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# Clusters of IIA and IIIA group metals: synthesis and reactivity

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**Abstract.** Experimental and theoretical data on the structure of clusters of Group IIA and IIIA metals are summarised. General trends in the properties of the clusters as a function of nuclearity are outlined, and special points on the dependences, corresponding to the so-called magic numbers, are identified. Data on the reactivity of clusters in the gas phase are used to establish the anomalies corresponding to these points. It is shown that the reactivity of mixed clusters obeys more complex relationships, determined by their electronic structure and geometry. A new type of organomagnesium cluster is described, and shown to be promising as a component of catalytic systems. The cryochemical synthesis of giant clusters of transition metals, which offer a high reactivity and catalytic activity, is described. The bibliography includes 176 references.

## I. Introduction

Metal clusters occupy an intermediate position between metal atoms (which display the greatest possible dispersion) and bulk metals, and they constitute a new type of metallic state. According to the generally accepted terminology[1] clusters are species containing between 2 and $10^5$ interconnected metal atoms, of size varying from 0.5 to several tens of nanometres. The boundary between the cluster and the metallic state is hard to define. Ultradispersed powders, and especially colloidal metals with a particle size of $10-10^3$ nm, show marked differences from bulk metals. They are often called giant or supergiant clusters. This terminology will be adopted here.

The special properties of the cluster state and the wide range of potential applications of clusters and colloidal metals in various areas of science and technology have stimulated an intense interest in this field of research. The results have been discussed in monographs[1-4] as well as in research papers. However, until recently most of the work had been aimed at clusters of the transition metals, and an interest in clusters of the typical (non-transition) elements has become evident only in the last few years. This new topic has come to the fore because of recent advances in experimental and (even more so) in computational methods, which have made the clusters of typical metals a promising field of study. Because of the great experimental difficulty met in the preparation and study of clusters we have witnessed an unusual state of affairs in which theoretical studies have outstripped the experimental work.

This review is aimed at clusters and colloidal solutions of metals from Groups IIA and IIIA. It does not attempt to provide comprehensive information on the physics and the physical chemistry of these materials: its object is to draw attention to the least fully investigated and yet the most interesting aspect of the problem: the chemical properties and the likely applications of clusters of typical metals.

## II. Preparation of clusters in solution

The characteristic properties of the metals in Group IIA are the presence of an occupied *s* shell and the absence of *p* electrons. In terms of the general propositions of the theory of valence the bond of the $M_2$ dimer is not likely to be strong: occupied bonding and antibonding $\sigma$ MO are formed from the two *s* AO. Not surprisingly, therefore, no successful attempts to prepare homonuclear clusters of IIA group metals by 'classical' methods have so far been reported. Only one paper[5] describes the reduction of the tetramer of *o*-phenylmercury by magnesium in tetrahydrofuran (THF), which gave a crystalline complex of the tetramer of *o*-phenylmagnesium with THF. Each magnesium atom in the complex contributes to the formation of one $\sigma$ bond and two bridging $\delta$ bonds with the phenyl radicals, and it is also coordinated with one molecule of THF. Under these conditions the distance between the magnesium atoms lies between 3.546 and 2.804 Å. The latter value formally justifies the assignment of this compound to the cluster type. However, the lack of data on the direct interaction between the magnesium atoms makes this assignment ambiguous.

A different state of affairs is found with the Group IIIA metals. The presence of a valence *p* electron allows the formation of a covalent metal–metal bond, and the preparation of cluster compounds by conventional chemical methods seems more likely. Significant differences are noted between aluminium, which has a stable (3+) and an unstable (1+) oxidation state,

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and gallium and indium. The latter metals have, in addition, an even less stable state (2+). The synthesis of their cluster compounds by the dimerisation of derivatives of the bivalent metals immediately suggests itself:

$$2MX_2 \rightleftharpoons X_2M{-}MX_2.$$

In reality the dimers of the halides of bivalent indium and gallium are ionic species, $M^+[MX_4]^-$, and do not contain metal–metal bonds.[6] There are two methods of stabilising the cluster halides of indium and gallium. The first consists in complex formation with dioxan or other organic donors. In the resulting complexes of composition $M_2X_4 \cdot 2D$ (where D is a donor) the length of the Ga–Ga bond[7–9] is 2.40 ± 0.02 Å, and that of the In–In bond[10] is 2.775 Å. The cluster nature of these compounds was confirmed by X-ray diffraction and from their vibrational spectra. Complexes can also be prepared by the interaction of suitable donors with the metal dihalides in a hydrocarbon medium (for example, in benzene). Anion salts ($M_2X_6^-$) are another type of compound of these metals. Thus, in the ammonium salts $[R_4N]_2^+Ga_2Cl_6^{2-}$ the Ga–Ga distances are 2.39 Å (R = Me)[11] and 2.42 Å (R = Pr$^i$),[12] and in the triphenylphosphonium salts[13] they are 2.407–2.415 Å. In spite of the short interatomic distance the metal–metal bonds are weak, as shown by the low frequencies of the stretching vibrations (between 122 and 235 $cm^{-1}$ in the case of gallium[14] and between 120 and 150 $cm^{-1}$ for indium[15]). The dissociation energy of the metal–metal bond in these cluster halides was estimated[6] to be 25–35 kcal $mol^{-1}$. Another example of compounds containing a metal–metal bond are the gallium and indium chalcogenides, in which the Ga–Ga distance is 2.4–2.5 Å and the In–In distance is 2.75 Å. These compounds can be treated as salts of the simplest ($M_2^{4+}$) cluster cation.[16]

Only the simplest binuclear compounds have been obtained using classical methods of synthesis,[17] though the $In_6(C_5Me_5)_6$ hexamer (which is formally a cluster with an octahedral $In_6$ metal core) has been synthesised by the reaction between InCl and $Li(C_5Me_5)$. However, the In–In distances in this compound are so large (3.9 Å) that there is no justification for assuming the formation of metal–metal bonds. Even at 55 °C this product sublimes exclusively as a monomer.

Many attempts to prepare cluster compounds of aluminium in solutions have been reported. The formation of Al–Al bonds has been suggested, for example, in a mixed alkyl derivative of boron and aluminium synthesised by the reaction between $Al_2Me_6$ and $B_2(Me_4N)_4$, but no strict proof of this claim was advanced.[18,19] The same is true of the compound $[Bu^i_2Al]_2$, prepared[20] by treating $Bu^i_2AlCl$ with potassium.

X-Ray confirmation of the structure of the cluster compounds of aluminium synthesised under normal conditions has only recently been obtained. The reduction (with potassium) of the compound $[(Me_3Si)_2CH]_2AlCl$ gives a binuclear product with an Al–Al bond.[21] The reaction of the tetrameric complex of aluminium(I) chloride with $Mg(C_5Me_5)_2$ at −78 °C in the absence of water vapour and oxygen gave[22] the product $[Al(C_5Me_5)]_4$, containing a tetrahedral metallic core with an Al–Al distance[22] of 2.773 Å. The synthesis of a salt of composition $K_2[Al_{12}Bu^i_{12}]$, stable up to 150 °C and containing a metal core consisting of the $Al_{12}$ icosahedron (Al–Al distance 2.679 and 2.696 Å), has been reported.[23] This example offers the hope of a synthesis (in the near future) of cluster compounds of Al with metal cores in the form of regular polyhedra. One further example is provided by melts (prepared in a corundum crucible) of crystalline $Al_7Te_{10}$, in which the metal–metal distance (2.6 Å) is shorter than in the organic clusters.[24] However, the limitations of the classical approach cannot be ignored: there have been only two reports of the synthesis of cluster compounds with a substantial metal core, and there are no prospects to date of preparing ligand-free clusters by this method.

## III. Synthesis and properties of clusters in the gas phase

Fully developed methods of preparing and studying metal clusters in the gas phase are now available. The key stage in these methods is the flash evaporation of a relatively large amount of the metal, achieved (for example) by ion or electron bombardment. More recently, powerful laser pulses have been used for the same purpose. The evaporated atoms and ions are entrained in a stream of inert gas in which the clusters are formed. The temperature of the particles can be rapidly lowered to room temperature by suddenly expanding the flow. If necessary the ions can be selected by means of a quadrupole mass spectrometer. The final stage consists in the mass spectrometric detection of the particles, either directly or after appropriate physical or chemical perturbations.

Clusters of the Group IIA metals have not been studied extensively. For Be the dissociation energy of the dimer (0.1 eV) has been determined.[25] For $Mg_2$ the absorption spectra have been measured,[26] and a dissociation energy of 0.05 eV has been reported.[27] It was also shown that the ionisation potential of $Mg_2$ is 6.7 eV, which is much lower than for atomic magnesium, and that the dissociation energy of the charged $Mg_2^+$ ion is close to 1 eV.[28] Thus the removal of one electron strengthens the magnesium–magnesium bond quite substantially.

Aluminium clusters have been studied in greater depth. Experiments with ionised clusters have yielded reliable data on their electron affinities (EA) and ionisation potentials (IP), shown in Table 1. It can be seen that the ionisation potential increases significantly on going from the atom (6.0 eV) to the small clusters, but then gradually decreases. For $N > 14$ it falls below the value for the atom. However, it is still far from the electronic work function for the compact metal (4.24 eV). Even for $N = 55$ the IP stays at 4.95 eV.[29]

**Table 1.** Electron affinity and ionisation potentials of $Al_N$ clusters.

| $N$ | IP/eV | EA/eV | Ref. |
|---|---|---|---|
| 2 | 5.9–6.3 | – | 29–31 |
| 3 | 6.4–7.2 | – | 29–31 |
| 3 | – | 1.4–1.9 | 32–34 |
| 4–6 | 6.0–6.5 | – | 29–31 |
| 4–6 | – | 1.74–2.7 | 32, 33 |
| 7 | 6.0 | – | 29 |
| 7 | – | 2.0–2.6 | 32, 33 |
| 8–12 | 6.2 | – | 29 |
| 8–12 | – | 2.2–3.2 | 29, 32–34 |
| 13 | 6.4 | – | 31 |
| 13 | – | 2.8–3.5 | 32–34 |
| 14–22 | ⩽ 5.5 | – | 29, 31 |
| 14–22 | – | 2.5–2.8 | 32, 33 |
| 23 | – | 2.86 | 32 |
| 24–25 | – | 2.75 | 32 |
| 26–32 | – | 2.8–2.85 | 32 |
| 55 | 4.95 | – | 29 |

The electron affinity, which is negative for the atom, increases rapidly for $N = 2–3$, but beyond this point the growth becomes slower. In clusters with 24–32 atoms the EA increases at the rate of 0.1 eV per 8–10 metal atoms in the cluster.

