NYHOLM MEMORIAL LECTURE*

Ring, Cage, and Cluster Compounds of the Main Group Elements

By R. J. Gillespie
DEPARTMENT OF CHEMISTRY, MCMASTER UNIVERSITY, HAMILTON, ONTARIO, L8S 4M1, CANADA

1 Introduction

Although the borane and carbaborane cage and cluster compounds and a few cages and clusters of other main group elements such as P_4 and S_4N_4 have been known for some time, recent work has led to a considerable extension of our knowledge of cage and cluster compounds of the more electronegative main group elements.

My own interest in this subject stems from studies in our laboratories at McMaster University on the preparation of new polyatomic cations of sulphur, selenium, and tellurium, which have been found to have several novel cage and cluster structures. I will therefore first review the preparation and structures of these new cationic species. Then I will explore the relationships between the various structures and describe a framework into which they may be fitted. Finally I will discuss the relationships between the clusters of the electronegative main group elements, transition-metal clusters, and the electron-deficient boranes.

2 Polyatomic Cations of Sulphur, Selenium, and Tellurium

It has been found during the last ten years that sulphur, selenium, and tellurium may be oxidized by several different oxidizing agents to a variety of hitherto unknown polyatomic cations. The presently known species are summarized in Table 1. Some of these species had in fact been observed a very long time ago but had not been recognized as such. For example, as long ago as 1798 Klaproth reported that tellurium dissolves in ordinary concentrated 98% sulphuric acid to give a carmine-red solution.[1] It was also observed as early as 1804 that sulphur is dissolved by oleum to give blue, red, and yellow solutions depending on the concentration of the oleum and the time of reaction.[2] Similarly, selenium was reported, in 1827, to give green and yellow solutions in oleum.[3] The species

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*This paper was originally presented as the Nyholm Lecture for the session 1978/1979, at the 1979 Annual Congress of the Chemical Society, University of Bristol. Bristol, on April 3–5. 1979.

[1] M. H. Klaproth. *Phil. Mag*., 1798, **1**, 78

[2] C. F. Bucholz, *Gehlen's Neures J. Chem*., 1804, **3**, 7

[3] G. Magnus, *Ann. Phys. (Leipzig)*. 1827, **10**, 491; 1828, **14**, 328.

Table 1 *Polyatomic cations of sulphur, selenium, and tellurium*

M_{19}^{2+}	S_{19}^{2+}				
M_{10}^{2+}		Se_{10}^{2+}		$Te_2S_8^{2+}$	
M_8^{2+}	S_8^{2+}	Se_8^{2+}			
M_6^{2+}				$Te_3S_3^{2+}$	$Te_2Se_4^{2+}$
M_4^{2+}	S_4^{2+}	Se_4^{2+}	Te_4^{2+}	$Te_2Se_2^{2+}$	
M_6^{4+}			Te_6^{4+}		

giving rise to these colours were not identified with certainty although it came to be fairly generally believed that the deep blue colour of solutions of sulphur in oleum was due to the formation of the compound S_2O_3, described in older text books of inorganic chemistry as sulphur sesquioxide, since a deep blue solid of this approximate composition could be made by the direct reaction of sulphur and sulphur trioxide.[4] It was also believed that a similar compound $SeSO_3$ was present in solutions of selenium in oleum. It has now been established however that all these colours are due to various polyatomic cations of sulphur, selenium, and tellurium. For example, the deep green solutions of selenium contain the Se_8^{2+} cation, and the red solutions of tellurium the Te_4^{2+} ion.

Our interest in these systems arose as a result of our earlier work on the chemistry of solutions in highly acidic media and our discovery that the halogens may be oxidized to highly coloured polyatomic cations in such media, *e.g.* deep blue I_2^+, brown I_3^+, and red Br_2^+.[5] It seemed probable therefore that the long known, but poorly understood, solutions of sulphur, selenium, and tellurium in sulphuric acid and oleum also contain cationic species and this indeed proved to be the case.

3 Preparative Methods

Because oleum consists of a complex mixture of different polysulphuric acids and because it is viscous and has a high vapour pressure of SO_3 it is not a particularly convenient solvent for studying these cations. We found that HSO_3F is much more convenient to use and that in this solvent oxidation of the elements S, Se, and Te can be carried out in a quantitative and controlled manner by using $S_2O_6F_2$ as the oxidizing agent.[6] Thus reactions such as the following were carried out:

$$8Se + S_2O_6F_2 \rightarrow Se_8^{2+} + 2SO_3F^-$$
$$4Se + S_2O_6F_2 \rightarrow Se_4^{2+} + 2SO_3F^-$$

The course of the reactions was followed by cryoscopic and conductimetric measurements and by absorption spectroscopy and it was clearly established that selenium could be quantitatively oxidized under these conditions to the two

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[4] J. W. Mellor, 'Comprehensive Treatise on Inorganic and Theoretical Chemistry', Longmans Green, New York, 1930, Vol. 10, pp. 184–186 and 992.

[5] R. J. Gillespie and M. J. Morton, *Quart. Rev.*, 1971, **25**, 553.

[6] R. J. Gillespie and J. Passmore, *Adv. Inorg. Radiochem.*, 1975, **17**, 49.

species Se_8^{2+} and Se_4^+. The structures of such novel species were obviously of considerable interest and we were fortunate to obtain a crystalline material from an orange solution of selenium in oleum which proved to be the hydrogen disulphate of Se_4^{2+}, namely $Se_4(HS_2O_7)_2$. An *X*-ray crystallographic study showed that this ion has a simple square planar structure, and this will be discussed in more detail later.[7] The reaction between the element and oleum is, however, generally not a convenient preparative procedure. Crystallization from the viscous medium is slow and difficult and moreover the reactions are not readily controlled as excess of the oxidizing agent, SO_3, is always present.

It was clearly important to have simple and reliable preparative procedures for crystalline salts of these cations in order that their crystal structures could be determined. Although $S_2O_6F_2$ in HSO_3F was a somewhat better system with which to work it was found that crystalline salts could most easily be prepared by the use of SbF_5 or AsF_5 as an oxidizing agent in solution in an invert solvent such as SO_2.[6] HF and AsF_3 have also been used as solvents but most of the compounds that will be described have been prepared in SO_2 as solvent, *e.g.*

$$S_8 + 2AsF_5 \xrightarrow{SO_2} S_8^{2+}(AsF_6)_2 + AsF_3$$

Another preparative method that is useful for some cations has been developed by Corbett and his co-workers.[8] This involves the reaction of the element with a chloride of the element and $AlCl_3$ in the molten state, *e.g.*

$$SeCl_4 + 15Se + 4AlCl_3 \rightarrow 3Se_8(AlCl_4)_2$$

All of these preparative methods have one feature in common, namely that they provide an anion which is insufficiently basic to react with the cation, which is in general highly electrophilic and highly susceptible to disproportionation to the element and a species containing the element in a higher oxidation state. None of these cations are stable in aqueous media, for example, or in any solvent containing even small amounts of water, as they undergo disproportionations such as

$$2Se_4^{2+} + 6H_2O \rightarrow 7Se + SeO_2 + 4H_3O^+$$

Hence the need for solvents such as $H_2S_2O_7$, HSO_3F, SO_2, and AsF_3, all of which have very low basicities, and for counter anions such as SO_3F^-, $HS_2O_7^-$, SbF_6^-, Sb_2F_{11} , AsF_6^-, and $AlCl_4^-$, which are all the very weak conjugate bases of very strong acids.

4 Heteropolyatomic Cations

Although the preparation of 'mixed' or heteropolyatomic species containing two different elements, *e.g.* $Te_2Se_2^{2+}$, might appear to be of somewhat routine interest this turned out not to be the case as at least two new structural types were first discovered as a consequence of preparations of such mixed species. Three different preparative methods have been utilized:

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[7] I. D. Brown, D. B. Crump, and R. J. Gillespie, *Inorg. Chem.*, 1971, **10**, 2319.

[8] R. K. Mullen, D. J. Price, and J. D. Corbett, *Inorg. Chem.*, 1971, **10**, 1749.

(i) Oxidation of an alloy or mixture of two elements[9]

e.g.

$$\begin{matrix}\text{Se–Te}\\ \text{1:1 alloy or mixture}\end{matrix} \xrightarrow[SO_2]{SbF_5} Te_2Se_2(Sb_3F_{14})(SbF_6)$$

(ii) Reaction of an element with a cation of a different element[10]

e.g.

$$Se_8(AsF_6)_2 + 2Te \xrightarrow{SO_2} Se_8Te_2(AsF_6)_2$$

(iii) Reaction between cations of two different elements[11]

e.g.

$$Te_4(AsF_6)_2 + S_8(ASF_6)_2 \xrightarrow{SO_2} Te_3S_3(AsF_6)_2$$

These reactions cannot, however, be described as planned syntheses as the products usually cannot be predicted with any certainty and indeed have often proved to be completely unexpected. Moreover the reactions are generally complex and a number of products are formed of which only one has generally been crystallized out and identified. We are still in what may be described as the butterfly collecting era in this field of chemistry. Cotton has remarked in connection with metal clusters that 'The student of cluster chemistry is in somewhat the position of the collector of lepidoptera skipping observantly over the countryside and exclaiming with delight when fortunate enough to encounter a new species'.[12]

5 Structures

A. S_4^{2+}, Se_4^{2+}, Te_4^{2+}, and $Te_2Se_2^{2+}$.—*X*-ray crystallographic studies on the salts $S_4(S_7I)_4(AsF_6)_6$, $Se_4(HS_2O_7)_2$, $Se_4(Sb_8F_{33})(SbF_6)$, $Te_4(AlCl_4)_2$, $Te_4(Al_2Cl_7)_2$, and $Te_2Se_2(Sb_3F_{14})(SbF_6)$ have shown that the cations S_4^{2+}, Se_4^{2+}, Te_4^{2+}, and $Te_2Se_2^{2+}$ have square planar structures (Table 2). The bond lengths in the four

Table 2 *Bond lengths in the square planar* S_4^{2+}, Se_4^{2+}, Te_4^{2+} *and* $Te_2Se_2^{2+}$ *ions/pm*

	M_4^{2+}	*Single bond*	*Crystal structure*	*Ref.*
S_4^{2+}	198	204	$S_4(S_7I)_4(AsF_6)_6$	13
Se_4^{2+}	228	234	$Se_4(HS_2O_7)_2$, $Se_4(Sb_8F_{33})(SbF_6)$	7, 14
Te_4^{2+}	266	274	$Te_4(AlCl_4)_2$, $Te_4(Al_2Cl_7)_2$	15
trans-$Te_2Se_2^{+}$	247	254	$Te_2Se_2(Sb_3F_{14})(SbF_6)$	9

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[9] P. Boldrini, I. D. Brown, R. J. Gillespie, E. M. Marahajh, and J. F. Sawyer, to be published.

[10] P. Boldrini, I. D. Brown, R. J. Gillespie, P. R. Ireland, W. Luk, D. R. Slim, and J. E. Vekris, *Inorg. Chem.*, 1976, **15**, 765.

[11] R. J. Gillespie, W. Luk, E. Maharajh, and D. R Slim, *Inorg. Chem.*, 1977, **16**, 892.

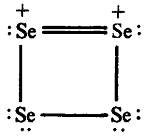
[12] F. A. Cotton, *Quart. Rev.*, 1966, **20**, 397.

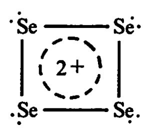
[13] J. Passmore, personal communication.

[14] R. J. Gillespie, J. Sawyer, and J. E. Vekris, to be published.

[15] D. J. Prince, J. D. Corbett, and B. Garbisch, *Inorg. Chem.*, 1970, **9**, 2731.

ions are slightly shorter than the normally accepted values for the corresponding single bonds. This is consistent with a valence-bond description of these ions in terms of four equivalent resonance structures such as (1), or alternatively with a simple molecular orbital description in which three of the four π molecular orbitals, the two almost non-bonding (e_g) orbitals and the (a_{1g}) bonding orbitals, are filled and the antibonding (b_{2u}) orbital is empty. Thus these molecules may be described as 6π electron 'aromatic' systems (2).


