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A statistical analysis of magic numbers of valence electrons in small clusters of transition metals using the Cambridge Crystal Structure Database

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Abstract

Distribution of small clusters of transition metals M_n with $n = 3$ to 6 metal atoms over the number of valence electrons in metallopolyhedra, N_{val}, has been analysed using the Cambridge Crystal Structure Database (10 sets, total 923 crystal structures). The occurrence of peaks related to magic numbers N_{val} has been found for trinuclear (48e), tetranuclear (60e) and hexanuclear (86e) carbonyl clusters of metals of the Fe and Co subgroups. However, similar distributions for pentanuclear carbonyl clusters of the same metals, for tri- and tetranuclear carbonyl-phosphine derivatives of metals of the Ni subgroup, and also for the $M_4(\mu_3\text{-}X)_4$ type clusters with mixed cubane-like frameworks (where X is a halogen or chalcogen) are more uniform and exhibit no predominance of specific "magic" numbers. Among tri- and tetranuclear metal complexes of the Cu subgroup, the more common and typical are those with no metal–metal bonds, in which every metal atom has a 17-, 18-, or 19-electron valence shell. On going from metals of the Fe and Co subgroups to post-transition elements, the strength of metal–metal bonds and the descriptive ability of magic numbers decline. The following magic numbers were found for octahedral "inorganic" clusters of early transition metals: $N_{val} = 74$ for clusters of the $M_6(\mu_3\text{-}X)_{12}$ type (where X is a halogen) and a more strictly obeyed number $N_{val} = 84$ valid for more rigid frameworks $M_6(\mu_3\text{-}X)_8$, (X is halogen or chalcogen).

Introduction

Magic numbers of electrons are a well known feature in cluster chemistry. The rules available for such compounds (i.e. the effective atomic number (EAN) rule and Wade's "$2n + 2$" rule [1] with its further modifications [2–5]), known also as "counting schemes for polyhedron electrons" and as the "theory of skeletal electron

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pairs" [4], describe the geometry of a cluster as a function of the number of valence or skeletal * electrons in its polyhedron. Magic numbers were initially proposed for clusters involving middle-transition metals in a carbonyl ligand environment [1]. Later, several papers providing theoretical substantiation and ways to determine magic numbers for a wider class of polynuclear compounds were published [3–5].

Today, the total number of clusters with known structure is in excess of one thousand and rapidly increasing. The abundance of experimental evidence allows the regularities of electronic and spatial structure of a given type of compound to be considered using an alternative approach, viz. an empirical study based on a statistical analysis of structural data. In the last few years, investigations of this kind, relying on the Cambridge Crystal Structure Database (CCSD) [6] as their principle tool (which presently covers more than 55,000 compounds with "organic" carbon atoms) have resulted in formulation of several important regularities of geometric and electronic structures of organic molecules [7].

In the present work, we are concerned with finding "empirical" magic numbers of valence electrons in small clusters of transition metals which contain metallopolyhedra M_n with $n = 3$ to 6 ** metal atoms.

Using CCSD, we have obtained distributions of structurally investigated clusters of the same type over values of N_{val} in their metallopolyhedra. Whenever there is an increased thermodynamic stability of clusters having some specific values of N_{val}, these values would show up in histograms in the form of related maxima. It is interesting to compare values of "statistical" magic numbers with those predicted by the EAN and "$2n + 2$" rules for M_n clusters with the appropriate value of n. This work is a continuation of our research into the nature of magic numbers and the conditions for their existence [9,10].

The small clusters we are concerned with make up a major part of all the structurally analysed metalloclusters and, in view of their large number, they can be treated statistically. The set of clusters which have been subjected to X-ray or neutron diffraction analysis may be viewed as being fairly representative since cluster chemistry is characterized by the large proportion of compounds which have been investigated structurally. On these grounds, the distributions obtained herein of structurally studied clusters as functions of N_{val} are likely to express general laws which hold for the whole gamut of compounds of a given type. In several cases, samples of structural data retrieved from CCSD were supplemented by data from the literature on compounds of a similar type with no "organic" carbon atoms (these are primarily octahedral clusters of early transition metals in a halogenide or chalcogenide environment and also some carbonyl and nitrosyl derivatives), and from data published recently on small clusters of Pd and Pt. In all such cases we tried our best to include as many references as possible.

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* The numbers of valence, N_{val}, and skeletal, N_{skel}, electrons in a cluster of transition metal atoms obey a straightforward relationship, $N_{val} = N_{skel} - 12n$, where n is the number of metal atoms in the cluster; see ref. 1.

** The relation between the structure of the trinuclear clusters and the number of their valence electrons has been considered in a review by S.P. Gubin [8].

Data selection and processing

References to structural studies of transition metal clusters with 3 to 6 metal atoms were retrieved from the BIB file (1985 version) of CCSD by running the BIBSER program on an EC-1060 computer in the Computer Centre of the USSR Academy of Sciences. The data have been taken from publications up to the middle of 1984. From a total of 1340 references, the following sets were formed.

A. Fe, Co, Ru, Rh, Os, and Ir clusters with predominance of carbonyl ligands in coordination environments: trinuclear (MCO3, 343 references), tetranuclear (MCO4, 142 references), pentanuclear (MCO5, 56 references), and hexanuclear (MCO6, 61 references). Apart from the CCSD data, structural data on clusters with carbonyl ligands only (9 references) were also included with MCO5 and MCO6 samples. No compounds with isolated mononuclear fragments of the σ-metallocenic type, i.e. those having no metal–metal bonding with the main metallopolyhedron, were incorporated into this group.

B. Ni, Pd, and Pt clusters with carbonyl, phosphine, and η-olefine ligands: trinuclear (NIPT3, 32 references) and tetranuclear (NIPT4, 16 references). Because of their small size, these sets were supplemented by recently published data which had not yet been taken up into CCSD (8 references in all).

C. Multinuclear Cu, Ag, and Au complexes having a connected fragment built up of metal atoms: trinuclear (CUAU3, 37 references) and tetranuclear (CUAU4, 117 references). No compounds with isolated mononuclear or binuclear fragments and intrafragmental metal-to-metal distances greater than 4 Å were included in these sets.

D. Tetrahedral clusters of middle-transition metals in which atoms of transition metals are part of cubane-like frameworks $M_4(\mu_3\text{-}X)_4$ or $M_3M'(\mu_3\text{-}X)_4$, (where X is a halogen or chalcogen) were made up into the TETR set (67 references). The CCSD set of derivatives of metals of the Fe and Co subgroups was expanded to include published data on derivatives of V, Cr, and Mn subgroup metals (23 references). Another set based entirely on data taken from the literature was formed, which covered another type of “inorganic” cluster: the octahedral clusters of early transition metals with halogenide and chalcogenide ligands (the OCTA set comprising 52 structures).

In all, 923 cluster structures were used, of which 840 were retrieved from CCSD and 83 were taken from original papers. The inclusion of data not contained in CCSD could not substantially affect the results obtained for the nine “Cambridge” sets. However, in the case of small sets, it did improve their representativeness. At the same time, thanks to our “paper-based” set OCTA, a very interesting group of octahedral halogenide and chalcogenide clusters could be analysed, which are obviously related to other small clusters of transition metals.

Throughout this work, a structural investigation of an individual chemical compound was treated as a unitary piece of information. Whenever results of several studies of the same cluster were available (such as refinements, brief and full reports, independent determinations of the structure by different groups of authors, availability of both X-ray and neutron diffraction data), only one inclusion of the cluster into the set was made. The same rule was applied to situations when several crystal modifications or different crystallosolvate forms of the same cluster had been studied. However, salt structures with similar cluster ions but different counter-ions were counted independently, unless reported in one paper in which case only one reference was used.

Since all we need to calculate N_{val}, is the structural formula of the cluster, no special checks were made on the accuracy of a given structural investigation, except that data on structures where not all of the ligands had been determined were discarded as were those on which, as a result of serious disorder, no conclusive judgement could be made as to the character of the bonding of ligands to the metallopolyhedron.