The most interesting observation is the presence of several special points in the dependence of these parameters on the size of the cluster. Thus the electron affinity of $Al_6$, $Al_{23}$, and especially $Al_{13}$ is significantly higher than for their neighbours. The low ionisation potential of the $Al_7$ cluster is also noteworthy. This implies an abnormally high stability for the $Al_6^-$, $Al_7^+$, $Al_{13}^-$, and $Al_{23}^-$ systems, which contain 19–20, 40, and 70 valence electrons. This is an example of the law of magic

numbers, well known in the chemistry of clusters, according to which systems having certain numbers of valence electrons have anomalously high stabilities.

Experimental tests of the magic numbers in terms of the dissociation energies of neutral clusters have not yet been carried out. We only know that the dissociation of $Al_2$ requires[35] an energy of 1.34 eV. More data are available for charged clusters. The high thermal stability of several $Al_N^+$ clusters, including easily identifiable clusters with 20 valence electrons (of composition $Al_7^+$),[36] has been demonstrated. A similar result has been reported[29,37] for cationic clusters of aluminium, which show a tendency for an increase in stability with nuclearity: anomalously high stabilities were found in the clusters with 7, 13, 14, and 23 aluminium atoms, containing 20, 38, 41, and 68 valence electrons respectively. This is consistent with data on clusters obtained[38] by bombarding an aluminium target with $Xe^+$ ions having an energy of 9 eV: in this case a stability maximum was again observed for the clusters with 7, 14, and 23 metal atoms. Less striking examples of the same effect were found in trinuclear clusters (8 electrons). Detailed studies of the photodissociation of $Al_N^+$ clusters revealed the existence of two main dissociation paths:

$$Al_N^+ \longrightarrow Al^+ + Al_{N-1}, \quad (1)$$

$$Al_N^+ \longrightarrow Al_{N-1}^+ + Al. \quad (2)$$

Path (1) is more typical of clusters with 5–7 and with 9 atoms; path (2) usually corresponds to 8 or 10–17 metal atoms.[39] The dissociation energies vary between wide limits (from 1.5 to 2.6 eV) and are anomalously high (3.1 eV) in cationic clusters with 7 and 13 aluminium atoms. Data[30] for small clusters ($N \leqslant 7$) differ quantitatively from other reports,[39] but they also point to a large increase in the strength of the bond on going from $N = 6$ ($E_{diss} = 1.55$ eV) to $N = 7$ (2.25 eV). Surprisingly, the elimination of $Al^+$ or Al from $Al_3^+$ ($E_{diss} = 1.3$ or 1.12 eV) is more difficult than the dissociation of $Al_2^+$ or $Al_4^+$.

The existence of magic numbers has been confirmed also for anionic clusters. In a mass spectrometric study of anionic clusters of aluminium containing up to 70 atoms the species $Al_{13}^-$ (40 electrons) was found to have a very high stability, and a jump was noted also for $Al_{13}^-$ (70 electrons).[40]

Gallium and indium clusters show the same magic numbers as the aluminium clusters, the effect being most marked for the $M_7^+$ clusters.[36]

The experimental determination of the electronic state of the clusters is a difficult problem. Measurements[41] of the magnetic moments of $Al_N$ particles ($N = 2-25$) led to the conclusion that these clusters are in low-spin states: doublet for odd $N$ and singlet or triplet for even $N$. In ESR studies of the $Al_3$ trimer (prepared by condensation of aluminium from the gas phase into an adamantane matrix[42]) it was found that the spectrum corresponds to a particle having the form of a regular triangle and in a quartet state. The state of the simplest ($Al_2$) particle is also not entirely clear. An analysis of the electronic spectra of the aluminium, indium, and gallium dimers, which have (when in a matrix) two groups of bands at $(1.3-1.5) \times 10^4$ and $(2.4-3.0) \times 10^4$ cm$^{-1}$, led to the assignment of both groups of bands to transitions from a $^1\Sigma_g^+$ state.[43] However, an analysis of the vibrational spectra and of the emission spectra suggests that the ground state is $^3\Sigma_g^-$.[44] We shall show in the next section that this ambiguity arises from the existence of several almost degenerate states.

## IV. Structure and properties of clusters from quantum chemical calculations

Most of the currently available information on the clusters of typical metals has been obtained by quantum chemical methods. Let us examine the results in some detail.

Theoretical studies can be subdivided into two groups: quantitative calculations and calculation of a qualitative or semiquantitative character, based on the spherical shell model.

The spherical shell model[44,45] starts from the assumption that the metal core is most closely packed when in a spherical symmetry. The whole system is divided into two spheres: an inner (core) and an outer sphere (shell). The core includes the nucleus and all the electrons except the valence electrons, and the shell includes the valence electrons. It can easily be seen that in the case of a spherical symmetry this description is formally identical to the description of an atom in the one-electron approximation. Therefore the wave functions of the electrons in the shell can be split into a radial and an angular part. Like the spherical harmonics of the atom the angular functions will have $s$, $p$, $d$, $f$ AO symmetry depending on the orbital angular momentum. The maximum numbers of electrons in the subgroups of this pseudoatom are the same as the typical numbers for atoms: 2, 6, 10, 14, etc. However, the greater diffuseness (as compared with the AO) of the cluster functions results in a number of differences. In particular, the normal sequence of increasing energies for the AO,

$$ns < np < (n+1)s \approx nd < (n+1)p < (n+1)d \approx nf$$

is replaced by

$$ns < np < nd < (n+1)s < nf < (n+1)p < ng < (n+1)d.$$

The following electron configurations are the most stable in this model: $1s^2p^6$, $1s^2p^6d^{10}2s^2$, $1s^2p^6d^{10}f^{14}2s^2p^6$, $1s^2p^6d^{10}f^{14}g^{18}2s^2p^6$, $1s^2p^6d^{10}f^{14}g^{18}2s^2p^6d^{10}3s^2$, containing 8, 20, 40, 58, and 70 electrons respectively. We can easily see that these are the same magic numbers as those which had been discovered experimentally. According to the model the species $Al_3^+$, $Al_7^+$, $Al_{13}^-$, $Al_{19}^-$, and $Al_{23}^-$ should be the most stable. This is consistent with the IP and EA data quoted above, and with the corresponding cluster stabilities. The increased stability of $Al_{14}^+$, $Al_{23}^+$, etc. can be attributed to the fact that the occupancy of their electron shells is the closest to the stable configuration in the $Al_N^+$ series.

The simple and objective description of the clusters, and especially the possibility of predicting the magic numbers, are the strong points of the spherical shell model. Its limitations, however, are equally obvious. For small $N$ values the real symmetry of the core is far from spherical. In general, as was pointed out by DeHeer et al.,[45] the predictions of the model are satisfactory for $N > 40$. The most serious limitation arises from the failure of the model to take account of the real geometry of the cluster. This limitation can be partially eliminated by adopting a variant of the theory which offers a compromise: the stipulation of a spherically symmetrical potential is retained, and departures of the geometry from the ideally spherical are treated as perturbations. Thus, the geometry of the sodium, magnesium, aluminium, and lead clusters has been optimised[46] by treating the ions of the core as exposed to a spherically averaged potential not identical to the potential of the simplest model.

Most of the cluster calculations were carried out by *ab initio* methods at various levels, or in the approximation of the local density functional (LDA). The electron correlation was allowed for by the Møller–Plesset theory at different levels (MP-2, MP-4, etc.) or by introducing the configurational interaction (CI) with allowance for singly and doubly perturbed states (CISD), as well as the CI for different initial configurations (MRCI, MRCI-SD).

### 1. Be clusters

The main result obtained at the SCF level was that the stability of the $Be_2$ dimer is very low and that the dissociation energy increases rapidly with $N$. Whereas the atomisation energy of one metal atom ($D/N$) at this level of calculation is only 0.05 eV for $Be_2$, in $Be_3$ it already has double that value and in $Be_4$ $D/N$ is 0.43 eV.[47] This is explained by the rapid growth of the degree of $sp$ hybridisation attributed to the relatively similar sizes of the $2s$

and $2p$ AO, which favour the formation of hybrid $sp$ AO. SCF calculations also point to a large increase of the electron affinity with increase of $N$ in the $Be_N$ clusters. Even in the tetramer we find[48] EA $\approx$ 1 eV. For the neutral tetrahedral $Be_4$ molecule at the SCF (or a more precise) level a $D/N$ value of 0.6 eV has been calculated,[47] with an interatomic distance of 2.08 Å.

Calculations allowing for electron correlation[49-54] have identified a series of important properties of the structure of Be clusters: a rapid increase in $D/N$ with $N$ (up to a value in excess of 0.9 eV for $Be_{13}$) with approximately constant values of Be–Be distance (2.0–2.2 Å) in the clusters, a similarity in the energies of different isomers (for example, the $Be_{13}$ clusters of $D_{3h}$ and $D_{3d}$ symmetry differ by 5% in energy), and a singlet ground state. All the published papers have stressed the important role of the electron correlation, but according to Rubio et al.[51] in the case of large clusters ($N \geqslant 7$) good qualitative results can also be obtained without allowing for CI.

Small Be clusters ($N = 3-7$) have been studied[55-57] in great detail in recent years. The structures illustrated in Fig. 1 are available to these species. We can see that regular polyhedra of the highest possible symmetry are characteristic for Be. The bond length is 2.50 Å in the dimer, 2.23 Å in the trimer, and less than 2.10 Å in the $Be_4$ tetramer. The dissociation energies calculated per atom are 0.3, 0.8, and 0.9–1.0 eV for $Be_3$, $Be_4$, and $Be_5$ respectively. Thus even relatively small Be clusters can be treated as stable molecules.

Unlike other metals of interest in the present discussion Be has been the object of nonempirical calculations[58,59] for relatively large clusters (from $Be_{51}$ to $Be_{69}$). However, in this case electron correlation effects were ignored. As we have already pointed out, in large clusters this omission is unimportant. The clusters are in a singlet ground state, with a bond energy (not allowing for correlation effects) of about 1.1 eV per atom for $N = 51$, 57, and 63 and about 1.2 eV per atom for $N = 69$. Allowing for correlation would bring these values to about 1.4–1.5 eV. A large decrease in the ionisation potential as compared with that of the atom and of the small clusters (IP = 3.62 eV) has been pointed out. As could have been expected, in large clusters a very effective $sp$ hybridisation takes place: even in $Be_{51}$ more than one electron of the central atom is transferred from a $2s$ AO to a $2p$ AO. Unlike the atoms of the outer layer, the central atoms of these clusters can be treated as indistinguishable from atoms in the bulk state.

## 2. Mg clusters

Magnesium clusters have a low bond energy. Calculations not allowing for correlation give a negative stabilisation energy for the dimer and the trimer, and a negligibly small stability (0.03 eV) for the tetramer.[48,60,61] The results of detailed calculations for neutral Mg clusters are summarised in Table 2.

All the $Mg_N$ clusters with $N \leqslant 13$ are in a singlet state.[63-66] It can be seen from Table 2 that the tendency to form regular polyhedra is suppressed even for $N = 5$, and clusters with $N \geqslant 8$ have a low symmetry. Their geometry is determined by two opposing tendencies. Regular polyhedra are the best configuration for maximising the number of covalent bonds and for optimising the conditions leading to $sp$ hybridisation. However, a high symmetry unavoidably produces degenerate electronic states which destabilise the molecule through the Jahn–Teller effect. In $Mg_N$ clusters the stability of the M–Mg covalent bond is low, the role of this effect should be small, and the departures from the 'ideal' geometry are not very substantial.