(1)


(2)

B. S_8^{2+} and Se_8^{2+}.—*X*-ray crystallographic studies of $S_8(AsF_6)_2$ and $Se_8(AlCl_4)_2$ have shown that the structures of S_8^{2+} and Se_8^{2+} are very similar. Figure 1 shows the structure of the S_8^{2+} cation and Figure 2 gives the bond lengths and bond angles for S_8^{2+} and Se_8^{2+}.[16,8] They consist of an eight-membered ring with an *exo–endo* conformation and a rather long transannular bond which is relatively shorter and stronger in the case of Se_8^{2+}. This, at first sight, curious structure may be regarded as being half-way between the structures of the cage molecule S_4N_4 and the crown-shaped ring of S_8 and Se_8. Indeed since S_4N_4 has

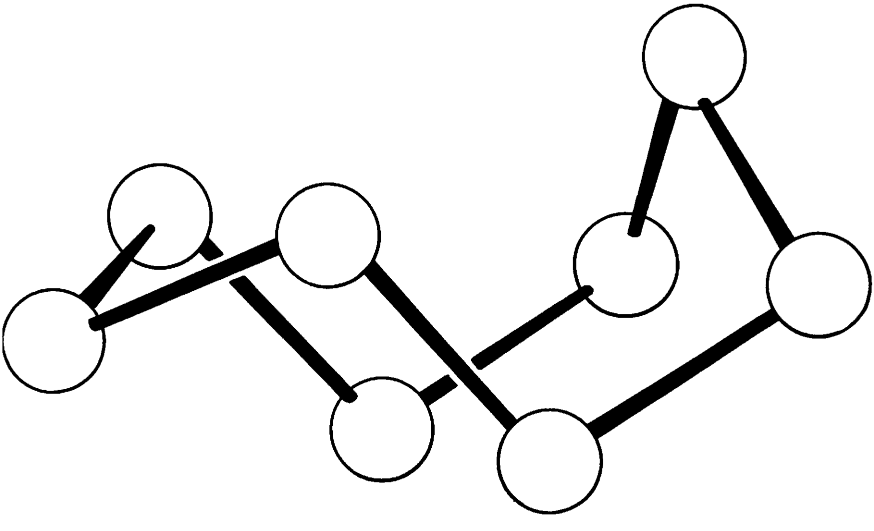


Figure 1 *The structure of* S_8^{2+} *and* Se_8^{2+}

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[16] C. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg Chem.*, 1971, **10**, 2781.

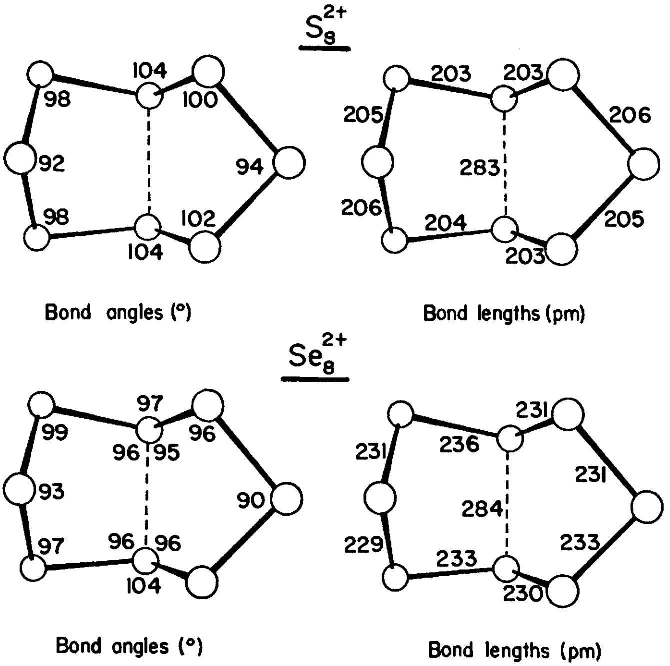


Figure 2 *Bond lengths and bond angles in* S_8^{2+} *and* Se_8^{2+}

two electrons less than S_8^{2+} and is isoelectronic with the unknown S_8^{4+} (which appears to be unstable with respect to S_4^{2+}) we may imagine that as two electrons are removed from S_8 one end folds up and a transannular bond forms. Then, with the removal of two more electrons, the other end folds up and another bond forms to give the S_4N_4 structure (Figure 3).

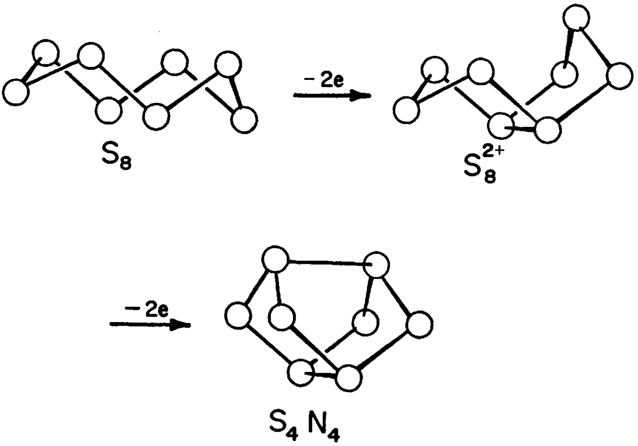


Figure 3 *Relationships between the structures of* S_8, S_8^{2+}, *and* S_4N_4

C. **Se_{10}^{2+} and $Te_2Se_8^{2+}$**.—The reaction between Te and $Se_8^{2+}(AsF_6)_2$ leads to the formation of the black crystalline compound $Te_2Se_8(AsF_6)_2.SO_2$ which was the first example of a ten-atom polyatomic cation.[10] Subsequently the compound

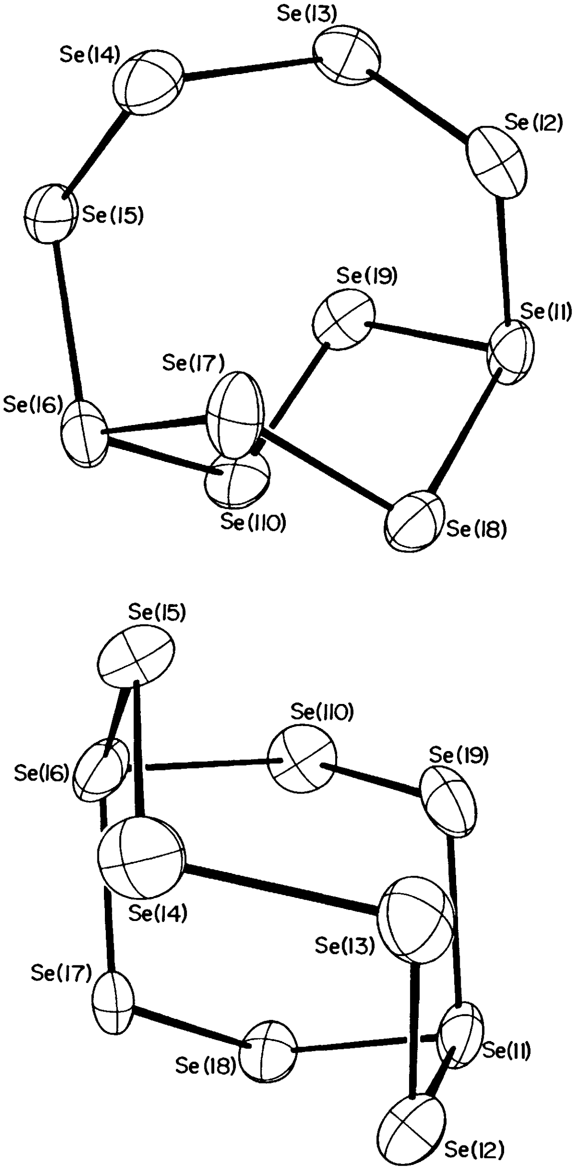
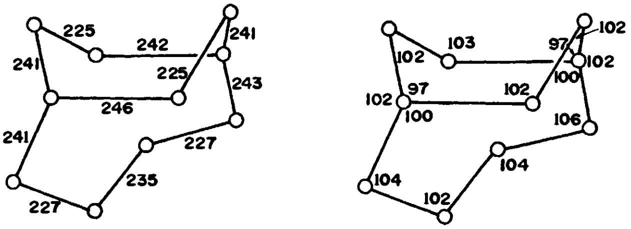
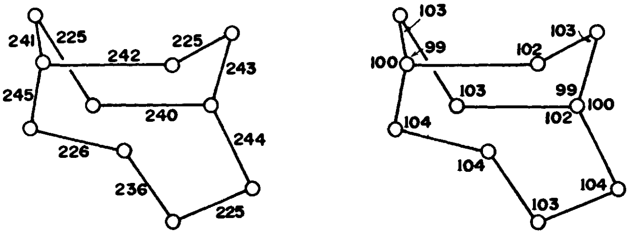


Figure 4 *Two views of the structure of* Se_{10}^{2+}

$Se_{10}(AsF_6)_2$, which contains the homopolyatomic cation Se_{10}^{2+}, has been prepared.[17] Both ions have the same basic structure which consists of a six-membered boat-shaped ring bridged by a chain of four atoms to form an eight-membered ring. Figure 4 shows the structure of the Se_{10}^{2+} ion and bond lengths and bond angles for Se_{10}^{2+} and $Te_2Se_8^{2+}$ are given in Figures 5 and 6, respectively.



Cation 1



Cation 2

Bond lengths (pm) Bond angles (°)

Figure 5 *Bond lengths and bond angles in* Se_{10}^{2+}. *Values are given for the two crystallographically non-equivalent* Se_{10}^{2+} *ions in the structure*

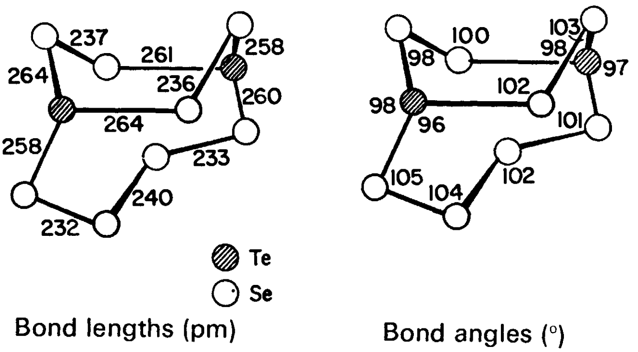


Figure 6 *Bond lengths and bond angles in* $Te_2Se_8^{2+}$

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[17] R. C. Burns, W Chan, R. J. Gillespie, W. Luk, J. F. Sawyer, and D. R. Slim, *Inorg. Chem.*, to be published

D. $Te_2Se_4^{2+}$ and $Te_3Se_3^{2+}$.—The six-atom homopolyatomic species S_6^{2+} and Se_6^{2+} have never been observed and although compounds formulated as $Te_6(AsF_6)_2$ and $Te_6(AlCl_4)_2$ have been prepared, no crystals have been obtained which were suitable for an *X*-ray crystallographic determination of their structures.[15,18] However, in studies of the preparation of mixed cations, the compounds $Te_2Se_4(SbF_6)_2$, $Te_2Se_4(AsF_6)_2$, and $Te_3S_3(AsF_6)_2$ were isolated and their crystal structures have been determined.[11]

Both cations have very similar structures consisting of a three-membered ring to which is attached a three-atom chain forming a five-membered ring (Figure 7).

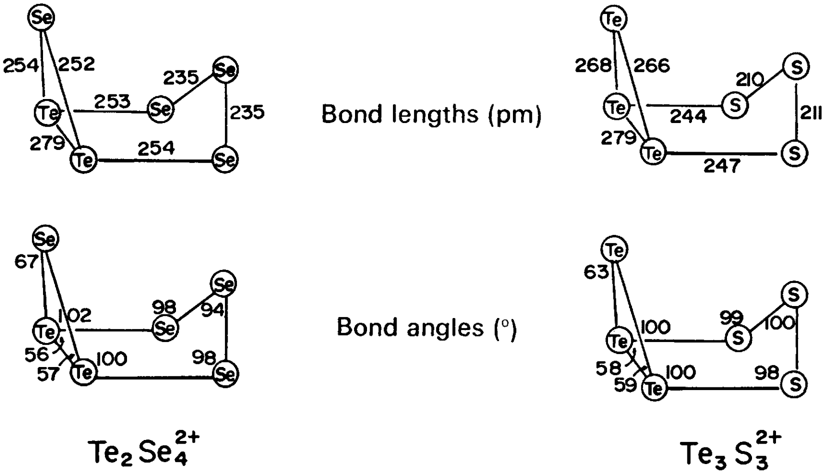

Figure 7 *Bond lengths and bond angles in* $Te_2Se_4^{2+}$ *and* $Te_3S_3^{2+}$

Alternatively the structure may be described as an overall six-membered ring with a pronounced boat conformation and one cross-ring bond.

