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Intermetallic Studies and Bonding Concepts

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This essay for EurJIC's cluster issue on polar intermetallics, clusters and cluster complexes introduces the reader to the difficulties in finding new and novel intermetallics among a wide variety of possibilities, inasmuch as most of the elements of the periodic table are metals. Like metal atoms may form naked clusters or be differently charged, such as Zintl cations or polyanions. Discrete clusters may also be incorporated as building blocks in polar intermetallics or be condensed into infinite one-, two-, or three-dimensional arrays. In all cases, it is important to explore the unknown before (physical) properties can be measured and applications come into view.

What a wonderful collection of articles the editors have assembled! The heavy emphasis on the new or growing areas of solid-state chemistry that concern metal compounds, clusters, intermetallics, and related materials is perfect. Overall, one can discern continued evolution of some areas of research that date "from the beginning", others that have developed anew and matured over the interim years, broadening our perspectives, capabilities, and understanding, and still other research directions that are still in their infancy. And my perspectives or bias certainly enter into sorting through these too.

Fifty years ago it was difficult to focus and readily "find gold" in this area because so many systems and principles were unexplored, some binary systems included, and there was even some uncertainty as to what you were looking for in this brave new world and why. ("What properties will these new compounds have?" – really!) New metal–halogen cluster systems discovered for earlier transition elements were also more diverse than those in the traditional niobium and molybdenum families, principally because these were all stabilized by a range of interstitial atoms, mostly our impurities in the early days. These additional variables also allowed many of the new rare-earth–metal-halide systems (and others) to be condensed into a variety of metal-rich arrays and networks, and such discoveries continue today. Substitutions of more conventional ligands in the exo positions on such excised clusters were also achieved (by others) and thence new solution chemistry. On the other hand, pertinent $ThCr_2Si_2$-type analogues of the earlier transition metals are only of a more recent vintage.

Zintl phases as they were understood years ago were a logical and a fairly productive research area, and once you thought more about phase stabilities, even the addition of mixed cations would give you new products. Extensions of real or imagined Zintl phase systems into molecular solvents, using "crypt" or crown ethers to sequester the cations, turned out to be simple entrées into what has grown into a major thrust, molecular (main group, mostly) clusters beyond one's imagination.[1] Novel results regarding solid-state Zintl phases and their near neighbors are to be found in this work and in the current literature. Some broader and generally electron-richer systems are found that span the transition metals, for example, ternary systems of an active metal, an early-to-late transition metal, and a post-transition main group metal or metalloid. The latter pairs of elements often generate large condensed networks that are stuffed by the cations, especially when these are in smaller proportions. The active-metal components of such ternary (or higher) systems also exert fairly regular effects on the symmetry (or complexity) of the polyatomic anionic frameworks; the lowest-field alkali-metal cations usually correspond to relatively higher symmetry structures and space groups compared with those that contain the increasingly smaller fractions of higher-field alkaline-earth or rare-earth metals in analogous networks of lower symmetry. A considerable variety of the more electronegative elements in such networks are also illustrated in the following manuscripts.

Systematic extensions of Zintl phases into electron-poorer systems, that is, those in which one or more of the more electronegative elements lies a little (or well) to the left of the Zintl border (between groups 13 and 14), takes us to a large number of basically unexplored systems and compounds therein, and new conceptual territory for many

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inorganic chemists. Early explorations suggest that the new products may entail a wide variety of electron- and spin-poor intermetallic phases with uncommon properties (for chemists), metallic phases that lack the usual valence rules and concepts together with quasicrystals and approximants, complex Hume–Rothery (and other?) electronic effects, and maybe the unpredictable. Strong interelement bonding is the rule, with relativistic gold (and others?) playing a strong and special role, and with the onset of delocalized metal–metal bonding that is evidenced by the higher heteroatomic coordination numbers that appear in the structures. It would appear that many of these opportunities have been left unexplored because these particular systems or regions do not afford good examples of useful properties, viz., higher temperature superconductivity, strong magnetic coupling, etc.

This type of effort fills our knowledge base systematically but at a very limited rate because of the large fraction of the periodic table that is still "dark". Blanket descriptions are not needed or perhaps wise, but enough coverage to afford useful generalities and good predictions is desired. Overall, we see a wide range of interests, needs, and opportunities among the attached articles, but the frequent orientation on application often results in poor breadth, or even spotty coverage of phase compositions. A simple example of breadth over broad ignorance follows my current interests, broadly speaking, the chemistry in major unknown areas in which the compounds are metallic, or synthesized from metals. A few discoveries therein that follow on quasicrystal-approximant interests illuminate some big holes, so to speak; numerous new phases for which there was no precedent for novelty. A simple consideration of phase space also suggests that limiting initial explorations to only ternary (plus lower-order) systems is necessary or highly desired: about 61 elements are stable metals, and even half of the independent ternary combinations still amount to ~1.1×10^4 systems! The simplest of searches would seem to require good control of stoichiometry and some painstaking care. The choice of metallic components emphasizes that chemistry and chemists will be unable or unwilling to predict bonding, structure, and so forth without a familiar nonmetal or metalloid to hang their hat on.

Some other problems also come to mind. How are current studies of isolated quaternary, even quinary, phases (loc cit) going to be usefully organized and used; just via search engines? Reactions in which there is poor, or no, control of stoichiometry seem to pose a general problem too. Do we need to know all or most of the phases in a given ternary, or would 50 or 75% do? And although the initial thought was that new structure and bonding features would be sufficient reason to search, this simplicity ignores the details of the many other properties and phenomena and, in the end, applications. Still the very existence of a phase would seem to be the minimum necessity. And some (or many) of these will be unprecedented, after which we can consider subsequent property and application studies.

Go and seek!

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[1] S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chem. Int. Ed.* **2011**, *50,* 3630-3670.