We also see from Table 2 that the normal dependences of various properties on $N$ are also displayed by $Mg_N$: an increase in the stability and in the electron affinity with $N$, and a decrease in the IP. Calculations can predict small peaks corresponding to the magic numbers on these otherwise monotonic curves. In particular, a marked increase in stability is found on passing from $Mg_3$ to $Mg_4$ (8 electrons). The magic number 20 is not so clearly recognisable, but nevertheless the stability of $Mg_{10}$ ($D/N = 0.83$ eV) is higher than that of $Mg_9$ (0.78 eV) and of $Mg_{11}$ (0.79 eV).[66] Calculations reveal a correlation between the stability and the population of the $3p$ level. For $N \leqslant 13$ the maximum $p$ population corresponds to $N = 10$ (0.3); a second local maximum (0.2) corresponds to $N = 4$. It should also be noted that the stability of the clusters is relatively low for $N \leqslant 8$.

In spite of the small bond energy the excitation of $Mg_N$ produces long-lived excited states. The thermal decomposition of $Mg_N^*$ requires surmounting a high activation barrier[67] ($\geqslant 0.4$ eV in the case of $Mg_2$). Excitation can be induced by exposure to

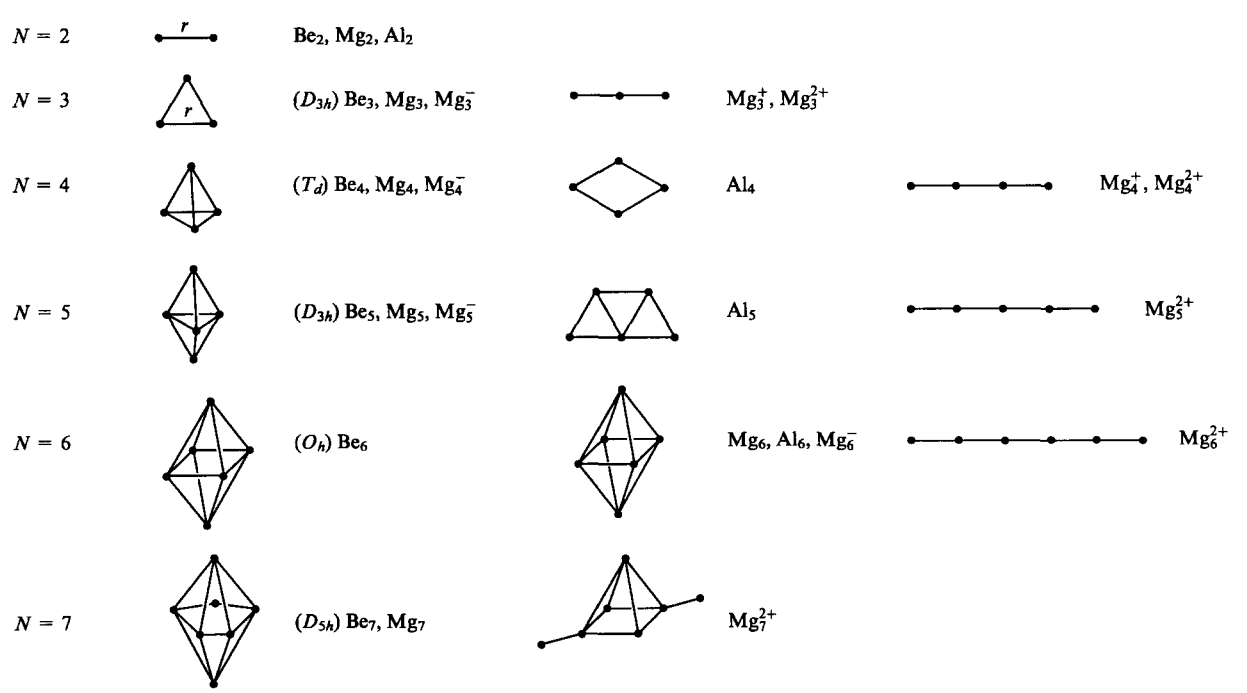



**Figure 1.** Typical geometric forms of small clusters of Group IIA and IIIA elements.

**Table 2.** Results of calculations on $Mg_N$ clusters.

| $N$ | Method of calculation[a] | Geometry | $r_{Mg-Mg}$/Å | $(D/N)$/eV | IP/eV | EA/eV | Ref. |
|---|---|---|---|---|---|---|---|
| 2 | *Ab initio*, STO 6-31G, MR | $D_{\infty h}$ | 2.82 | – | – | – | 54 |
| | VB | $D_{\infty h}$ | – | 0.026 | 6.2 | – | 62 |
| | LDA (LSD approximation) | $D_{\infty h}$ | 3.6 | 0.11 | 6.42 | 0.39 | 63, 64 |
| | LDA | $D_{\infty h}$ | – | 0.115 | – | – | 65 |
| 3 | *Ab initio*, STO 6-31G, MR | $D_{3h}$ | 2.76 | – | – | – | 54 |
| | VB | $D_{3h}$ | – | 0.05 | 5.6 | – | 62 |
| | LSD | $D_{3h}$ | 3.15 | 0.26 | 6.43 | 0.93 | 63, 64 |
| | *Ab initio*, CI | $D_{3h}$ | 3.38 | 0.13 | – | – | 56 |
| | LDA | $D_{3h}$ | – | 0.284 | – | – | 65 |
| 4 | *Ab initio*, STO 6-31G, MR | $T_d$ | 2.59 | – | – | – | 54 |
| | VB | $T_d$ | – | 0.08 | 5.3 | – | 62 |
| | LSD | $T_d$ | 2.97 | 0.5 | 6.61 | 1.0 | 63, 64 |
| | *Ab initio*, CI | $T_d$ | – | 0.18 | – | – | 56 |
| | LDA | $T_d$ | – | 0.53 | – | – | 65 |
| 5 | LSD | Trigonal bipyramid | 2.88 (3.20)[b] | – | 5.71 | 1.14 | 63, 64 |
| | LDA | " | 2.88 (3.20)[b] | 0.5 | – | – | 65 |
| 6 | LSD | Rectangular bipyramid | 3.08, 3.6 (3.13)[b] | – | – | – | 63, 64 |
| | | " | 3.08, 3.6 (3.13)[b] | 0.53 | 5.76 | 1.46 | 63, 64 |
| | LDA | " | 3.08, 3.6 (3.13)[b] | 0.566 | – | – | 65 |
| 7 | LSD | Pentagonal bipyramid | 3.21 (3.06)[b] | 0.6 | 5.87 | 1.52 | 63, 64 |
| | | " | – | 0.641 | – | – | 65 |
| 8 | LDA | Pentagonal bipyramid with an additional apex | – | 0.694 | – | – | 65 |
| | | Two-cornered trigonal prism | – | 0.63 | 5.5 | 1.9 | 66 |
| 9 | LDA | Three-cornered trigonal prism | – | 0.809 | – | – | 65 |
| | | " | – | 0.78 | 5.9 | 1.9 | 66 |
| 10 | LDA | Four-cornered trigonal prism | – | 0.83 | 5.6 | 1.4 | 66 |
| 13 | LDA | Asymmetric structure based on two trigonal prisms | – | 0.82 | 5.3 | 2.0 | 66 |

[a] VB, valence bond method; LSD, local spin density method.
[b] The Mg–Mg distance in the base is shown without parentheses; that in the edges is shown in parentheses.

light or by chemical action (for example, with sulfur atoms). As has been pointed out,[67] the stability of the excited states of Mg clusters suggests the possibility of developing a new type of laser based on this material.

Neutral and anionic magnesium clusters decompose by splitting off one metal atom:[64]

$$Mg_N \longrightarrow Mg_{N-1} + Mg,$$

$$Mg_N^- \longrightarrow Mg_{N-1}^- + Mg.$$

The geometry of the anionic clusters is similar to that of the neutral clusters. The interatomic distances in the anionic clusters are slightly smaller than in the neutral species, and the bond energy per single atom is approximately 0.2 eV higher.[63,64]

The highest singly occupied MO in $Mg_N^-$ have a completely $p$ character for $N = 2$, 3, 6, and 7, and an approximately 67% $p$ character for $N = 4$ or 5.[64]

Removing one electron alters the geometry of the cluster. Thus, the structure of $Mg_3$ and $Mg_3^-$ is an equilateral triangle, whereas that of $Mg_3^+$ is linear. The $D_{3h}$ symmetry characterises a saddle point rather than a minimum on the potential energy surface (PES) of $Mg_3^+$.[62] Two structures have been proposed for $Mg_4^+$; an approximately square structure and an equilateral triangle with a central atom.[68] A calculation allowing for CI suggests that the energies of these molecules are equal: 0.51–0.53 eV per atom.[69] An analysis in the approximation of the valence bond method showed that the presence of many isomers with approximately equal energies is a distinguishing feature of the cationic Mg clusters.[62]

The geometry calculated for $Mg_4^+$–$Mg_6^+$ in the local spin density functional approximation[63,64] is different from the value calculated by Durand.[62] These results are compared in Table 3. They all suggest[62–64] that the singly charged clusters are much more stable than the neutral clusters, especially for small $N$. As for $Mg_N^-$ and $Mg_N$ their decomposition takes place by the detachment of one Mg atom. Small $Mg_N^{2+}$ clusters are thermodynamically unstable, and undergo the so-called coulombic explosion: a decomposition induced by the coulombic repulsion of the nuclei.

**Table 3.** Cationic $Mg_N^+$ clusters.[63,64]

| $N$ | Geometry | $(D/N)$/eV | $r_{Mg-Mg}$/Å |
|---|---|---|---|
| 2 | $D_{\infty h}$ (linear) | 0.76 | 2.98 |
| 3 | " | 0.85 | 2.99 |
| 4 | " | 0.83 | 2.96 |
| 5 | $D_{3h}$ (trigonal bipyramid) | 0.93 | 3.04 (3.01)[a] |
| 6 | Rectangular bipyramid | 0.84 | 3.54, 4.07 (3.06)[a] |
| 7 | Distorted pentagonal bipyramid | 0.90 | 2.96 – 4.10[a] |

[a] The Mg–Mg distance in the base is shown without parentheses; that in the edges is shown in parentheses.

A calculation in the LDA approximation[70] showed that $Mg_N^{2+}$ clusters are stable only for $N > 14$. An alteration effect has been noted: the maxima in the curves of energy against number of atoms correspond to $N$ values of 5, 10, 18, 21, 30, and 35 (with 8, 18, 34, 40, 58, and 68 electrons respectively), i.e. the number of electrons is equal or close to the magic numbers. The simplest decomposition scheme,

$$Mg_N^{2+} \longrightarrow Mg^+ + Mg_{N-1}^+.$$

takes place only in special cases. The general rule is that the preferred decomposition is the process in which both fragments have a number of electrons differing by unity from the magic number (an exact correspondence is impossible because the number of electrons in $Mg_N^+$ is odd).

