Solid-state chemistry of cluster compounds with metals in the left part of the periodic table is described. As a function of the metal valence electron concentration (VEC), characteristic changes occur with stepwise changing features. Strongly metal–metal-bonded and ligand-encapsulated clusters exist for large values of VEC. At decreased values, endohedral atoms stabilize the clusters, and with the lowest values, only clusters exist with no ligand shell. This general trend holds for systems with discrete, as well as condensed, clusters as illustrated for d metals, including the lanthanides, alkaline earth and alkali metals.

Keywords: clusters; condensed clusters; suboxides; subnitrides; hydride halides; rare earths

1. Introduction

Today, the term metal cluster is frequently used for entities containing a limited number of metal atoms, no matter whether these atoms are bonded to each other. In the following, the term will be used in its original meaning, as introduced by Cotton (1964), i.e. referring to units where an excess of metal valence electrons is involved in metal–metal ($M–M$) bonding. Particularly, metals on the left-hand side of the periodic table exhibit a unique solid-state cluster chemistry. These metals become increasingly less electropositive and valence electron poor the further left they are, resulting in a stepwise change of cluster character. Starting with transition metals in groups 7–5, the number of electrons available for $M–M$ bonding is large, and a plethora of clusters with strongly bonded $M_n$ cores surrounded by non-metal atoms is known. Also, with metals of groups 4 and 3, including the lanthanides, a rich chemistry of $M–M$-bonded compounds exists. Clusters of the rare earth (RE) metals are still entirely encapsulated by non-metal atoms, and thus enclosed in an ionic shell; however, they need to be stabilized by endohedral atoms, and the bonding to the endohedral atoms is also heteropolar. A drastic change comes when we move on to cluster compounds of groups 2 and 1 metals. Now, the metal atoms arrange around non-metal atoms, and the encapsulation is lost. Along the line described, the characteristic features of the clusters change from a metal atom core with heteropolar bonding...
to the outside, via heteropolar bonding to both inside and outside, finally to heteropolar bonding only to the inside. Thus, $M$–$M$ bonding is turned from inside to outside.

So far, the focus has been on discrete clusters and the consequence of decreasing metal valence electron concentration (VEC). A second systematic change originates from ligand deficiency. An incomplete encapsulation of the $M_6$ core by ligands results in cluster condensation via $M$–$M$ bonds between adjacent clusters. Such condensed cluster phases comprise oligomers as well as one-dimensional, two-dimensional and three-dimensional interconnected systems. An impressive number of metal-rich phases of transition metals with $p$ elements exhibit structures to be described within this concept (Simon 1981). Whereas the cluster cores are empty at a sufficiently large VEC, the combined ligand and electron deficiency leads to an occupation of the cluster cores by endohedral atoms, as in the case of discrete clusters. One meets the scenario nearly exclusively in the extended new chemistry of metal-rich halides of the RE elements. It is no surprise that such condensation also occurs with the bare clusters of metals of groups 1 and 2.

The ideas outlined above have been illustrated with a multitude of examples originating from quite different sources (Simon 1995). Here, the short review focuses on a few representatives selected from a vast number of compounds. The review covers some textbook knowledge, as well as recent results that corroborate the above ideas and add new facet to chemistry of discrete and condensed clusters in solids. The selection is mainly limited to clusters based on or derived from octahedral $M_6$ units for the sake of simplicity.

### 2. Ligand-encapsulated clusters

In his pioneering work, Brosset (1945) showed that divalent molybdenum forms a cluster $[\text{Mo}_6\text{Cl}_4^{8+}]$ that consists of an octahedral Mo$_6$ core surrounded by Cl atoms above all faces. Some years later, similar hexanuclear clusters, $[\text{Nb}_6\text{Cl}_2^{12+}]$ and $[\text{Ta}_6\text{Cl}_2^{12+}]$, were identified with all 12 edges of the octahedron being coordinated by Cl atoms (Vaughan et al. 1950). The two prototypes of hexanuclear clusters are shown in figure 1a,b.