E. Te_6^{4+}.—In some of our early work on the oxidation of tellurium, evidence was obtained for the formation of a yellow-brown cation Te_n^{n+} in solution in HSO_3F and SO_2 and for compounds of empirical composition $TeSbF_6$ and $Te_2S_3O_{10}$, which appeared to contain the same cation Te_n^{n+}.[18,19] However no crystal structures were determined and it was not possible from the solution measurements to determine *n* with certainty. Recently this species has been reinvestigated and two compounds have been isolated which have been found, by *X*-ray crystallography, to have the composition $Te_6(AsF_6)_4.2AsF_3$ and $Te_6(AsF_6)_4.2SO_2$ and to contain a trigonal prismatic Te_6^{4+} cation[20] (Figure 8).

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[18] J. Barr, R. J. Gillespie, G. P. Pez, P. K. Ummat, and O. C. Vaidya, *Inorg. Chem.*, 1971, **10,** 362.

[19] J. Barr, R. J. Gillespie, G. P. Pez, P. K. Ummat, and O. C. Vaidya, *J. Amer. Chem. Soc.*, 1970, **92,** 1081.

[20] R. C. Burns, R. J. Gillespie, W. Luk, and D. R. Slim, *Inorg. Chem.*, in the press.

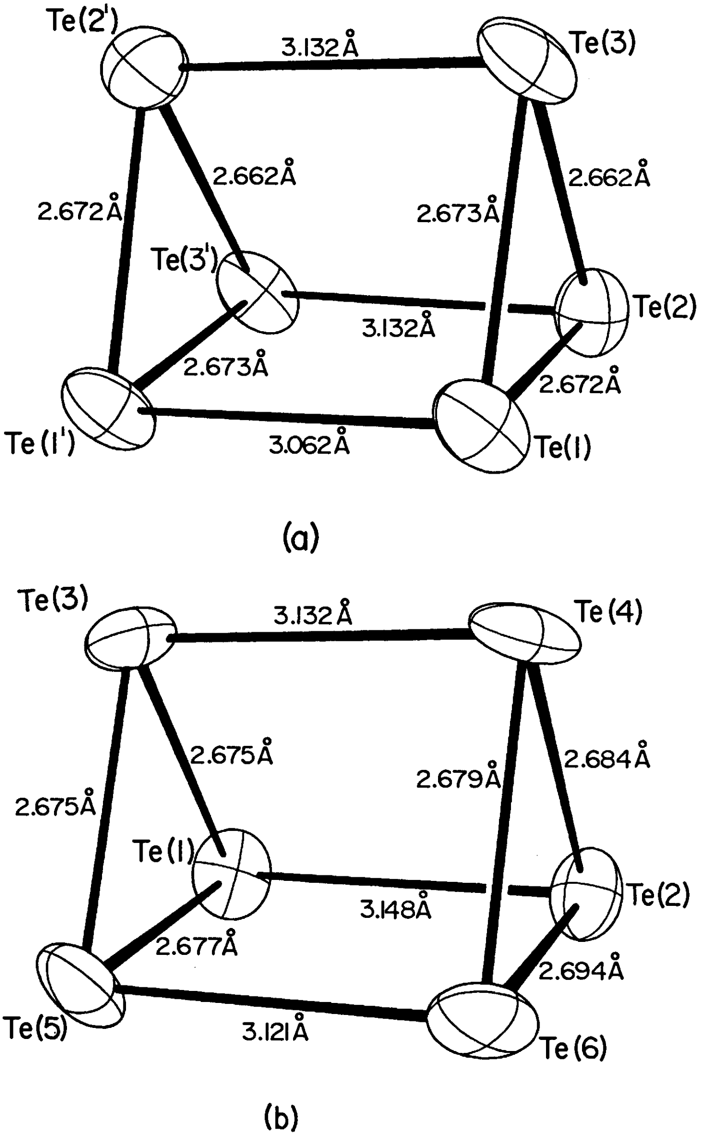

Figure 8 *The structure of* Te_6^{4+}: (*a*) *in* $Te_6(AsF_6)_4.2AsF_3$ *and* (*b*) *in* $Te_6(AsF_6)_4.2SO_2$

This represents the first known example of a simple six-atom trigonal prism molecule.

F. S_{19}^{2+}.—The first product of the oxidation of sulphur in oleum or with SbF_5

in HF or SO_2 was found, in our early work, to be a red species that was identified as S_{16}^{2+} from solution studies and from analytical data on a compound which appeared to be $S_{16}(AsF_6)_2$.[21] No crystals of the substance were obtained at that time but very recently, after many unsuccessful attempts, some rather unstable red crystals were eventually grown from a 2:1 mixture of SO_2 and SO_2ClF and a structural determination led to the surprising result that the material has the composition $S_{19}(AsF_6)_2$.[22] It contains the S_{19}^{2+} cation (Figure 9) with an unexpected structure consisting of two seven-membered rings joined by a five-atom chain. One ring has a boat conformation and the other consists of a 4:1 mixture of chair and boat conformations. Bond distances and bond angles are given in Figure 10.

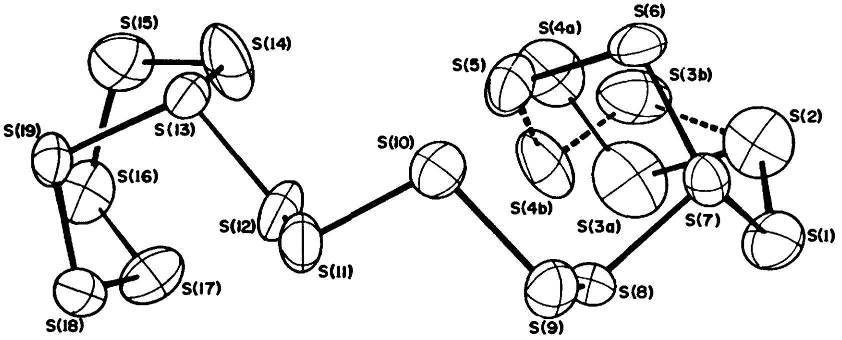

Figure 9 *The structure of* S_{19}^{2+}

6 Structural Relationships among the Cations of Group VI Elements

We have already noted the relationships between the structures of S_8, S_8^{2+}, and S_4N_4. In particular when two electrons are removed from an S_8 ring it folds up into an *exo–endo* conformation and a weak cross-ring bond is formed (Figure 3). The ions $Te_3S_3^{2+}$ and $Te_2Se_4^{2+}$ have pronounced boat conformations although the neutral S_6 ring has the expected chair conformation. Presumably neutral Te_3S_3 and Te_2Se_4 rings would have the same chair conformation. The removal of two electrons thus leads to the folding up of the molecule into a pronounced boat conformation and the formation of a cross-ring bond which, in this case, is rather strong (Figure 11). This is quite analogous to the structural changes that occur when S_8^{2+} is formed from S_8. Furthermore Te_6^{4+}, which has two electrons less than $Te_3S_3^{2+}$ and $Te_2Se_4^{2+}$, has a trigonal prism structure. Thus Te_3S_3 and Te_2Se_4 have structures intermediate between the chair structure of S_6 and the trigonal prism of Te_6^{4+}. As electrons are removed from the neutral six- and eight-membered rings there is a strong tendency for them to fold up into more closely packed cluster structures.

The $Te_3S_3^{2+}$ structure can also be obtained from the P_4S_3 structure by removal

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[21] R. J. Gillespie, J. Passmore, P. K. Ummat, and O. C. Vaidya, *Inorg. Chem.*, 1971, **10**, 1327.
[22] R. C. Burns, R. J. Gillespie, and J. F. Sawyer, *Inorg. Chem.*, in press.

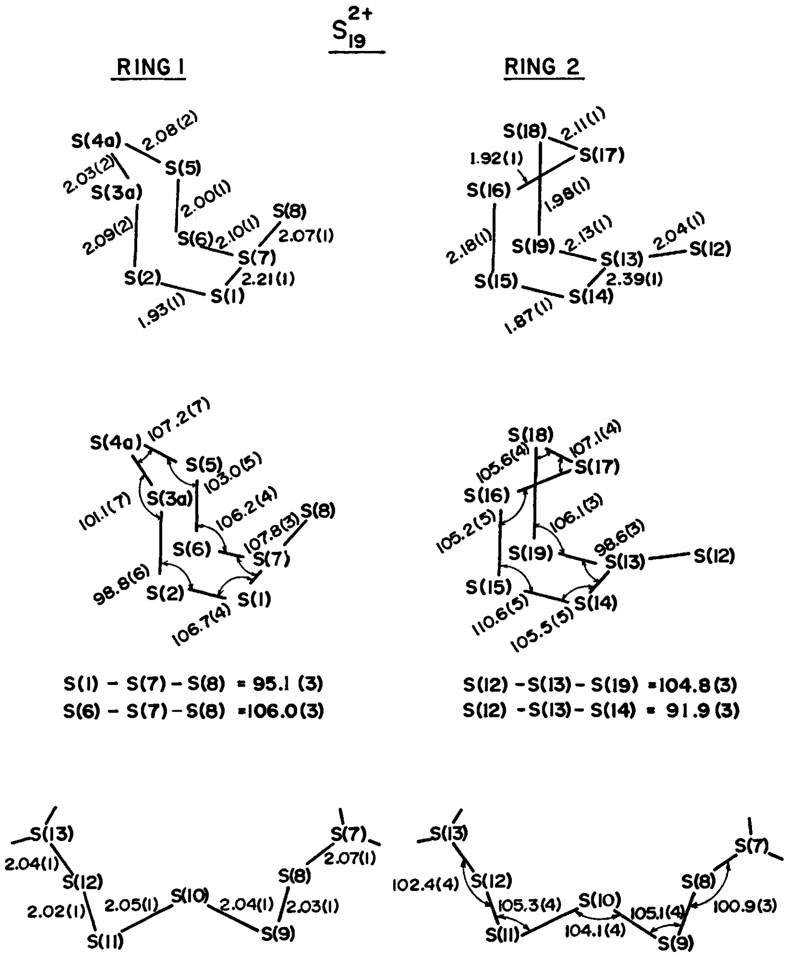


Figure 10 *Bond lengths and bond angles in* S_{19}^{2+}

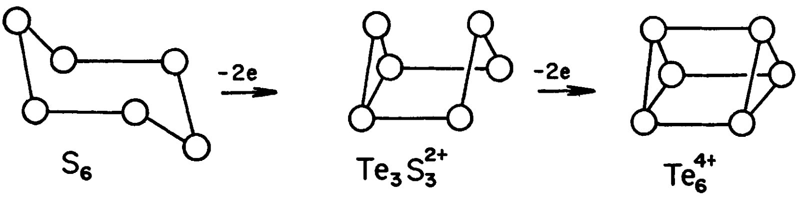


Figure 11 *Relationships between the structures of* S_6, $Te_3S_3^{2+}$, *and* Te_6^{4+}

of one S atom, the S—P bonding electron pairs remaining in place as unshared pairs (Figure 12). These interesting relationships suggest that it might be possible to fit all these main group element cage and cluster structures into a common framework.

