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Main group element chemistry at the millennium

Norman N. Greenwood

School of Chemistry, The University of Leeds, Leeds, UK LS2 9JT

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Some of the highlights of main group element chemistry during the past decade are reviewed. There are now 47 elements in the s- and p-blocks of the Periodic Table, ranging from the oldest (and lightest) element in the universe, hydrogen, to the most recently synthesised (and heaviest) known element, ^{293}[118], which was first reported in 1999. On the basis of the astonishing discoveries and developments that have been made in chemistry during the first two millennia of the present era, the only safe prediction for the third millennium is that there will be even more spectacular, perplexing, exhilarating, satisfying and potentially useful discoveries in main group element chemistry to be expected in the years that lie ahead.

1. Introduction

Chemistry, like history, is no respecter of decades, or centuries, or even millennia. These are convenient though entirely arbitrary time intervals, which do not usually correspond with the timing of actual developments or events. In chemistry we have been wonderfully served since 1904 by having our *Annual Reports on the Progress of Chemistry*. These are yearly anniversary presents, but a longer time-scale is necessary to enable us to perceive the general trends that are occurring and to gauge the significance of the developments that are taking place.

On the occasion of the sesquicentennial of the Chemical Society/Royal Society of Chemistry in 1991 there was an opportunity to chart the resurgence of main group element chemistry during the preceding 45 years (*i.e.* from 1946, which was the first complete year after World War Two).[1] In the present article I shall extend the Perspective to incorporate selected results from the massive amount of work that has been published during the past decade. The optimistic note on which I concluded the earlier survey seems to have been well justified by the advances achieved. However, those closer to the laboratory bench than I have myself been in recent years will no doubt also be painfully aware of the problems and difficulties entailed in maintaining this forward momentum.

The review will be structured around specific individual elements or groups of elements in the Periodic Table.

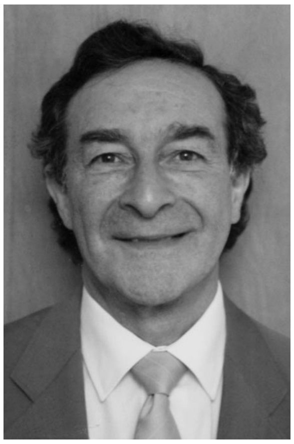
2. The chemistry of hydrogen

An unexpectedly varied coordination chemistry is emerging for hydrogen. Despite the fact that the element has but a single electron, stable compounds are known in which hydrogen has a coordination number not only of 1 as expected, but also of 2, 3, 4, 5 or even 6. Examples are:[2]

2 – boranes such as B_2H_6, *i.e.* $[H_2B(\mu_2\text{-}H)_2BH_2]$;
3 – the tetrahedral cluster $[(\mu_3\text{-}H)_4Co_4(C_5H_5)_4]$;
4 – the anion $[(\mu_4\text{-}H)Ru_8(CO)_{21}H]^{2-}$;
5 – the deuteride $\beta\text{-}Mg_2NiH_4(d_4)$;
6 – encapsulated H in $[HNb_6I_{11}]$, $[HRu_6(CO)_{18}]^-$, *etc.*

Such compounds provide continuing incentives to deepen and refine our concepts of chemical bonding. Likewise, the burgeoning field of dihapto dihydrogen complexes of the transition elements in Groups 5–10, which feature three-centred $(\eta^2\text{-}H_2)M$ bonds involving the pair of electrons in H_2.[2] Typical examples involve d^0, d^2, d^4, d^6 and d^8 metal centres predominantly from Group 6 onwards, though a moderately stable cationic niobium complex $[(\eta^5\text{-}Cp')_2Nb(\eta^2\text{-}H_2)L]^+$ has been isolated by protonation of the corresponding neutral hydride using CF_3CO_2H, where $Cp' = \{C_5H_4(SiMe_3)\}$ and $L = PMe_2Ph$.[3]

Interest in the nature of the hydrogen bond and its important structural ramifications continues unabated. A particularly thoughtful and beautifully illustrated review of the concept of



Norman N. Greenwood

Norman Greenwood was born in 1925 in Melbourne, Australia, where he received both his undergraduate and initial research degrees. After a PhD from Cambridge he held academic appointments in Nottingham (1953–61), Newcastle upon Tyne (1961–71) and Leeds (1971–) where he is now Emeritus Professor of Chemistry. He has published extensively in the fields of solid state chemistry, Mössbauer spectroscopy and main group element chemistry and has written several influential monographs and textbooks. Appointments include President of the Dalton Division of the RSC, President of the Chemistry Section of the British Association, President of the Inorganic Division of IUPAC, Chairman of the International Atomic Weights Commission, and numerous visiting professorships throughout the world. He holds honorary doctorates from the University of Nancy (France) and Toho University (Tokyo), was elected FRS in 1987 and Foreign Member of the French Academy of Sciences in 1992. Throughout his career he has received many Prizes, Awards and Lectureships, the most recent being the Humphry Davy Lectureship (2000) of the Royal Society.

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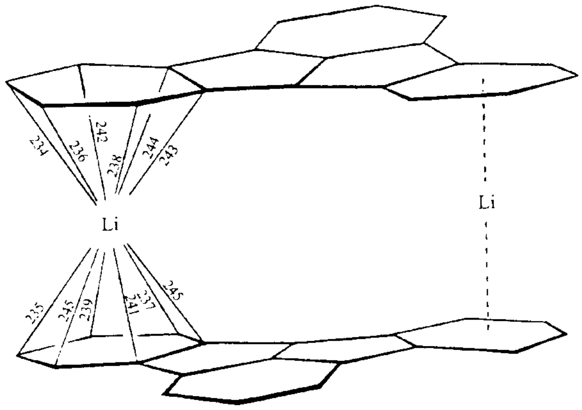
the hydrogen bond in relation to molecular structure and crystal engineering provides a useful summary.[4] In addition, an entirely new type of interatomic interaction, the H···H or dihydrogen bond has been recognised.[5] Thus, comparison of the melting point of ethane, H_3CCH_3 (−181 °C) with that of the precisely isoelectronic ammonia–borane, H_3NBH_3 (+104 °C) suggested the possibility of unusually strong intermolecular interactions in the latter despite the absence of lone pairs. A trawl of structural data bases revealed many other examples of such H···H bonds which operate between a conventional hydrogen-bond donor such as an NH or OH group acting as the weak acid component on the one hand, and an element–hydride bond EH on the other, where the element E can be a transition metal or boron. The interaction, which involves the close approach of protonic and hydridic hydrogen, has been characterised not only by crystallography (including neutron diffraction data) but also by other physical and theoretical methods. The resulting E–H···H–X systems have close intra- or inter-molecular H···H contacts in the range 175–190 pm, compared with normal non-bonding H···H contacts of >240 pm. Their heats of interaction are substantial (12–29 kJ mol^{-1}) and lie in the range found for conventional hydrogen bonds. In addition to numerous examples among the aminoboranes, intramolecular Ir–H···H–N bonds have been revealed in several six-coordinate iridium complexes, and an intermolecular Re–H···H–N bond has been identified in the yellow crystalline complex $[ReH_5(PPh_3)(indole)]$.[5]

3. The elements in Groups 1 and 2

Exciting developments have occurred in the chemistry of these elements during the past two decades that have completely rejuvenated what had previously appeared to be a largely predictable and worked-out area of chemistry. This efflorescence is particularly striking for lithium whose rich and extremely varied coordination chemistry now transcends even that of most transition metals.[6,7] These advances have been made possible by the imaginative use of bulky ligands, the burgeoning number of metal amides, alkoxides, enolates and organometallic compounds, and the exploitation of multidentate crown and cryptand ligands. As a result, lithium is now known in more than 20 coordination geometries with coordination numbers ranging from 1–12.[8] Thus, the bulky ligand bis(trimethylsilyl)methyl forms monomeric molecules of $[LiCH(SiMe_3)_2]$ in the gas phase, *i.e.* 1-coordinate Li. Two-coordinate Li can be either linear, as in the anion $[Li\{(SiMe_3)_3\}_2]^-$, or bent, as in polymeric $\{LiCH(SiMe_3)_2\}_\infty$, which also features 5-coordinate C_α. Likewise, 3-coordinate Li can be planar, pyramidal or angular, 4-coordinate Li is tetrahedral and 5-coordinate Li can be trigonal bipyramidal, square pyramidal or even planar depending on the hapticity and steric requirements of the ligand(s). Of particular note is the highly unusual planar 6-coordination in the unique structure of Li_3N; examples of octahedral, pentagonal pyramidal and irregular 6-coordination are also well established, and so on through coordination numbers 7, 8, 9 and 10 up to 12 (hexagonal prismatic) in the lithium 7b*H*-indenofluorenide dimer $[Li_2(\mu\text{-}C_{19}H_{12})_2]$ (diagram at top of next column).

The well established ring-stacking and ring-laddering principles have recently been extended to the synthesis of well defined mixed Li–Na and Li–Na–K compositions, for example $[\{[(PhCH_2)_2N]_2LiNa\cdot OEt_2\}_2]$ and $[\{[Bu^tN(H)]_2LiNa\cdot tmeda\}_2]$.[7] An intriguing new class of Li–Mg amides based around oxo (O^{2-}) or peroxo (O_2^{2-}) cores has been described (see Figs. 1 and 2).[9,10] Note the planar coordination about the central oxygen in Fig. 1.