The number of valence electrons in the metallopolyhedron was found as the total of valence electrons of all atoms in the cluster and ligand-donated electrons minus the cluster charge. When the cluster had an interpolyhedral atom, all its valence electrons were assumed to have been drawn into the polyhedron. The numbers of electrons donated by ligands were as is usually assumed in metalloorganic chemistry (terminal σ-R, σ-Ar, X (halogen), SR-, CN-ligands – 1e; carbonyl, η^2-olefine and isonitryl ligands – 2e, μ_2-X(halogen), NO – 3e, η^6-arene – 6e, etc., see [11]). When it was impossible to derive N_{val} unambiguously from the stoichiometric composition of the cluster and the title of the referenced paper, the crystal structure of the cluster had to be considered. In group "*A*" and in the TETR set, we also included mixed clusters of the $[MoFe_5C(CO)_{17}]^{2-}$ (EACRFB *) type with a "heteroatom" of an early or middle-transition metal. Clusters that could have qualified for a given set because of the number of metal atoms in their main polyhedron, but having an extra vertex-cap superstructure, were not included in the set. Clusters in which the main polyhedron of transition metals is bonded to a AuL, CuL, or HgX bridge fragment (L is a two-electron donor and X is a halogenide ligand), and which plays the part of a structural analogue of a hydride ligand, were included. No mixed clusters with either Ni, Pd, Pt, Cu, Ag, or Au atoms in the main polyhedron were entered for consideration. The composition of the sets and CCSD codes of individual clusters, listed in the order of their valence electron number, can be found in the Appendix.

Discussion of results

The distribution of structurally investigated small clusters over the value of N_{val} is shown in the form of histograms in Figs. 1, 4–6. To see how different factors contribute to the existence of magic numbers of electrons in the analysed clusters, sets of compounds were made, which differed, (i) in the nature of metal atoms forming the polyhedron, (ii) in their number, (iii) and in the character of the ligand environment of the cluster. Sets of the "*A*" group (MCO3–MCO6) were chosen so as to encompass carbonyl derivatives of the most "clusterable" metals, such as Fe, Co, and their analogues. Included in the "*B*" group, were tri- and tetranuclear derivatives of the nearest neighbours of these metals in the periodic system, being elements of the Ni subgroup. In selecting clusters for the "*B*" group (NIPT3 and NIPT4), we tried to limit our choice to clusters with ligands particularly close to those typical for the "*A*" group, even at the expense of set size. The "*C*" group represents sets of polynuclear complexes of post-transition metals of the Cu

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* The CCSD code of the compound is given in parentheses.

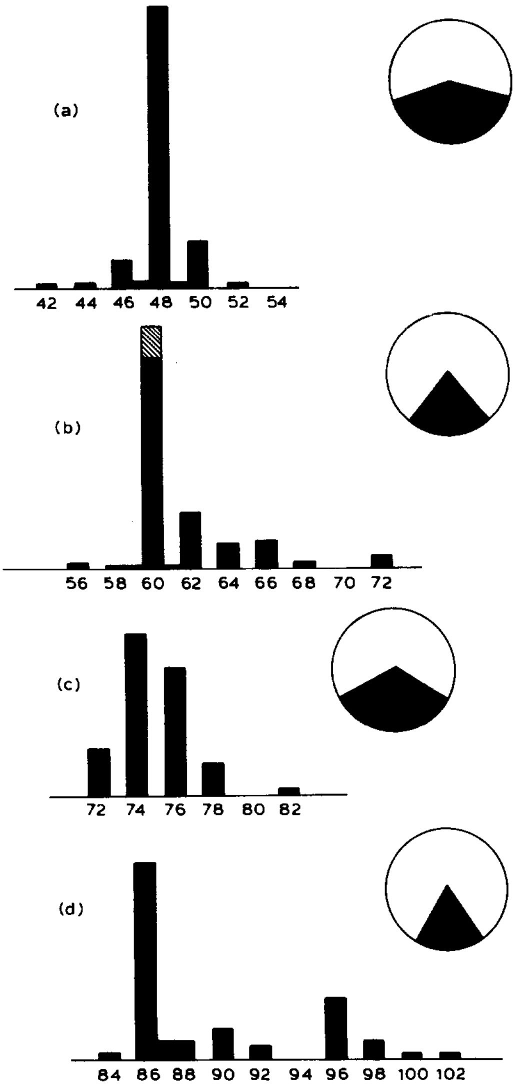

Fig. 1. Distribution of carbonyl clusters of Fe and Co subgroups over the numbers of valence electrons in metal core: (a) three-nuclear M_3; (b) four-nuclear M_4 (the shaded part corresponds to 60-electron open moieties which are completed by ligands to octahedron); (c) five-nuclear M_5; six-nuclear M_6. (M is transition metal). Black sectors correspond to the part of hydride clusters in each set.

subgroup, mostly derivatives of Cu itself (CUAU3 and CUAU4). Finally, the "*D*" group contains data on tetrahedral clusters of middle-transition metals (in fact those forming clusters in the "*A*" group) with μ_3-halogenide and μ_3-chalcogenide ligands (the TETR set) and on octahedral clusters of early transition metals (the OCTA set, compiled from original papers). The comparison of the distributions of crystal structures over N_{val} for all four cluster groups is undoubtedly important for understanding the nature and stability of magic numbers.

Carbonyl clusters of metals of Fe and Co subgroups

Initially, it was structural studies of these clusters that led to the formulation of the electron counting rules, determining magic numbers N_{val} for metallopolyhedra. Indeed, looking at histograms for tri-, tetra- and hexanuclear clusters (Fig. 1a–1d), one can easily make out the magic numbers, N_{val}, equal to 48, 60, and 86. The first two numbers coincide with the magic numbers for a M_3 triangle, and a M_4 tetrahedron, given by the EAN rule, while the third one matches the Wade's rule prediction for an octahedron M_6 [1]. In fact, most clusters with these values of N_{val} do have the predicted structure. Hence we see, that clusters (Fig. 2) with the N_{val} magic numbers indeed have a greater thermodynamic stability, which is the reason for their predominance over the other clusters with the same number of metal atoms. Another obvious feature of the histograms shown in Fig. 1 is that there are many more compounds with even values of N_{val} than with odd ones, this reflects the instability of unfilled electron shells.

The histogram with the simplest shape relates to trinuclear clusters (Fig. 1a), the distribution of which expressed as a function of N_{val} is apparently close to normal (with the predominance of closed electron-shell compounds taken into account). The histograms for larger clusters from the MCO4 (Fig. 1b) and MCO6 (Fig. 1d) sets are markedly less symmetrical, with the right-hand side acquiring a much more characteristic form, related to opening of closo-polyhedra in clusters with the number of electrons in excess of the major magic number. Alternative magic numbers are often observed in this region. They are also predicted by the existing rules: $N_{val} = 62$ for "butterfly" clusters and $N_{val} = 64$ for planar quadrangles in the MCO4 set (Fig. 1b); $N_{val} = 90$ for triangular prisms and $N_{val} = 96$ for two isolated triangles $(M_3)_2$ in the MCO6 set (Fig. 1d). It follows that an increased thermodynamic stability does not simply occur by virtue of a cluster having a magic number N_{val} (as determined by electron counting rules), but is rather a property due to particular geometric configurations (see Fig. 2). It is interesting that in the case of tetranuclear clusters, the "statistical" magic number $N_{val} = 60$ relates not only to tetrahedral structures (solid part of the bar in Fig. 1b), although they prevail, but also to clusters with "butterfly" and planar quadrangle configurations, completed to octahedron by bridging ligands (hatched part).