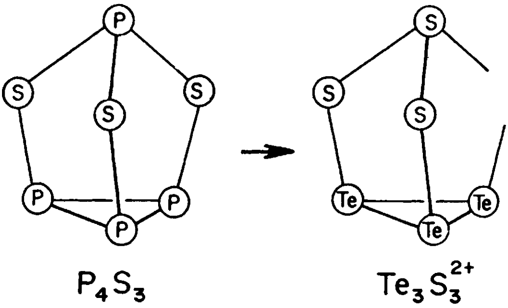
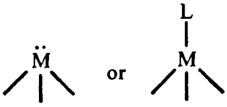


Figure 12 *Relationship between the structures of* P_4S_3 *and* $Te_3S_3^{2+}$

7 Basic Cluster Structures for the Main Group Elements

It has become customary to describe cage and cluster molecules, particularly those formed by many transition metals, in terms of the polyhedral structures of the *closo* borane anions $B_nH_n^{2-}$ and carbaboranes $C_2B_{n-2}H_n$. However, the cage and cluster molecules of the more electronegative main group elements, such as P_4S_3, the trigonal prismatic Te_6^{4+}, and cubic molecules such as $Al_4N_4Ph_8$, do not fit easily into this pattern. These molecules may be described as electron-precise or electron-rich and their description in terms of the electron-deficient boranes does not seem very appropriate. It is not surprising that the qualitative schemes of Lipscomb[23] and Wade,[24] which treat the cluster electrons as partially or completely delocalized and which provide a satisfactory basis for rationalizing the structures of boranes, are not applicable to electron-precise cages and clusters.

It seems more satisfactory to attempt to describe the main group element electron-precise clusters in terms of localized bonding and non-bonding electron pairs. We assume that in their cage and cluster compounds these elements generally obey the octet rule, *i.e.* that they do not exhibit the higher valencies that are observed in their compounds with more electronegative elements such as fluorine. Thus the basic structures of the electron-precise main group element clusters are those in which each atom forms three cluster bonds and has either an external lone pair or forms an external bond to a ligand, *i.e.* each atom has the configuration:



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[23] W. N. Lipscombe, 'Boron Hydrides', Benjamin, New York, 1963.
[24] K. Wade, *Adv. Inorg. Radiochem.*, 1976, **18**, 1.

Possible structures for clusters of 4, 6, 8, and 10 atoms have been described by a number of authors mainly in connection with the problem of the valence-isomers of the annulenes C_nH_n. Balaban[25] has given a complete listing and has shown that there is only one structure for a four-atom cluster, namely the tetrahedron, two structures for a six-atom cluster, five for an eight-atom cluster, and twenty for a ten-atom cluster. No structures of this type are possible for clusters containing odd numbers of atoms. The two possible structures for a six-atom cluster are the trigonal prism and a structure which has the form of a Möbius strip and has been called Benz-Möbiustripane. A number of the structures for eight and ten atoms are also of this type but none have been synthesized and will not be considered further. Figure 13 shows the cluster frameworks for 4, 6, 8, and 10 atoms of which there are known examples or of which derivatives are known. The possible structures differ in the number of different sized faces. They are consistent with Eulers rule for convex polyhedra which states that

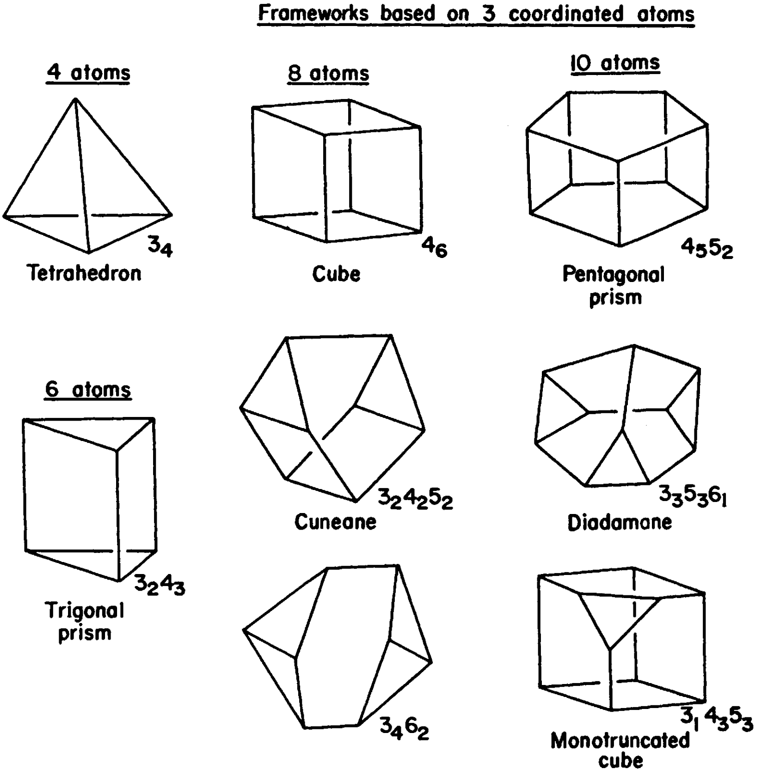

Figure 13 *Frameworks based on three-co-ordinated atoms*

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[25] A. T. Balaban, *Revue Romaine de Chimie*, 1966, **11**, 1097.

$$C + F = E + 2$$
$$\text{corners} + \text{faces} = \text{edges} + 2$$

This can be restated[26] in chemical terms as

$$\text{atoms} + \text{rings} = \text{bonds} + 2$$

Thus for an eight-atom cluster of three-connected atoms there must be $3 \times 8/2 = 12$ bonds and hence a total of six rings. The three structures shown in Figure 13 are the cube which has six squared faces and is designated 4_6, the cuneane structure which has two three-membered rings, two four-membered rings, and two five-membered rings and is designated $3_2 4_2 5_2$ and the $3_4 6_2$ structure. For ten atoms the pentagonal prism $4_5 5_2$ and two other structures are shown in Figure 13.

The shapes of all the known cage and cluster compounds of the main group elements can be derived from the basic structures in Figure 13. Any molecules which have one of these basic shapes in which each atom is bonded to three others and has one external ligand or unshared pair will be described as cluster. Any group of atoms in which some are bonded only to two others and which therefore has a more open structure will be referred to as a cage. An electron-precise cluster will contain $5n$ electrons, $3n$ bonding electrons, and $2n$ non-bonding. A cage has more electrons and will necessarily have a more open structure. In the limit when all the atoms are only two-cordinated the total number of electrons is $6n$ and a ring structure results.

8 Examples of cluster molecules

The number of known examples of true cluster structures among the main group elements is rather limited. Tetrahedral molecules are exemplified by P_4, As_4, and Sb_4. The only examples of a trigonal prism molecule are the ion Te_6^{4+} and derivatives of the hydrocarbon prismane C_6H_6 such as hexamethyl prismane. There are several examples of cubic molecules including the hydrocarbon cubane C_8H_8, the aluminium–nitrogen compound $(PhAlNPh)_4$, and thallium alkoxides $[Tl(OR)]_4$. The cuneane structure is known only in the form of the hydrocarbon cuneane C_8H_8 and its derivatives. The only known 10 atom cluster is the hydrocarbon diademane $C_{10}H_{10}$.[27] However these cluster structures are the basic structures from which all the cage structures may be derived as we will now show.

9 Derivation of the Structures of Cages from the Basic Cluster Structures

The structures of cages may be derived from the basic cluster structures by means of the following rules:

(i) One or more edges of a cluster A_n may be replaced by a bridging atom B.

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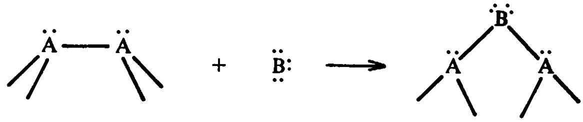
[26] H. G. von Schnering in 'Homoatomic Rings, Chains and Macromolecules of Main Group Elements', ed. A. L. Rheingold, Elsevier Scientific Publishing Co., Amsterdam, 1977.

[27] A. de Meijnere, D. Kaufmann, and O. Schallner, *Angew. Chem., Internat. Edn.*, 1971, **10**, 417.

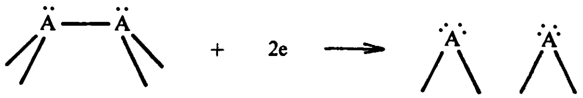
(ii) One or more edges of a cluster may be broken by the addition of an electron pair, so that a bonding electron pair is replaced by two non-bonding pairs.*

(iii) One or more atoms may be removed from a cluster leaving the bonding electron pairs in place as non-bonding pairs.
The same transformations may obviously be carried out on a cage structure to give a still more open cage and it is convenient to specify a fourth process

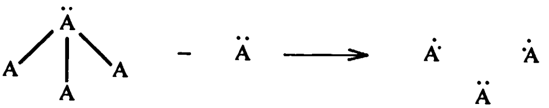
(iv) consisting of the removal of a two-co-ordinated bridging atom **B** from a cage, the result of which is the same as the addition of an electron pair to an edge of the corresponding cluster structure (ii).



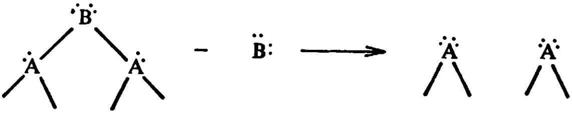
(1)



(2)



(3)



(4)

These rules are summarized in equations (1)—(4). It is an important feature of these rules that in processes (2), (3), and (4) in which bonding electron pairs are replaced by non-bonding pairs the atoms nevertheless remain clearly, if weakly, bonded to each other and although the interatomic distance necessarily increases the overall structure still retains the same general shape. Since the main group element cages contain predominantly, if not entirely, P, S, and heavier elements it is reasonable to suppose that the attractive force between formally non-bonded atoms arises from the presence of unfilled orbitals, *e.g.* *d* orbitals on these heavy atoms. These vacant orbitals permit some delocalization of electron density from the formally non-bonding pairs on neighbouring atoms and thus these non-bonding pairs become slightly bonding. Process (2) can be described in molecular orbital terms as the filling of the anti-bonding orbital associated with the A—A bond. However, rather than the resultant situation

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* Mingos has previously pointed out the relationships between some cages and clusters based on the application of this rule.[17a]

[17a] D. M. P. Mingos, *Nat. Phys. Sci.*, 1972, **236**, 99.

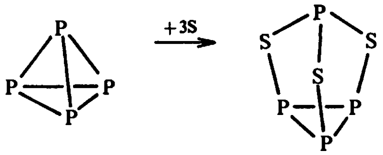
being somewhat antibonding, as is usually assumed, it is slightly bonding. Since two pairs of electrons are involved in this interaction it can be described as a weak double bond. Indeed the formation of an ethylenic double bond from two CH_2 molecules is quite analogous, except that in this case the double bond is strong because low-lying stable orbitals on C are involved

$$H_2C: + :CH_2 \rightarrow H_2C::CH_2$$

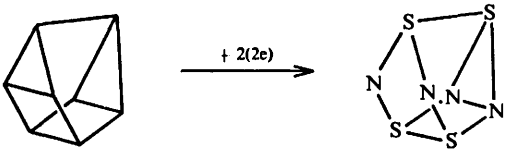
compared to the much less stable *d* orbitals on the heavier elements.

The following are examples of each of these processes:

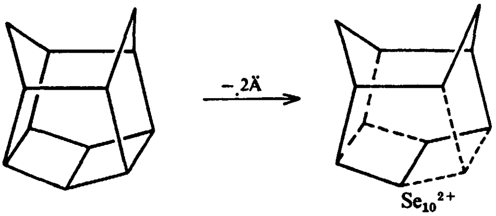
(i) Bridging three of the edges of a P_4 tetrahedron with S atoms gives the P_4S_3 cage molecule,



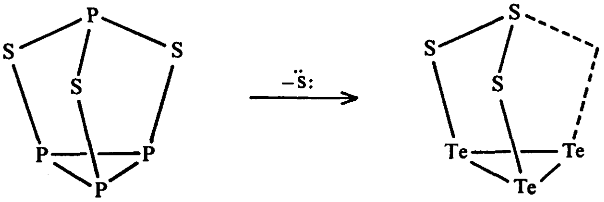
(ii) Adding two pairs of electrons to each of two edges of the cuneane structure, *e.g.* hypothetical $S_4N_4^{4+}$, gives the S_4N_4 cage,



(iii) Removal of two atoms from a doubly bridged pentagonal prism structure gives the Se_{10}^{2+} cage,



(iv) Removal of S^{2+} from P_4S_3 gives the $Te_3S_3^{2+}$ structure,

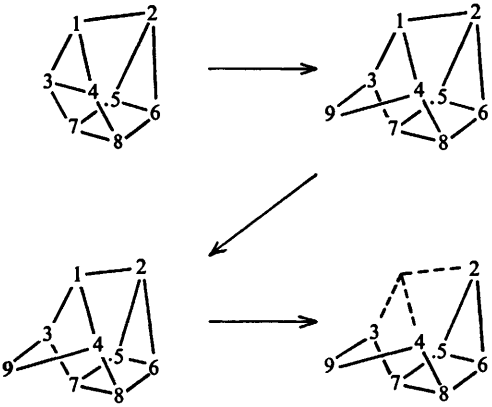


10 Derivation of the Structures of the Polyatomic Cations of the Group IV Elements

The generalizations presented above can be used to rationalize the structures of the polyatomic cations of the Group VI elements.