In the nomenclature of Schäfer & Schnering (1964), the Cl atoms are marked as $X^i$-type. Additional $X^a$-type atoms coordinate the corners of the octahedron. A large number of compounds are derived from these characteristic units, e.g. via ligand exchange. A visual description of chemical bonding was developed early on by Kettle (1965): with ligands above the eight faces of the octahedron, two-centre-two-electron bonds are formed along the 12 edges, and in the case of 12 ligands above the edges, three-centre-two-electron bonds into the eight faces exist. As the $M$–$M$ bonds share a metal-to-ligand antibonding contribution, the cluster VEC frequently deviates from the closed-shell configurations of 24 and 16 electrons, respectively, depending particularly on the type of ligands.

Drastic electron deficiency creates a qualitatively new feature. The cluster cores incorporate additional atoms forming strong heteropolar bonds with the surrounding $M$ atoms at the expense of the weak $M$–$M$ bonding. A first example (Simon 1967) was found with Nb$_6$I$_{11}$, whose structure is made up of $[M_6X_8]$-type clusters interconnected according to $[\text{Nb}_6\text{I}_8]\text{I}_{6/2}$. The low value of VEC = 19 is

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the reason for a reversible incorporation of a hydrogen atom into the cluster centre, see figure 1c. Formally, the H atom adds one electron to the cluster, but actually it acts as an acceptor forming H\(^-\) (Fritsche et al. 1984). The then even electron number of the cluster changes the paramagnetic behaviour into non-magnetic at low temperature. The ‘voluntary’ uptake of an atom into the [Nb\(_6\)I\(_8^+\)] unit becomes a necessary condition for cluster formation with the neighbouring element zirconium, and a variety of compounds based on [Zr\(_6\)X\(_{12}\)] clusters, where Z comprising atoms of main group and transition elements is known (Corbett 1981). A particularly interesting case is found with the homologue thorium. In part, owing to its larger atomic size, the [M\(_6\)X\(_{12}\)]-type cluster is overcrowded with seven hydrogen atoms in [Th\(_6\)Br\(_{12}\)H\(_3^+\)], each providing one electron to the cluster (Braun & Simon 1996). This reaches the ‘magic’ electron count 16. Recalling the description of M–M bonding in the [M\(_6\)X\(_{12}\)]-type cluster in terms of eight electron pairs in the octahedral faces, the H\(^-\) ions represent a kind of colouring of these multi-centre bonds, see figure 1d. One molecule H\(_2\) per cluster can be desorbed before the compound [Th\(_6\)Br\(_{12}\)H\(_5\)]Br\(_{6/2}\) decomposes into other phases. Proceeding to the RE metals, the electron deficiency is further increased. Yet, numerous compounds based on the [M\(_6\)X\(_{12}\)] topology are formed, provided the units are stabilized by endohedral atoms and additional electron donors outside the clusters. As a novelty, the cluster centres can also be occupied by molecular anions like the ethanide ion C\(_{6^-}\), e.g. in the Sc\(_6\)I\(_{12}\)C\(_2\) cluster (Dudis & Corbett 1987) shown in figure 1e. Through backbonding, the C–C distance is shortened to approximately 140 pm.

[M\(_6\)X\(_{12}\)Z]-type clusters are frequently present in metal-rich RE halides, but may not be immediately recognizable. The crystal structure of the ‘Al-contaminated monoiodide LaI\(_{Al_x}\)’ can be refined to \(R = 0.04\) with an NaCl-type structure on the basis of the Bragg reflections ignoring diffuse scattering effects. However, taking the observed spheres of diffuse scattering

**Figure 1. Clusters with octahedral M\(_6\) core:** (a) [Mo\(_6\)Cl\(_8\)], (b) [Nb\(_6\)Cl\(_{12}\)], (c) [Nb\(_6\)I\(_8\)H], (d) [Th\(_6\)Br\(_{12}\)H\(_7\)] and (e) [Sc\(_6\)I\(_{12}\)(C\(_2\))].
around the Bragg reflections into account, shown in figure 2a, together with the calculated intensities in figure 2b, a structure of Al-centred [La₆I₁₂Al] clusters in a uniform (not random) distribution is derived (figure 2c) and refined on the basis of measured intensities in the entire reciprocal space (Oeckler et al. 2005).