In principle, the predominance of certain values of N_{val} in histograms of Fig. 1 could be due not only to a higher stability of the corresponding clusters but also to concentrated efforts of those who synthesized them, provided the directed cluster synthesis had been a reality, as is proclaimed in some papers. Hypothetically then, the attention payed by chemists to clusters with particular geometric structures (or,

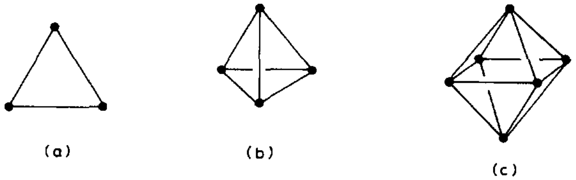

Fig. 2. Geometries of metal polyhedra with the statistically dominating magic numbers of N_{val}: (a) M_3 triangle, (b) M_4 tetrahedron, (c) M_6 octahedron.

for example, to clusters with specific magic numbers N_{val}) could severely affect the observed distribution profiles. Unfortunately for cluster chemistry (and luckily for statistical processing of its results!) the present state of the art of directed synthesis of polynuclear systems does not allow a positive prediction of the stoichiometry of the reaction products (and, occasionally, even of the number of metal atoms in the molecule). As a consequence, the structure of most cluster synthesis products is determined by thermodynamical factors alone. Circumstantial evidence of unpredictability of the structure of most polynuclear products of synthesis (be it directed or not) is provided by an extremely high share of structural studies in cluster chemistry.

A general condition for obtaining clusters with more atoms is to increase reaction temperature, that is to carry out the synthesis under more rigorous conditions [12]. The rigidity of reaction conditions can be measured from a reduction in the fraction of hydride derivatives (which have higher reactivity), displayed on circle diagrams in Fig. 1. The increasing rigidity in conditions of synthesis in the sequence M_3–M_4–M_6 is seen to produce no effect on the existence of predominant magic numbers. So, interest of investigators in this or other types of cluster (which, in the end, is often influenced by the stability of synthesized compounds), is, in the context of this study, nothing more than just a factor enhancing the empirical regularity actually existing.

An additional demonstration of the fact that behaviour of clusters in group "*A*" is governed thermodynamically and is independent of research interests of individual investigators can be obtained by considering the distribution in N_{val} of structures of pentanuclear derivatives in the MCO5 set (Fig. 1c). Unlike other group "*A*" sets, this histogram has a much wider peak (N_{val} region 72 to 78) displaced to the right of the $N_{val} = 72$ magic number of Wade's closo-polyhedron (trigonal bipyramid), which merely produces an indistinct satellite maximum. It is inexplicable, from the general standpoint, why octahedral "Wade's" closo-clusters should attract greater interest of chemists than "Wade's" trigonal-bipyramidal closo-polyhedra. So, here we have some strong evidence for a "statistical" character of synthesis of new polynuclear compounds. Another peculiar feature of pentanuclear clusters is the existence of several nearly equally distributed polyhedra for the two most distinctive numbers $N_{val} = 74$ and 76; some observed configurations of metal frameworks are shown in Fig. 3. It is interesting to note that despite an even greater number of theoretically possible cluster configurations in the MCO6 set than in MCO5 set, to which it is comparable in size, it is in fact the closo-polyhedra with the magic number $N_{val} = 86$ that prevail in MCO6. We see, therefore, that the existence of a prominent "statistical" magic number among all other rule-based magic numbers N_{val} is in no way an inherent cluster property, and is observed only with metallopolyhedra of appropriate nuclearity.

In terms of their number of atoms, pentanuclear clusters occupy an intermediate position between frameworks with localized bonding and polyhedra with electron delocalization. For derivatives of the first type, which predominate among tri- and tetranuclear clusters (the MCO3 and MCO4 sets), magic numbers N_{val} are to be found by the EAN rule and for the second type polyhedra by Wade's rule (the most typical example of such polyhedra is provided by octahedral clusters). An "intermediate" position of pentanuclear derivatives is manifested not only in the existence of a wide variety of geometrical configurations of the clusters, among which are

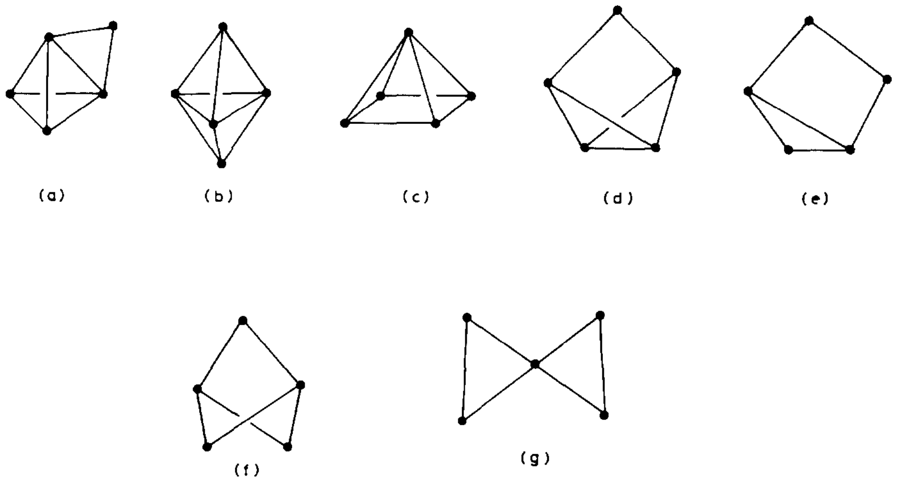

Fig. 3. Metal polyhedra in five-nuclear clusters: (a) $N_{val} = 74$, (b) $N_{val} = 72$ or 76, (c) $N_{val} = 74$, (d) $N_{val} = 76$, (e,f,g) $N_{val} = 78$.

polyhedra of both types (with localized and delocalized bonding, Fig. 3), but also in the occurrence of two or more almost equally "popular" values of N_{val} in clusters with similar frameworks (as was previously observed for trigonal bipyramids in refs. [2,9]). The observed broadening of the maximum in the MCO5 set (Fig. 1c) can apparently be attributed to the effect of all these factors. It is interesting to note that tetragonal-pyramidal nido-clusters M_5 with rare exceptions have Wade's $N_{val} = 74$. This is still another demonstration of the importance of the "$2n + 2$" rule for octahedron-based clusters (see [9]).

Small clusters of post-transition metals

Clusters of this type are represented by tri- and tetranuclear compounds of metals belonging to the nickel (NIPT3, NIPT4) and Cu subgroups. Larger clusters of these metals have been less studied and the few structural investigations that are available cannot possibly be treated statistically. In fact, the NIPT3 and NIPT4 sets are not very large either, nevertheless they do make it possible to analyse qualitative trends involved in passing from clusters of middle-transition metals to polynuclear derivatives of post-transition elements. Small clusters of platinum [13] and gold [14] have recently been the subject of quantum-chemical studies, which, however, were unable to identify unique magic numbers for known geometrical configurations.

Unlike Fe, Co and their analogues, purely carbonyl derivatives of the Ni subgroup metals are less common (and those of palladium have not yet been reported); typically, these metals form derivatives with mixed carbonyl-phosphine, phosphine-hydride or other coordination environment that involves phosphine ligands. This type of cluster constitutes a major part of the "*B*" group samples. The distributions of such clusters over the various N_{val} (Fig. 4) were found to be markedly different from those relating to clusters of the Fe and Co subgroups. An important feature of the "*B*" group histograms is the absence of a unique dominant statistical magic number of valence electrons, as is found in the MCO3, MCO4 and MCO6 sets. In trinuclear clusters of the NIPT3 set (Fig. 4a), a "smearing" of the

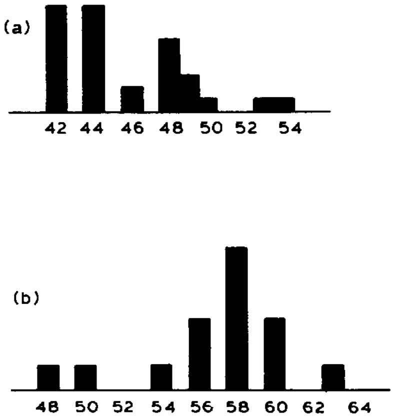

Fig. 4. Distribution of small clusters of Ni, Pd and Pt over N_{val}: (a) three-nuclear; (b) four-nuclear.

characteristic value of N_{val} can be seen to take place, similar to that observed in MCO5, i.e. there are three maxima close to each other in height corresponding to 42, 44, and 48 valence electrons in the metal polyhedron. It is interesting to note that the $N_{val} = 42$ value occurs mainly among platinum clusters, whereas $N_{val} = 44$ is generally related to palladium compounds. Meanwhile, $N_{val} = 48$ is found in both triangular Ni clusters with metal–metal bonding and in trinuclear Pd and Pt complexes containing only weakly-bonded atoms with square planar coordination.