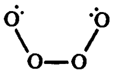
A. S_8^{2+} and Se_8^{2+}.—These ions have an *exo–endo* conformation with a long transannular bond. Their structures can be derived from that of cuneane by the following transformations:

Bond 3–4 is replaced by the bridging atom 9, bond 5–6 is broken and then atom 1 is removed.



It would appear to be the weak attractive force between the lone pairs on atoms 3, 4, and 2 represented by the dashed lines in the structure above that holds this ion in its *exo–endo* conformation, *i.e.* that causes the retention of the cuneane structure for seven of the atoms.

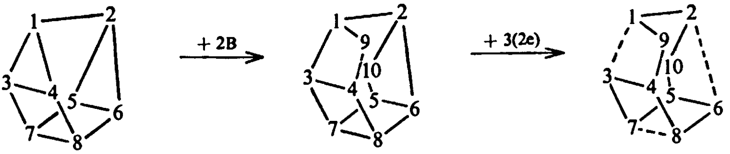
We note the presence in this structure of pentagonal rings of five electron pairs of the type



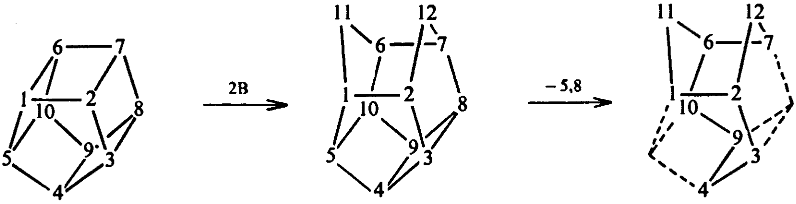
These are a feature of many cage structures and the formation of a weak double bond in this situation seems to be particularly favoured.

B. Se_{10}^{2+} and $Te_2Se_8^{2+}$.—These two ions have the same cage structure which can be derived from cuneane by bridging two edges and breaking three bonds.

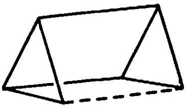
The conformation of the four-atom chain that bridges across the six-membered ring is such as to form two five-electron pair rings with four coplanar atoms and two lone pairs, of the same kind as described above for S_8^{2+} and Se_8^{2+}.



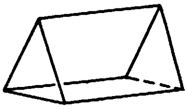
The presence of these five electron pair rings is clearly shown if the Se_{10}^{2+} structure is derived from a doubly bridged pentagonal prism by removing two of the atoms.



C. Te_6^{4+}.—According to the rules outlined above the structure of this ion should be obtained by adding two electrons to, and thus breaking, one of the bonds of the trigonal prism structure, *e.g.* the unknown Te_6^{6+} ion. One might expect this to give a distorted trigonal prism with one bond longer than the others. In fact Te_6^{4+} has a regular trigonal prism structure although the bonds between the triangular faces are longer than those in the triangular faces. Presumably the structure can be described in terms of the three equivalent resonance structures (3) each of which contains one broken bond with possibly some contribution from the six equivalent structures (4).

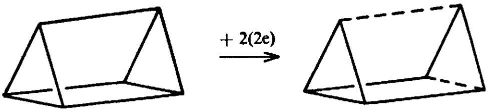


(3)



(4)

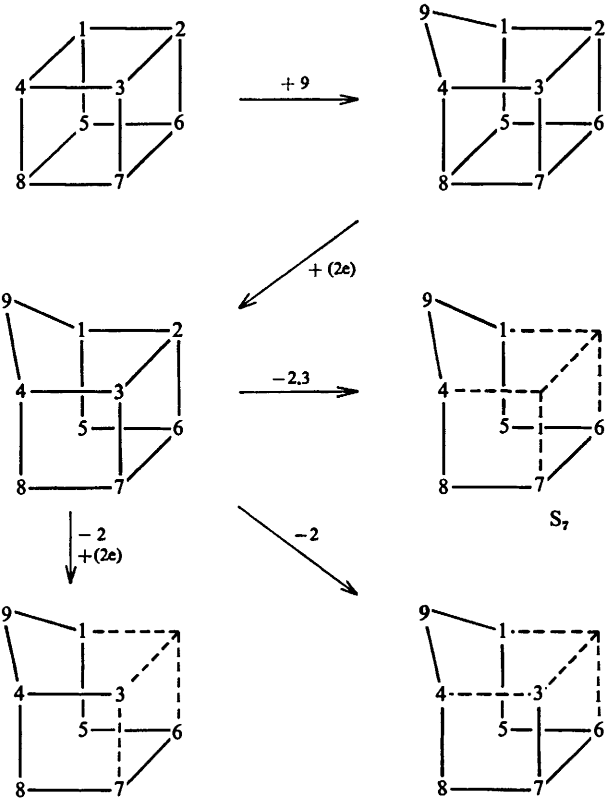
D. $Te_3S_3^{2+}$ and $Te_2Se_4^{2+}$.—These two ions have the same bicyclic structure containing a three-membered ring (5) and a five-membered ring with a pronounced boat conformation (6). This structure can be obtained by breaking two of the bonds of the trigonal prism cluster structure (5).



(5) (6)

The pronounced boat conformation can be ascribed to the broken bond, *i.e.* the weak double bond between the two triangular faces. It is also interesting to note that the structures of these ions can be obtained from the P_4S_3 structure by removing one of the S atoms leaving the two bonding electron pairs as non-bonding pairs as shown in Figure 12. It is these two non-bonding pairs of electrons which provide the weak double bond that holds these ions in the same conformation as the P_4S_3 molecule.

E. S_{19}^{2+}.—Before discussing the structure of S_{19}^{2+} it will be convenient to mention some simpler but related molecules. S_7 has a chair conformation[28] that can be derived from the cube as shown below. S_7I^+ and S_7O also have the same chair conformation[29,30] with the substituent atom occupying what appears to be a rather sterically hindered position. Their structures can also be derived from the cube as shown. The position of the substituent atom 3 appears to be closely connected with the weak bonding interaction 3 - - - 7.



S_7

S_7I^+ S_7O

ring 1 of S_{19}^{2+}

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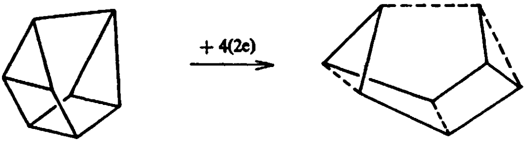
[28] R. Steudel, R. Reinhardt, and F. Schuster, *Angew. Chem., Internat. Edn.*, 1977, **16**, 715.
[29] J. Passmore, P. Taylor, T. K. Whidden, and P. White, *J. C. S., Chem. Comm.*, 1976, 689.
[30] R. Steudel, R. Reinhardt, and T. Sandow, *Angew. Chem., Internat. Edn.*, 1977, **16**, 716.

Ring 1 of S_{19}^{2+} is similar to S_7I^+ and S_7O except that the substituent which, in this case, is the first sulphur atom of the five atom chain, although occupying approximately the same position relative to the ring, is bonded to a different ring sulphur atom. Its structure can also be related to the cube as shown above.

Ring 2 of S_{19}^{2+} has a boat conformation which can be derived from cuneane as follows:



ring 2 of S_{19}^{2+}

11 The Structures of Some Other Cage Molecules

The cage structures of a number of different phosphorus and arsenic sulphides and selenides and some related molecules can all be derived from the tetrahedron, the trigonal prism, or the cuneane structure using the rules given above, as shown in Figure 14.

Some derivatives of the cube are shown in Figure 15. These include P_{11}^{3-},[31] trishomocubane $C_{11}H_{14}$,[32] and homocubane C_9H_{10}.[33] Derivatives of the pentagonal prism which include homopentaprismane $C_{11}H_{12}$,[34] $(Bu^tBN_2H_2)_4$,[35] and Se_{10}^{2+} [17] are also shown in Figure 15.

12 The Relationship between Cluster Structures and Sphere Close-Packings

A cluster is an arrangement of atoms that are packed closely together. Since most of the space occupied by an atom is made up of its valency shell electrons which surround a rather small central core it is reasonable to suppose that in a cluster the valency shell electrons are also closely packed. In one simple form of the VSEPR theory for predicting the shapes of molecules of the type AX_n each bonding pair is assumed to have a spherical shape and the arrangement of these spherical electron pairs is that in which they are packed as closely as possible around the core of the central atom A. Thus four such electron pairs have a tetrahedral arrangement, five a trigonal bipyramid arrangement, and six an octahedral arrangement, *etc.*, as has been discussed in detail elsewhere.[36] It is logical to conclude that when a number of atoms are packed as closely as possible together in a cluster then all the valency electron pairs will constitute one overall close-packed arrangement. These close-packed arrangements are the same as those found in AX_n molecules but they have no central core, being held

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[31] W. Wichelhaus and H. G. von Schnering, *Naturwiss*, 1973, **60**, 104.
[32] G. R. Underwood and B. Ramamoorthy, *Tetrahedon Letters*, 1970, 4129.
[33] W. G. Dauben and D. L. Whalen, *Tetrahedron Letters*, 1966, 3343.
[34] G. R. Underwood and B. Ramamoorthy, *J.C.S., Chem. Comm.*, 1970, 12.
[35] P. C. Thomas and I. C. Paul, *J.C.S., Chem. Comm.*, 1968, 1130.
[36] R. J. Gillespie, 'Molecular Geometry', van Nostrand Reinhold, London, 1972.

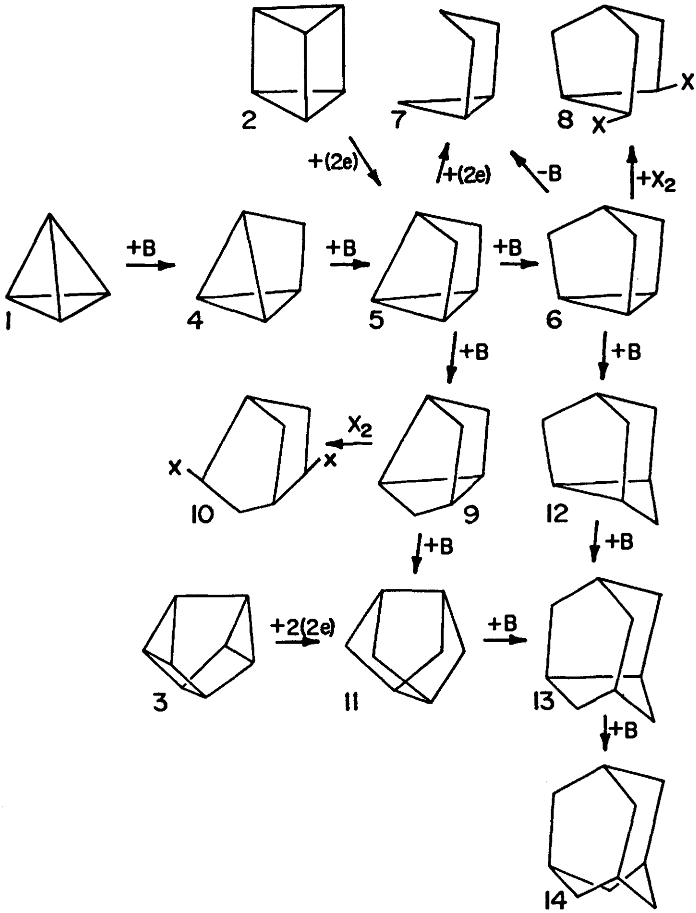

Figure 14 *Derivatives of the tetrahedron, the trigonal prism, and cuneane:* 1, *tetrahedron,* P_4; 2, *trigonal prism*; 3, *cuneane*; 4, –; 5, –; 6, P_4S_3, Sb_7^{3-}; 7, $Te_3S_3^{2+}$, $Te_2Se_4^{2+}$; 8, β-$P_4S_3I_2$; 9, –; 10, α-$P_4S_3I_2$; 11, S_4N_4, α-P_4S_4; 12, β-P_4S_4, α-P_4S_5*; 13, P_4S_7*; 14, P_4O_6, *adamantane*, P_4S_9* (+2e *signifies the addition of two electrons*; +B *signifies the addition of a bridging atom*; –B *signifies the removal of a bridging atom*; X_2 *signifies a halogen molecule*; **these molecules contain one or more externally bonded sulphur atoms*)

together instead by four or more cores which occupy appropriate holes in the close-packed arrangement of electron pairs.