The simplest metallocene sandwich, the lithocene anion $[LiCp_2]^-$, has been synthesized as large yellow-brown crystals of $[PPh_4]^+[Li(\eta^5\text{-}C_5H_5)_2]^-$ by mixing $[Li(C_5H_5)]$ and Ph_4PCl in the molar ratio 2 : 1 in thf.[11] The anion, which features 10-coordinate lithium, has D_{5d} symmetry with coplanar, staggered (centrosymmetric) C_5H_5 rings and the Li–Cp bonding is to be regarded as highly ionic with Li–$Cp_{centroid}$ 200.8 pm. It is therefore quite unlike the precisely isoelectronic beryllium and boron analogues $BeCp_2$ and $[BCp^*_2]^+$ ($Cp^* = C_5Me_5$) which are more



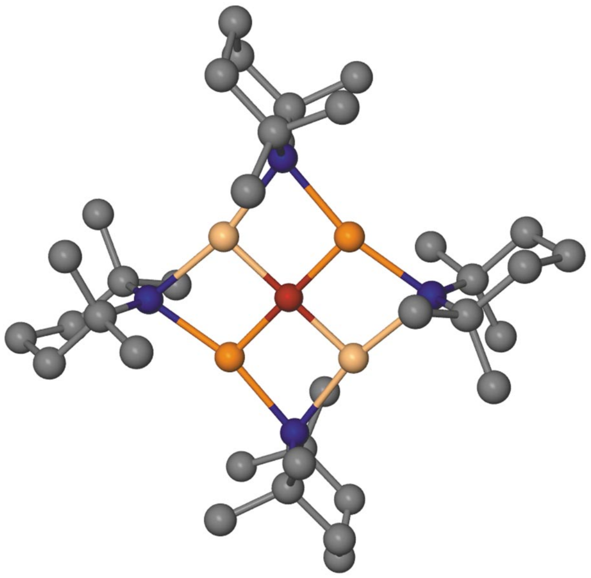


Fig. 1 Molecular structure of $[\{Me_2C(CH_2)_3CMe_2N\}_4Li_2Mg_2O]$ showing the square coordination of the central O atom.

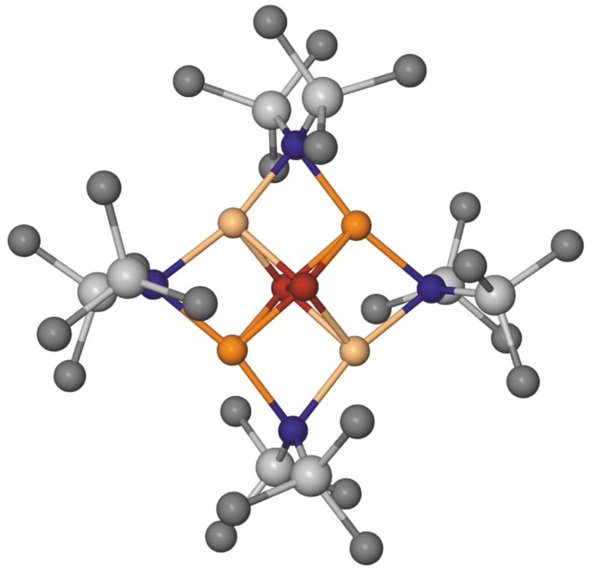


Fig. 2 Molecular structure of $[\{(Me_3Si)_2N\}_4Li_2Mg_2(O_2)]$ showing the central peroxo group, O_2^{2-}.

covalently bonded, with one η^5 and one η^1 ligand, but is strikingly similar to the D_{5d} structure of the diagonally related [$MgCp_2$]: Li–C_{av} 231.8 pm, Mg–C_{av} 230.4 pm.

The first dialkyllithiate, $[Li(thf)_4]^+[LiR_2]^-$, where R = $(Me_3Si)_3C$, had been prepared in 1983 by reacting tris(trimethylsilyl)methane with methyllithium in thf.[12] The corresponding reaction of methylsodium in ether, in the presence of tmen [= $Me_2N(CH_2)_2NMe_2$], yielded the first dialkylsodiate as colourless plates of $[Na(tmen)_2(Et_2O)]^+[NaR_2]^-$: the ether could be rapidly and completely removed under reduced pressure and the anion features linear 2-coordinate sodium, as expected from the lithium analogue, with the unusually short Na–C distance of 247.9 pm.[13] A potassium potassiate polymeric contact ion pair was synthesized by metallation of a *cyclo*-dihydrotriazine derivative with n-butylpotassium in thf; pale yellow crystals of $[K(thf)]^+[KR_2(thf)_2]^-$ were isolated where R = C(Ph)=NC(Bu^nBu^t)N=C(Ph)N.[14] The anionic potassium was N-bonded to two dihapto *cyclo*-triazine moieties and two thf ligands in distorted tetrahedral configuration with the angle N–K–N 132° and the K–N distances 281 and 287 pm respectively.

A fascinating analogy has been drawn between the solvated electron in liquid ammonia solutions, the crystalline electride salts of J. Dye, and the species now identified as the products of absorption (dissolution) of alkali metal atoms in crystalline zeolites.[15] It had been known that absorption of guest sodium atoms from the vapour phase into dehydrated Na^+-containing zeolites gave paramagnetic tetrahedral Na_4^{3+} clusters. It was subsequently found, remarkably, that the formation of Na_4^{3+} or K_4^{3+} was independent of the nature of the incoming alkali metal atom (M) but was determined by the cation of the host zeolite:

$$M^0 + 4Na^+_{zeolite} \rightarrow M^+ + Na_4^{3+}\ [\textit{i.e.}\ (Na^+)_4\cdot e^-]$$
$$M^0 + 4K^+_{zeolite} \rightarrow M^+ + K_4^{3+}$$

Linear, diamagnetic clusters of Cs_4^{2+} have also been identified in zeolites and diamagnetic Na^- is also known.

4 The elements in Group 13

Boron

The extraordinary efflorescence of innovative research which continues to be published on boron chemistry has ensured that, uniquely, this element remains the only main group element to have a separate chapter devoted to its advances in the RSC's *Annual Reports on the Progress of Chemistry*; indeed it has enjoyed this status for the past two decades. In addition, a spate of anniversary volumes dedicated to distinguished borane chemists, and the published Proceedings of the regular series of International Meetings on Boron Chemistry (IMEBORON) have ensured a continuing flow of review papers and reports of new results.[15–23]

The extent to which metallic elements mimic boron (in having fewer electrons than orbitals available for bonding) has been a fruitful cohering concept in the development of metalloborane chemistry for several decades.[1,24–26] Indeed, metals have been referred to as 'honorary boron atoms' or even as 'flexiboron atoms'. The converse of this relationship is clearly also valid and further insights can be obtained by contemplating "the metallic face of boron".[27,28] Another seminal idea has been the notion that boranes and their derivatives, far from being 'electron deficient', can usefully be exploited as versatile polyhapto ligands in appropriate circumstances.[29–31] An interdisciplinary area of continuing interest is the use of isotopically enriched boron-10 compounds for use in the neutron capture therapy of brain tumours.[32,33] Although definitive clinical breakthroughs have not yet been secured, the encouraging results of several trials sustain the belief that an effective procedure may be available in the foreseeable future.

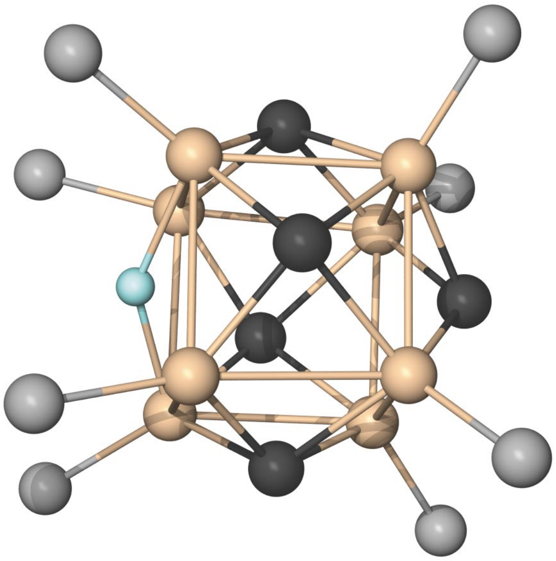


Fig. 3 Molecular structure of the carbaalane $(AlMe)_8(CCH_2Ph)_5H$ showing the slightly distorted Al_8 cube capped by five 5-coordinate C-benzyl groups (the 5 Bz omitted for clarity) and the unique diagonally bridging H atom (angle Al–H–Al 145°).

Other recent developments include (a) the use of carbaboranes as a new class of weakly coordinating anions for strong electrophiles, oxidants and superacids,[34] and (b) new synthetic approaches to the so-called 'megaloboranes' involving cluster fusion reactions of various species with molten decaborane.[35] Supramolecular assemblies formed from *o*-, *m*- and *p*-carborane are also attracting attention.[36]

Aluminium, gallium, indium and thallium

The unequivocal synthesis and definitive structural characterisation of digallane, Ga_2H_6, after half a century of uncertainty and error is arguably the most impressive *tour de force* of the past decade.[37] Success was finally achieved by first preparing dimeric monochlorogallane, $\{H_2Ga(\mu\text{-}Cl)\}_2$, by reaction of $GaCl_3$ with Me_3SiH at −23 °C and then reducing a freshly prepared sample of this liquid with freshly prepared $LiGaH_4$ under solvent-free conditions at −30 °C in an all-glass apparatus. The volatile product, obtained in about 5% yield, condensed as a white solid at −50 °C and decomposed into its elements at ambient temperatures. In the vapour phase digallane has the diborane structure with Ga–H_t 152 pm, Ga–H_μ 171 pm, Ga···Ga 258 pm and angle Ga–H_μ–Ga 98°. In the solid state, gallane tends to aggregate further *via* Ga–H_μ–Ga bonds to give $(GaH_3)_n$, with *n* perhaps equal to 4 but, in contrast to the structure of polymeric α-AlH_3, some terminal Ga–H_t bonds remain. The closely related mixed hydrides $GaBH_6$ (*cf.* B_2H_6), 2-GaB_3H_{10} (*cf.* B_4H_{10}), and $H_tGa(\eta^2\text{-}BH_4)_2$ (note the pentacoordinated central Ga atom) have also been prepared and structurally characterised by gas-phase electron diffraction analysis.[38] It is doubtful whether the hydrides InH_3 and TlH_3 have yet been prepared.