It is worth noting that, given the relatively small size of the NIPT3 (32 structures), the obtained regularities are of a somewhat conjectural nature. The histogram for an even smaller-sized set NIPT4 (16 structures, Fig. 4b), representing tetranuclear clusters, is seen to suggest a similar pattern: a wide spectrum of observable N_{val} values (from 48 to 63 electrons) with a slight peak at $N_{val} = 58$. A large "electron capacity" of tetranuclear phosphine-hydride clusters was noted previously [15].

On the whole and notwithstanding the scarcity of experimental material, it can be concluded from our statistical analysis that small clusters of the "*B*" group have a more uniform distribution over values of N_{val} than metallocomplexes of the Fe and Co subgroups. Because of this, the magic numbers of valence electrons, quite significant in some "*A*" group samples, are not just replaced by others in the "*B*" group, but become less meaningful altogether. This inference is in agreement with the results of a quantum-chemical calculation (by Mingos) of small Pd and Pt clusters which show that, in a stable cluster electron configuration, the values of N_{val} are functions of the relative orientations of ML_2 fragments making up the polyhedron (where L is a phosphine ligand) [13]. Earlier, we argued for the non-existence of magic numbers for the compounds in question by considering some examples of carbonyl-phosphine clusters [9].

The above-mentioned tendency of the "*B*" group clusters for disappearance of magic numbers becomes quite obvious in tri- and tetranuclear metallocomplexes of the Cu subgroup (the "C" group structures, sets CUAU 3 and CUAU4). The N_{val} values found with these clusters have a very wide range (40 to 57 in CUAU3 and 48 to 84 in CUAU4) and there is no clear-cut peak in the region of electron deficient clusters (the left-hand part of the diagrams in Fig. 5). Other distinctive features of

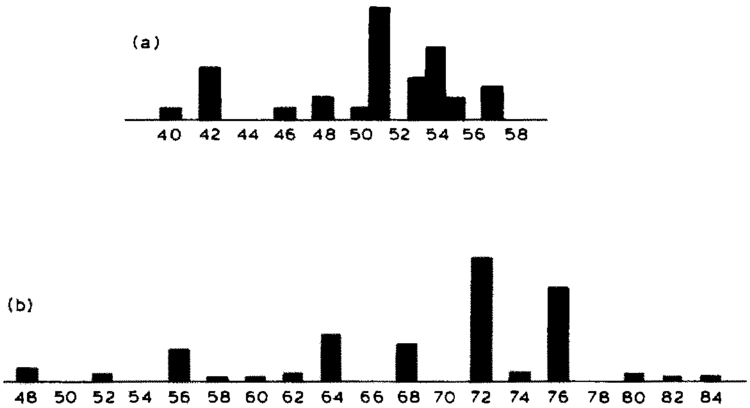

Fig. 5. Distribution of polynuclear derivatives of Cu, Ag and Au over N_{val}: (a) three-nuclear, (b) four-nuclear.

"*C*" group clusters (actually of Cu derivatives, which largely make up this group) are a very broad range of observed M–M distances and an increased stability of compounds with open electron shells of metal atoms. The former means that metal–metal bonding is virtually non-existent except in clusters with greatest electron deficiency (such as Cu_4 parallelograms in compounds of the type $Cu_4[(\mu_2\text{-}C_5H_4CH_2NMe_2)FeCp]_2$ [CUMFEP, see set CUAU4, $N_{\mathrm{val}} = 48$] with Cu–Cu distances 2.35–2.50 Å). The second feature relates to the existence of paramagnetic trinuclear complexes with $N_{\mathrm{val}} = 51$ (Fig. 5a). The "*C*" group sets are mainly composed of compounds in which every metal atom has a 17-, 18-, or 19-electron shell and metal-metal exchange ineraction between atoms is relatively weak at distances of about, and exceeding, 3.0 Å. The linking of metals in such polynuclear complexes seems to be largely due to the binding action of bridge ligands. Apart from these, in the "*B*" group there are complexes which have "almost isolated" groups of 16-electron atoms in a square planar ligand envrironment and also (in Au compounds) groups of 14-electron linearly-coordinated atoms that are probably involved in metal–metal bonding over large distances (see [3,9,14] and references therein). On the whole, the basic trend observed in the electronic structure of small clusters as we pass from Fe and Co derivatives and their analogues to post-transition metal compounds appears to be the weakening of the metal–metal bonding. As a consequence of such weakening, the magic numbers N_{val}, which in the case of group "*A*" carbonyl clusters are connected to electronic properties of the metallopolyhedron, become immaterial for compounds of the Ni and Cu subgroups, as they are replaced by characteristic numbers of electrons in polynuclear complexes with no metal–metal bonding. On these grounds, it did not seem very useful to search for magic numbers N_{val} for small clusters of post-transition metals – at any rate, it was empirically unsubstantiated. At the same time, a greater polyhedron nuclearity and especially the appearance of atoms inside the polyhedron are found to produce a stabilizing effect on the cluster. Accordingly, magic numbers N_{val} are known to exist for larger centered gold clusters of the type $[Au_nL_{n-1}]^q$ with $n = 8$ to 13, and are related to electronic properties of the central atom [3].

Clusters with halogenide and chalcogenide ligands

Along with the type of atoms making up the polyhedron and its geometrical arrangement, there are other factors which govern the number of valence electrons in a stable electron shell of the cluster, namely the nature and structure of the ligand environment [1]. In order to evaluate the effects of ligand environment and to obtain magic numbers in "inorganic" clusters that do not follow the EAN and "$2n+2$" rules, the TETR and OCTA sets were analysed. The TETR set consisted of CCSD-stored structures of clusters of the Fe and Co subgroups metals (supplemented by published data on derivatives of metals from the V, Cr, and Mn subgroups) having M_4X_4 frameworks in which metal atoms are arranged in a tetrahedron linked to a cubane-like skeleton by μ_3-X ligands (X is a halogen or chalcogen). The OCTA * set includes octahedral clusters of metals belonging to the first half of the transition series with halogenide and chalcogenide ligands in $M_6(\mu_2\text{-}X)_{12}$ and $M_6(\mu_3\text{-}X)_8$ frameworks.

By analogy with carbonyl derivatives (MCO4), the number $N_{val} = 60$ is widely thought to be a "magic" one for clusters represented in the TETR set. The choice of appropriate values of N_{val} for octahedral clusters in the OCTA sample is still a matter for discussion [1,9]; the few known carbonyl analogues with metallopolyhedra built up from atoms of same metals (mainly rhenium) largely follow the "$2n+2$" rule.

Several interesting points can be made concerning histograms of TETR and OCTA cluster distributions over N_{val} (Fig. 6). Contrary to what might be expected by analogy with carbonyl derivatives, no prevailing peak (not even a broad one) corresponds to the "magic" number $N_{val} = 60$. Instead, there is a series of small peaks in the histogram in the interval 54 to 76 valence electrons. When data from the publications are combined with those from the TETR set, the observed pattern becomes even more pronounced (unhatched columns in Fig. 6a). Comparable frequencies in a wide range of N_{val} values of several electronic (and related geometric) structures of cubane-like clusters, arising from competing electron requirements of the cubane framework and its tetrahedral fragments M_4 and X_4, is quite consistent with the "electron depot" function served by such clusters in biochemical systems [16].

The calculation of numbers N_{val} for OCTA clusters (Fig. 6b) is complicated by frequent occurrences in their structures of infinite motifs (layers and chains) with bridging ligands, by a wide interval of $M \cdots X$ distances in such motifs, and also by a recently recognized presence of atoms of light elements inside several previously investigated inorganic clusters (see [19]). Even after all these qualifications, the histogram in Fig. 6b exhibits almost total absence of the "carbonyl" magic number $N_{val} = 86$ (the sole exception is the $Cp_6Ti_6O_8$ cluster [20]). The histogram also has two prominent peaks, each one relating to its own type of octahedral cluster structure: the wide peak in the N_{val} region 72 to 76 corresponds to clusters of the $M_6(\mu_2\text{-}X)_{12}$ type and that at $N_{val} = 84$ to $M_6(\mu_3\text{-}X)_8$ structures. So, (in line with Wade's hypothesis [1] and contrary to our own conclusion as to the non-existence of magic numbers N_{val}, drawn previously from limited experimental data [9]) there

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* Some of the published data which has been incorporated into the TETR and OCTA sets were taken from reviews [16–18].