As long as the $M_6$ unit in a cluster compound is fully encapsulated by ligands above edges/faces and corners, the general feature of such an arrangement is that of sub-nano-sized pieces of a metal distributed in a dielectric matrix. This feature is schematically illustrated for the structure of $Nb_6F_{15} = [Nb_6F_{12}]F_{6/2}$ (Schäfer et al. 1965) in figure 3. The loading of the $Th_6$ octahedra by hydrogen in the isostructural compound $Th_6Br_{15}H_7$ (Braun et al. 1996) thus reminds us of the chemical behaviour of the bulk metal thorium, which can absorb a huge amount of the gas.

So far, entirely ligand-encapsulated clusters have been discussed. The $M-M$-bonded cores in the compounds are well separated, and hence semiconducting or insulating behaviour results. As a first step towards ligand deficiency,
one can remove the atoms in front of the corners of the \( M_6 \) octahedron. As long as the closed electronic configuration is preserved, the compounds are still semiconducting; however, electron deficiency may lead to electronic delocalization between clusters and metallic properties via charge transfer through appropriate ligands. Chevrel phases and the various phases based on the molybdenum chalcogenide cluster \([\text{Mo}_6\text{X}_8]\) serve as examples. A critical next step is the interconnection of adjacent \( M_6 \) cores via \( M-M \) bonding as a consequence of further ligand deficiency. The mode of interconnection varies from corner, via edge to face sharing. Corner sharing allows for one-dimensional, two-dimensional and three-dimensional \( M-M \)-bonded systems and occurs most abundantly with reduced Nb oxides (Köhler et al. 1992; Svensson et al. 1999). Edge sharing frequently occurs in trans-position leading to one-dimensional systems as in molybdenum oxides (McCarley 1990), but also two-dimensional systems are known with the examples of zirconium monohalides (Corbett 1981). An obvious way of interconnection via opposite faces is also frequently found in ternary molybdenum chalcogenides (Chevrel & Sergent 1986). Intermediates comprise oligomeric clusters formed from varying numbers of condensed \( M_6 \) units. It is amazing to see extremely close structural relationships in the chemistry of seemingly very different metals like, e.g. molybdenum and RE metals.

Figure 4 depicts some anionic oligomeric clusters as they are found in reduced oxomolybdates. They are based on the \([M_6X_{12}]\)-type cluster and are the starting members of a general series \( M_{4n+2}X_{6n+6} \), which contains linear oligomeric clusters, the largest observed being composed of five condensed \( M_6 \) octahedra, and which ends with the infinite polyanion \([\text{Mo}_4\text{O}_{6}^-]\). Taking into account the loss of three valence electrons when moving from Mo to RE, the formation of topologically similar clusters calls for a replacement of the oxygen by less electron demanding halogen atoms as ligands and stabilization of the clusters by endohedral atoms. Indeed, numerous carbide halides have been synthesized and structurally characterized, which contain the discrete \([\text{RE}_6\text{X}_{12}\text{C}_2]\) cluster, as well as oligomers formed from up to three such discrete units, which all contain \( \text{C}_2 \)

Figure 4. (a–c) Oligomeric \([\text{Mo}_{4n+2}\text{O}_{6n+6}]\) clusters for \( n = 2, 3, 5 \), as found in reduced oxomolybdates and (d,e) same type of clusters based on \( \text{C}_2 \)-centred octahedra in La carbide iodides.
units (Mattausch et al. 2006). Even the kind of connection between the clusters via bridging non-metal atoms is, in part, identical in these compound classes of Mo and RE.