Interest in polyaluminium species continues to be intense, often arising from an interest in nanoparticles or precursor compounds for semiconductor fabrication. Of particular note is the first polyhedral carbaalane $(AlMe)_8(CCH_2Ph)_5H$ which has an Al_8C_5 skeleton (Fig. 3).[39] It was prepared as colourless crystals by the hydroalumination of an aluminium alkynide:

$$11Me_2AlH + 5Me_2AlC{\equiv}CPh \rightarrow (AlMe)_8(CCH_2Ph)_5H + 8AlMe_3$$

The 8Al occupy a slightly distorted cube with five of the faces being capped by the 5-coordinate C atoms of the five C-benzyl groups and the sixth face being diagonally bridged by the unique H atom with Al–H 191 pm. The Al–Al distances around this H-bridged face are relatively long (av. 279.7 pm) but those on the remaining edges, at 260.9 pm, are close to those in $\mathrm{Al_2Me_6}$ (260.5 pm).

A new route to large cluster compounds of main group element metals has been developed with spectacular results. It is known that metastable solutions of AlX and GaX (X = Cl, Br, I) disproportionate even under mild conditions to give the corresponding metal and trihalide. However, by substituting the halide with suitable ligands this process can be delayed so that compounds containing clusters of metal atoms can be captured as intermediates and even crystallised before they form metals. Thus, the new $\mathrm{Al_{12}}$ cluster, $\mathrm{Al_{12}R_8^-}$ [R = $\mathrm{N(SiMe_3)_2}$], resembling a section of the pure aluminium metal lattice, has been prepared by reacting AlCl solutions with $\mathrm{LiN(SiMe_3)_2}$.[40] Milder conditions yielded $\mathrm{Al_7R_6^-}$.[41] The largest known metal cluster yet to be characterised by X-ray analysis, $[\mathrm{Al_{77}\{N(SiMe_3)_2\}_{20}}]^{2-}$, was obtained similarly by adding a solution of AlI in toluene/diethyl ether at −78 °C to a solution of base-free $\mathrm{LiN(SiMe_3)_2}$ and slowly warming it to 60 °C. The product was obtained as black crystals, thermally stable at room temperature but highly sensitive to attack by air and moisture.[42] The $\mathrm{Al_{77}}$ core features a central Al atom surrounded by three concentric polyhedral shells containing 12, 44 and 20 Al atoms, respectively, stabilized by the 20 organic ligands which prevent further aggregation to the bulk metal. Charge balance was provided by two complex lithium cations $[\mathrm{Li(OEt_2)_3(\mu\text{-}I)Li(OEt_2)_2}]^+$ and there were two toluene molecules of crystallisation. [Note added in proof: an even larger cluster $[\mathrm{Ga_{84}\{N(SiMe_3)_2\}_{20}}]^{4-}$ has been made by reacting GaBr and $\mathrm{LiN(SiMe_3)_2}$ at −78 °C; the shiny black crystals are stable up to 400 °C and feature a central multiply bonded $\mathrm{Ga_2}$ group sitting inside a hollow football-like structure composed of 32 Ga atoms which, in turn, are surrounded by 30 more ‘naked’ Ga atoms which wind around the central structure in planar $\mathrm{Ga_{10}}$ rings; finally 20 $\mathrm{Ga\{N(SiMe_3)_2\}}$ groups complete the cluster (*Angew. Chem.*, 2001, **113**, 734; see also *Chem. Br.*, May 2001, 17).]

A related route has led to large gallium cluster compounds. Thus, reaction between solutions of GaBr and LiR {R = $\mathrm{Si(SiMe_3)_3}$} on slow warming from −78 °C yielded $\mathrm{(RGa)_4Br_4}$ and black crystals of $\mathrm{Ga_{22}R_8}$. The neutral metal–metal cluster (Fig. 4a) is unique in having a central Ga atom (dark green) surrounded by 13 further Ga atoms (mid-green) at Ga–Ga (av.) 294.2 pm (Fig. 4b).[43] This shell of 13Ga—within which Ga–Ga (av.) is 286.7 pm—has similar coordination to a cuboctahedron but with one of the $\mathrm{M_3}$ faces becoming $\mathrm{M_4}$ (*i.e.* $\mathrm{M_3 : M_6 : M_3}$ becomes $\mathrm{M_4 : M_6 : M_3}$). As a consequence, this polyhedron has eight square faces each of which is then capped by a Ga atom bearing a tris(trimethylsilyl)silyl ligand (Fig. 4a). These eight outer Ga atoms (pale green) form a slightly distorted square antiprism.

Several new forms of In cluster have been achieved by similar types of reaction starting with lower valent organometallic compounds of indium. For example $\mathrm{In(C_5Me_5)}$ reacts with $\mathrm{NaR^*}$ ($\mathrm{R^* = SiBu^t_3}$) to give black-green $\mathrm{In_8R^*_6}$, in which a distorted cube of 8 In atoms is surrounded by the 6 supersilyl ligands.[44] Again, thermolysis of $\mathrm{R^*_2InInR^*_2}$ in boiling heptane (≈100 °C) yielded black-violet crystals of $\mathrm{In_{12}R^*_8}$ which were sensitive to moisture and air.[45] The basic cluster (Fig. 5) has a novel framework which is not icosahedral but rather a ‘stretched ellipsoid’.

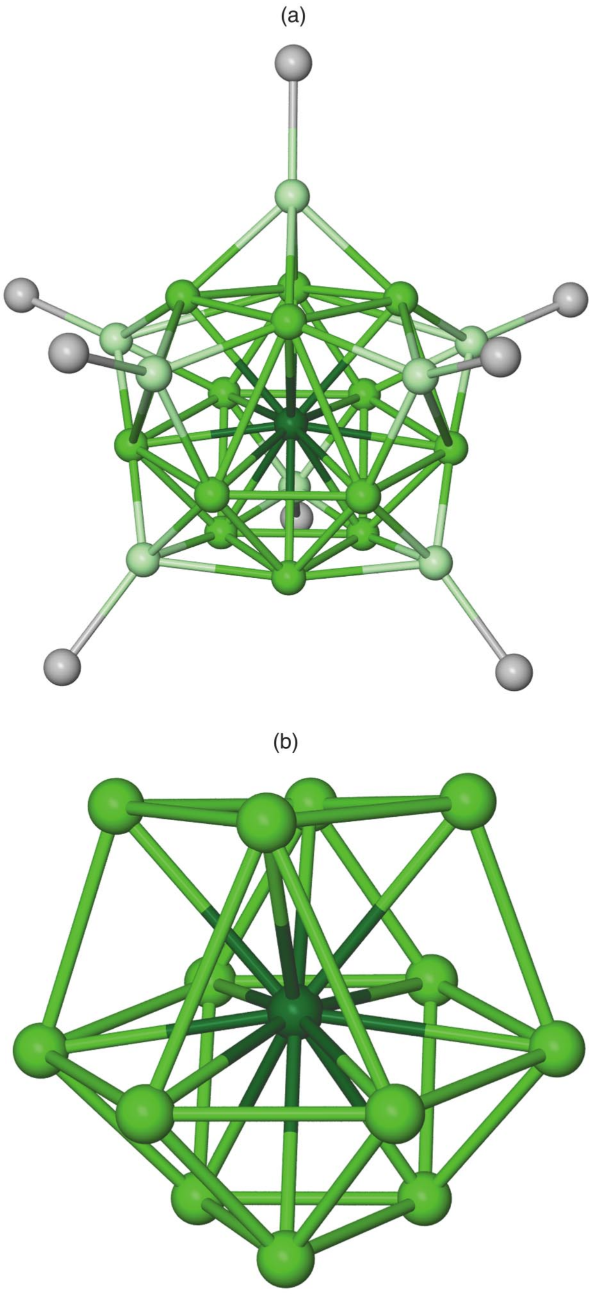


Fig. 4 (a) The molecular structure of $[\mathrm{Ga_{22}\{Si(SiMe_3)_3\}_8}]$; the central $\mathrm{Ga{\cdot}Ga_{13}}$ core is surrounded by a mantle of eight $\mathrm{GaSi(SiMe_3)_3}$ groups (omitting the 24 $\mathrm{SiMe_3}$ groups for clarity). (b) The central $\mathrm{Ga{\cdot}Ga_{13}}$ core of $[\mathrm{Ga_{22}\{Si(SiMe_3)_3\}_8}]$.

5. The elements in Group 14

The fullerenes

Just as the chemistry of the Group 14 elements is dominated by carbon, so the chemistry of carbon itself has been dominated during the past decade by that of the fullerenes. The dramatic developments which followed the discovery of a series of soluble molecular modifications of carbon in September 1985 has been reviewed many times[46] and the outlines of their chemistry were soon established as a result of the intense interest throughout the world. Macroscopic amounts of pure $\mathrm{C_{60}}$ and $\mathrm{C_{70}}$ were first isolated on 22 August 1990 and many other allotropes are now known *e.g.* $\mathrm{C_{76}}$ (chiral), three isomers each of $\mathrm{C_{78}}$, $\mathrm{C_{82}}$ and $\mathrm{C_{84}}$, *etc.* The 1996 Nobel Prize for Chemistry was awarded to R. F. Curl, H. W. Kroto and R. E. Smalley for their pioneering discoveries in this unforeseen area of chemistry.[47] The sheer bulk of new chemistry emerging (which now exceeds 15 000 publications and is increasing at some 3000 papers per year), coupled with the ready accessibility of numerous reviews and monographs,[46,48–51] dictate that the present account be limited to a few illustrative examples of some of the most recent novel findings.