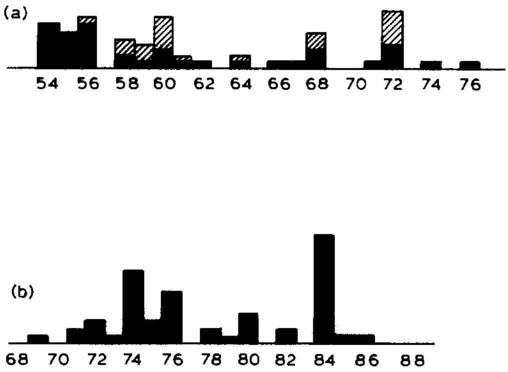

Fig. 6. Distribution of inorganic clusters over N_{val}: (a) cubane-like moieties M_4X_4 (M is middle-transition metal, i.e. from V to Co subgroups, X is halogen or chalcogen); (b) octahedral clusters of the early-transition (from Sc to Mn subgroups) metals with halogen or chalcogen atoms as bridging ligands.

seem to exist some analogues of magic numbers N_{val} for inorganic octahedral clusters, which are different for various-ligand environment structures of polyhedra. The "stringency" with which $M_6(\mu_3\text{-}X)_8$ clusters keep to the $N_{val} = 84$ number and the "loose" nature of the number $N_{val} = 74$ for $M_6(\mu_2\text{-}X)_{12}$ clusters can be attributed to the fact that clusters of the first type have a more rigid framework.

Conclusions

By analysing distributions of small clusters of transition and post-transition metals over the number of valence electrons in their polyhedra, we were able to show the existence of "favourable" stoichiometries related to statistically prevailing magic numbers of valence electrons, N_{val}, in certain clusters. It also follows from our analysis that in some cases established ideas as to the domain of magic number existence have to be revised. The magic numbers $N_{val} = 48$ for triangular and $N_{val} = 60$ for tetrahedral clusters (predicted by the EAN rule) and also $N_{val} = 86$ for octahedral clusters (the "$2n + 2$" rule) correspond to the most thermodynamically favourable and typical configurations among tri-, tetra-, and hexanuclear carbonyl clusters, respectively, with Fe and Co subgroups metals and show up in the histograms in the form of distinctly shaped peaks. By contrast, pentanuclear carbonyl clusters, which are at the margins of the domains covered by the EAN and "$2n + 2$" rules, as well as small metalloclusters of the Ni subgroup, that do not follow these rules at all, have a diffuse distribution with N_{val} featuring no single prevailing peak. On going from middle-transition metal clusters to those of the Ni subgroup and further on to Cu, a reduction in the strength of the metal–metal bonding is observed, as exemplified by tri- and tetranuclear clusters, also the individual magic numbers of electrons are ceasing to exist and structures of polynuclear complexes with no direct metal–metal bonding become predominant. The replacement of carbonyl ligands in the cluster coordination environment with halogenide and chalcogenide ones is also found to cause the disappearance of related "carbonyl" magic numbers. Depending on the flexibility of the metallo-ligand framework in such clusters, a broad interval for $M_4(\mu_3\text{-}X)_4$ or a narrow interval for

$M_6(\mu_2\text{-}X)_{12}$, of nearly equally represented values of N_{val} is observed, whereas for a rigid framework $M_6(\mu_3\text{-}X)_8$ there is a single predominant magic number $N_{val} = 84$.

As we have seen, "statistical" magic numbers N_{val} provide additional evidence for the validity of the EAN and Wade rules in their domain of application (small carbonyl clusters of middle-transition metals). Furthermore, having identified this domain, both time and effort can be saved by giving up trying to define new magic numbers of cluster types for which they are apparently non-existent. Interestingly, the N_{val} values prevailing in carbonyl cluster samples arise from closo-polyhedra, while magic numbers obtained by electron counting rules for more open structures show up in diagrams in the form of "satellite" peaks, thus upsetting the distribution symmetry.

The results of the statistical investigation of magic numbers in clusters are consistent with theoretical findings on similar systems [2,13,14] and make it possible to identify some promising areas for future calculations. Thus, a quantum-chemical study of the effect of ligand environment on the stability of different electron configurations in slightly altered polyhedra would be of considerable interest. Another important direction of research that we see is the recently initiated analysis of factors responsible for the structures of middle-sized and large clusters of transition metals [21,22]. The appropriate rules for this domain (as well as their application limits) can apparently be worked out by using statistical processing of experimental data along with methods employed in solid state physics and molecular physics.

Appendix

Distribution of structures of small clusters of transition metals over N_{val} in the various sets

For each of the ten collected sets (see Fig. 1, 4–6) all N_{val} numbers and corresponding CCDB codes are listed. Clusters with hydride ligands in MCO3–MCO6 sets are prepresented separately. For compounds which are not in the CCDB files, their formulae and references are used.

I. MCO3 set. Three-nuclear metal clusters of Fe and Co subgroups with CO ligands in coordination environment.

A. Non-hydride

$N_{val} = 42$: BOGMIT BOZYUK PHGECO.

$N_{val} = 44$: BUBWEA CLECRU OCHTPI

$N_{val} = 46$: ASCORU AZNBFE BAWWUR BEJBIB BIZYAK BOWBEU BUNCFE FARSFC10 FBUPFE HCMBRU10 OTPBOS PAFECO TPCOOS.

$N_{val} = 47$: BDCEFG CEPBEE CDPPCO MPHPRU.

$N_{val} = 48$: AEBCCO ALCTRU APFCFE ASCORU10 AXMYCO AZTRUC10 BADLUN10 BAHSOS BAHPEF BAJBIX BASTEU10 BAYCEY BBRMYC BCMYCO BCOCRU BEBJOH BEBJUN BEBKEY10 BEFKEC BEHVAL BELVUJ BEMYUN BENDON10 BEVTOL BEXPUP BEZMAU BIKBAY BICRUC10 BIMSOF BIZTEJ BOSMEB BRFOSA10 BRFOSB BUBZIH BUGMOF BUHHER BUHXRU BUNMEC BUPXEP BUPYAM BUPYOA BUZMIS CABGIV CACCAK CAGKAW CAKYOC CAMKEG CAMZIZ CATCUV CAVVEA CAVVIE CAVVOK CAXTUQ CAXVAY CAZHOA CCPHFC CCPZRC CEBBEQ CEDGIB CEDKAX CEDVOW CEGCIA CEGCOG CEJFOM CEJGAZ CELROA CEMVAR CFPARH CHPRUS10 CMCPRH10 CMNCOD CMPPFE10 COTTRU10 CPBUOS10 CPMCCO CPMTRH CPRHCT01 CPSCOB CPTCCO CPYLFE CRHPIM CRUHEP CTMHFE CTXMCO CYPCOO DAZRUC10 DCASRU DMPCCO10 DPACOS10 DPDZFE DPHTRH EFFACO ETAFEA ETPHOT ETYTCO EYCPCO FCBFEC FECPAC HMTLCO HPTRUC LICOCO MASCFE MASCOA MBPSRU MEDYCO10 METCOP MGERUC10 MOPCOS MSCOFE MSICCO MSIPRU10 MSTCOA MVCPFE NBPCCO OCAFBR OCNMPO OMPMCO OXBUDC10 PACPFE

PCOCOC PCOMES10 PENRUC PHOFEC10 PMBRUB PMCECO PMHTRU PSCORH SCHICO SIPCRU SPENRU10 TBUOSC10 TEAFEA10 TEAFEB10 TETCCO THCXCO TPBAOS10 UNCTRU.