For the clusters of the more electronegative main group elements the atomic cores are always found in positions of three-co-ordination, *i.e.* in trigonal holes which when capped with an unshared pair or with a bonding pair shared with an external ligand become tetrahedral holes. We first restrict our discussion to such structures and we will add the further restriction that each electron pair is situated between only two nuclei, *i.e.* it forms a localized two-centre single bond.

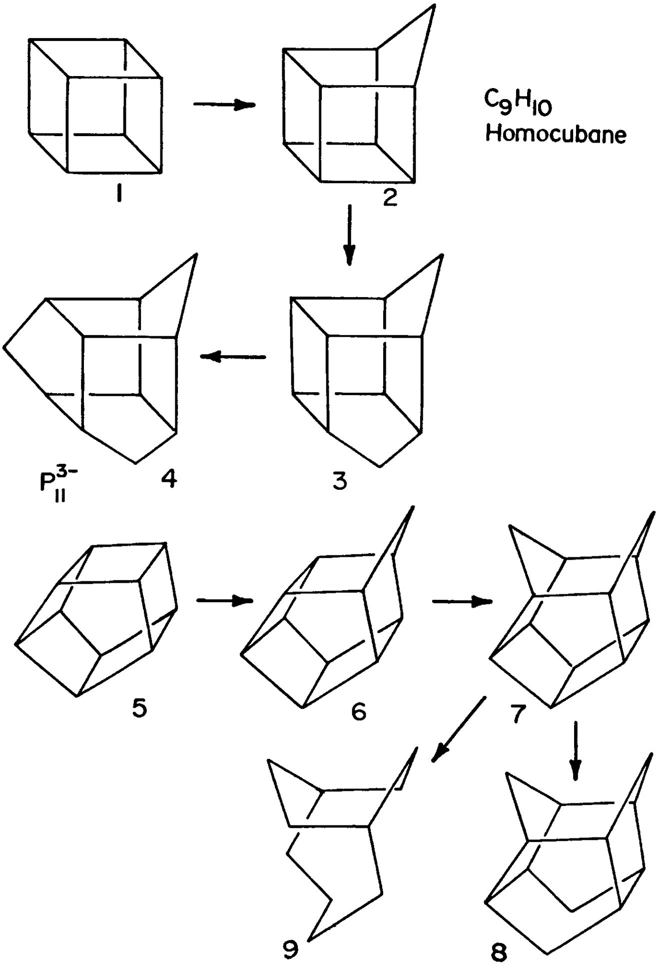

Figure 15 *Derivatives of the cube and the pentagonal prism:* 1, *cubane* C_8H_8; 2, *homocubane* C_9H_{10}; 3, —; 4, $P_{11}{}^{3-}$ *trishomocubane* $C_{11}H_{14}$; 5, —; 6, *homopentaprismane*; 7, —; 8, $(Bu^tBN_2H_2)_4$; 9, $Se_{10}{}^{2+}$, $Te_2Se_8{}^{2+}$

Table 3 summarizes the possible clusters of this type and the corresponding electron-pair arrangements.

Such clusters are only possible for even numbers of atoms and the cases of four to ten atoms are considered. Each cluster contains 1.5*n* electron pairs, *i.e.* 6, 9, 12, and 15 electron pairs, respectively. Six and nine electron pairs have the octahedral and tricapped trigonal prism arrangements which correspond to the closest packings of spheres on the surface of an inner sphere—in this case the surface of the central hole (Figure 16).

The closest packing of 12 electron-pair spheres is the icosohedral arrangement

Table 3 *Electron pair arrangements in two-centre-bonded three-co-ordinated clusters*

Number of nuclei	*Number of electron pairs*	*Arrangement of electron pairs*	*Arrangement of nuclei*	*Examples*
4	6	Octahedron (3,3′)	Tetrahedron	P_4, As_4, Sb_4
6	9	Tricapped trigonal prism (3,3′,3)	Trigonal prism	C_6H_6 (prismane)
8	12	Cubo-octahedron (4,4′,4)	Cube	$[Tl(OR)]_4$
10	15	Bispentagonal antiprism (5,5′,5)	Pentagonal prism	

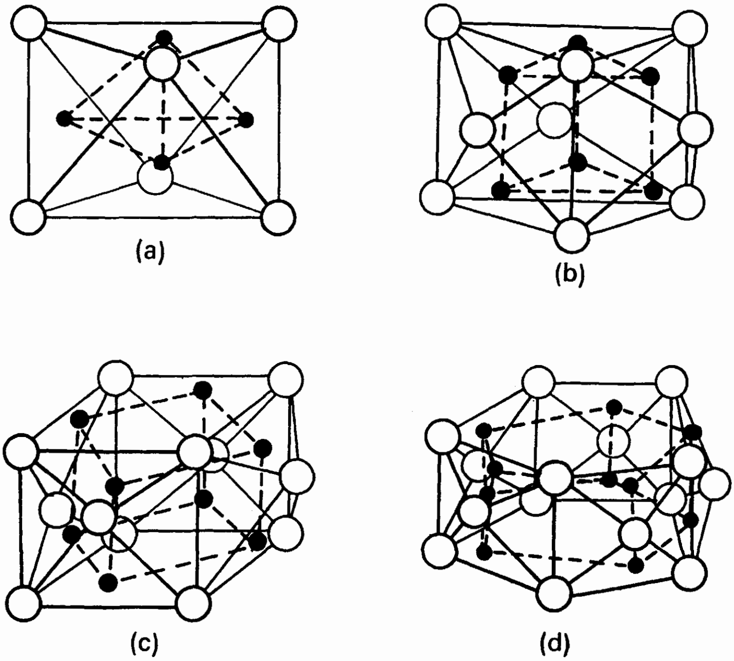

Figure 16 *Close packed arrangements of electron pairs: (a) octahedral arrangement of six electron pairs with four nuclei occupying trigonal holes and having a tetrahedral arrangement; (b) tricapped trigonal prism arrangement of nine electron pairs with six nuclei occupying trigonal holes and having a trigonal prism arrangement; (c) cubo-octahedral arrangement of twelve electron pairs with eight nuclei occupying trigonal holes and having a cubic arrangement; (d) pentacapped pentagonal prism (5,5′,5) arrangement of fifteen electron pairs with ten nuclei occupying trigonal holes and having a pentagonal prism arrangement*

but this is not suitable for three-co-ordinated clusters and a more suitable but not quite close-packed arrangement is the cubo-octahedron which may be described as a 4,4′,4, arrangement where 4′ indicates a square of electron pairs having a staggered arrangement with respect to the square layers above and below. This cubo-octahedral arrangement of 12 electron pairs can be derived from a three-dimensional cubic-close-packed stack of thirteen electron pair spheres by removing the central sphere. The cubo-octahedron has eight trigonal holes in which the eight cores of a cubic cluster are located (Figure 16c).

For the fifteen electron pairs of a ten-atom framework the appropriate arrangement is the nearly close-packed bispentagonal antiprism or 5,5′,5, arrangement. This gives rise to the pentagonal prism structure when ten atomic cores are placed in ten trigonal holes (Figure 16d).

The two other eight-atom three-co-ordinated networks in Figure 16 are also based on a cubo-octahedral arrangement of twelve electron pairs. In order to obtain the cuneane structure two cores are moved from two triangular faces of the cubo-octahedron to two adjacent triangular faces as shown in Figure 17. If

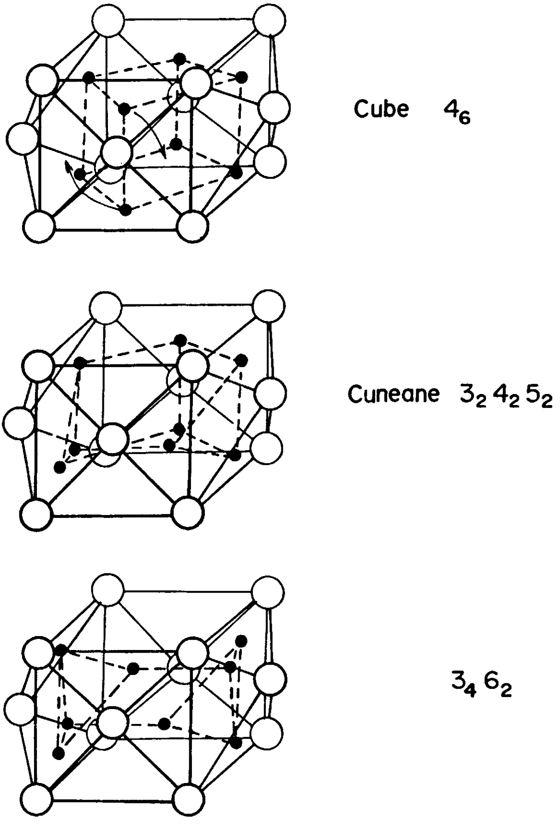

Figure 17 *The cube, the cuneane, and the* $3_4 6_2$ *cluster frameworks and their relationship to a cubo-octahedral arrangement of electron pairs*

this process is repeated on two more opposite faces of the cubo-octahedron the 3_46_2 structure is obtained.

It is interesting to note that the close-packed electron pair model gives a satisfactory explanation of the apparently unusually small bond angles in the smaller clusters. For example in tetrahedral molecules such as P_4 the bond angle is apparently only 60°. The model shows that each atomic core is, however, surrounded tetrahedrally by four electron pairs but the centres of the electron pair spheres are not located on the core–core directions, *i.e.* the apparent bond directions. In other words the bonds may be described as bent as has frequently been previously suggested. Similarly the apparent bond angle of 90° in cubane again corresponds to bent bonds.

13 Four Co-ordination of Atomic Cores and Multicentre Bonding

The range of possible cluster compounds based on close-packed arrangements of electron-pair spheres is considerably increased if atomic cores can occupy square holes, *i.e.* four-co-ordinated sites in addition to the three co-ordinate sites so far considered. The square pyramid, the trigonal bipyramid, and the octahedron, which are not found for the main group elements so far discussed then become possible cluster shapes. Another possibility is that atomic cores occupy sites in such a way that electron pairs are three- or four-co-ordinated, *i.e.* form three- or four-centre face bonds in addition to occupying two-co-ordinated sites or forming edge bonds as so far considered. Table 4 summarizes all the close-packed and nearly close-packed arrangements of from four to thirteen electron pairs and the cluster shapes based on these electron pair arrangements.

These additional types of clusters are found mostly among the transition metals although some examples are known for boron and some of the more metallic of the main group elements. The classical examples of compounds containing multicentre bonds are those of boron. Among the possible cluster compounds B_4Cl_4 can be described as having a tetrahedral arrangement of electron pairs each of which forms a three-centre face bond and $B_5H_5^{2-}$ and $B_3C_2H_5$ can be described in terms of a trigonal prism arrangement of six electron pairs each of which forms a three-centre face bond; the cation Bi_5^{3+} can also be described in the same way. Other possibilities for multi-centre bonding include a trigonal bipyramidal arrangement of five electron pairs giving a trigonal prism cluster with both three- and four-centre bonds and six electron pairs in an octahedral arrangement giving a cubic structure with six four-centre face bonds. No examples of these two types of cluster are however known. Although some of the smaller electron-deficient clusters of boron and some of the more metallic elements can be described in localized electron pair terms, in general this approach is not satisfactory for electron-deficient compounds and delocalized models are more appropriate.