**Table 4.** Decomposition of the $Mg_N^{2+}$ clusters.[64]

| $N$ | Decomposition scheme | Energy barrier/eV |
|---|---|---|
| 2 | $Mg_2^{2+} \rightarrow 2Mg^+$ | 0.48 |
| 3 | $Mg_3^{2+} \rightarrow Mg_2^+ + Mg^+$ | 0.77 |
| 4 | $Mg_4^{2+} \rightarrow 2Mg_2^+$ | 0.90 |
| 5 | $Mg_5^{2+} \rightarrow Mg_3^+ + Mg_2^+$ | 0.98 |
| 6 | $Mg_6^{2+} \rightarrow 2Mg_3^+$ | 1.03 |

The coulombic repulsion favours the linear $Mg_N^{2+}$ structure with positive charges located mainly at the chain ends.[63,64] Clusters with $N \leqslant 6$ are linear, but for $N = 7$ the structure becomes a pentagonal bipyramid. The linear molecule has an energy only 0.08 eV higher. The potential energy curves for the dissociation have also been calculated;[64] the results are summarised in Table 4. Because of their kinetic stability the unstable $Mg_N^{2+}$ clusters can play an important role as intermediates in the reactions of neutral magnesium clusters.

## 3. Ca clusters

The energy gap between the 4*s* and 4*p* shells of Ca is smaller by a factor of 1.5 than the gap between the *s* and *p* valence shells of Be and Mg. This should favour *sp* hybridisation, but at the same time the more diffuse structure of the 4*p* AO suppresses the hybridisation. The compensation of these opposing factors should make the properties of the Ca clusters similar to those of the Mg clusters. Few calculations on the Ca clusters have been reported. At the SCF level a dissociation energy of about 0.2 eV per atom has been obtained for $Ca_4$. This is greater than for $Mg_4$ but smaller than for $Be_4$.[61] The $Ca_3$ trimer is even less stable ($\sim$0.11 eV per atom for an internuclear distance of $\sim$4 Å).[71]

No calculations have been reported for Ba or Sr.

## 4. Al clusters

The valence shell of Al contains an unpaired *p* electron which permits the formation of a $\sigma$ bond with *sp* hybridisation. A relatively high stability can therefore be expected for the small Al clusters. This has been confirmed experimentally and by quantum chemical calculations.

The presence of isomers having similar energies and the small depth and large width of the minima in the PES make it difficult to obtain reliable calculated results. A recent analysis[72] has shown that in order to give an adequate description of $Al_N$ clusters the chosen basis should include the *d* AO. Electron correlation effects account for up to one half of the stabilisation energy of the cluster, but their inclusion does not markedly affect the calculated geometry.[73] The main difficulty is the presence of several almost degenerate states having different geometries and multiplicities.

Specially meaningful results were obtained in calculations on the $Al_2$ dimer. Different ground states had been suggested for this species: $^1\Sigma_g^+$, $3\Pi_g$ (see Ref. 50) and $^3\Sigma_g^-$ (see Ref. 74), but more recently it was shown that this state is $^3\Pi_u$ (see Refs 75 and 76). This state is almost degenerate with $^3\Sigma_g^-$ ($\Delta E = 174$ cm$^{-1}$), and the $^1\Sigma_g^+$ energy is substantially higher (by 2000 cm$^{-1}$).[77] A similar state of affairs was noted for $Al_3$ (see Refs 78–81). The results of calculations for small Al clusters are shown in Table 5: we can see that $Al_N$ clusters show a number of special features in addition to the more general properties such an increase in EA and in stability with increasing $N$. The most striking of the special features is a tendency to form planar structures (except in the case of $Al_6$). This is probably a consequence of the absence of *sp* hybridisation during cluster formation, which can destabilise the molecule. Therefore the three-dimensional structures most conducive to the formation of *sp* hybrid orbitals are difficult to produce. It should be noted that a planar structure is not consistent with the close packing postulated in the spherical shell model. Nevertheless, as was pointed out above, the model can successfully predict (at the qualitative level) many important properties of the clusters, and departures from the spherical symmetry can be treated as perturbations while retaining the model.[78]

The similarity in structure between the Al clusters and the crystalline metal have been analysed at the LDA level.[62] In the metal the cubo-octahedron can be chosen as the structural unit. In clusters, even when large, a packing based on the icosahedron as the structural unit is more stable. It is replaced by the cubo-octahedron only for $N > 2000$. The energy differences between the corresponding isomers calculated for $N = 13-55$ were found to be very small: not more than 2% of the total energy. Calculations of the IP[82] show that even for $N = 19$ the value obtained for the cluster (6.18 eV) is higher than for the Al atom (5.77 eV), and that it becomes significantly lower (5.04 eV) only for $N = 55$. Experimental results give a similar dependence of the IP on $N$, but the equality of the IP values for the atom and the cluster is seen at $N \approx 19$.

**Table 5.** Small aluminium clusters.

| $N$ | Method of calculation | Geometry | Ground state | $(D/N)$/eV | $r_{Al-Al}$/Å | IP/eV | EA/eV | Ref. |
|---|---|---|---|---|---|---|---|---|
| 2 | *Ab initio*, MRCI | $D_{\infty h}$ | $^3\Pi_4$ | 0.7 | 2.76 | – | – | 77 |
| | *Ab initio*, MRCI | $D_{\infty h}$ | $^3\Pi_4$ | 0.62 | 2.70 | – | – | 73 |
| | VB | $D_{\infty h}$ | $^3\Pi_4$ | 0.77 | 2.62 | 6.02 | 0.09 | 78 |
| | *Ab initio*, CI | $D_{\infty h}$ | $^3\Pi_4$ | 0.60 | 2.76 | – | – | 75 |
| 3 | *Ab initio*, MPY | $C_{2v} \sim D_{3h}$ | $^2A_1{}^4A_2$ | 1.1 | 2.6 | 6.38 | – | 81 |
| | *Ab initio*, CI | $D_{3h}$ | $^4A_2$ | 0.92 | 2.64 | – | – | 75 |
| | *Ab initio*, CI | $D_{3h}$ | $^2A_1$ | 0.90 | 2.60 | – | – | 75 |
| | VB | $C_{2v} \sim D_{3h}$ | $^2A_1$ | 1.07 | 2.62 | 6.31 | 1.43 | 78 |
| 4 | VB | $D_{2h}$ (rhombus) | $^1A_1$ | 1.12 | 2.6 | 6.46 | 1.50 | 78 |
| | *Ab initio*, CI | $D_{2h}$ (rhombus) | $^1A_1$ | 1.09 | 2.67 | – | – | 75 |
| 5 | VB | $C_{2v}$ (rectangular pyramid) | $^2B_1$ | 1.06 | 2.72–2.92 | 5.57 | 1.91 | 78 |
| | *Ab initio*, CI | $C_{2v}$ (planar configuration) | $^2B_1$ | 1.15 | – | – | – | 75 |
| 6 | VB | Distorted octahedron | $^3B_1$ | 1.22 | 2.78–2.81 | 6.55 | 2.16 | 78 |
| | *Ab initio*, CI | Octahedron | $^3B_1$ | 1.42 | – | – | – | 75 |

### 5. Ga and In clusters

Experimental data on Ga and In clusters are adequately consistent with the predictions of the spherical shell model.[83] A strict calculation allowing for the CI has been reported only for the Ga dimer.[84] The ground state of the dimer is $^3\Pi_u$ ($r_{Ga-Ga}$ = 2.762 Å), with a dissociation energy of 1.4 eV, and a $^3\Sigma_g^-$ state lying close to it (IP of the dimer 5.62 eV, EA = 1.04 eV). The anion of the dimer is more stable, with a dissociation energy of 2.2 eV, $r_{Ga-Ga}$ = 2.562 Å, ground state $^4\Sigma_g^-$. The stability of the $Ga_2^+$ cation in the $^2\Sigma_g^+$ ground state is close to that of $Ga_2$ (1.5 eV, $r_{Ga-Ga}$ = 3.24 Å).

## V. Semiempirical and empirical calculations on clusters

Nonempirical calculations in wide basis sets which allow for electron correlation offer adequate descriptions of small clusters. However, in the case of large clusters their requirements of computer time are excessive. Therefore the search for promising methods of calculating the structure and the characteristics of these clusters by semiempirical approaches is now an urgent problem.

We are not aware of any successful attempts to describe clusters of Group IIA metals by these methods. Reported calculations of $Mg_N$ clusters by the MNDO and CNDO/2 methods (*sp*, *spd*, and split *spd* basis sets) did not give satisfactory results: the bond energies were unacceptably high and the internuclear distances were too short.

**Table 6.** Calculation of Al clusters by semiempirical methods.

| *N* | Method | Geometry | *s* | (*D*/*N*)/eV | IP/eV | Ref. |
|---|---|---|---|---|---|---|
| 2 | CNDO/2 | $D_{\infty h}$ | 3 | 1.0 | 7.21 | 84 |
| | MNDO | – | – | 0.66 | 5.57 | 85 |
| | INDO | $D_{\infty h}$ | – | 0.67 | 6.37 | – |
| 3 | CNDO/2 | $C_{2v} \sim D_{3h}$ | 2 | 2.04 | 7.18 | 84 |
| | MNDO | – | – | 0.8 | 6.15 | – |
| | INDO | $D_{3h}$ | – | 1.12 | 6.13 | 85 |
| 4 | CNDO/2 | $C_{2v} \sim D_{4h}$ | 1 | 2.43 | 7.75 | 84 |
| | MNDO | – | – | 0.9 | 6.2 | – |
| | INDO | Rhombus | – | 1.37 | 6.44 | 85 |
| 5 | CNDO/2 | $C_{4v}$ | 2 | 2.60 | 7.12 | 84 |
| 6 | CNDO/2 | $O_h$ | 1 | 2.97 | 7.51 | 84 |

Better results were obtained for Al clusters. The results of a calculation[84] by the CNDO/2 method using corrected parameters are summarised in Table 6. As can be seen, the calculation gave reasonable values of the parameters *D*/*N* and IP, and it offers a correct description of the geometry of these clusters. However, a comparison with the data of Table 5 shows some quantitative discrepancies, less marked in the case of the MNDO calculations. Thus the shortcomings of these methods include a 10%–20% reduction of the internuclear distance as compared with the *ab initio* calculations.

Satisfactory results were obtained[85] by a special modification of the INDO method which gives internuclear distances and structures in good agreement with experiment.[82] It was used[85] in calculations for large clusters with $N \leqslant 49$. In clusters with $N \leqslant 43$ good results were obtained by the SINDOI method.[86] Thus the use of semiempirical methods in conjunction with special parametrisation provides an adequate description of Al clusters. Evidently, suitable alternative parametrisations can be produced also for other metals.