$N_{\text{val}} = 49$: ACXIRU BASMUD CPCOSI PLNCOA10.

$N_{\text{val}} = 50$: BAXZEF BENPIT BEYCUD BEZPIF BIMSFE10 BINMUG BIPKOA BIPKUG BITMIA BOWCAR10 BUSNEI BUXVOF BUYMAJ CABHUI CABJAQ CABJEU CAKHOL CAPPUE CARLOW CARLUC CATZOM CAVSUN CERKAL CONPOT CYPCOS MIFECO MOXCOS MTSOCO10 MTSOSC10 NFECMP10 OSCTAM POHYOS TCFPAS TIMSFE TCRUCP.

$N_{\text{val}} = 52$: BAMDOI BINJUD CATROE CDEFGH10. A total of 203 structures.

B. Hydride

$N_{\text{val}} = 42$: HRHMOP.

$N_{\text{val}} = 44$: HPHIRB PCHIRH10.

$N_{\text{val}} = 46$: ACICFE BAHSIM BEJHIH BEYHRU BICFUO BUHCUC BUWGEF BUZZIF CAFCUH CBOSIC10 HCOSPP NCHPOS.

$N_{\text{val}} = 47$: ABCDEF BACKUL.

$N_{\text{val}} = 48$: ACREOS10 BABVIJ BADGOC BADGUI BAGBEO BAGGUH BAHSAE BAHSEI BAJBET BAJXEP BAJXIT BAMZEU01 BAPVET BARHIL BATLIR10 BATLOX10 BECFIY BEGKAZ BEHKEE BEHMUW BEKBIC BEKTOA BEMYIB BENDUT10 BENFAB10 BEPKUC BEVTIF BEVTUR BEVVAZ BEXJIX BEXJOD BEXJUJ BICLEE BICLII BIDKII BIFMAE BIHPUD10 BIHZOH BIYXAI BODGUW BOVLIH BOWBUK10 BOXGUQ BUBZON BUHOSC BULNEB BULVOT BUNJEZ BUPTUB BUPYEQ BUPYUG BUTMOS BUXVIZ BUZNEP CAFHIA CAFJOI CAFJUO CAMYEU CASVIB CATZEC CAWSOI CAWYOO CEBCIV CEJFUS CERWUR CESCAE CHVINO DCHMOS DCTPHO DCTRIM10 DMFHRU DPOSCO ETSCOS EYHFEC FBOSHC FIMCOS10 HACORU HAZTOS HBOCDO HCMBRU10 HEIOSA HEIOSB HMBZOS HMCBFE HMECOS HMIBOS HNCPHR HOCPRH10 HOSETP HOSTBC10 HPCOFE HPROSA HPROSB HSFOSA HSFOSB HTCPRH10 HTSAOS HXDYOS HYBIOS IMCBFE IPSHFE MALCRU MAMOSA MBTRUC10 MCERUC10 MEBYRU MPFMOS MPSHFE MTEYOS10 MXCBRU NCEYRU PIMOSS STILOS TCBOSD10 TEMFCH TFOOSC10.

$N_{\text{val}} = 50$: BAHHOH BATLUD10 BELVIX BIGZIA BITVAB CYDRUC10 OSCEYP10. 140 structures in total. For the whole set of structures: N_{val} – no. of clusters (%): 42e – 4 (1.17), 44e – 5 (1.46), 46e – 25 (7.29), 47e – 6 (1.75), 48e – 253 (73.75), 49e – 4 (1.17), 50e – 42 (12.24), 52e – 4 (1.17), a total of 343 (100%) structures, hydrides 40.8%.

II. MCO4 set. Four-nuclear metal clusters of Fe and Co subgroups with CO ligands in coordination environment.

A. Non-hydride

$N_{\text{val}} = 56$; BAYWED.

$N_{\text{val}} = 58$: CESFOV.

$N_{\text{val}} = 59$: CPICPF.

$N_{\text{val}} = 60$: ACTOSA * ACTOSB * ALLCOA BADKOG BADMIC BAFFET BAFFIX BALYES10 BAWKIT BECNOM10 BEFYEQ BICIRC10 BIFCUO BIFGAY BIWZEM * BNCHRU * BNZCTC BOBTIV BTNRUA * BULYOW * BUSWAM BUZYAH CECXUD CEHXUI CDTRUC10 CIROCD COFARS COFERH * CPFTEC CPHCOS10 CPNRUC10 CPRHIC10 CYOYRU DPMRHC EACMFE * EAMICO IRCOAS10 IRDTPP IRTTPP MAMOSB MOCOCP MSTCOB PACCRU * PDCOCO01 * PERUHC10 PHCOIR PIMNFE PIMRHC PIMUFE PMCPCO POPRHC PPCORU PPHCIR10 PRACCO PRUFEA PYFEFE TBZOFE TCOCAC * TMAZRU10 XYLCTC.

$N_{\text{val}} = 61$: BACRUN10.

$N_{\text{val}} = 62$: ACBRUA BACYUZ BADMAU10 BAHDIX BAXKOA10 BECKAV BICGAV BISNAS BUCYUT BUKWOT BYNFEC CENZEA EAENFE10 IPVRUB PHCORH PHIMRU PRUFEB10.

$N_{\text{val}} = 64$; BADHUJ BETVIF BIXKEY BOBTOB BODHOR CESWUS CEFZUI CPSCOD RHCBIM

$N_{\text{val}} = 66$: BODHUX BUGXEG BUGXIC CAPCEB CASWAU CEGBAR CNCRCO MCPFEC MTFESL.

$N_{\text{val}} = 68$: ACBRUB MXACIR.

$N_{\text{val}} = 72$: DAZFEC PHACFE SBCLFC SBPCOB. A total of 105 structures.

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* Open moiety M_4 (tetragonal or butterfly) is completed to octahedron by ligands.

B. Hydride

$N_{val} = 58$: HXPTOS.

$N_{val} = 60$: AMOSHC BAJSUA01 BAXGUC BEDCIW BEDCOC BELBEZ BEXMAS BIXFIX BMHOSA BMHOSB BOPZAH BUCNUI BUTBUN CATNUG CECGAS CECGEV CEFRUA COMHOS HMPCIC01 HNIOSB * HPECRU HPETOS HRUTPC10 HYOSWC10 IMPOSC MSTCOC PIHFRB10 PINCOS TMBFCO01 TRIIRC UCHXOS.

$N_{val} = 62$: BETVAX10 BITRAX HMYCFE01 PIMFEB01.

$N_{val} = 66$: AFBACO. In total 37 structures. For the whole set N_{val} – no. of clusters (%): 56e – 2 (1.41), 58e – 1 (0.70), 59e – 1 (0.70), 60e – 91 (64.09) 60e open – 12 (8.45), 61e – 1 (0.70), 62e – 21 (14.79), 64e – 9 (6.34), 66e 10 (7.04), 68e – 2 (1.41), 72e – 4 (2.82), a total of 142 structures, hydrides 26.1%.

III. MCO5 set. Five-nuclear carbonyl and carbonyl-containing clusters of metals of Fe and Co subgroup.

A. Non-hydride

$N_{val} = 72$: BUMRAC PIMOSI $Os_5(CO)_{16}$ [23].

$N_{val} = 74$: BACGOB BAMLUW10 BEMYOH BOVHOJ BUCDIM BUFBUZ CABRIG CABROM CASPAR CARRET COTPRU10 EACRFA MXPPOS10 PHSRUA PHSRUB $Fe_5C(CO)_{15}$ [24], $Ru_5C(CO)_{15}$ [25], $Os_5C(CO)_{15}$ [26].

$N_{val} = 76$: BAGZOY BEDVOV10 CAPCAX CAVXAY CEBFEU CEBFIY CEPNUG ICORHA10 ICORHD10 NBAIRH PACIOS.

$N_{val} = 78$: BIHDOL BOBZEX CAYCEK, $Os_5(CO)_{19}$ [27].

$N_{val} = 82$: BIFMUY. A total of 37 structures.

B. Hydride

$N_{val} = 72$: CAWTUP CAWVAX HPACOS PIOSCO10.