Early work on the direct fluorination of solid $\mathrm{C_{60}}$ with $\mathrm{F_2}$ gas at 70 °C gave a mixture of partially fluorinated derivatives

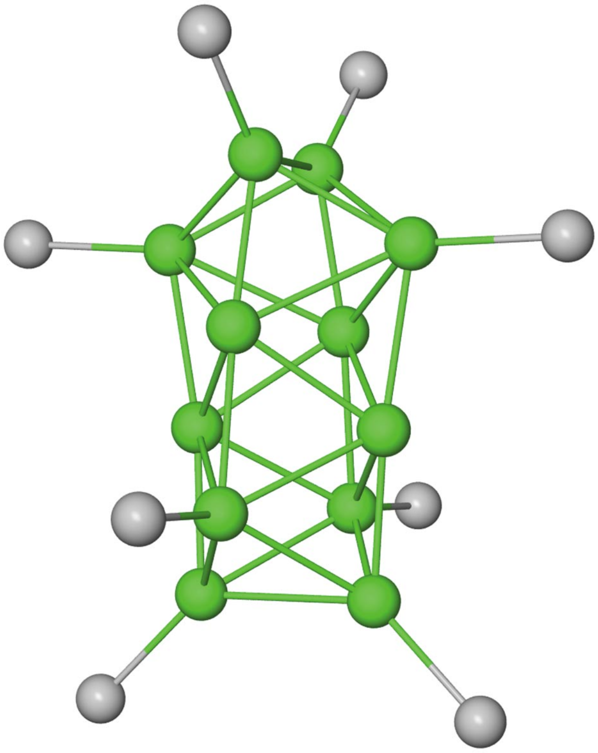


Fig. 5 View of the non-icosahedral In_{12} cluster in $[In_{12}(SiBu^t_3)_8]$ showing the 'stretched ellipsoid' of In_{12} comprising two fused octahedral In_6 subclusters. The In–In distances range from 281 to 331 pm, the average of the eight In–In distances between the two subclusters being 303 ± 3 pm (*cf.* 325–338 pm in In metal).

together with the unique, colourless, fully fluorinated product $C_{60}F_{60}$.[46] By contrast, $C_{60}F_{48}$ alone has over 20 million possible isomers but, astonishingly, the high-yield synthesis of just one of these was achieved by heating a mixture of C_{60} and NaF under F_2 at 275 °C for several days.[52] (Actually it is a racemic mixture of two chiral enantiomers.) Partial fluorination by metal fluorides such as K_2PtF_6 at 465 °C followed by HPLC separation of products led to the isolation of numerous other fluoro derivatives such as $C_{60}F_2$, $C_{60}F_{16}$, $C_{60}F_{18}$ and $C_{60}F_{36}$ (two isomers), *etc.*[53] Use of an MnF_3/KF fluorinating mixture gave larger amounts of $C_{60}F_{18}$, plus $C_{60}F_{20}$, both of which have quite extraordinary structures. Thus, $C_{60}F_{18}$ features a flattened fullerene cage with all the fluorine atoms bound to one hemisphere of the C_{60} cluster and symmetrically surrounding an unsubstituted C_6 benzenoid ring (Fig. 6).[54] This hexagonal ring has all six C–C distances equal at 137.2 pm whereas the six C atoms directly bound to this ring have C–C 147.6 pm. The longest C–C distances are 167.2 pm and there are four groups of C–F distances in the range 136.1–139.6 pm. The second compound, $C_{60}F_{20}$, is computed to have a jagged equatorial belt of fluorine atoms (Fig. 7) which distorts the quasi-spherical geometry of the parent C_{60} into an oblate spheroid with the distance between the (three coordinate) polar caps being only 629 pm as compared to 785 pm between the tetrahedral (four coordinate) carbon atoms on opposite sides of the equator. The shape of this ringed cluster has suggested the trivial name of 'saturnene' for this compound.[53]

Many other fluoro and oxofluoro derivatives have been separated and await full structural characterisation; among these are $C_{60}F_nO$ ($n = 4, 6, 8$), $C_{60}F_{18}O$ (three isomers), $C_{60}F_{18}O_2$ (seven isomers) and forty-nine derivatives of C_{70}, as well as numerous fluorides of higher members of the series such as $C_{76}F_n$ ($n = 36, 38, 40, 42, 44$), $C_{78}F_n$ ($n = 38, 42$), $C_{82}F_{44}$, $C_{84}F_{40}$ and $C_{84}F_{44}$.[53] Further structural surprises can confidently be anticipated.

Another aspect of fullerene chemistry is the synthesis and structural characterisation of clusters containing encapsulated metals, typically lanthanides.[46] A recent development in this area is the characterisation of the first fullerene-encapsulated metal carbide $(Sc_2C_2)@C_{84}$ (as distinct from $Sc_2@C_{86}$).[55a] The compound, with others, was found in the soot produced by an arc discharge between Sc_2O_3/graphite composite rods, and has a pale green colour in CS_2 solution. The detailed structure (Fig. 8) was established by Rietveld analysis of the synchrotron X-ray powder diffraction pattern and led to values of the interatomic distances within the encapsulated Sc_2C_2 cluster of Sc · · · Sc 429 pm, C · · · C 142 pm and Sc–C 226 pm.

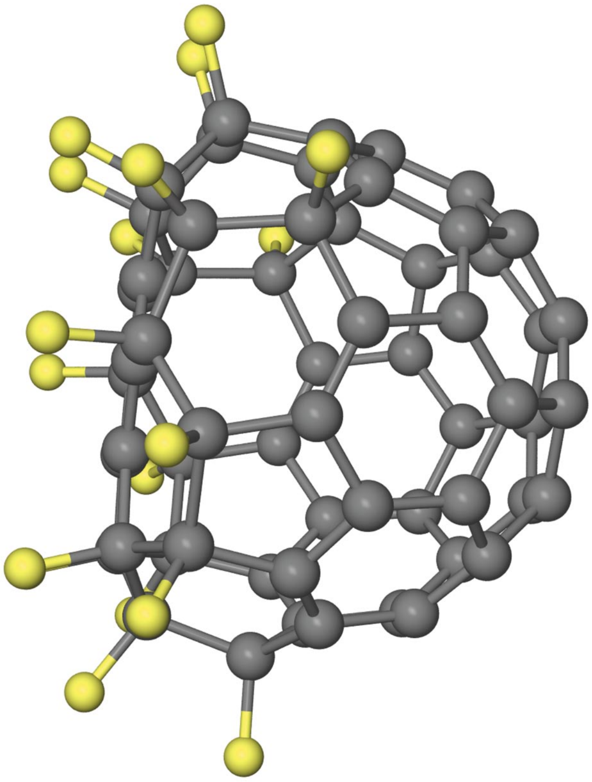


Fig. 6 Molecular structure of $C_{60}F_{18}$ showing the flattened C_{60} cluster.

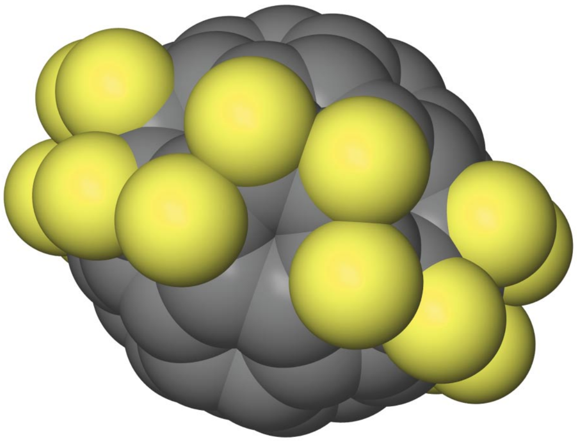


Fig. 7 Molecular structure of $C_{60}F_{20}$ ('saturnene') showing an oblate spheroid of C_{60} ringed by a jagged equatorial belt of 20 F atoms.

The burgeoning field of nitrogen heterofullerenes has been reviewed.[55b] For the related heterofullerenes $C_{60-2n}(BN)_n$ and $C_{60-n}B_n$ see ref. 46.

Carbon

Carbon is now known in more than a dozen different stereochemistries featuring all coordination numbers from 1 (as in CO) to 8 (see below).[56] Thus, in addition to the classical organic stereochemistries of linear (2), planar (3) and tetrahedral (4)

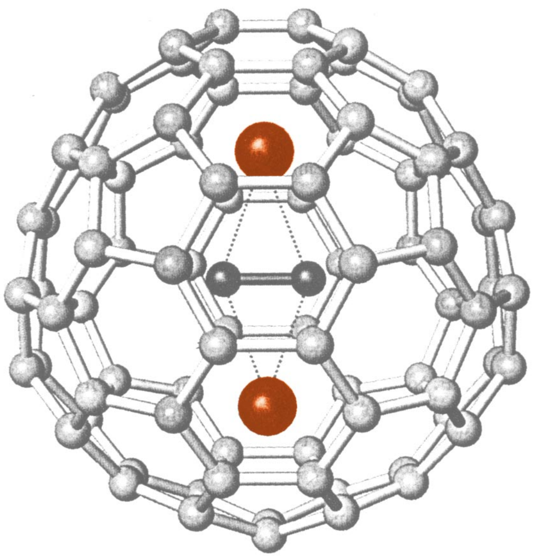


Fig. 8 Molecular structure of $[(Sc_2C_2)@C_{84}]$. (Reproduced by permission from *Angew. Chem., Int. Ed.*, 2001, **40**, 397.)