The low bond strength and the important role of the van der Waals interactions justify the use of empirical potentials for the intermolecular interactions when considering the structure and properties of the clusters. Thus, Halicioglu and Pamuk[87] have used a modified Lennard–Jones potential which gave stabilisation energies (1.226 and 1.274 eV per atom for $Al_4$ and $Al_5$ respectively) in good agreement with the results of nonempirical calculations. The same potential was used to calculate the activation energies of the regrouping of isomers. The activation barrier to the rearrangement of the tetrahedral $Al_4$ cluster into a rhombic cluster was 12.5 kJ mol$^{-1}$. In the case of $Al_5$ the conversion of a trigonal bipyramid into a square bipyramid requires surmounting a barrier of ~4 kJ mol$^{-1}$. These calculations[87] suggested the initial formation (in the gas phase) of the less stable $Al_4$ and $Al_5$ clusters, which are then transformed into the more stable planar structures. Thus the use of empirical potentials in calculations of the dynamics of the regrouping of small clusters can give satisfactory results. The conclusion that the barriers to isomeric regrouping are small has been shown[88] to apply also to magnesium.

## VI. Reactions of clusters in the gas phase

The reactions of clusters have attracted great interest among research workers as models of the elementary stages of processes in heterogeneous catalysis. They are also of interest from the standpoint of the synthesis of unusual chemical compounds containing weak metal–metal bonds.

The interaction of $Al_N^+$ with oxygen destroys the cluster.[89] Most of the oxygen interacts with the uncharged core of the cluster to form particles of the $Al_5O_2$ and $Al_4O_2$ type. Products of the interaction of the charged core of the clusters with oxygen have also been detected: the $Al_2O^+$ and $Al_3O^+$ cluster oxides. The order of the changes in reactivity of neutral and cationic clusters of aluminium towards the reaction with oxygen has been established:[90] the reactivity decreases in the sequence dimer > atom > trimer. The rate of the process was slowest with $Al_3^+$, probably because of the stability of the 8-electron shell present in this species. Studies of the reactions of $O_2$ with neutral $Al_N$ particles also revealed a high reactivity of the dimer, decreasing in the series $Al_2 > Al_3 > Al_4$ (Cox et al.[91]). Beyond this point the reactivity begins to increase again with the nuclearity. Notwithstanding the generally held view that the highest activity of a metal is found in the atomic state the reactivity of the clusters was found to be even higher.[92] Thus, the $Al^+$ and $Al_N^+$ ions ($N$ = 2–8) require collision energies of 3.5 and 0–0.25 eV respectively to react with oxygen.[92]

The nonmonotonic dependence upon nuclearity of the activity of clusters towards the reaction with $O_2$ is clearly seen in the anionic $Al_N^-$ clusters. In keeping with the spherical shells model the most stable and unreactive clusters are $Al_7^-$, $Al_{23}^-$, and $Al_{43}^-$ (see Refs 93 and 94).

It is interesting to note that the reactivity of $Al_N^-$ and $Al_N^+$ towards reactions with oxygen is weakly dependent on the sign of the charge, and that according to kinetic data[95] the effect of nuclearity in a series of clusters carrying the same charge is markedly stronger. For $Al_N^+$ with $N$ between 1 and 33 the following oxygenated products have been obtained: $AlO_x^+$, $Al_2O_x^+$, $Al_3O_x^+$, $Al_3O_3^+$, and $Al_5O_2^+$. The rate constants $k_2$ of these reactions lie in the range of (1–2) × 10$^{-12}$ cm$^3$ s$^{-1}$ for $N$ = 2, 3, 5, 9, 10, 17–33, and for $N$ = 4, 8, and 14–17 they are 1.5–5.0 times lower. For $Al^+$, $Al_6^+$, and $Al_7^+$ the reaction is totally suppressed ($k_2 < 10^{-16}$ cm$^3$ s$^{-1}$).

Anionic clusters react by the scheme

$$Al_N^- + O_2 \longrightarrow \begin{cases} Al_{N-2}^- + Al_2O_2 \\ Al_{N-1}^- + AlO_2^- \\ Al_{N-1}O + AlO^- \end{cases}$$

The rate constants $k_2$ lie between 10$^{-13}$ and 10$^{-11}$ cm$^3$ s$^{-1}$. No interaction was detected for the magic clusters $Al_{13}^-$ and $Al_{23}^-$.

The reactions of aluminium clusters with other molecules have been studied in less depth. The interaction with hydrogen (and deuterium) is hindered, and its rate is measurable only for

clusters with $N = 6-8$ ($Al_6 \gg Al_7 \gg Al_8$). The process probably takes place in two stages: [91]

$$Al_N + D_2 \longrightarrow Al_ND_2,$$

$$Al_ND_2 + Al \longrightarrow Al_ND + AlD.$$

The reactivity of the $D_2$ molecule towards the interaction with $Al_6$ is 1500 times lower than that of $O_2$.

The reactions of aluminium clusters with hydrogen have been analysed in terms of the modified spherical shells model.[96] Two factors play an important role: the stability of the cluster (magic numbers) and its structure (from the point of view of inserting a hydrogen atom into it). The icosahedral $Al_{12}$ cluster has an internal cavity large enough to accept a hydrogen atom. On the other hand in the case of $Al_{13}$, in which the insertion of hydrogen seems even more favourable (since the total number of electrons in this case increases to the magic value), the cavity is absent and the hydrogen can be accommodated only with great difficulty.

The interaction of the lower Al clusters with molecular hydrogen has been examined theoretically in an *ab initio* study[97] of the heat of dissociative chemisorption of $H_2$ on $Al_N$. According to these calculations the process is endothermic for $N \leqslant 5$, and a small energy gain (approximately 5 kJ $mol^{-1}$) is observed only for $N = 6$. This effect can be treated in terms of the spherical shell model as a manifestation of the filling of the valence shell of the cluster superatom: in $Al_6H_2$ we reach the magic number of electrons (20). The results of the calculation agree satisfactorily with experimental data.[91]

Aluminium clusters ($Al_N$) can react with compounds containing a hydroxyl group. With methanol they give the adducts $Al_N(CH_3OH)_m$, where $m = 1-3$, the reactivity being a maximum for $N = 16$, 17, with a minima at $N = 7$, 14, 23. The rate of the reaction with methanol is only slightly lower than the rate of the reaction with oxygen.[91] It is interesting to note that water is approximately an order of magnitude less active than methanol. Adducts with the same composition as those formed with methanol are obtained with $D_2O$. The formation of oxides or hydroxides has not been observed.[91] The lower neutral clusters ($N = 2-7$) react with water to a negligible extent, whereas the cationic $Al_N^+$ clusters ($N = 1-3$) react with water, with formation of cluster hydroxides and evolution of hydrogen.[90]

In addition to the above, reactions of the $Al_N$ clusters with carbon monoxide[91] and with acetone[98] have been observed. In the latter case particles of $Al_NMeCO$ ($N = 1-15$) are formed as well as the $Al_NMe_2CO$ adducts. The interaction of $Al_N^+$ ($N = 1-3$) with ethylene breaks down the hydrocarbon molecule:

$$Al_N^+ + C_2H_4 \longrightarrow Al_NCH_2^+ + \dot{C}H_2.$$

The $Al^+$ and $Al_2^+$ ions are much more active than $Al_3^+$.[90] With ammonia the $Al_N$ clusters give the adducts $Al_N(NH_3)_m$, $m = 1-3$. Under the influence of radiation the ammonia is desorbed without dissociation of the cluster.[31] Aluminium clusters do not react with methanol in the gas phase.[91]

There have been effectively no studies of the gas-phase reactions of clusters of other metals of Groups IIA and IIIA. Only theoretical calculations have been carried out for some systems. The structures and energies of the $Be_NH$ cluster hydrides have been calculated at the SCF level (without allowing for CI).[71] These molecules are much more stable than the corresponding Be clusters. The binding energy of the hydrogen increases rapidly with the nuclearity $N$: even for $N = 4$ it is close to the energy of sorption on the bulk metal. *Ab initio* calculations of the complexes of $Be_2^{2+}$ with molecular hydrogen[99] identified two stable complexes formed by the reactions:

$$Be_2^{2+} + 2H_2 \longrightarrow \left[H_2\text{---}Be\text{—}Be\text{---}H_2\right]^{2+}, \quad (+2.45\ eV)$$

$$Be_2^{2+} + 4H_2 \longrightarrow \left[(H_2)_2\text{---}Be\text{—}Be\text{---}(H_2)_2\right]^{2+}. \quad (+3.27\ eV)$$

In these complexes the hydrogen is not dissociated: the $H_2$ molecules are located at right angles to the Be—Be bond. These complexes may be formed as intermediates in the interaction of charged Be clusters (and probably also Mg and Ca clusters) with molecular hydrogen.

Theoretical studies of the cluster compounds of magnesium[100-102] have shown that the addition of an $Mg_2$ dimer to F—F, Cl—Cl, H—H, and H—F bonds is more favourable than the addition of an Mg atom. The gain in energy is between 2 and 12 kJ $mol^{-1}$. For Ca the calculation also predicts the possibility of forming cluster compounds of the F—Ca—Ca—F type. As reported,[102] the interaction of the $Mg_2$ cluster with HF can take place through a four-atom transition state to give the cluster compound HMgMgF. However, in every case the calculated difference between the heats of reaction of Mg and $Mg_2$ is not large. It should not be forgotten that the calculation[100-102] can give erroneously low results for the clusters because of the failure to allow for electron correlation effects. The results of calculations on the magnesium—methyl halide system are discussed below, because this reaction has been observed in a condensed but not in a gaseous phase.

Only fragmentary information on the structure, properties, and reactivity of the clusters in the gas phase is available at present. Nevertheless we can formulate some general conclusions. The clusters of all metals in Groups IIA and IIIA are labile formations, with bonds having a strength intermediate between the weak van der Waals bonds and covalent bonds. The presence of numerous geometric isomers and of electronic states with similar energies leaves little doubt that clusters can easily become rearranged into a structure more favourable to the reaction. The low stability of the M—M bond allows us to observe both processes without decomposition of the cluster core (reactions with $H_2$, MeOH, CO) and reactions with dissociation (with $O_2$) under conditions of low activation energy. Two problems are still controversial. Firstly, it is not clear whether homogeneous gas-phase catalysis involving clusters is possible. The Be, Mg, and Al clusters can activate and split bonds with low reactivities such as H—H, C—C, etc. However, there is no evidence of the regeneration of the clusters from the resulting adducts. Secondly, the reaction mechanisms have not been made clear. In an attempt[91] to treat these reactions as one-electron processes the reactivity was correlated with the reciprocal energy difference between the HOMO of the donor and the LUMO of the acceptor. However, the arguments put forward are not entirely convincing. For example, in this approach methane could be said to be more active than hydrogen. Furthermore the low reactivity of the Al atoms as compared with their small clusters (which have a high IP) is difficult to understand. We believe that the high reactivity of the clusters arises from the possibility of simultaneous interaction of a cluster with several atoms of the substrate molecule. Under these conditions the activation may be associated with both an electron transfer and a synchronous bond breaking act in the substrate, with formation of substrate—metal bonds. The thermodynamic characteristics and the activation parameters are found (as could have been expected) to be sensitive to the electronic state of the cluster. The magic clusters have a low reactivity (at least, in reactions involving the breakdown of the metal core).