$N_{val} = 74$: BAMOSC CAVWUR HETPOS OMPOSC, $HFe_5N(CO)_{14}$ [28], $H_2Os_5(CO)_{16}$ [29].

$N_{val} = 76$: BACGIV BALKUU BIHDIF CAVWIF CAVWOL CBMPOS CTCPOS ZEGDUK.

$N_{val} = 78$: BOVHUP. In total 19 structures. For the whole set of structures: 72e – 7 (%) (12.5), 74e – 24 (42.9), 76e – 19 (33.9), 78e – 5 (8.9), 82e – 1 (1.8), a total of 56 structures (100%), hydrides 34%.

IV. MCO6 set. Six-nuclear carbonyl and carbonyl-containing metal clusters of Fe and Co subgroups.

A. Non-hydride

$N_{val} = 84$: TBICOS10.

$N_{val} = 86$: BALKOO BEKMOT BEZXEJ BIDMAC BIDMEG BIJSUI BONYEI BOPFUH BUSWAN CANDUQ CAWYAA CAWYEE CELKEJ EACRFB ECORHA ECORHB MACHFE MARUCB10 MBZCIR MCYOSC MPPCRU PACORH PASCRU POSHRH RUCMES TBAMRC TRCORU, $Rh_6(CO)_{16}$ [30].

$N_{val} = 87$: BIGPAI BUHWAC TMAHCO10.

$N_{val} = 88$: BTNRUB BZYOSC TOSCOS10.

$N_{val} = 90$: BETVEB BOZBOH PIMNCO PPCHRH PPCOPC.

$N_{val} = 92$: BUDGAI COESRU.

$N_{val} = 96$: CACOBU10 CABPAW COHFCO COZRCP MCONCO TACCCO.

$N_{val} = 100$: CEPYOL.

$N_{val} = 102$: BUSVUI. A total of 50 structures.

B. Hydride

$N_{val} = 86$: PAHCRU PIHRUC PIMHCO10, $HRu_6C(CO)_{15}NO$ [31].

$N_{val} = 96$: BINGAG BINGEK CAFHEW DTMHOS.

$N_{val} = 98$: BUXROB BUXRUH BUXSAO. In total 11 structures. For the whole set of clusters (%): 84e – 1 (1.6), 86e – 32 (52.6), 87e – 3 (4.9), 88e – 3 (4.9), 90e – 5 (8.2), 92e – 2 (3.3), 96e – 10 (16.4), 98e – 3 (4.9), 100e – 1 (1.6), 102e – 1 (1.6), a total of 61 structures (100%), hydrides 18%.

V. NIPT3 set. Three-nuclear clusters of Ni, Pd and Pt with π-olefine, carbonyl and phosphine ligands

$N_{val} = 42$: BAJHEZ BESDAE BESDEI BIWTIK BOFNUF CASMUE CHXPCP PHSOPT PSDXPT.

$N_{val} = 44$: CEPHPD CHPPTC MICPDP SDBICP THIOPD, $Pd_3(CO)_3(PPh_3)_4$ [32], $Pd_3(CO)_2(PPh_3)_3$-$Sn_2(acac)_4$ [33], $[Pd_3(PPh_2)_2Cl(PPh_3)_3]^+$ [34], $[Pd_2Pt(PPh_2)_2Cl(PPh_3)_3]^+$ [34].

$N_{val} = 46$: CDOTNI PAEPPT10.

$N_{val} = 48$: BERFIN10 CETLAO COFBNI ESPNIB IPOXPD TAOANI10.
$N_{val} = 49$: BAMCNI BIGFUS TCPDNI01.
$N_{val} = 50$: BIGFOM.
$N_{val} = 53$: CPNISU.
$N_{val} = 54$: PCNTNI. For the whole set of clusters (%): 42e – 9 (28.1), 44e – 9 (28.1), 48e – 6 (18.8), 49e – 3 (9.4), 50e – 1 (3.1), 53e – 1 (3.1), 54e – 1 (3.1). A total of 32 structures (100%).

VI. NIPT4 set. Four-nuclear metal clusters of Ni subgroup with – olefine, phosphine and carbonyl ligands.
$N_{val} = 48$: $[Pt_4H_2(PBu^t_3)_4]^{2+}$ [15].
$N_{val} = 50$: BAYHID.
$N_{val} = 54$: $[Pt_4H_7(PBu^t_3)_4]^+$ [15].
$N_{val} = 56$: BAJHOJ PHTLPD, $Pd_4(CO)_2(OAc)_4$ [37].
$N_{val} = 58$: BUXZOJ CACGES COMPPD PCOPTP, $Pd_4(CO)_5(PPh_3)_4$ [32], $Pt_4(CO)_5(PEt_3)_4$ [32].
$N_{val} = 60$: BOGXAW HFBYNI10 TNITPP.
$N_{val} = 63$: TCPNIH11. A total of 16 structures.

VII. CUAU3 set. Three-nuclear complexes of Cu, Ag and Au.
$N_{val} = 40$: BENNOX.
$N_{val} = 42$: BOKDIO CACPOL ETIMAU SPPNAU TPAUOX.
$N_{val} = 46$: DPMECU.
$N_{val} = 48$: CEMTUJ TMPSCU10.
$N_{val} = 50$: BOZPAH.
$N_{val} = 51$: APROCV BOTBOB BOXTEN BOZBIB DAPOUL DAPRCV DAPRCX EHPECU TCUCAN TMSOCC TONCUR.
$N_{val} = 53$: BZOTCU CUEHAP DAPRCW PRAICU.
$N_{val} = 54$: BAHZOZ MOPAGB10 PAGSXA10 PAGSXF10 PPMICU TRTCUC.
$N_{val} = 55$: ACUESH ADEHCU10.
$N_{val} = 57$: BULWIO CUPRAL10 HPMBXC.
For the whole set of structures (%): 40e – 1 (2.7), 42e – 5 (13.5), 46e – 1 (2.7), 48e – 2 (5.4), 50e – 1 (2.7), 51e – 11 (29.8), 53e – 4 (10.8), 54e – 7 (18.9), 55e – 2 (5.4), 57e – 3 (8.1). A total of 37 structures (100%).

VIII. CUAU4 set. Four-nuclear derivatives of Cu, Ag and Au.
$N_{val} = 48$: AGMFFE CAGBIV CUMFER MSIMCU10.
$N_{val} = 52$: BEPLEN CAKPIN.
$N_{val} = 56$: BESBAC BESBEG BEXXIL CUTBUX DMTACU MCUBZA01 TCTFAC TCUBEN THACAU.
$N_{val} = 58$: ITPPAU.
$N_{val} = 60$: CUIPDT.
$N_{val} = 62$: BOBPOX CAYLID.
$N_{val} = 64$: AUPIPC BIGMIN CEDNOO CEMXUN CUTURS10 CBZTET10 DMAUHT HTUTCU10 IODOCU MPPICU MPYTCU NOBCUC PPTICU20 TPHCUB.
$N_{val} = 68$: BILLOX BINSOG BOFROD CAAECU CUBDPM CUCDPM CUIDPM10 ETUCUN MEACCU PPAAGB10 PSACLU.
$N_{val} = 72$: APMCUA BEPDAB BOMNEW BOZRAJ BPICCU BRTAGT BUFLOD BUGREA BUXLAH CAJNIK CAPFEE CARMAJ CAXFOW CEGTEN CERGOV CERGUB CERHIQ CUEIAB CUIPIP CUIPYR EAOCLC10 EASCUI EPCUBT EPCUCT EPCUIT ETSICU MACRCU MORCUI MPPCUI TEPAGB TEPAGC TEPAGI TPAGIN TPASIC TPCUBR10 TPCUCL01 TPHCUI TPPAGC10.
$N_{val} = 74$: BOFHIN CERTOI.
$N_{val} = 76$: APACUT APAECU APAECV BAEACU BEGZAO BOFHIN BOGCOP BOGMEP BOTBIV BRBAEC BUFTUR CABLUM CEAECU CPPOCU01 EAECUA EXTFCU10 ICBECU MAEOCU MPOCUC10 OCPYCU OCUQUO OHCTCH OXCLPC PICOCU PRAOCU TAMCUG TEENCU TPAECV XBPYRC.
$N_{val} = 80$: DAEOCU OEACAC10.
$N_{val} = 82$: BIZXIR.
$N_{val} = 84$: TPECUC
For the whole set of structures (%): 48e – 4 (3.4), 52e – 2 (1.7), 56e – 9 (7.7), 58e – 1 (0.9), 60e – 1 (0.9),

62e – 2 (1.7), 64e – 14 (12.0), 68e – 11 (9.4), 72e – 38 (32.4), 74e – 2 (1.7), 76e – 29 (24.7), 80e – 2 (1.7), 82e – 1 (0.9), 84e – 1 (0.9), a total of 117 structures (100%).