14 Transition Metal Clusters

The co-ordination sphere of a transition metal in a cluster is in general completed by a number of ligands, *e.g.* carbonyl groups. When the electrons

Table 4 *Cluster molecule shapes based on close-packed or nearly close-packed arrangements of electron pairs*

No. of electron pairs	*Electron pair arrangement*	*Number of cores in*		*Electron pair co-ordination*	*Cluster shape*	*Bonding*	*Example*
		3-co-ord. position	*4-co-ord. position*				
4	Tetrahedron	4	—	3	Tetrahedron	Face	B_4Cl_4
5	Trigonal Bipyramid	6	—	3, 4	Trigonal prism	Face	—
6	Octahedron	4	—	2	Tetrahedron	Edge	P_4
		8	—	4	Cube	Face	—
	Trigonal prism	2	3	3	Trigonal bipyramid	Face	Bi_5^{3+}
7	Monocapped octahedron	—	—	—	—	—	—
8	Square antiprism	4	1	2	Square pyramid	Edge	$Fe(CO)_{15}C$
	Cube	—	6	3	Octahedron	Face	$Nb_6Cl_{12}^{2+}$
9	Tricapped trigonal prism	6	—	2	Trigonal prism	Edge	—
		2	3	2	Trigonal bypyramid	Edge	$Os_5(CO)_{16}$
10	Bicapped square antiprism	—	—	—	—	—	—
11	Pentcapped trigonal prism	—	9	3, 4	Tricapped trigonal prism	Face	Bi_9^{5+}
12	Icosahedron	—	—	—	—	—	—
	Cubo-octahedron	8	—	2	Cube	Edge	$[Tl(OR)]_4$
		8	—	2	Cuneane	Edge	C_8H_8
		8	—	2	3_46_2	Edge	$Au(AuL)_8^{3+}$
		—	6	2	Octahedron	Edge	$Mo_6Cl_8^{4+}$
	Hollow hexagonal close-packing	—	6	2	Trigonal prism	Edge	—
13	Cubic close-packing	—	6	2	Octahedron	Edge and Centre	$Rh_6(CO)_{16}$
	Hexagonal close-packing	—	6	2	Trigonal prism	Edge and Centre	$Pt_6(CO)_{18}^{2-}$

Table 5 *Electron counts or 'magic numbers' for clusters*

No. of atoms, n	*Shape of cluster*	*Co-ord. no. of atoms, a*	*Co-ord. no. of electron pairs, p*	*No. of cluster bonding electron pairs*	*Total no. of cluster electrons*	
					Main Group	*Transition metal*
4	Tetrahedron	3	3	4	16	56
		3	2	6	20	60
5	Square pyramid	3, 4	3	4	—	66
		3, 4	2	8	—	74
5	Trigonal bipyramid	3, 4	3	5	—	66
		3, 4	2	9	—	72
6	Trigonal prism	3	3, 4	5	22	82
		3	2	9	30	90
		4	2	12	—	84
		4	2	13	—	86
	Octahedron	4	3	8	—	76
		4	2	12	—	84
		4	2	13	—	86
8	Cube	3	4	6	28	96
		3	2	12	40	108
		3	2	13	42	110

supplied by these ligands are counted in addition to those forming the cluster bonds the transition elements appear to conform, with very few exceptions, to the 18 electron rule. For the purposes of electron counting it is assumed that each ligand contributes two electrons to the cluster. The number of electrons associated with any cluster is then readily calculated. For a main group element cluster the total number of cluster electrons is $N = n\left[8 - 2a\left(\frac{p-1}{p}\right)\right]$ and for a transition metal $N = n\left[18 - 2a\left(\frac{p-1}{p}\right)\right]$ where n is the number of atoms in the cluster, a is the co-ordination number of each atom and p is the co-ordination number of each electron pair, *i.e.* $p = 2$ for a two-centre bond, $p = 3$ for a three-centre bond, *etc.* The numbers of electrons counted in this way for all the common polyhedra and for two, three, and four-centre bonding are summarized in Table 5.

15 Tetrahedral Clusters

The most common type of tetrahedral cluster is that having six two-centre edge bonds and a total of 60 electrons for a transition metal, 20 for a main group cluster, and intermediate numbers of electrons for mixed main group–transition metal clusters. Examples are given in Table 6.

A less common type of tetrahedral cluster is that having four three-centre face bonds. Examples are B_4Cl_4 and $H_4Re(CO)_{12}$. The bonding in the latter cluster which does not have the magic number of 60 electrons appropriate for edge bonding, has sometimes been described as unsaturated and resonance structures involving metal–metal double bonds have been proposed. Justification for the present description is provided by the fact that the metal–carbon bonds eclipse the tetrahedron edges, whereas in the 60 electron tetrahedral clusters the metal ligand bonds are staggered with respect to the tetrahedron edges. Assuming that the metal ligand bond pairs tend to have a staggered arrangement with respect to the metal–metal bonding pairs they are predicted to be staggered with respect to the tetrahedron edges in 60 electron clusters and eclipsed with respect to these edges in 56 electron clusters. It has also been concluded from an *X*-ray crystallographic study that the protons lie above the tetrahedral faces and not over the edges of the tetrahedron as in other tetrahedral hydrido complexes. Again this indicates that the metal–metal bonding pairs are in the tetrahedral faces.

16 Octahedral Clusters

Octahedral clusters can be based on either a cubo-octahedral arrangement of twelve electron-pairs, which gives twelve two-centre edge bonds or a cubic arrangement of eight electron pairs, which gives eight three-centre face bonds (Figure 18). The former arrangement has a total of 84 cluster electrons and the latter 76.

Examples of both these types of clusters are given in Table 7. In these cases also

Table 6 *Tetrahedral clusters*

	M_4	M_3A	M_2A_2	MA_3	A_4
No. of electrons for edge bonding	60	50	40	30	20
	$Ir_4(CO)_{12}$	$Cp_3CoS(CO)$	$(Ph_5C_5)Pd_2C_2Ph_2$	$Co(CO)_3As_3$	P_4
	$Co_4(CO)_{12}$	$(CO)_9FeCo_2S$	$Cp_2Ni_2C_2Ph_2$		As_4
	$Ir_4(CO)_9(PR_3)_3$	$Co_3(SiR)(CO)_9$			Sb_4
	$H_4Ru_4(CO)_{12}$	$MeCCo_3(CO)_9$			
	$H_6Re_4(CO)_{12}^{2-}$				
	$Fe_4(CO)_{12}^{2+}$				
	$Ni_4(CO)_6(PR_3)_4$				
	$CpRhFe_3(CO)_{11}$				
No. of electrons for face bonding	56				16
	$H_4Re(CO)_{12}$				B_4Cl_4

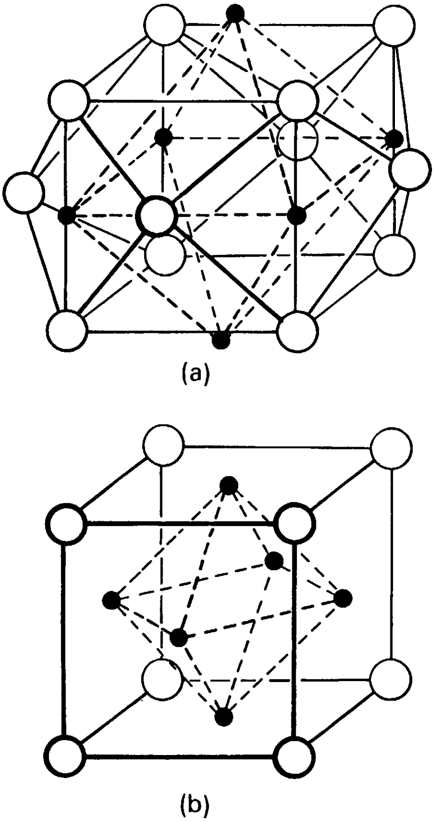

Figure 18 *(a) Cubo-octahedral arrangement of twelve electron pairs with six nuclei occupying four-co-ordinated holes and having an octrahedral arrangement; (b) cubic arrangement of eight electron pairs with six nuclei occupying four-co-ordinated holes and having an octahedral arrangement*

Table 7 M$_6$ *Octahedral clusters*

No. of electrons	76	84	86
Bonding	Face	Edge	Edge + Central
	$Nb_6Cl_{12}^{2+}$	$Mo_6Cl_8^{4+}$	$Ru_6(CO)_{18}^{2+}$
	$Au(PPh_3)_6^{2+}$	$Cu_6(PPh_3)_6^{6-}$	$Ru_6(CO)_{17}C$
		$Os_6(CO)_{18}$	$HRu(CO)_{18}^{-}$
	Pt_6Cl_{12}		$Rh_6(CO)_{16}$
			$Co_6(CO)_{15}^{2-}$
			$Ni_6(CO)_{12}^{2-}$
			$Rh_6(CO)_{15}I^{-}$

the geometry of the metal–ligand bonds is consistent with the proposed bonding since in the edge bonded compounds the metal–ligand bonds lie above the faces, *i.e.* staggered with respect to the edges, whereas in the face-bonded clusters the metal–ligand bonds lie above the edges.

A long standing problem with respect to the description of many octahedral clusters is that they contain a total of 86 rather than the 84 cluster electrons that is appropriate for edge bonding. This had led to the suggestion that they should be described in terms of the type of bonding proposed for the boranes in which seven electron pairs are required for an octahedral structure.[24] An alternative description of these clusters is suggested by the present approach when it is recalled that the cubo-octrahedral arrangement of 12 electron pairs has room for a thirteenth pair in its central hole to give a cubic close-packed stack of 13 electron pairs. Examples of this type of cluster are listed in Table 7. They may be described as having twelve edge bonds and a thirteenth central bond.

Another interesting aspect of octahedral clusters is that several of them contain a central interstitial atom. It is perhaps significant that these are all 86 electron clusters if the electrons provided by the interstitial atom are also counted. Typical examples are $Ru_6(CO)_{17}C$ and $Fe_6(CO)_{16}C^{2-}$. The interstitial carbon atom is situated at the centre of the octahedron, and therefore in the centre of the central electron pair. These clusters could alternatively be regarded as 84 electron clusters containing a C^{2+} ion occupying the central hole of the cubo-octahedral arrangement of twelve electron pairs.

17 Square Pyramid Clusters

These are based on a square antiprism arrangement of eight electron pairs with one four-co-ordinated atom in the apical position and four three-co-ordinated atoms in the basal positions (Figure 19). These require 74 electrons for M_5 clusters, 64 for M_4A clusters, 54 for M_3A_2 clusters, *etc.* There are a total of eight two-centre bonds, one along each edge of the square pyramid. $Fe_3S_2(CO)_9$ is an

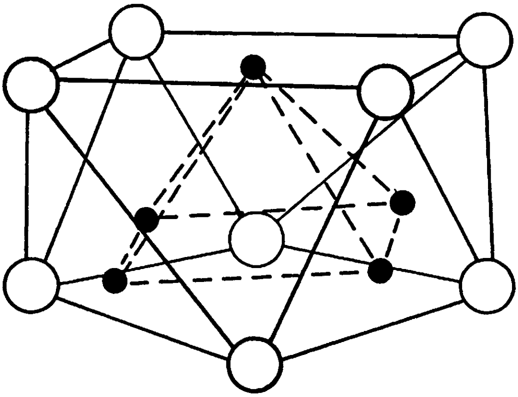

Figure 19 *Square antiprism arrangement of eight electron pairs in a square pyramid cluster*

example of a 54 electron M_3A_2 cluster and $Fe_5(CO)_{15}C$ is an example of a 74 electron M_5 cluster containing an interstitial carbon atom. The carbon atom is situated in the base of the square antiprism of electron pairs, *i.e.* slightly below the four basal iron atoms which occupy four of the eight trigonal holes of the square antiprism arrangement of electron pairs. It can then be regarded as participating in four three-centre bonds with the four pairs of iron atoms in the base of the square pyramid.

18 Trigonal Bipyramid Clusters

The tricapped trigonal prism arrangement of nine electron pairs that was used to describe trigonal prism clusters (Table 3) is also appropriate for the description of trigonal bipyramid clusters. Two atomic cores are situated in trigonal holes at the top and bottom of the tricapped trigonal prism and the other three cores are placed in square holes at the side. Thus two cores are three-co-ordinated and three cores are four-co-ordinated (Figure 20). There is a total of nine two-centre bonds and a total of 72 cluster electrons. An example is $Os_5(CO)_{16}$.