## VII. Heteronuclear clusters

Metals of Groups IIA and IIIA can form heteronuclear as well as homonuclear clusters. The mixed clusters $K_NMg$ were studied by Kappes et al.,[103] who found that these compounds did not satisfy the formal rules of the spherical shell model. In spite of

having eight valence electrons $K_6Mg$ does not show an enhanced stability, as observed in the 10-electron $K_8Mg$ cluster. The $MgLi^+$, $MgLi^{2+}$, $Mg_2Li^+$ clusters have been prepared by evaporation of the metals from the liquid phase using electron bombardment.[104] Experimental data on clusters of this type are few, and do not allow definite correlations to be identified. Theoretical studies have greatly outstripped the experimental work.

Mixed clusters containing Be and Mg are characterised by a moderately high symmetry and a tendency to form planar structures at low values of $N$. Typical geometric forms of $Li_NBe$ clusters[105] are shown in Fig. 2. Three-dimensional structures are first encountered with $Li_5Be$ in neutral clusters and with $Li_6Be^+$ in charged clusters. The bond is stronger in $LiBe_N$ clusters than in $Be_N$. The bond energies per atom are 0.25 eV in LiBe and 0.45 eV in $Li_2Be$. Similar effects were observed[106] for $Li_NMg$, the only difference being that $Li_3Mg$ has the form of a centred triangle. The introduction of Mg or Al as adatoms into $Li_N$ clusters produces a large increase in the stability of the cluster as a whole, with a corresponding decrease in the ionisation potential.[107]

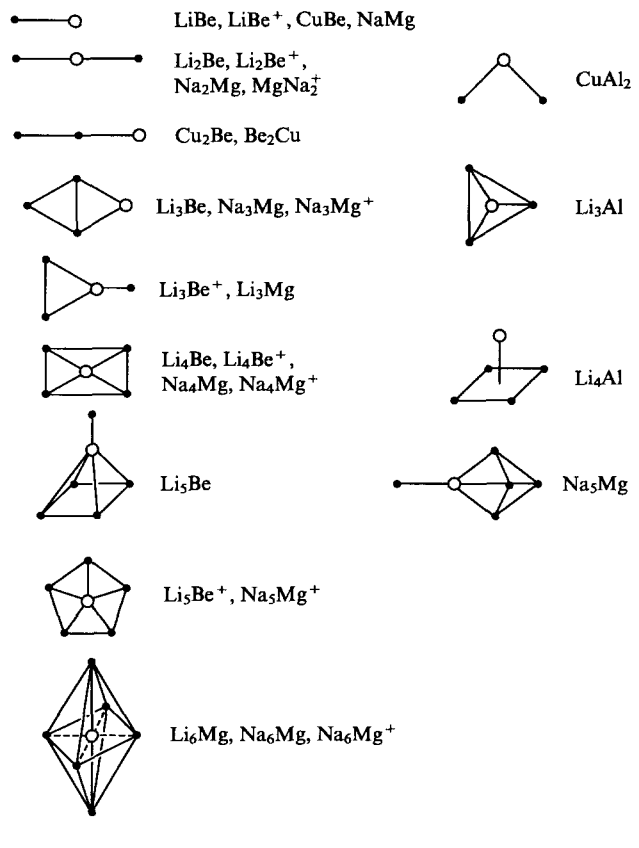



**Figure 2.** Typical forms of mixed clusters.

The $Na_NMg$ and $Li_NMg$ clusters were studied in great detail by Fantucci et al.,[108] who made *ab initio* calculations over a wide basis set allowing for CI. Though the geometry obtained for $Li_NMg$ was similar (on the whole) to previous reports[106] the $D/N$ and IP values were quite different. It was suggested[108] that the STO-6G basis used in the previous work[106] is inappropriate in this case and leads to unreal values of the energy. The MgNa and MgLi clusters are characterised by weak M – M′ bonds with $D/N < 0.1$ eV and internuclear distances of 3.59 and 3.2 Å. The stabilisation energy increases with $N$. The cations are much more stable. For example, the bond breaking energy is 0.87 eV in $MgNa_N^+$. The properties of the mixed clusters vary non-monotonically with $N$. In $MgLi_N^+$ and $MgNa_N^+$ even values of $N$ correspond to a stabilisation energy greater than in the odd values. The ionisation potential of clusters with even $N$ is also higher than that of their neighbours with odd $N$. The magic numbers expected on the basis of the spherical shell model are not clearly observed. In the neutral clusters an enhanced stability is found for 8, 9, and 10 electrons, and in the cationic clusters for 5, 7, and 9. This effect is probably due to the large departures of the geometry of the small $MgM_N$ and $MgM_N^+$ clusters from the spherical form.

The theoretical model was modified as follows in order to provide a satisfactory explanation of the experimental data.[109,110] It is assumed that the additive atom is located at the centre and creates a region in which the charge density is different from the density in the remainder of the core. With a reasonable choice of parameters the resulting model of 'a sphere within a sphere' provides a sequence of energy levels different from that given by the simplest model: $1s < 1p < 2s < 1d$ etc. In this case even a configuration of 10 electrons produces a closed shell: $1s^2p^62s^2$. Under these conditions the stability of the 10-electron cluster $K_8Mg$ is not surprising. The stipulation of a central location of the additive atom is clearly justified (see Fig. 2), as is also the assumption of a different charge density in the central region. For example, in the $Li_NMg$ clusters the central Mg atom carries a greater positive charge (1.1 – 1.33), and in the $Li_NAl$ clusters the charge on the Al atom is also greater than +1 (see Rao and Jene[107]). At the same time the departures from spherical symmetry become substantial.

The Al – B and Al – C mixed clusters are of interest from the standpoint of the spherical model. The clusters $Al_{12}B^-$, $Al_{22}B^-$, and $Al_{21}B_2^-$ have been shown (experimentally) to have a high stability.[111] Because B and Al are isoelectronic these clusters are analogues of the magic clusters $Al_{13}^-$ and $Al_{23}^-$. The low stability of the $Al_{11}B_2^-$ cluster, which is isoelectronic with $Al_{13}^-$, seems inexplicable at first sight. Allowing for the geometric factor now becomes important. Thus, $Al_{13}^-$ is an icosahedron with one central atom which can be replaced by B without substantial changes in geometry. On the other hand replacing a second atom in the outer sphere infringes the symmetry of the system and destabilises it. Two central atoms are present in $Al_{23}^-$, and both can be replaced without perturbing the structure: $Al_{21}B_2^-$ is therefore a very stable system.

The C atom differs little in size from the Al atom. Results analogous to those obtained[111] for the Al – B system could have been expected for $Al_NC^-$. However, a study of $Al_NC^-$ clusters with $5 \leqslant N \leqslant 38$ gave unexpected results: a high stability was observed[40] for $Al_7C_4^-$ and $Al_{24}C^-$. These clusters contain a nonmagic number of electrons: 26 and 77. Their stability was ascribed[40] to the formation of tightly bound AlC subunits in the cluster, which do not contribute to the formation of a valence shell. These clusters should be treated as $Al_6^-(AlC)$ and $Al_{23}^-(AlC)$ respectively, with shells of 19 and 70 electrons, in complete agreement with the model. The absence of a stable $Al_{13}^-(AlC)$ cluster can be attributed to the same effects as the absence of $Al_{11}B_2^-$. The $Al_{13}^-$ centred icosahedron simply does not have unoccupied sites for the interaction with an AlC subunit.

Mixed clusters containing transition and typical metals are of interest as models of new types of heterogeneous catalysts. They can be prepared in the gas phase or in solution. The reaction between diphenylmagnesium and CuBr in diethyl ether gave the $Cu_4Mg(C_6H_5)_6$ cluster, with a metal core consisting of a trigonal bipyramid having three Cu atoms at the base and Cu and Mg atoms at the apices.[112] The Mg – Cu distances are 2.75 Å, and the tetrahedral Mg configuration is produced by the coordination of ether molecules.

*Ab initio* calculations allowing for correlation[113] have been carried out for clusters containing Cu, Be, and Al. The CuBe cluster is much more stable than $Be_2$ ($D/N = 0.385$ eV), and CuAl has the same bond energy as $Al_2$. Both these clusters are almost nonpolar. It is interesting to note that asymmetric structure correspond to the more stable isomers of the linear

$Cu_2Be$ and $Be_2Cu$ clusters (see Fig. 2). The interaction of $Be_2$ with Cu greatly increases the stability of the Be–Be bond (dissociation energy 0.56 eV). The $CuAl_2$ cluster has a triangular structure; the energy needed to split off an atom is 2.28 eV for a Cu atom and 1.56 eV for an Al atom.

The reactivity of the mixed Al clusters has been studied for their interaction with hydrogen and oxygen. Hydrogen is not chemisorbed on solid Al, and does not react with Al atoms or clusters (except $Al_6$–$Al_8$). However, Co clusters are activated by introducing Al into them. Thus, the following activity series were obtained[114,115] for mixed Co–Al clusters with identical numbers of Co atoms:

$$Co_6 \approx Co_6Al \ll Co_6Al_2 > Co_6Al_3\,;$$

$$Co_8 \ll Co_8Al < Co_8Al_2 > Co_8Al_3\,.$$

Even one Co atom causes marked activation of the Al clusters. Thus, the $Al_{10}Co$ cluster has a high activity.

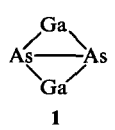
A different state of affairs is seen for $Nb_N$ clusters. The activity of small Nb clusters with $N = 4-7$ falls off steeply when Al is introduced. For example, $Nb_4Al_2$ reacts with $H_2$ to a negligible extent, whereas $Nb_4$ is quite active. On the other hand the deactivation of $Nb_N$ clusters with $N = 8-12$ by aluminium is relatively weak.

The effect of Al on the reactivity of $Co_N$ clusters has been ascribed[114] to a decrease in the IP. However, direct measurements of the IP of mixed clusters failed to detect a decrease when the number of Al atoms was increased, or a correlation with the reactivity of the cluster.[116] The activation of the Co clusters by aluminium is probably caused by electron transfer within the metal core from the Al to the Co.

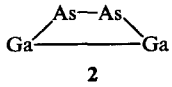
The reactivity of Nb clusters towards the reaction with $H_2$ is not correlated with the IP,[117] and the electronegativities of the Al and Nb atoms are not very different. The deactivation of small $Nb_N$ clusters by aluminium has been attributed to the structural blocking of the most reactive atoms of the transition metal. At high $N$ values the contribution from this effect is small.