The final member of the series of RE compounds, the infinite chain, e.g. in Gd$_4$I$_5$C$_2$, is well characterized. However, in figure 5, the high-resolution transmission electron microscopy image of a sample of related La carbide iodides (Kienle et al. 2008) exhibits a typical disorder that occurs quite frequently in this kind of phases, and which may be described as an epitaxial intergrowth of chains and oligomeric clusters of a general composition La$_{4n+2}$(C$_2$)$_n$I$_{5n+5}$ and evidences a source of varying clusters yet to be isolated in discrete well-ordered compounds.

3. Bare-metal clusters

Moving from the transition metals to the alkaline earth and alkali metals primarily changes the number and kind of valence electrons. However, these metals exhibit a rich and still growing cluster chemistry in the subnitrides and suboxides (Simon 1979, 1997, 2004), respectively. The structural features can be extrapolated from the criteria presented previously. Owing to the lower values of VEC, the clusters need to be stabilized by endohedral non-metal atoms, and, as a qualitatively new feature, the clusters have lost their ligand shell.

Alkali metal suboxides were discovered a century ago in admirable investigations by Rengade (1909). In spite of several attempts, their chemical nature was disclosed only many decades later. Early hints to the existence of Ba subnitrides came from the work of Addison et al. (1975); however, again their compositions and structures were unknown for several decades. The structures of Rb and Cs suboxides represent textbook knowledge and, hence, will be treated.
only very briefly in order to pave the way for the more complicated subnitrides. 

[Rb9O2] and [Cs11O3] clusters formed from two and three face-condensed $M_6$ octahedra around $O^{2-}$ ions are shown in figure 6a,b.

The surplus of metal valence electrons according to [Rb$^{+}_9$O$_2^{-}$]e$_5^-$ and [Cs$_{11}^+$O$_3^{2-}$]e$_5^-$ is used in $M$–$M$ bonding. Owing to the absence of a ligand shell, $M$–$M$ bonding is not confined to the discrete cluster, but also involves inter-cluster bonding. Detailed measurements of electrical and thermal properties indicate that the bonding in the solids Rb$_9$O$_2$ and Cs$_{11}$O$_3$ is like that in the elemental alkali metals, the single atoms being replaced by the corresponding clusters. Indeed, the clusters behave like ‘giant’ alkali metal atoms and combine with excess of metal to form a kind of intermetallic compounds. The binary phases Rb$_9$O$_2$ and [Rb$_9$O$_2$]Rb$_3$$\Leftrightarrow$Rb$_9$O have been structurally characterized, as well as Cs$_{11}$O$_3$, [Cs$_{11}$O$_3$]Cs$\Leftrightarrow$Cs$_4$O and [Cs$_{11}$O$_3$]Cs$_{10}$$\Leftrightarrow$Cs$_7$O. Interestingly, the very similar metals Rb and Cs are sufficiently different that they separate in space when forming ternary compounds such as [Cs$_{11}$O$_3$]Rb, [Cs$_{11}$O$_3$]Rb$_2$ and [Cs$_{11}$O$_3$]Rb$_7$. The crystal structure of the latter, as well as that containing one Rb atom per cluster is depicted in figure 7. The atoms between the clusters have no bonding to the $O^{2-}$ ions, but constitute a purely metallic matrix.

In the preceding section, the bonding in Nb$_6$F$_{15}$ based on ligand-encapsulated clusters was schematized in terms of sub-nano-sized particles of a metal regularly dispersed in a dielectric matrix (figure 3). In the case of Cs$_{11}$O$_3$, the bonding

Figure 6. Suboxide clusters (a) [Rb$_9$O$_2$] and (b) [Cs$_{11}$O$_3$] formed from two and three $M_6$O octahedra, respectively; subnitride clusters (c) [Ba$_{14}$CaN$_6$] composed of six condensed [Ba$_5$CaN] units with Ca in the centre; (d) [Ba$_{12}$Li$_8$N$_6$] cluster containing six condensed [Ba$_3$Li$_3$N] units; (e) [Ba$_{6}$Li$_{12}$N$_6$] cluster formed from condensed trigonal bipyramids [Ba$_3$Li$_2$N] indicated by shading; and (f) [Li$_{26}$N] cluster formed from four interpenetrating Li$_{12}$ icosahedra (one shaded) occupied by N in the central tetrahedron (shaded).
Figure 7. Crystal structures of: (a) $[\text{Cs}_{11}\text{O}_3]\text{Rb}_7$ and (b) $[\text{Cs}_{11}\text{O}_3]\text{Rb}$.

