16	42
d(Mo–X, 1×)	45	50	1	48	13	−14	−8
e(Mo–X, 2×)	−242	−243	−204	−241	−205	−154	−105
f(A–X, 6×)	23	21	26	18	23	8	105
g(A–X, 3×)	−10	−7	−15	−6	−12	−34	−136

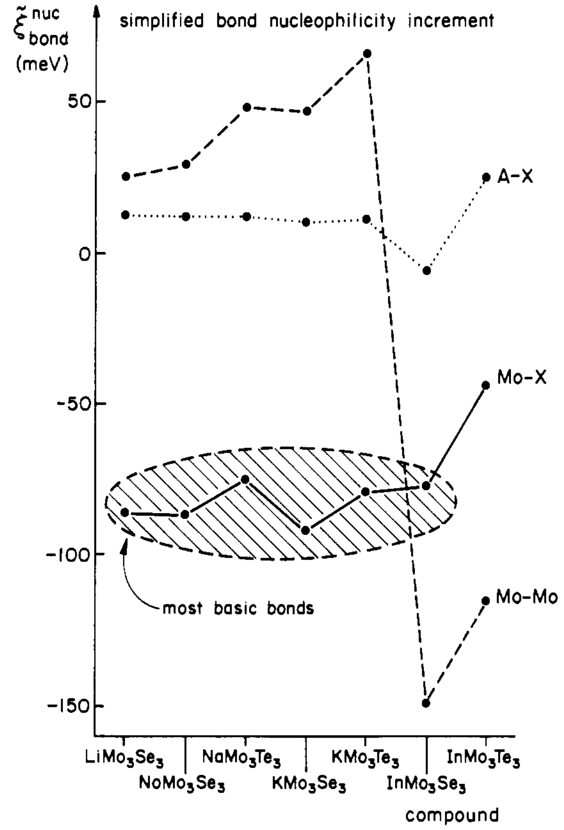

Figure 6. Average Mo–Mo, Mo–X, and A–X simplified bond nucleophilicity increments (meV) in AMo_3X_3 phases.

providing a high dielectric constant, could be promising reagents for "luring" the infinite Mo string out of its wrapping by X atoms. Of course, the detailed calculation of an actual solvation process lies far beyond our present approach. However, we want to stress that the Mo–X bonds are reasonable targets for acidic solvents, and they will be attacked first. Such a hypothesis can by no means be "extracted" from the static graphical representation of the AMo_3X_3 structure type in Figure 1.

To summarize, we have investigated the degree of bonding, reactivity, and acid–base behavior within the AMo_3X_3 family by means of electronic structure calculations. A bond-energy order of the form Mo–X > Mo–Mo > A–X is found, in accordance with typical graphical presentation and chemical preconceptions. Concerning reactivity, only Mo–X and A–X bonds but not Mo–Mo bonds, which appear to be highly inert, stand out. By the breaking down of reactivity into acidity and basicity, the solubility behavior of these compounds is rationalized in terms of the A–X bonds' strong acidities, which fit perfectly the basicity of the polar solvents. On the contrary, the highly basic character of all the Mo–X bonds throughout the series gives rise to the assumption that these bonds could be attacked (and probably be broken) by highly acidic solvents, eventually releasing a purely metallic chain that might condense with others, forming colloidal metal particles.

In general our calculations point to an a priori way to design directed reactions using solid-state compounds. Such an approach, well known in organic chemistry,[26] is desperately needed in solid-state chemistry. Moreover, the typical graphical representation of a solid-state compound, while it may bear structural truths, should not be indiscriminately used as a predictor of reactivity. It depends on the reaction.

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