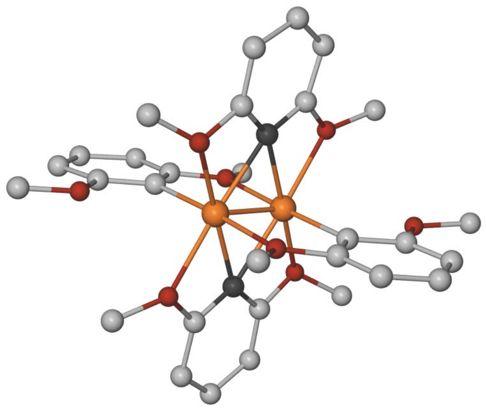


Fig. 9 Molecular structure of tetrakis(2,6-dimethoxyphenyl)-divanadium emphasising the planar 4-coordination around two of the carbon atoms (darker grey).

coordination, we now also recognise bent 2-coordination (in RP=C=PR), pyramidal 3-coordinate carbanions such as CPh_3^-, T-shaped 3-coordinate in organometallic tantalum vinylidene complexes and see-saw (C_{2v}, CN 4) in the carbido Fe_4 'butterfly' cluster $[Fe_4C(CO)_{13}]$. Higher coordination numbers are found in many compounds such as:

CN 5 – Al_2Me_6 and *closo*-$C_2B_4H_6$;
CN 6 – *closo*-$C_2B_{12}H_{12}$ and $[C(AuPPh_3)_6]^{2+}$;
CN 7 – crystalline $(LiMe)_4$;
CN 8 – BeC_2 (antifluorite) and $[Co_8C(CO)_{18}]^{2-}$.

To these can now be added the planar tetracoordination of carbon which has been recognised in an increasing number of organometallic compounds. The first crystallographically established example was in the divanadium complex shown in Fig. 9 and this particular aspect of the structure was noted at the time.[57] It has subsequently become clear that planar 4-coordinate carbon is stabilised when two metal atoms (MM or MM*) form a three-centre bond with the carbon atom. Examples are known from all parts of the Periodic Table: homometallic MM with M = Li; Ti, Zr, Hf; V, Nb, Ta; W; Re; Pd; Cu; Ce, Sm, and MM* with, for example, M = Ti, Zr, Hf and M* = B, Al, Ga as well as W/Re.[58,59] The structures with planar 4-coordinate C atoms are calculated to be generally about 50 kJ mol^{-1} more stable than the alternative state in which the sp^2 C atom forms three two-centre bonds.

Whilst still on the subject of the stereochemistry of carbon it is perhaps appropriate in this millennium review to correct a view, widely held by chemists generally, that the concept of the tetrahedral geometry of 4-coordinate carbon was independently advocated in 1874 by van't Hoff and Le Bel. Even worse, one frequently encounters solecisms such as "tetrahedral sp^3 hybridisation of tetravalent carbon seemed to be a rock solid concept since its proposal by van't Hoff and Le Bel".[59] In fact, the electron was not discovered by J. J. Thomson until 1897, the G. N. Lewis octet theory of valency dates from about 1916, and the concept of hybridisation was not developed by Linus Pauling until 1930. As for tetrahedral carbon itself, Le Bel spent several decades protesting emphatically against being credited with the tetrahedron theory (*e.g.* "I used the greatest efforts in all my explanations to abstain from basing my ideas on the preliminary hypothesis that the compounds of carbon of the formula CR_4 have the shape of a regular tetrahedron") and he wrote several articles arguing against the van't Hoff theory.[60,61] He tended to favour a square-based pyramidal stereochemistry for CR_4 with carbon at the apex, and subsequently spent many years in fruitless attempts to resolve into optical isomers citraconic and mesaconic acids (*i.e.* methylmaleic and methylfumaric acids). *The tetrahedral stereochemistry of 4-coordinate carbon should be credited to van't Hoff alone*.

The deep significance and great synthetic utility of G. A. Olah's work on carbocations was recognised by the award of the 1994 Nobel Prize for Chemistry.[62] Two limiting types of carbocation are recognised: classical carbenium ions of which CH_3^+ is the parent, and non-classical carbonium ions of which CH_5^+ is the parent. Further discussion and leading references will be found in ref. 15, pp. 351–373 and in ref. 18.

Silicon, germanium, tin and lead

Steady progress rather than dramatic discoveries has characterised the recent advances in the chemistry of the heavier elements of Group 14. The first tricoordinated silylium ion, R_3Si^+ (R = mesityl) has been successfully prepared from allyltrimesitylsilane by removal of the allyl group with $[Et_3SiCH_2CPh_2]^+[B(C_6F_5)_4]^-$; it gives a ^{29}Si NMR signal at δ 225.5 which is static in the presence of aromatic solvents that are known to coordinate with the less hindered Et_3Si^+.[63] The frustrations and partial successes attending previous attempts to prepare silylium ions, R_3Si^+, have been reviewed,[64] as has the active field of transition metal complexes of silylenes (R_2Si:), silylynes (RSi⋮), silenes ($R_2C{=}SiR_2$) and disilenes ($R_2Si{=}SiR_2$).[65]

Work on polyhedral silaboranes continues apace. The first silicon analogue of an *ortho*-dicarbaborane, *closo*-[1,2-$(MeSi)_2$-$B_{10}H_{10}$] has been synthesised by reacting a benzene solution of decaborane under reflux with $MeHSi(NMe_2)_2$;[66] X-ray analysis showed the Si–Si distance to be 230.8 pm which is slightly shorter than the 'normal' single bond Si–Si distance (233–234 pm). The compound is also notable in being the first example of a *formal* derivative of a disilyne, MeSi≡SiMe. Subsequently the *nido*-silaborane $[B_{10}H_{12}(SiMe)]^-$ was shown to react with Et_3NBH_3 to eliminate $2H_2$ and give the first *closo*-monosilaborane $[B_{11}H_{11}SiMe]^-$ in excellent yield.[67] Contemporaneously, the first *arachno*-silaborane [6-$(MeSi)B_9H_{12}$-9-$(NHMe_2)$], which is isostructural with $B_{10}H_{14}^{2-}$, was prepared by reacting *arachno*-$B_9H_{13}(SMe_2)$ with $Si(NMe_2)_2MeH$.[68]

Polymeric $(SiCl_2)_\infty$ is extremely insoluble, but it has recently proved possible to isolate single crystals and to determine their structure by X-ray analysis.[69] The pale yellow crystals consist of infinite parallel chains of $SiCl_2$ (all-*trans*) with unusually long Si–Si bonds: 241.4 pm, compared with the typical value of 234 pm. A consistent theoretical framework for polyhedral (cluster) compounds of the heavier Group 14 elements Si, Ge, Sn and Pb has been established and leads to computed strain energies of these and their carbon analogues.[70] An unusual species,

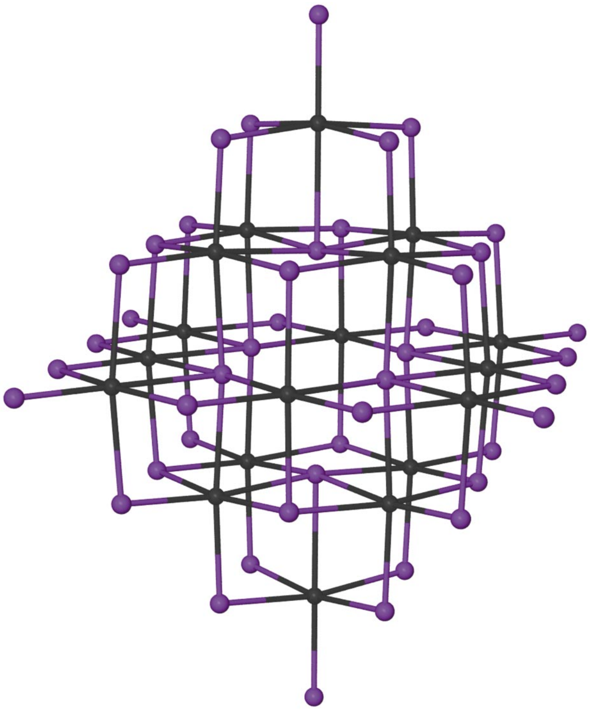


Fig. 10 Structure of the $Pb_{18}I_{44}^{8-}$ anion in its tetrabutylammonium salt.

$Pb_{18}I_{44}^{8-}$ (molecular weight 9313) (Fig. 10), has been made by treating an acetone/ether solution of PbI_2 and NaI with $Bu^n{}_4NPF_6$. The complex anion has D_{4h} symmetry in which each Pb atom is octahedrally coordinated to 6 I; these octahedra are connected through layers comprising 1, 4, 8, 4 and 1 Pb atoms in a 'Chinese puzzle' type of arrangement.[71] Neglecting the vacant site at the centre of the polyanion the complex can be described as a fragment of the NaCl structure. Pb···Pb distances are in the range 471–480 pm (*cf.* 456 pm in PbI_2 itself) indicating the absence of Pb–Pb bonds. The Pb–I distances vary considerably (295.9–352.5 pm) depending on whether the I atom is terminal, μ, μ_3 or μ_5.