Figure 8. (a) Crystal structure of $\text{Cs}_{11}\text{O}_3$. (b) The shading shows the metallic bonding between the clusters and the exclusion of the conduction electrons from the cluster centre.

The situation is reversed. Now, the presence of Coulomb bubbles of $3 \times \text{O}^{2-}$ ions inside the clusters leads to a confinement of the conduction electrons to the space between the clusters, as indicated in figure 8.

The structure corresponds to a void metal exhibiting a regular array of regions that are forbidden for the conduction electrons. This general structure principle becomes even more explicit with subnitrides. The most obvious analogy to the structures of alkali metal suboxides is found with $[\text{Ba}_6\text{N}]\text{Na}_{16}$: bare $\text{Ba}_6\text{N}$ octahedra are surrounded by pure sodium (Snyder & Simon 1994). However, such simple arrangements are rather the exception with subnitrides and more complex clusters are the rule.

Figure 6c shows the characteristic cluster $[\text{Ba}_{14}\text{Ca}_6\text{N}_6]$ present in numerous subnitride phases (Steinbrenner & Simon 1996). It is formed from six face-sharing $\text{Ba}_5\text{Ca}$ octahedra, each centred by an $\text{N}^{3-}$ ion with $\text{Ca}$ in the middle. The core of the cluster, $[\text{Ba}_8\text{Ca}_6\text{N}_6]$, according to $[\text{Ba}_8^{2+}\text{Ca}_2^{2+}\text{N}_6^{3-}]$ is electroneutral and structurally represents one unit cell of (anti)perovskite. Such a sub-nano-sized piece of salt is surrounded by six Ba atoms that provide electrons for $M-M$ bonding according to $[\text{Ba}_{14}^{2+}\text{Ca}_2^{2+}\text{N}_6^{3-}]^{e^{-12}}$ and a metallic skin to the cluster, as in the case of the alkali metal suboxides. The analogy is even closer, as stoichiometric compounds exist where the clusters are arranged in a matrix of

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alkali metal. A whole series of phases [Ba$_{14}$CaN$_6$]Na$_n$ has been characterized via single-crystal-structure investigations, where $n$ takes the values 7, 8, 14, 17, 21 and 22 (Vajenine & Simon 2001). They all represent regular dispersions of sub-nano-sized pieces of a salt in a metal. As an example, the structure of [Ba$_{14}$CaN$_6$]Na$_{17}$ is depicted in figure 9 (Simon & Steinbrenner 1996).

All attempts failed to substitute the sodium by heavier alkali metals. The cluster does not bind to K, Rb and Cs, very much like elemental Ba that does not mix or form compounds with these metals. Of course, one could have expected a partial substitution within the alkali metal substructure, as binary compounds such as Na$_2$K and Na$_2$Rb are known. However, an unexpected reaction occurs: in contact with K, a part of Na is extracted from the subnitrides to form liquid Na/K alloy. The reaction can be used for the systematic preparation of phases with low values of $n$ by performing the nitridation reaction in an Na/K melt of appropriately chosen composition.