IX. TETR set. Cubane-like clusters $M_4(\mu_3\text{-}X)_4$ where M is a middle-transition metal, X is halogen or chalcogen.

$N_{val} = 54$: AFESES BINDUX BZMSFE CAPGAB CATTOG EAFEST FESTPH HETSFE.
$N_{val} = 55$: AMTFEW BUTFAX BZTFEA ETFEMO PSFEEA SBTMOI.
$N_{val} = 56$: BAMDUO10 BEWTAY BEZGAO10 BIFJIJ BIZDUJ BUYJUA CAYGOY PHTMFW, $(C_5H_4Me)_4V_4S_4$ [36].
$N_{val} = 58$: BOXSEM FESBAS10, $Cp_3Cr_3FeS_4(OOCBu^t)$ [36], $Mo_4S_4(S_2CNEt_2)_6$ [37], $[(C_5H_4Pr^i)_4Mo_4S_4]^{2+}$ [37].
$N_{val} = 59$: BEICOI, $[Cp_4Cr_4S_3O]^+$ [36], $[(C_5H_4Pr^i)_4Mo_4S_4]^+$ [37], $Mo_4S_4(EDTA)_4$ [37].
$N_{val} = 60$: BASFNF, SLCOCR, $Fe_4S_4(NO)_4$ [38], $(C_5H_4Pr^i)_4Mo_4S_4$ [37], $Cp_4Cr_4O_4$ [39], $(C_5H_4Me)_4Cr_4S_4$ [36], $Cp_3Cr_3CoS_4(CO)$ [36], $(C_5H_4Me)_4Cr_4OS_3$ [36], $[Mo_4S_4(CN)_{12}]^{8-}$ [40].
$N_{val} = 61$: BIBMOO, $[Cp_4Cr_4S_4]^-$ [36].
$N_{val} = 62$: FLTHFE.
$N_{val} = 64$: BUANCO, $Cp_3Cr_3CoS_4(CO)_3$ [36].
$N_{val} = 66$: TCPFES.
$N_{val} = 67$: CPEFTS.
$N_{val} = 68$: COSCYP CPCOPT CPEFES, $Mo_4S_4(NC_6H_4Me)_4[S_2P(OEt)_2]_4$ [37], $[Mo_4S_4(NO)_4(CN)_8]^{8-}$ [37], $Mo_4S_4(NC_6H_4Me)_4(S_2CNBu^t_2)_4$ [37].
$N_{val} = 71$: COPSPF.
$N_{val} = 72$: BZRUOH10 COCPST MASYFE10 NBRFBY, $[Cr_4(OH)_4(CO)_{12}]^{4-}$, $[Cr_4(OMe)_4(CO)_{12}]^{4-}$ [41], $W_4(OH)_4(CO)_{12}H_4$ [41], $Mo_4(OH)_4(CO)_8(NO)_4$ [41], $Re_4(OH)_4(CO)_{12}$ [41], $Re_4F_4(CO)_{12}$ [42].
$N_{val} = 74$: AMXACO.
$N_{val} = 76$: BEWDUC. For the whole set of structures (%): 54e – 8 (11.9), 55e – 6 (9.0), 56e – 9 (13.4), 58e – 5 (7.5), 59e – 4 (6.0), 60e – 9 (13.4), 61e – 2 (3.0), 62e – 1 (1.5), 64e – 2 (3.0), 66e – 1 (1.5), 67e – 1 (1.5), 68e – 6 (9.0), 71e – 1 (1.5), 72e – 10 (14.8), 74e – 1 (1.5), 76e – 1 (1.5). A total of 67 structures (100%).

X. OCTA set. Octahedral clusters of early-transition metals with halogenide and chalcogenide ligands.

$N_{val} = 69$: Zr_6Cl_{15} [43].
$N_{val} = 71$: $[Zr_6I_{14}]^-$ [44], $Zr_6I_{14}(K)$ [45].
$N_{val} = 72$: $Zr_6Cl_{12}\cdot M_2ZrCl_6$ [46], $[Zr_6Cl_{13}(Be)]^-$ [19], $[Sc_6Cl_{12}]^{3-}$ [43].
$N_{val} = 73$: $Zr_6Cl_{14}(B)$ [19].
$N_{val} = 74$: $[Nb_6Cl_{18}]^{2-}$ [47], $[Nb_6Br_{12}Cl_6]^{2-}$ [48], $[Nb_6Br_6Cl_6Br_6]^{2-}$ [48], $[Ta_6Cl_{18}]^{2-}$ [49], $Zr_6Cl_{12}(Be)$ [19], $Zr_6Cl_{14}(O)$ [19], $[Zr_6Cl_{15}(C)]^-$ [19], $Zr_6Cl_{15}(N)$ [19], $[Zr_6Cl_{15}(B)]^{2-}$ [19], $[Zr_6Cl_{16}(Be)]^{4-}$ [19].
$N_{val} = 75$: Nb_6Cl_{15} [50], Ta_6Cl_{15} [51], Ta_6Br_{15} [51].
$N_{val} = 76$: Nb_6Cl_{14} [50], Ta_6I_{14} [52], Mo_6Se_8 [53], $[Nb_6Cl_{18}]^{4-}$ [54], $Ta_6Cl_{14}\cdot 7H_2O$ [55], $Zr_6I_{12}(C)$ [19], $[Ta_6Cl_{12}(CN)_6]^{4-}$ [56].
$N_{val} = 78$: W_6Cl_{18} [57], $Mo_6S_6Br_2$ [58].
$N_{val} = 79$: Nb_6I_{11} [59].
$N_{val} = 80$: $[Nb_6I_{11}]^-$ [60], Re_6Te_{15} [61], $Mo_6S_3Br_6$ [62], $[Tc_6Br_6(Br,OH)_6]^{2-}$ [63] *. $N_{val} = 82$: W_6Br_{16} [64], $Nb_6I_8(NH_2Me)_6$ [65].
$N_{val} = 84$: W_6Br_{12} [66], W_6Br_{14} [66], Mo_6Br_{12} [66], $[Mo_6Br_{13}]^-$ [66], $[Mo_6Br_{14}]^{2-}$ [66], $Mo_6Br_{12}(OH_2)_2$ [66], Mo_6SeCl_{10} [67], $Re_6Se_8Cl_2$ [68], $[Mo_6Cl_{14}]^{2-}$ [69], $Re_6Se_4Cl_{10}$ [70], $[W_6Cl_8Br_6]^{2-}$ [64], Mo_6Cl_{12} [71], $[Re_6S_{10}(S_2)]^{4-}$ [72,73], $[Re_6S_{11}]^{4-}$ [61], $[Mo_6SCl_{13}]^{3-}$ [74], $[Mo_6Cl_8Br_6]^{2-}$ [75].
$N_{val} = 85$: $[Re_6S_{10}(S_2)_{1.5}]^{4-}$ [76].
$N_{val} = 86$: $Cp_6Ti_6O_8$ [20]. For the whole set of structures (%): 69e – 1 (1.9), 71e – 2 (3.8), 72e – 3 (5.6), 73e – 1 (1.9), 74e – 10 (18.9), 75e – 3 (5.6), 76e – 7 (13.2), 78e – 2 (3.8), 79e – 1 (1.9), 80e – 3 (5.6), 82e – 2 (3.8), 84e –16 (30.2), 85e – (1.9), 86e – 1 (1.9). A total of 53 structures (100%).

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* Not used in statistics.

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