The first example of a transition metal–germanium triple bond has been found in $[(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Ge(C_6H_3Mes_2\text{-}2,6)]$ (Mes = mesityl = 2,6-$Me_2C_6H_3$).[72] The compound was made by direct reaction between $Na[CpMo(CO)_3]$ and [2,6-$Mes_2C_6H_3GeCl$] in thf at 50 °C: it features an almost linear (172.2°) Mo–Ge–R skeleton and an Mo–Ge distance of only 227.1 pm, some 35 pm shorter than the normal single-bond length.

6. The elements in Group 15

Many of the themes described in the sesquicentennial review[1] continue to excite attention a decade later and the work has frequently been extended from nitrogen and phosphorus to their heavier congeners arsenic, antimony and bismuth. Thus, the coordination chemistry of N_2 (isoelectronic with CO) is still being actively pursued as is the extremely important aspect of protonation of these complexes.[73] The elusive species of pure, adduct-free NI_3 has finally been prepared by direct reaction of BN with IF in $CFCl_3$ at low temperatures:[74]

$$BN + 3IF \rightarrow NI_3 + BF_3$$

The compound is a deep red, volatile solid which is very unstable (explosive) at room temperature and which reacts readily with NH_3 at −45 °C to give the familiar dark green polymeric adduct $[NI_3{\cdot}3NH_3]$. NI_3 is soluble in $CFCl_3$ to give a deep red solution which is fairly stable at −60 °C but which decomposes rapidly at 0 °C. The low-temperature Raman spectrum confirms the expected pyramidal structure.

In contrast to the ubiquitous NO, whose ligand properties have also been well investigated, few spectroscopic data have so far been reported for PO, though it is probably the most abundant P-containing molecule in interstellar clouds. It is now found[75] that reaction of the diphosphadinickelatetrahedrane species $[(Cp^4Ni)_2(\mu,\eta^2\text{-}P_2)]$ (where $Cp^4 = \eta^5\text{-}C_5HPr^i{}_4$) (see Fig. 11a) with $[W(CO)_5(thf)]$ gives the square-based pyramidal cluster $[W(CO)_4(Cp^4{}_2Ni_2P_2)]$ (Fig. 11b) which, in turn, can be oxidised with bis(trimethylsilyl)peroxide to give the corresponding bis(PO) derivative (Fig. 11c) as oxygen-sensitive black crystals.

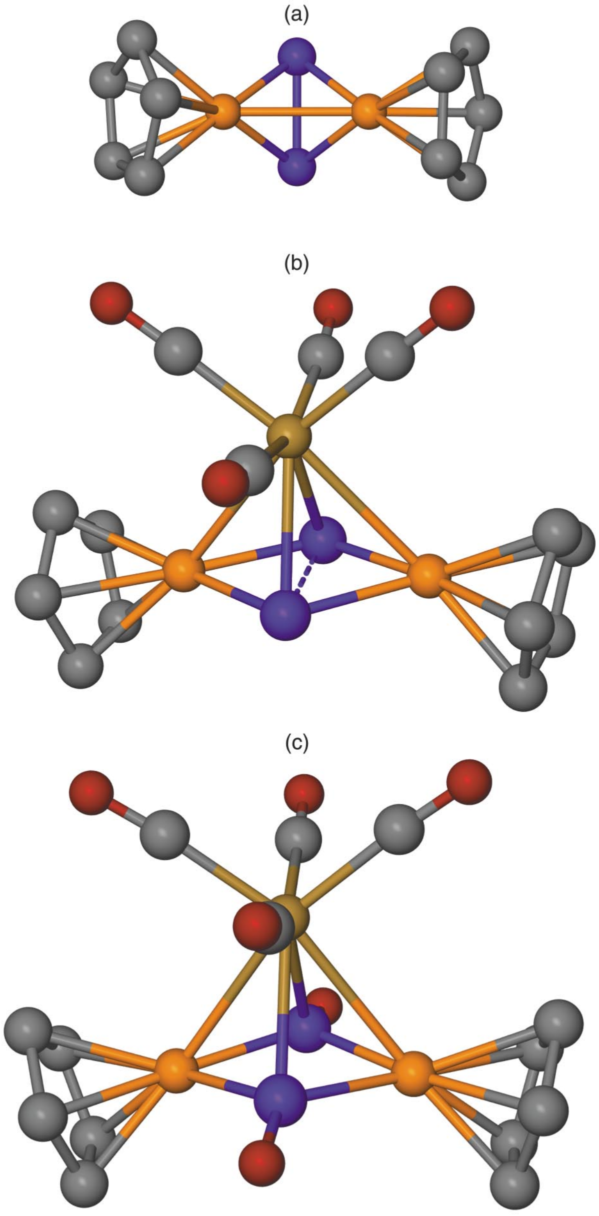


Fig. 11 (a) Structure of the diphosphadinickelatetrahedrane species $[Ni_2(\eta^5\text{-}C_5HPr^i{}_4)_2(\mu,\eta^2\text{-}P_2)]$ $[(Cp^4Ni)_2(\mu,\eta^2\text{-}P_2)]$ with the eight isopropyl groups omitted for clarity. (b) Structure of the square-based pyramidal structure of $[W(CO)_4(Cp^4{}_2Ni_2P_2)]$. (c) Structure of the bis(PO) derivative $[W(CO)_4\{Cp^4{}_2Ni_2(PO)_2\}]$.

The sequence 11a → 11b → 11c is accompanied by progressive increase in the diagonal P···P distance from 205.3 through 230.4 to 262.4 pm (*i.e.* from bonding to non-bonding). The P=O distances in (11c) are 146 and 148 pm (*cf.* 148 pm in the free PO molecule).

It has long been recognised that Group 15 atoms are isolobal with the CH group. Extensive work on the all-P and all-As analogues of the ligands *cyclo*-C_4H_4, *cyclo*-$C_5H_5^-$ and benzene have been reviewed, as well as E_n ligands (E = P, As: n = 1, 2, 3 and >8).[76] Heterocyclic analogues such as $(Bu^tCP)_{2,3,4\ldots}$ are also being constructed by oligomerisation of RC≡P, the tetrameric ligands yielding either tetraphosphacubane or tetraphosphabarrelene derivatives (see Fig. 12).[77]

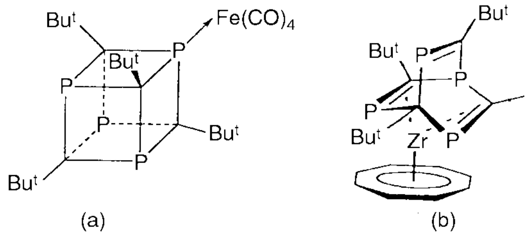


Fig. 12 Schematic representation of typical adducts of the tetraphosphacubane and tetraphosphabarrelene clusters (a) $[\{\eta^1\text{-}(Bu^tC)_4P_4\}\text{-}Fe(CO)_4]$ and (b) $[\{\eta^4\text{-}(Bu^tC)_4P_4\}Zr\{\eta^8\text{-cot}\}]$ (cot = cyclooctatetraene).

Novel organoantimony homocycles such as the Sb_3 ring in $(RSb)_3$ [R = $(Me_3Si)_2CH$] and the polycycles R_4Sb_8 and R_5Sb_7, as well as transition metal complexes with $Bu^t_4Sb_4$ or $Bu^t_3Sb_4$ as ligands, have been prepared.[78] Antimony analogues of the above P and As ligands were reported at the same time, *e.g.* clusters comprising Mo_2Sb_2, $MoSb_3$, $MoSb_5Mo$ and the *cyclo*-Sb_6 ligand. The synthesis of the first organobismuth monocycles $(RBi)_n$ has also been achieved ($n = 3$, 4; R = $(Me_3Si)_2CH$).[78] Mixed rings such as $[(Bu^tC)_2P_2Sb]^-$,[79] and $[C_2HBu^t_2P_2Sb]$[80] have also been devised as ligands to Rh and Ir centres[79] and cobalt[80] respectively.

A useful review of the structure of the Group 15 E(III) halides and halogeno anions (E = As, Sb, Bi and occasionally P) illustrates the great advances that have recently been made in this field.[81] Thus, EX_3 give rise to over a score of anion types, ranging from the mononuclear EX_4^-, EX_5^{2-} and EX_6^{3-} to many polynuclear derivatives of these such as $E_2X_8^{2-}$, $E_2X_9^{3-}$, $E_2X_{10}^{4-}$, *etc.* through oligomeric $E_4X_{16}^{4-}$, $E_4X_{18}^{6-}$ $E_5X_{18}^{3-}$, $E_6X_{22}^{4-}$, $E_8X_{28}^{4-}$ and $E_8X_{30}^{6-}$ to various polymeric species. The structures are firmly based on X-ray crystallographic evidence. Cationic halogeno species are less numerous though NF_4^+ (1980), NCl_4^+ (1990) and EX_4^+ (E = P, As; X = F, Cl, Br, I—most post 1990) are known.[82] $SbCl_4^+$ is also known and now the newest tetrahedral cation, $SbBr_4^+$, has been synthesised as its $[Sb(OTeF_5)_6]^-$ salt by oxidation of $Sb(OTeF_5)_5$ with Br_2.[82] No BiX_4^+ is yet known.