In contrast to the heavy alkali metals, the light homologue Li participates in subnitride formation, and it does it in a dual way. Li has affinity to both Ba and N, as indicated by the existence of Ba/Li intermetallic compounds and the very stable nitride Li$_3$N. It should therefore be able to enter the subnitride cluster, as well as the purely metallic region between the clusters. Indeed, [Ba$_{14}$LiN$_6$]Na$_{14}$ can be synthesized, which is isotypic, with the cubic Ca-containing compound, and only the central Ca atom being replaced by Li. When the relative amount of Li is increased, the metal also becomes part of the region between the clusters. [Ba$_{14}$LiN$_6$]Li$_4$Na$_{11}$ and [Ba$_{14}$LiN$_6$]Li$_5$Na$_{10}$ crystallize in different well-ordered structures which are closely related to that of [Ba$_{14}$LiN$_6$]Na$_{14}$, in spite of the deviation in alkali metal content (Smetana et al. 2008a,b). It is remarkable that, in these mixed metal phases, bonding between Li and Na occurs, although the binary Li/Na system exhibits an extended range of immiscibility. Obviously, the neighbourhood of the Ba atoms has a subtle influence on the bonding capability of
the ternary phase [Ba$_{19}$Li$_{13}$]Na$_{29}$, a short Li–Na distance of only 319 pm clearly indicates a chemical bond. The compound will be addressed once more later.

In the cluster [Ba$_{14}$LiN$_6$], the octahedra surrounding the N atoms contain one Li atom. Increasing the Li:Ba ratio results in the new cluster [Ba$_{12}$Li$_8$N$_6$] shown in figure 6d (Smetana et al. 2007a,b). Here, the N atoms are surrounded by Ba$_3$Li$_3$ octahedra, which are condensed in a way that the Li atoms collect in the inner part of the cluster, and the Na atoms are arranged outside. Following the structural principle of the suboxides and subnitrides presented so far, these clusters are again dispersed in a metallic matrix according to [Ba$_{12}$Li$_8$N$_6$]Na$_{15}$.

For the sake of simplicity, the topology of an $M_6$ octahedron was chosen throughout this review to outline the ideas about encapsulation, stabilization by endohedral atoms, cluster condensation and loss of encapsulation. Of course, there are many more closely related systems; however, these are based on different topologies. In the following, two examples are briefly mentioned to be more complete. In the large structure of Ba$_{39}$Li$_{80}$N$_9$, two types of subnitride clusters have been found (Smetana et al. 2006). The first, [Ba$_6$N] octahedra, is known from the structure of [Ba$_6$N]Na$_{16}$. The second cluster, [Ba$_6$Li$_{12}$N$_6$], is composed of six distorted condensed trigonal bipyramids [Ba$_3$Li$_2$N], see figure 6e. A particularly interesting case is related to the ternary phase Ba$_{19}$Li$_{13}$Na$_{29}$ mentioned earlier. The complex structure contains Li$_{26}$ Mackay clusters formed from four tetrahedrally arranged interpenetrating icosahedra. This type of cluster, though consisting of different atoms, is well known from γ-brass. There is experimental evidence that the central Li$_4$ tetrahedron is empty; however, detailed investigations show that it can also be occupied by, for example, N. The entity [Li$_{26}$N] as the most metal-rich cluster discussed in the context of this review is shown in figure 6f (Smetana et al. 2008a,b).

The last section started from single $M_6$ octahedra encapsulated by ligands. Cluster condensation resulted in oligomers and finally infinite arrays of varying dimensionality. The structural chemistry of bare-metal clusters described so far closely follows this general pathway, and only the final step is left to be demonstrated. As examples, chain compounds formed from face-sharing octahedral units are chosen.

In figure 10, the structures of In[Mo$_3$Se$_3$] (Hönle et al. 1980) and [Ba$_3$N]Na (Rauch & Simon 1992) are compared. Both exhibit hexagonal rod packings of such chains. Whereas the electron-rich Mo$_6$ clusters are entirely encapsulated by anions bonding to additional cations between the chains, the electron-poor Ba forms bare chains of octahedra centred by N$_3^{-}$ ions and bonded to metallic Na between the chains, as in the structures of suboxides and subnitrides with discrete clusters illustrated before. Similar to the latter, the chain compound also allows a variation of the extension of the metallic region, e.g. with [Ba$_3$N]Na$_5$ (Snyder & Simon 1995), as well as Ba$_3$N (Steinbrenner & Simon 1998), which only contains [Ba$_3$N] chains in metallic bonding.