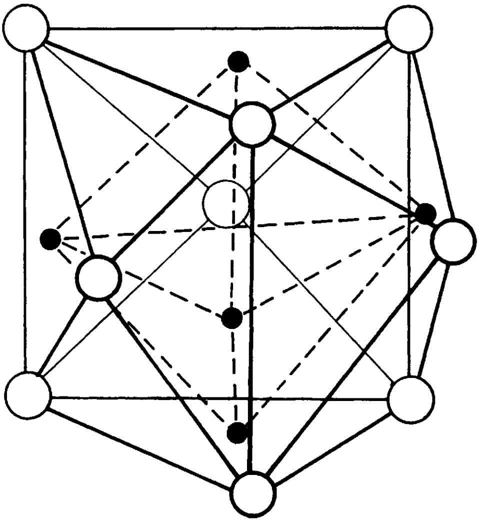

Figure 20 *Tricapped trigonal prism arrangement of nine electron pairs in a trigonal bipyramid cluster*

Alternatively a trigonal bipyramid cluster may be based on a trigonal prism arrangement of electron pairs with the atomic cores occupying the middle of the two triangular faces and the three square faces so that each electron pair is three-co-ordinated and forms a three-centre bond in each of the six faces of the trigonal bipyramid. The apical metal atoms are three-co-ordinated and the equatorial atoms four-co-ordinated. Although there are no transition metal examples the Bi_5^{3+} cluster appears to be of this type.[37] It has a total of 11 electron

[37] R. C. Burns, R. J. Gillespie, and W-C Luk, *Inorg. Chem.*, 1978, **17**, 12.

pairs of which six are three-centre bonding pairs and the remaining five are non-bonding pairs.

It seems appropriate to mention the Bi_9^{5+} cluster at this point as it has a related structure and as it has not previously been satisfactorily accounted for using a localized electron pair approach. The nine bismuth atoms occupy the corners of a tricapped trigonal prism.[38] It can be described in terms of a pentacapped trigonal prism arrangement of electron pairs, *i.e.* a 1,3,3′,3,1 arrangement. Eight of the electron pairs form three-centre bonds and three form four-centre bonds and each bismuth core is situated in a four-co-ordinate position, or when the unshared pairs are included each bismuth is surrounded by a square pyramidal arrangement of five electron pairs (Figure 21).

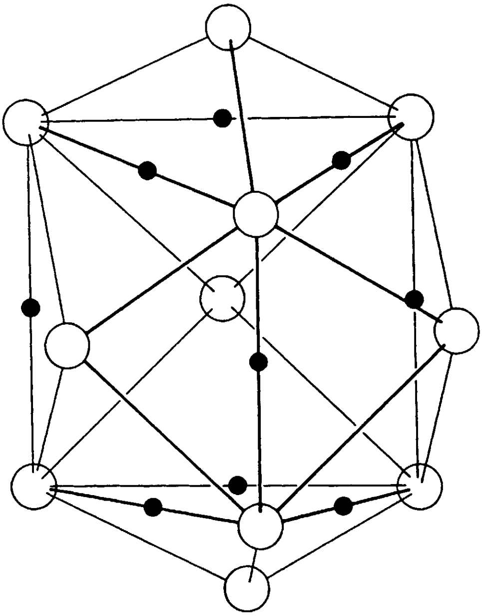

Figure 21 *Pentacapped trigonal prism arrangement of eleven electron pairs in a tricapped trigonal prism cluster*

19 Trigonal Prism Clusters

There appear to be three possible electron pair arrangements for a trigonal prism cluster. Apart from the trigonal bipyramid arrangement of five pairs of which there are no known examples, a trigonal prism cluster can be based on the tricapped trigonal prism arrangement of nine electron pairs or on a hexagonal close-packed arrangement of twelve or thirteen pairs. In the former case the total number of cluster electrons is 90 of which 18 are used to form nine two-

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[38] R. M. Friedman and J. D. Corbett, *Inorg. Chem.*, 1973, **12**, 1134.

centre edge bonds (Figure 16). The only known example appears to be the $Rh_6(CO)_{15}C^{2-}$ ion in which the C^{4+} core is situated in the central hole of the close-packed arrangement of nine bonding electron pairs. Alternatively, a trigonal prism cluster can be based on a hollow hexagonal close-packed arrangement of twelve electron pairs or a true hexagonal close-packed arrangement of thirteen electron pairs. The electron pair arrangement and the corresponding metal–metal bonds are shown in Figure 22. There are a total of 84 or 86 electrons as in the cubic close-packed octahedral clusters. Of these there are twelve bonding pairs of which six form edge bonds in the triangular faces and the remaining six form three double bonds between the triangular faces. There may in addition be a thirteenth bonding pair forming a central bond. A cluster of this type is the $[Pt_6(CO)_9\mu(\text{-}CO)_9]^{2-}$ ion[39] which has 86 cluster electrons including a central bonding pair.

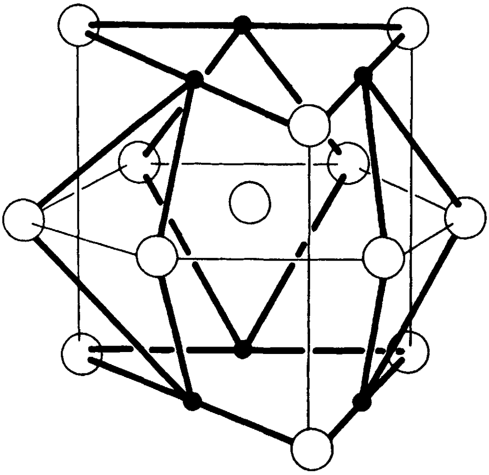

Figure 22 *Hexagonal close packed arrangement of thirteen electron pairs in the* $[Pt_6(CO)_9(\mu\text{-}CO)_9]^{2+}$ *trigonal prism cluster*; Pt—Pt *bonds are shown as heavy lines.*

20 Cubic Clusters

These are based on the cubo-octahedral arrangement of 12 electron pairs with eight atomic cores occupying the eight trigonal holes. Each atom is three-coordinated and there are a total of twelve bonding pairs (Figure 16). The total number of cluster electrons in this case is 120 for an M_8 cluster, 80 for the rather common M_4A_4 clusters, and 40 for an A_8 cluster. Examples of these types of clusters are given in Table 8. It is possible, in principle, to have an additional electron pair in the centre of the cubo-octahedron, as described for octahedral clusters, to give a total of 122 cluster electrons or 82 in the case of M_4A_4 clusters. It is perhaps surprising that no clusters of this type have yet been reported.

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[39] J. C. Calabrese, L. F. Dahl, Z. Cavalieri, P. Chini, G. Longoni, and S. Martinengo, *J. Amer. Chem. Soc.*, 1974, 96, 2616.

Table 8 *Cubic clusters*

	M_8	M_4A_4	A_8
No. of electrons	120	80	40
	$Ni(CO)_8(\mu_4PCoH_5)_6$	$Mu_4(CO)_{12}(SEt)_4$ $Os_4(CO)_{12}O_4$ (CuIL) $(CO)_{12}Co_4Sb_4$	C_8H_8 $[Tl(OR)]_4$

21 Gold Clusters

Gold clusters have been found to have some rather unique structures and have caused a considerable amount of discussion. Octahedral clusters such as $[(p\text{-tolyl})_3P]_6Au_6{}^{2+}$ have a total of 76 cluster electrons which is the number required for a face bonded octahedral cluster.

More unusual are the clusters with a central gold atom such as $Au(AuL)_8{}^{3+}$ and $Au(AuL)_{10}{}^{3+}$.[40,41] The first has the three-co-ordinated 8 atom 3_46_2 structure with a central gold atom (Figures 13 and 17). There are twelve pairs of electrons available for bonding if it is assumed that each gold atom provides three electrons for bonding and thus has a d^8 configuration. These twelve electron pairs have the slightly distorted close-packed cubo-octahedral arrangement appropriate for the 3_46_2 structure. Thus each peripheral gold atom forms three cluster bonds and one bond to an external ligand, the four bonds having an approximately tetrahedral arrangement. The centre of the cluster is occupied by an Au^{3+} ion. This seems to be a satisfactory description of these clusters although it should be noted that the gold atoms do not obey the 18 electron rule, each of the peripheral atoms having only 16 valency shell electrons.

The cluster $Au(AuL)_{10}{}^{3+}$ can be described in a similar manner as a three-co-ordinated 10 atom monotruncated cubic cluster (Figure 13) with an Au^{3+} ion occupying the central hole. Again the peripheral gold atoms have only 16 and not 18 electrons in their valency shells.

22 Localized Bonding in Transition Metal Clusters

It has been the object of this brief discussion of transition metal clusters to show that a localized bond model is an attractive alternative to the generally accepted model based on the borane structures in accordance with Wade's rules.[24] Although there are exceptions to the present model, as there are to Wade's rules, it seems clear that a large number of transition-metal cluster compounds can be conveniently described in terms of localized two-centre or three-centre bonds between the metal atoms, with each metal atom obeying the 18 electron rule. This model gives a simple and useful picture of the bonding and has some predictive value in

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[40] P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, and M. Sansoni, *J.C.S., Chem. Comm.*, 1971, 1423.

[41] P. L. Bellon, M. Manassero, L. Naldini, and M. Sansoni, *J.C.S., Chem. Comm.*, 1972, 1035.

so far as each possible cluster shape has only a few characteristic numbers of electrons, although when alternative shapes are possible for the same number of electrons no choice between the alternative shapes can be made. It is perhaps important to note that even the remarkable metal clusters containing interstitial metal atoms such as the gold clusters described above and $[Rh_{13}(CO)_{12}(\mu\text{-}CO)_{12}H_3]^{2-}$ and $[Rh_{15}(CO)_{14}(C)_2]^-$ can all be described in terms of localized two-centre metal–metal bonds forming a polyhedron surrounding a central charged metal atom and in the latter case two C^{4+} cores. We note also that the sphere close-packing model provides an explanation for the 86 electron pair octahedral clusters which have otherwise proved a stumbling block for the localized electron pair model as they have one pair of electrons in excess of the number needed for twelve edge bonds.

23 Review of the Factors Determining the Shapes of Clusters

Having shown that the more electronegative main group element clusters and the transition-metal clusters can be described in terms of arrangements of localized electron pairs, it seems appropriate to review in general the factors that control the structures of clusters. The three interactions that must be considered are core–core repulsions, core–electron attractions, and electron–electron repulsions. The cores stay relatively far apart and can therefore be considered to repel each other according to Coulombs law. If the core–core interactions dominate the cores will take up those positions which minimize their mutual repulsion. These arrangements are the well-known arrangements of points on a surface of a sphere repelling each other according to Coulombs law.[36] Core–core interactions will be expected to be dominant when the ratio of the number of electron pairs to cores is small. For the borane anions $B_nH_n^{2-}$ and the carbaboranes there are only $n + 1$ electron pairs for n cores and core–core repulsions dominate the structure. Alternatively it may be said that there is an insufficient number of electron pairs to give a close-packed arrangement with sufficient holes for the cores. In such a case the electrons must be regarded as delocalized and the core–core interactions become the dominant factor in determining the structure. The structures of these compounds are indeed in accord with this prediction. Only in the case of the smallest clusters is the number of electron pairs sufficient to give a close-packed or nearly close-packed arrangement with sufficient holes to accommodate the atomic cores in three-co-ordinate sites. Thus in B_4Cl_4 there is a close packed tetrahedral arrangement of four electron pairs and in $C_2B_3H_5$ a nearly close packed trigonal prism arrangement of electron pairs. Nevertheless in general in these electron deficient compounds core–core repulsions determine the structures and the electron–electron interactions are relatively unimportant.

On the other hand in clusters with large electron-pair:atomic-core ratios the core–electron attractions and the electron pair–electron pair repulsions (represented in our model by the hard sphere electron pairs) tend to cause the electron pairs to adopt close-packed arrangements leaving the atomic cores to occupy suitable holes in the close-packed arrangement. In these cases, as in the main group clusters, the structure is determined by the electron pair packing and the core–core repulsions no longer dominate the structure. Since transition-metal clusters should be regarded as electron rich it seems appropriate to use a localized electron model in these cases also and we have shown this model is indeed satisfactory in a large number of cases.

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