7. The elements in Group 16

The great catenating abilities of S, Se and Te continue to be exploited and have yielded an amazing variety of elemental molecular allotropes, E_n, as well as numerous polyatomic cations and anions, E_n^{x+}, E_n^{x-}.[83]

The resplendent blue colour of lapis lazuli and ultramarine is known to be due to the presence of paramagnetic S_3^- and S_2^- colour centres in the zeolitic host, sodalite. It has recently been found that incorporation of paramagnetic Se_2^- into the sodalite cages yields a brilliant red pigment, and it is even possible to accommodate the substantially larger radical and diradical species Te_2^- and Te_2 to generate blue to greenish pigments depending on the preparative procedures used.[84] Again, the new bicyclo polycation Te_8^{2+} has been quantitatively synthesised as blue-black crystals of $Te_8[WCl_6]_2$ by reducing WCl_6 with elemental Te in an evacuated, sealed glass ampoule at 150 °C.[85] Many mixed Te/S and Te/Se cations are also known. Another recent addition is the cation Se_{17}^{2+}, *i.e.* $[(cyclo\text{-}Se_7)SeSeSe(cyclo\text{-}Se_7)]^{2+}$.[86] Three interesting mixed chalcogen anions can also be mentioned: $[Te(\eta^2\text{-}S_5)_2]^{2-}$, $[Te(\eta^2\text{-}S_7)_2]^{2-}$ and $[Te(\eta^2\text{-}S_5)(\eta^2\text{-}S_7)]^{2-}$.[87]

An astonishing number of complex zintl-type anions and related species are being characterised among which are the yellow adamantane-like $[Sn_4Se_{10}]^{4+}$,[88] the black $[Sn(\eta^2\text{-}Se_2PSe_3)_3]^{5-}$,[89] and the orange-coloured extended anion $[Sn_2Se_4(PSe_5)_2]^{6-}$ which features an 11-membered chain $[\mathbf{SeP}(Se)_2\text{-}\mathbf{SeSeSn}(Se)(\mu\text{-}\mathbf{Se})_2\mathbf{Sn}(Se)\mathbf{SeSeP}(Se)_2\mathbf{Se}]^{6-}$.[89] Discrete anions of $[P_8Se_{18}]^{6-}$ in the orange potassium salt are also notable (synthesised in high yield from KSe, red P and Se at 510 °C).[90]

The burgeoning field of metal chalcogenide cluster chemistry has been extensively reviewed.[91,92] Although there are vestigial similarities between the polyselenometalates and polytelluro-metalates on the one hand and the well known polyoxo- and polythio-metalates on the other, it is now clear that the combined effects of decreasing electronegativity and increasing size and covalency down the group ensure substantial dissimilarities in the structures encountered with the heavier congeners. A vast novel and exciting area of structural chemistry is emerging.[92]

Catenation is also a notable feature of the vast new realms of sulfur/nitrogen chemistry.[93] A potentially enormously important development is the possibility of making electrically conducting molecular wires of $(SN)_x$ chains.[94] The exploitation of numerous S/N sequences as unusual ligands also continues apace,[93,95,96] and other simpler species have continued to attract attention: for example, the coordination chemistry of thionitrosyl (NS), thioazate (NSO^-), disulfidothionitrate (S_3N^-), sulfur monoxide (SO) and disulfur monoxide (S_2O)—*i.e.* the S analogues of NO, NO_2^-, NO_3^-, O_2 and SO_2—has been reviewed.[97]

The chemistry of the ubiquitous atmospheric pollutant SO_2 continues to be actively studied and a case has been made that SO_2 is the most versatile ligand/complexing agent known.[98] It is amphoteric, behaving as a Lewis acid or base, a mild oxidant or reductant, or an oxygen donor or acceptor. It is an excellent non-aqueous solvent when liquified at −10 °C and coordinates to many types of compound. SO_2 can bond strongly to low-valent metals (*cf.* CO or NO) or completely reversibly (*cf.* O_2 or H_2). Examples of both *O*-bonded and *S*-bonded complexes are known: it can be monohapto, dihapto or bridging, and there has recently been a dramatic increase in our knowledge of the rich variety of its reaction chemistry, fuelled no doubt by environmental concerns.

Finally in this group, we can turn our attention to the elusive species $SeCl_2$ which, surprisingly, evaded isolation and characterisation in the pure form until 1999.[99] It can be made by reacting Se with SO_2Cl_2: it is an unstable red oil but is stable for 24 hours at room temperature when dissolved in thf or dioxane. It also forms 1:1 and 1:2 adducts with tetramethylthiourea and tetrahydrothiophene, respectively. Halogen exchange between $SeCl_2$ and Me_3SiBr in thf yields a solution of the thermally unstable $SeBr_2$ (^{77}Se NMR and Raman spectra). Two other surprisingly coy simple binary halogeno species of selenium are the recently prepared anions $[Se_2Cl_2]^{2-}$ and $[SeCl_6]^{2-}$.[100]

8. The halogens and noble gases

Halogens

The great propensity of iodine to catenate is well known: polyiodides in particular continue to provide a bizarre range of stoichiometries which exhibit a wide variety of geometrical arrangements that are frequently not readily apparent from their overall formulae.[101] In addition to symmetrical and unsymmetrical linear I_3^-, V-shaped I_5^- and trigonal pyramidal I_7^-, one encounters *Z*-shaped I_8^{2-} (*i.e.* $I_3^-{\cdot}I_2{\cdot}I_3^-$) and the more complex I_9^-, I_{12}^{2-}, I_{13}^{3-}, I_{16}^{2-} and I_{16}^{4-}.[101,102] The largest such unit to be structurally characterised so far is I_{22}^{4-} in $[PMePh_3]_4I_{22}$: the polyanion can be viewed as comprising two L-shaped I_5^- units bridged by an I_2 molecule and completed by two end-on I_5^- groups.[103]

The crucial rôle of oxychlorine species in the chemistry of the stratosphere and upper atmosphere and the seasonal fluctuation of the ozone hole have stimulated intense world-wide studies of these fugitive species during the past 25 years.

The seminal studies emanating from the laboratories of P. J. Crutzen, M. J. Molina and F. S. Rowland were recognised in 1995 by their joint award of the Nobel Prize for Chemistry, and their Nobel Lectures provide very useful and authoritative reviews of work in this field.[104]

Cationic halogen species become progressively less stable with decrease in atomic number, as expected. Thus, I_5^+ and Br_5^+ are both known[105,106] but no indication has been obtained for the Cl_5^+ cation. Likewise, detailed structural information on $I_3^+AsF_6^-$ and $Br_3^+AsF_6^-$ has been available for some years[107,108] but it was not until 1999 that X-ray diffraction data were obtained for the yellow salts of Cl_3^+ with the anions AsF_6^-, SbF_6^-, $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$.[109] Depending on the particular anion, the Cl–Cl distance was in the range 197–199 pm and the bond angle was 104.5–105.6° (*i.e.* larger than the values of 102.5° for Br_3^+ and 101.8° for I_3^+). The paramagnetic species Cl_2^+ has proved even more elusive and previous reports that the deep violet solutions obtained by reacting Cl_2 with $O_2^+SbF_6^-$ in anhydrous HF contained this species have been shown to be in error. The cation is actually the unusual trapezoidal tetra-atomic species $Cl_2O_2^+$ (see Fig. 13) in which the Cl_2 and O_2 edges (191.6 pm and 118.5 pm respectively) are held together by π^*–π^* interactions ($Cl \cdots O$ 242.5 pm).[109] The crystalline salts $Cl_2O_2^+SbF_6^-$ and $Cl_2O_2^+Sb_2F_{11}^-$ are violet-black. The cation persists when the salts are dissolved in HF solution, but above −30 °C it slowly decomposes to the yellow Cl_3^+ species mentioned above.

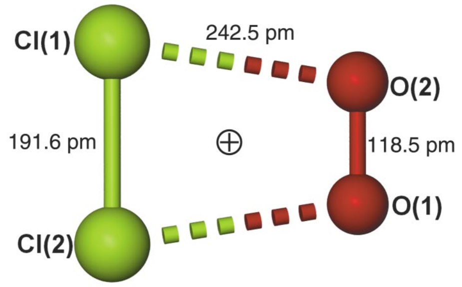


Fig. 13 Structure of the trapezoidal tetra-atomic cation $Cl_2O_2^+$ in its SbF_6^- salt.

The rich oxide, oxyacid and oxyanion chemistry of chlorine and iodine is not matched by a similarly extensive range of oxybromine species. Indeed, it has been remarked that the atomic combination of bromine and oxygen is possibly the most unfavorable one in nonmetal chemistry. A timely review of the bromine oxides themselves[110] indicates that, apart from the transient diatomic gas-phase radicals BrO and BrO_2, the only well established (meta)stable compounds are dark brown Br_2O, orange-yellow Br_2O_3 and colourless Br_2O_5: their structures in the solid state have been determined as bent Br–O–Br, Br–O–BrO_2 and O_2Br–O–BrO_2, respectively.