Condensation of [Ba$_6$N] octahedra is found in the structure of Ba$_2$N, which consists of Ba–N–Ba layers with metallic bonding between them (Reckeweg & DiSalvo 2002). The structure of the new compound [Ba$_2$LiN] (Smetana et al. 2007a,b) exhibits layerwise cross-linked [Ba$_5$LiN] units (figure 11), which have been mentioned earlier as the constituent of the [Ba$_{14}$LiN$_6$] cluster. These few
Figure 10. Crystal structures of: (a) \(\text{In}[\text{Mo}_3\text{Se}_3]\) with anionic chains of condensed \(\text{Mo}_6\) octahedra encapsulated by Se atoms and cations between them and (b) \([\text{Ba}_3\text{N}]\text{Na}\) with bare \([\text{Ba}_3\text{N}]\) chains and metallic bonding between the chains and additional Na.

Figure 11. Crystal structure of: (a) \(\text{Ba}_2\text{N}\) formed from condensed \([\text{Ba}_6\text{N}]\) units and (b) \(\text{Ba}_2\text{LiN}\) containing layers of crosswise condensed \([\text{Ba}_5\text{LiN}]\) units.

Examples give some impression of an extended chemistry of metal-rich compounds yet to be explored. The recent discovery of a new class of suboxides may underline this remark.

Elemental Cs reacts with oxides \(\text{A}_2\text{O}_3\) \((\text{A} = \text{Al}, \text{Ga}, \text{In}, \text{Fe})\) at moderate temperature around \(200^\circ\text{C}\) to form the isostructural compounds \(\text{Cs}_9\text{AO}_4\) (Hoch et al. 2009). It is amazing to see that the very stable high-temperature ceramic material \(\text{Al}_2\text{O}_3\) dissolves under such mild conditions, the large excess of Cs with respect to a normal valence compound is remarkable and, even more, the existence

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of Fe$^{3+}$ in an environment of highly reducing Cs is exciting. The structure depicted in figure 12 reveals a general arrangement that is closely related to, for example, the structure of [Ba$_3$N]Na. Clusters of composition [Cs$_{12}$AO$_4$] shown in figure 12a are condensed into chains according to [Cs$_{8/2}$Cs$_4$AO$_4$] = [Cs$_8^+$ (AO$_4$)$_5^-$] e$_3^-$ with M–M bonding within the chains, between them and to additional Cs atoms that have no bonding contacts to the anions. The phases Cs$_9$AO$_4$ extend the spectrum of metal-rich compounds from those containing monoatomic entities such as H, O, N, etc. in metal clusters via diatomic species such as C$_2$ to complex groups such as AO$_4$. These phases could represent the tip of an iceberg with many more examples to follow.

4. Conclusions and final remarks

This short review covers a part of cluster chemistry and its development over a long period, from its origin to most recent work. Mainly structural aspects have been addressed. Details of the structures give insight into a significant variability with many more results to come. Beyond the details, general features have been briefly touched, which ascribe the structures to regular dispersions of sub-nanosized pieces of a metal in a salt-like matrix and, vice versa, pieces of a salt in a metallic matrix. Such general features relate to interesting physical properties as exemplified for the alkali metal suboxides, which show a very low work function owing to the electronic confinement and concomitant quantum size effects.

It is interesting to note that the chosen examples Nb$_6$F$_{15}$ and Cs$_{11}$O$_3$ exhibit similarity with much investigated electronic devices, the so-called quantum dot and anti-quantum dot arrays, respectively. The first consist
of arrays of discrete nanoscopic pieces of highly conducting semiconductor material, the latter of conducting layers with an ordered pattern of holes. Confinement of the electrons to the dots or to the region between the holes leads to a bunch of fascinating properties. To use these terms, Cs$_{11}$O$_3$ represents a self-organized three-dimensional anti-quantum dot array, as Nb$_6$F$_{15}$ may be viewed as the corresponding quantum dot array. The main difference lies in the scale. The arrays in the compounds are nearly two orders of magnitude smaller than those constructed from semiconductors. Perhaps, they will become a target of interest when miniaturization enters this limit.

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