A phenomenon analogous to the magic numbers effect has been observed for anionic Al clusters in the reactions of $VAl_N^-$, $NbAl_N^-$, and $VNbAl_N^-$ with oxygen.[94,118] It was found that $NbAl_4^-$ and $VAl_6^-$ have an anomalously low reactivity. Any attempt to reconcile this result with the spherical shell model must take account of the number of electrons contributed by the transition metal. The valence shell of V and Nb have the $3d^34s^2$ and $4d^45s^1$ structure. It is not clear whether the *d* electrons are correlated in the cluster. In the case of $NbAl_4^-$ the participation of all the electrons produces a stable 18-electron shell. In this case we obtain a 24-electron configuration for $VAl_6^-$, which is far from the magic number. It may be assumed that only the *s* electrons are involved (or, more strictly, one *s* electron). The prospects of describing the reactions of mixed clusters containing transition and typical metals in terms of simple models are not favourable at present.

Before proceeding to other topics we should mention the mixed clusters of gallium and arsenic. Interest in these species was stimulated by their possible application in the production of gallium–arsenic semiconductor materials. Clusters of this type are prepared by the laser evaporation of gallium arsenide.[119] The ground state of GaAs is $^3\Sigma^-$, that of $GaAs^+$ is $^4\Sigma^-$ (see Knight and Petty[120]). The most stable of the binary clusters[121] is $GaAs^-$. The $Ga_NAs_M$ clusters are characterised by the presence of several isomers with similar energies.[122] For example, in $Ga_2As_2$ we find the structures **1** and **2**, both unstable (though structure **1** is relatively more stable). The energy of the dissociation of cluster **1** into two GaAs molecules is greater than 3 eV (*ab initio* + MRCISD).[123]




**1**




**2**

These results exemplify the multiplicity of structures and of composition available to the mixed clusters. It is not unreasonable to suggest the possibility of preparing these compounds for any pair of metals and for many metal–nonmetal combinations.

## VIII. Preparation of clusters and their reactions at low temperatures

So far we have dealt with clusters prepared and studied in the gas phase. Another, no less important approach to the problem relies on the cryochemical synthesis of cluster compounds.

Metal clusters can be prepared by the aggregation of atomic metal being condensed from the gas phase. Their stabilisation in a matrix or on a solid carrier surface allows their chemical properties to be studied. The nuclearity of the clusters is difficult to establish in solid-phase experiments because mass spectrometric detection is not available.

Studies in which the clusters are prepared by condensation from the gas phase can be divided into two groups: studies of small clusters and studies of giant clusters and of even larger species. The preparation and the chemical properties of moderately large clusters (tens of hundreds of atoms) have received little attention because of the difficulty of identifying these species in condensed phases. Let us examine the case of small clusters.

The spectra of small clusters of calcium and magnesium have been studied by Klabunde and coworkers.[124,125] For example, for Ca the following bands were observed: 374 ($Ca_2$, $^1\Pi_u \leftarrow {}^1\Sigma_g^+$), 415 (Ca, $^1P_1 \leftarrow {}^1S_0$), 448 (Ca, $^1D_2 \leftarrow {}^1S_0$), 470 ($Ca_x$, $x > 2$), 505 ($Ca_2$, $Ca_x$), 550 ($Ca_x$), 648 nm ($Ca_2$, $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$). Bands corresponding to clusters with $N$ between 1 and 4 can be resolved for Mg; total absorption was observed for clusters with $N \geqslant 5$. The spectra of Al, Ca, and In dimers were reported by Douglas et al.[43]

The study of the reactivity of Al clusters is complicated by the very high activity of Al atoms towards the majority of reactants in the solid phase. At temperatures of about 77 K Al atoms react with ethylene,[126] propene,[127] butadiene,[128] tetrahydrofuran and halogen derivatives,[129] benzene,[130] and even methane.[131] Nevertheless the cluster halide $Al_2Cl_4$ was prepared by the simultaneous condensation of aluminium and chlorine in an inert matrix: the structure of its Al–Al bond was established by IR and ESR spectroscopy and by quantum chemical calculations.[132]

The cryochemical reactions of the elements of Group IIA, whose atoms are less reactive than those of aluminium, are of special interest. The formation of organomagnesium compounds (OMC) by the simultaneous condensation of Mg and organic halides was established 20 years ago.[133] More recently reactions between Mg clusters and relatively unreactive molecules such as $C_6H_5F$ and $CCl_4$ (Refs 134 and 135) have been carried out. Similar reactions have been observed[136] also for Ca and Sr. In the course of this work it was shown that the formation of OMC is favoured by the same conditions as the aggregation of Mg atoms.[137] Furthermore, products of the Wurtz reaction can be obtained instead of the OMC under conditions conducive to the isolation of atoms.[138] This underlines the important role of the aggregation of metals in the synthesis of OMC. Strict proofs of these conclusions have been formulated[139,140]. It was shown that in an Ar matrix the Ca clusters (but not the Ca atoms) react with $CH_3Br$ and $CH_3I$, and that only the $Mg_N$ clusters with $N \geqslant 4$ react with $CH_3F$.

The low reactivity of Mg and Ca atoms can be understood by considering the mechanism of formation of the OMC. The direct addition of the atoms to the carbon–halogen bond is symmetry forbidden,[141] and the activation energy of the process should be at least 30–40 kJ $mol^{-1}$ (see Davis[142]). Typically, in the gas phase the Mg atoms do not react with RCl molecules, irrespectively of the nature of R; radical detachment of Cl with formation of MgCl is observed only in the reaction with $Cl_2$.[143]

The formation of OMC requires an intermediate one-electron transfer whose possibility is determined by the ionisation potential of the metal-containing particles. As was pointed out above, the IP of $Mg_N$ clusters decreases with increasing nuclearity, and the reaction becomes possible above a certain value of $N$. By starting from this simple scheme we can propose an alternative role for the aggregation in the case of Al. In the Al clusters the IP initially increases with increasing nuclearity, and small clusters can have a low activity towards reactions with RCl.

The addition of $Mg_N$ to the bonds of organic halogen derivatives (RX) should lead to the formation of cluster compounds which we can call organopolymagnesium halides (OPMH). It has been suggested[140] that these compounds cannot be stable, and that they should decompose or react with the excess of RX when the matrix is allowed to warm up. Indeed, as reported,[101,102] the additional stabilisation energy of the OMC clusters (as compared with the Grignard reagent) is not more than 24.8 kJ $mol^{-1}$, and falls to zero as $N$ increases to 5. We consider these conclusions[140] premature. Firstly, as can be seen from the calculated potential energy surfaces for Mg* and $Mg^{2+}$, these species should have a high kinetic stability. The activation energy for their decomposition could be quite large. Secondly, the published calculations[101,102] do not allow for electron correlation effects, which can predominate in the stabilisation of cluster compounds. For example, the *ab initio* calculation of the stable cluster tetramer $Al_4(C_5Me_5)_4$ isolated in a pure form[22] suggests that this species cannot be prepared.[144] This conclusion is quite correct, in spite of the neglect of correlation effects, but for $Mg_N$ the correlation effects may be more important than for Al. Therefore the reported[101,102] stability of OMC clusters of the $RMg_NX$ type appears to be too low.

The stability of OPMH under normal conditions has now been confirmed experimentally in the case of phenylpolymagnesium halides.[145,146] These compounds, of the general formula $PhMg_NX$ ($N = 2-4$; X = F, Cl, Br, I), can be prepared by cryochemical synthesis and are stable in solution for many weeks at 295 K: they can be isolated in a polycrystalline form and analysed. The effective state of oxidation of the Mg is less than 2. The action of water on OPMH causes hydrogen evolution according to the equation

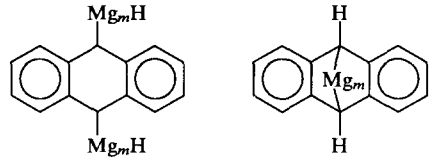
$$PhMg_NX + (2N-1)D_2O \longrightarrow$$

$$\longrightarrow PhD + MgX(OD) + (N-1)Mg(OD)_2 + (N-1)D_2.$$

The decomposition of $PhMg_NX$ requires a temperature close to 100 °C. Compounds with alkyl substituents are less stable, and their structure is not entirely clear.[147]

The composition of $RMg_NX$ is determined by the nature of the reagent X, and to a large extent by the stability of the C–X bond. Allyl bromides, which have the weakest bonds, give the classical Grignard reagents $C_3H_5MgX$ ($N = 1$). With the stronger C–Br and C–I bonds, and also C–C, the parameter $N$ takes the value 2 (on average). Lastly, from PhCl and PhF we obtain $PhMg_NX$ compounds in which the average value of $N$ is 3–3.5 (X = Cl), and even 4 (X = F). The dependence of the nuclearity of the OPMH on the strength of the C–X bond is due to the competition between the metal aggregation process and the addition at the C–X bond. In $C_3H_5X$ the bond is very weak, and the Mg atoms arriving from the gas phase react with the organic molecule faster than they can aggregate. The reaction probably takes place by a radical mechanism with intermediate removal of a halogen atom. Dimers and trimers react with the stronger C–Br and C–Cl bonds, whereas only the tetramers of larger particles can react with the strongest bonds (H–F). This explains the selectivity of the clusters in terms of activity as a function of the stability of the C–X bond.

The formation of cluster compounds of Group IIA is not confined to halogen derivatives. There is strong evidence for the existence of compounds of the $RMg_NH$ type, formed by the simultaneous condensation of the metal and of aromatic hydrocarbons. Under these conditions, Al, Ca, and Mg form bright green condensates which become black when heated. It is assumed that complexes are formed in the first stage, and are then decomposed with formation of the dispersed metal.[129,148] However, in addition to this process we observe the activation of the C–H bonds of the aromatic with formation of hydride derivatives. The yield of hydrides during the interaction of alkylaromatic compounds with magnesium was thought to be a few per cent.[149] During the interaction of calcium with benzene a quantitative yield of hydrides is formed,[150] but their nature is not entirely clear. By analogy with the formation of organopolymagnesium halides we may suggest the addition of magnesium clusters to strong C–H bonds. More definite data are available for the magnesium–anthracene system. In this case a solid product of composition $C_{14}H_{10}Mg_N$ was obtained on removing the excess of ligand, with $N$ varying between 4 and 8. Hydrolysis of these materials produces hydrogen, anthracene, and 9,10-dihydroanthracene, which suggests[151] the formation of the compounds **3** and **4**:




**3** **4**

$m \approx 4$.

The cluster compounds of Mg are more reactive than their mononuclear analogues. For example, the cross-combination of the $PhMg_2X$ (X = I, Br) compounds with allyl bromide is faster by an order of magnitude[145] than the reaction of PhMgX. The course of the reaction is also different. The compounds $PhMg_3Cl$ and $PhMg_4F$ ($N = 3$ and 4) react with allyl bromide by exchanging organic radicals, and under these conditions cross-combination is almost never observed.