Noble gases

The chemistry of the elements in Group 18 continues to be dominated by work on xenon, though some advances have been secured with its lighter congeners.[111] Of particular note is the unambiguous characterisation by infrared spectroscopy of the neutral compound HArF, formed by photolysis of HF in a solid argon matrix at 7.5 K.[112] The three new bands that appear in the spectrum were assigned (using samples isotopically enriched in ^{40}Ar, ^{36}Ar or ^{2}D) to the three expected vibrational modes ν(Ar–H), ν(Ar–F) and δ(H–Ar–F), and the bands were found to decrease in intensity at temperatures above 27 K. A weak chemical bond involving argon had earlier been proposed on the basis of spectroscopic studies on the fugitive matrix-isolated species $ArCr(CO)_5$.[113]

Little new work has recently been reported on compounds of krypton.[111] The linear molecule KrF_2 remains the only stable binary fluoride and this is the starting point of all new chemical syntheses such as the cationic derivatives KrF^+, $KrF^+\cdot xKrF_2$, $Kr_2F_3^+$ and $Kr_2F_3^+\cdot KrF_2$. Use of anhydrous HF as a solvent provides routes to the adducts $2KrF_2\cdot MnF_4$, $KrF_2\cdot MnF_4$ and $KrF_2\cdot CrOF_4$ and the use of KrF_2 as a specialist fluorinating agent is also noteworthy. Some of the most interesting developments, however, concern the identification of bonds from krypton to elements other than fluorine. The first example of a Kr–O bond was found in the thermally rather unstable $Kr(OTeF_5)_2$,[114] and the first Kr–N bonds were identified in the cations of $[HCN–KrF]^+[AsF_6]^-$ and $[R_fCN–KrF]^+[AsF_6]^+$.[115]

The chemistry of the radioactive gas radon has not advanced significantly during the past decade: ‘early’ work reliably indicated the existence of RnF_2, $[RnF]^+[SbF_6]^-$ and the corresponding salts with TaF_6^- and BiF_6^-, but claims for a higher fluoride and for oxo species such as RnO_3, the cation $[HRnO_3]^+$ and the anions $[HRnO_4]^-$ and $[RnO_3F]^-$ are less certain.[111]

The number of elements known to form chemical bonds to xenon has now moved into double figures. In addition to the well established compounds which feature bonds of Xe to F, O, N and C,[116] can be added those with bonds from Xe to H, Si, S, Cl, Br, I, Au and even Xe itself. Thus, species identified following UV irradiation of a variety of compounds in noble-gas matrices at low temperatures include the linear species $[Xe–H–Xe]^+$,[117] XeH_2 (and XeD_2),[118] [H–Xe–OH],[119] [H–Xe–SH][120] and HXeX (X = Cl, Br, I).[121] The novel gaseous cation $[Xe–SiF_3]^+$, formed by nucleophilic displacement of HF from protonated SiF_4 by Xe has the expected C_{3v} symmetry.[122] Thermally more robust combinations have also been characterised. The existence of the dark-green cation Xe_2^+ (first reported over twenty years ago) has been confirmed by an X-ray structural analysis of its $[Sb_4F_{21}]^-$ salt:[123] the Xe–Xe bond length was found to be 308.7 pm, which is longer than for any other element–element bond (*cf.* 304.1 pm for Re–Re in $Re_2(CO)_{10}$). Likewise, although individual molecules of the neutral compound $XeCl_2$ were detected spectroscopically in matrix isolation experiments in 1967/8, no compounds with thermally stable Xe–Cl bonds were isolated until 1999:[124] the synthetic strategy was to react the electrophilic cation $C_6F_5Xe^+$ with appropriate chlorine sources of reduced electrophilicity in CH_2Cl_2 solutions. Thus, $[C_6F_5Xe][AsF_6]$ reacted with 4-$ClC_5H_4N\cdot HCl$ to yield the colourless solid C_6F_5XeCl (decomp. without melting at 36 °C), and with Me_3SiCl to give a 91% yield of the colourless solid $[C_6F_5Xe–Cl–XeC_6F_5][AsF_6]$ (decomp. 100 °C). An X-ray structure determination of the latter compound showed Xe–Cl distances of 284.7 and 278.4 pm, angles C–Xe–Cl 176.0° and 178.8°, and angle Xe–Cl–Xe 117.0°. Another recent significant structural study has established that the XeF_7^- anion in $CsXeF_7$ is capped octahedral rather than pentagonal bipyramidal:[125] the Xe–F_{cap} distance of 210 pm is substantially longer than the average of the other six C–F_{oct} distances, 195 pm. The definitive structures of $[NO_2]^+[Xe_2F_{13}]^-$ (*i.e.* $XeF_6\cdot XeF_7^-$)[125] and $[NO]^+[XeOF_5]^-$ (*O*-apical, pentagonal pyramidal C_{5v} anion)[126] are also notable—this latter stereochemistry is unique in fluorine chemistry, *cf.* the symmetrical C_{3v} symmetry of the precisely isoelectronic species IF_6^-. Another dramatic extension of xenon chemistry is the synthesis of the tetraxenonogold(II) cation $[AuXe_4]^{2+}$, isolated at −78 °C as the dark red crystalline salt $[AuXe_4]^{2+}[Sb_2F_{11}]^-{}_2$. The compound is stable below −40 °C and features square-planar coordination about Au with Xe–Au 274 pm. Not only is it the first compound with an Xe–Au bond, but it is also one of the few true Au^{2+} salts known.[127] Clearly, the story of noble-gas compounds is still actively expanding.

9. The heaviest main group elements

Although xenon ($Z = 54$) is the heaviest non-radioactive member of the noble-gas Group 18, it is salutary to note that it now lies less than half way down the periodic table of known elements. The recent extension of the table beyond element [112] (the last member of the fourth transition series) as a result of the synthesis of individual atoms of elements [114], [116] and [118] means that there are now, potentially, three new members of the main-group elements. Their chemistry will necessarily remain unexplored unless or until rather more stable isotopes of these new elements can be synthesised in viable yields, but the current view is that they may reasonably be tentatively classified as 'ekalead', 'ekapolonium' and 'ekaradon'. Pending this development, we can only marvel at the stupendous technical and intellectual virtuosity of the groups that have achieved their synthesis and characterisation.

The nuclear stability of the transfermium elements ($Z > 100$) progressively decreases due to more rapid α-particle decay and spontaneous fission. Thus, the half-life of the longest-lived isotope for successive elements steadily diminishes from 65 seconds for [104] to less than 1 ms for [112]. However, it has been appreciated for many years that nuclear stability should increase again as one approaches the next 'magic number' nuclei which have closed shells of either protons or neutrons. The peak of this 'island of stability' is expected to occur at the double magic number of 114 protons and 184 neutrons, i.e. ^{298}[114] but enhanced stability should become noticeable for nuclei with more than about 168 neutrons. The secret of success in synthesising such massive nuclei without shattering them during synthesis is to use the heaviest possible magic-number nuclei for both the projectile and the target. Using this method a single atom of element 114 was synthesised and characterised towards the end of 1998 by bombarding a target of enriched ^{244}Pu (98.6%) as PuO_2 for 32 days with a current of the rare and very expensive doubly magic numbered heavy isotope ^{48}Ca (natural abundance 0.19%). The 5.2×10^{18} projectiles of $^{48}Ca^{5+}$ produced just one nucleus of ^{289}[114] (in line with expectations) and this underwent α-decay in 30.4 seconds:[128]

$$^{244}_{94}\text{Pu} + {}^{48}_{20}\text{Ca} \rightarrow 3\text{n} + {}^{289}[114] \xrightarrow[30.4\text{ s}]{-\alpha} {}^{285}[112] \xrightarrow[15.4\text{ min}]{-\alpha} {}^{281}[110] \xrightarrow[1.6\text{ min}]{-\alpha} {}^{277}[108] \xrightarrow[16.5\text{ min}]{} \text{SF}$$

The long initial decay time and the succession of long-lived α-decay products down to ^{277}[108] which then underwent spontaneous fission (SF) after 16.5 min indicated that the shores of the island of stability were being approached. Subsequently a similar experiment, in which a target of $^{242}_{94}$Pu (97%) in the form of PuO_2 was bombarded with 7.8×10^{18} projectiles of $^{48}_{20}Ca^{5+}$, produced the isotope ^{287}[114] which decayed by α-emission after 1.32 seconds:[129]

$$^{242}_{94}\text{Pu} + {}^{48}_{20}\text{Ca} \rightarrow 3\text{n} + {}^{287}[114] \xrightarrow[132\text{ s}]{-\alpha} {}^{283}[112] \rightarrow \textit{etc.}$$

It is important to note that the decay times quoted above are not half-lives—they are the actual elapsed time intervals for each successive event, starting from the formation of the single observed atom of ^{289}[114] or ^{287}[114]. For example, the emission of the α-particle from ^{287}[114] occurred 1.32 seconds after the formation of the new nuclide; this corresponds statistically to a half-life of 5.5^{+10}_{-2} s. The computation of a statistically meaningful 'half-life' from a single decay event, or even a small number of events, inevitably involves unsymmetrical uncertainties and, in itself, raises some intriguing mathematical and philosophical concepts.[130]

Still heavier elements were synthesised by bombarding the heaviest stable isotope of lead (the doubly magic $^{208}_{82}$Pb) with ions of the heaviest stable isotope of krypton, $^{86}_{36}$Kr.[131] This generated three observed atoms of the new element [118] which then decayed with a half-life of 120^{+180}_{-60} μs *via* α-particle emission to the further new element [116] which had a half-life of 600^{+180}_{-60} μs:

$$^{208}_{82}\text{Pb} + {}^{86}_{36}\text{Kr} \rightarrow \text{n} + {}^{293}[118] \xrightarrow{-\alpha} {}^{289}[116] \xrightarrow{-\alpha} {}^{285}[114] \rightarrow \textit{etc.}$$

The new elements [114], [116] and [118] are expected to be the heavier congeners of lead, polonium and radon, respectively. Without doubt, exciting prospects lie ahead.

10. Conclusion

This Millennium Perspective has concentrated on describing some of the most important recent developments and trends in the synthetic and structural chemistry of the 47 main group elements. It has not been possible to give similar prominence to the equally fascinating and important contemporary studies on the mechanisms of reactions involving main group element compounds or to the growing volume of work on catalysis. Nor has justice been done to the computational and theoretical aspects of the chemistry of these elements. Equally, there has not been space to discuss the numerous applications of this new chemistry though, of course, it is the tantalising prospect of ingenious new applications which provides the motivation of much of the work. The impact of new and more powerful instrumental techniques and the ubiquitous influence of computer technology in obtaining and disseminating these new results will, however, have been strikingly evident.

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