The high reactivity of organopolymagnesium halides can be attributed to a number of causes. These compounds contain the relatively weak Mg–Mg bonds, whose homolysis can lead to reactions which lower the nuclearity of the cluster. This could be the mechanism of the thermal breakdown of the cluster compounds at high temperatures. We should stress that the ionisation potential of the cluster OMC can be much lower than in RMgX, as shown by semiempirical calculations for model compounds.[146] One-electron transfer plays a fundamental role in many reactions of organomagnesium compounds.[152] Therefore a decrease in the IP should produce a strong activation of the molecule. Furthermore the coordination of the reacting molecules at several centres of the cluster simultaneously can be important, as it is in gas-phase reactions. For example, in the $RMg_4X$ compounds all the magnesium atoms are coordinationally unsaturated, and the unsaturation persists even after dimerisation of these cluster molecules. In the absence of donor solvents these species will be reversibly coordinated to reagents which favour their interaction. From this point of view the exchange reaction discussed above can be represented by the scheme:

$$RMg_NX + R'Y \rightleftharpoons \begin{matrix} R & & Y \\ & Mg_N & \\ X & & R' \end{matrix} \rightleftharpoons R'Mg_NX + RY.$$

The high activity of cluster compounds offers new possibilities in organometallic synthesis. However, the use of these compounds in catalysis has attracted the greatest interest. The reversible coordination of the cluster core to various reagents creates the possibility of obtaining catalytic cycles. Thus, in the $C_6H_5F-n\text{-}C_8H_{17}Cl-C_6H_5Mg_4F$ system the yield of chloro-benzene and octyl fluoride exceeds the molar amount of magnesium by a substantial factor, suggesting a catalytic process.

Cluster organometallic hydrides are of special interest from the viewpoint of catalysis. The magnesium–anthracene system discussed above can be used as a hydrogen transfer system. In the presence of hydrogen donors such as alkylaromatic hydrocarbons the yield of $CHCl_3$ in reactions with $CCl_4$ exceeds the amount of magnesium by an order of magnitude or more.[151] Evidence of a high catalytic activity towards the polymerisation, alkylation, and isomerisation of olefins in the combined condensates of magnesium with aromatic hydrocarbons and $TiCl_4$ has recently been obtained.[153] In the absence of the aromatic hydrocarbon the activity of the catalyst is much lower, or completely absent.

The cluster compounds of nontransition metals are of considerable interest as the components of homogeneous catalytic systems. From the standpoint of heterogeneous catalysis the giant and supergiant clusters are the most promising. These are similar in size to the powders obtained by dispersing metals or by reducing their salts in solutions. However, the giant clusters prepared by the cryochemical method have a number of distinguishing features, not found in ordinary metals, which justify a separate discussion within the present review.

## IX. Giant clusters prepared by cryosynthesis

In the previous section we discussed the interaction of small metal clusters with reactive matrices, leading to the formation of cluster compounds. The use of relatively inert matrices, and of compounds giving only low-stability metal adducts, offers a new pathway for the reaction: the aggregation of the metal with formation of giant clusters.

The most important methods of studying these systems include electron microscopy and UV and IR spectroscopy. Various theoretical models (Maxwell–Garnet, Drude, etc.[154, 155]) have now been developed to describe the spectra of highly dispersed metals. However, even by allowing for the cluster nature of the absorbing species these models fail to describe their IR spectra exactly.[156] A satisfactory quantitative description of the spectra is obtained by abandoning the use of all parameters relating to the bulk metal and allowing for the quantum effects associated with the small size of the absorbing species.[157] This model can be used to describe the spectra of large clusters of Al and other metals in the gas and the condensed phase.[158, 159]

Electron microscopic and spectral data show that ultradispersed particles of practically any size can be obtained by varying the condensation regime and the metal : inert matrix ratio. Under typical conditions (pressure of metal vapour $\sim 0.1$ Torr and metal : Ar matrix ratio $\sim 10$) almost all metals give particles having a diameter of the order of 1000 nm.[160] The particle size depends (among other factors) on the nature of the matrix and of the diluent gas. As a function of the latter factor it increases in the sequence: He < Ar < Xe (see Wada [161]). By varying the preparation regime of Mg clusters in the presence of tetrahydrofuran and of inert gases the size of the clusters can be varied between 2 and 100 nm or more (i.e. from $10^2$ to $10^7$ atoms).[162] Particles of about the same disperseness can be produced also without using inert matrices. Thus the condensation of Al vapour, both with and without hydrogen, gives crystalline particles of octahedral, cubo-octahedral, and trigonal bipyramid form having an average size of 40–200 nm.[163]

The giant clusters prepared by condensation in an inert gas matrix or on the surface of an inert carrier are similar in properties to the massive metals, the only difference being a very large specific surface area. The situation is entirely different for the products of the simultaneous condensation of the metal and of a formally inert organic compound. After removal of the excess of organic compound cocondensates of Mg with hexane and tetrahydrofuran are deeply coloured pyrophoric powders much more reactive than the Mg powders obtained by traditional methods.[164] The corresponding Ca condensates have been used [165] to prepare Ca analogues of the Grignard reagents.

Studies by electron microscopy of simultaneous condensates of Mg and tetrahydrofuran (after removing the excess of the latter) showed the formation of clusters approximately 35 nm in diameter. These condensates can absorb hydrogen at 200 °C, whereas dispersed magnesium prepared by any other method absorbs only at 350–450 °C. Treating the condensate with perylene increases the rate of sorption of hydrogen more than 10-fold.[166] This large increase in activity is due (at least in part) to an almost fourfold increase in specific surface area as compared with the most active samples of the compact metal. However, the main role is played by the specific structure of the clusters, resulting from the high proportion of organic substance. The condensate has the overall formula $Mg(C_xH_yO_z)_{0.0274}$, where $x:y = 3:1$.[167] The high catalytic activity of the condensate towards the H–D exchange reaction is observed even at 0 °C.[168] The sorption activity depends on the condensation conditions and on the shape and size of the clusters. Though in every case the arrangement of Mg atoms in the condensate corresponds to a hexagonal lattice, the morphology of the clusters is different: layered aggregations are formed in THF, whereas in a diethyl ether matrix the aggregates are columnar. A substantial activation of the condensate is achieved by adding 1%–2.5% of copper. Under these conditions the specific surface is increased by 1–2 orders. The copper is finely dispersed in the excess of magnesium and accelerates the sorption of hydrogen.[169] Similar results were obtained with cocondensates of magnesium and nickel. The nickel forms clusters 0.8–3.5 nm in diameter enclosed within larger aggregations containing an organic Mg species.[170]

The giant metal clusters obtained by cryochemical condensation have the size of colloidal particles. Therefore colloidal solutions are often produced by dissolving these condensates.[171] Giant clusters can also be synthesised by passing a flow of metal clusters or atoms in a stream of inert gas through a liquid solvent.[172] The possibility of formation and the stability of the colloidal metals obtained in this way are determined by the character of the interaction of the surface of the ultradispersed metal with the medium.

The colloidal solutions of aluminium have been studied in most detail. Thus, the dark blue solution in ethanol contains particles 30 nm in diameter. Bands at 215, 250, and 550 nm have been identified in its spectrum.[172] The solution is stable for one month: this has been attributed to the formation of a stabilising oxide film on the metal surface. The nature of the stability of the colloid is the same as in the Al colloid prepared by the aerosol method.[173]

The more active Ca metal also forms a light blue colloidal solution in ethanol. However, its lifetime is not more than 10–12 min, possibly because of the low strength of the oxide film. Stable colloids are not obtained even when the metal particles are combined with paraffins.

The mechanism of the stabilisation of colloids of typical metals prepared by cryochemical synthesis is not completely understood at present. Firm criteria defining their optimum formation conditions have not been formulated. It may be assumed that reactions on the surface of the initial clusters play a dominant role. Clearly, if the matrix is very active and reacts with atoms and small clusters in the solid phase a colloidal solution cannot be formed: for example, in calcium (or magnesium)–hydrocarbon halide systems. As in the case of the alkanes, inertness of the matrix does not stabilise particles of

colloidal dimensions because of coagulation and sintering effects. The best matrices have a moderately high reactivity: they are inactive during the preparation of the solid sample at low temperatures, and do not suppress the primary aggregation process in the solid phase, but they block the surface of the giant cluster by reacting with it near the melting point.

This simple criterion has been used in the synthesis of stable colloidal solutions of Mg in amines (triethylamine, dimethylamine, etc.[174,175] Heating the cocondensates of Mg and amines leads to the formation of coloured or colourless solutions containing (according to measurements by UV spectroscopy and electron microscopy) particles having dimensions between 30 and several hundred nanometers, depending on the amine. The interaction begins in the solid phase with formation of ion–radical particles, as shown by the characteristic ESR signal, which disappears upon heating the sample. Two competing processes apparently take place under these conditions: the aggregation of the small clusters formed during the condensation into larger formations and the conversion of the ion–radical species into compounds with stable chemical bonds. As a result we obtain relatively large metal particles with a surface coating of organometallic compounds. The formation of strong bonds is confirmed by the detection of up to several per cent of the organic component after pumping out the amine and lengthy vacuum heat treatment of the residue.

A slightly different stabilisation mechanism takes place in the magnesium–pyridine system. In this case very large aggregates (up to 2000 nm) are present in the solution. A strong ESR signal persists after the sample is melted. Pyridine has a high electron affinity, and therefore the ion radicals are reasonably stable on the metal surface. The resulting electric double layer stabilises the particles and prevents their coagulation. Oxygen additions cause the breakdown of this layer and destroy the colloidal solution.

Mg colloidal solutions have a high reactivity. They can be used in preparative work as a source of very active magnesium. However, their catalytic and initiating properties are the most interesting. They can activate various organic molecules, including hydrocarbons. In the presence of colloidal magnesium the catalytic migration of the double bond in olefins takes place effectively at room temperature. Normal alkanes are isomerised into isoalkanes, but the extent of reaction does not exceed 2%–4%. Colloidal magnesium is used as a powerful initiator of the radical addition of polyhalogenomethanes ($CCl_4$, $CHCl_3$, etc.) to the multiple bonds in olefins. The yield of product at 80 °C can be as high as 400 mol per mole of Mg per hour.[176] We note for comparison that the activity of one of the best initiators of this process (magnesium decacarbonyl) is several times lower at 120 °C and high pressure.

* * *

The study of the chemical reactions of clusters of the transition metal in the condensed phase and of the reactivity and catalytic properties of the resulting cluster compounds is only beginning. However, it is already evident that this work will generate new and very active homogeneous and heterogeneous catalysis systems. The stability of many cluster compounds of the transition metals in solutions opens new pathways to the realisation of unusual transformations and to the synthesis of new types of organometallic derivatives. Complex systems containing both clusters of the transition metals and compounds of these metals are of special interest. In this case we can expect the achievement of very high catalytic activities. The number of publications in this field will undoubtedly continue to increase.

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