

Atypical compounds of gases, which have been called ‘noble’†

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In this *critical review* I describe fascinating experimental and theoretical advances in ‘noble gas’ chemistry during the last twenty years, and have taken a somewhat unexpected course since 2000. I also highlight perspectives for further development in this field, including the prospective synthesis of compounds containing as yet unknown Xe–element and element–Xe–element bridging bonds, peroxide species containing Xe, adducts of XeF₂ with various metal fluorides, Xe–element alloys, and novel pressure-stabilized covalently bound and host–guest compounds of Xe. A substantial part of the essay is devoted to the—as yet experimentally unexplored—behaviour of the compounds of Xe under high pressure. The blend of science, history, and theoretical predictions, will be valued by inorganic and organic chemists, materials scientists, and the community of theoretical and experimental high-pressure physicists and chemists (151 references).

1 Lead-in

They say *noblesse oblige*.¹ Nothing more inaccurate and misleading than that has been said, however, in the context of the heavier gaseous elements of Group 18 (Rn, Xe, Kr), which

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† This essay is dedicated to Roald Hoffmann, on the occasion of his 70 birthday, who has taught me to feel the pulse of science.



Wojciech Grochala

Wojciech Grochala was born in 1972 in Warsaw, Poland, where he received his MSc, PhD and DSc from the University of Warsaw. He has studied chemistry with Roald Hoffmann in Ithaca (Cornell, USA) and with Peter P. Edwards (then at Birmingham, UK). Inorganic solid state chemistry and mountaineering are Wojciech's real passions. He entered the field of noble gas chemistry through the back door, when studying the most

potent oxidizers available to chemistry (higher fluorides of Ag).¹⁴⁴ His scientific interests encompass superconductivity,¹⁴⁵ quantum modelling of solids and molecular materials, hydrogen³⁷ and energy storage, hydrogen transfer catalysis,¹⁴⁶ applications of high pressures in chemistry,¹²⁰ molecular devices, unusual oxidation states of the chemical elements,¹⁴⁷ and more. He now heads the Laboratory of Technology of Novel Functional Materials, a joint enterprise of the ICM and of the Department of Chemistry at Warsaw University. Wojciech is the happy husband of Liliana and father of three kids: Ilona Maria, Oliver Lucian and Leonard Karol.

for a century have been colloquially called ‘noble’. Since the discovery of argon (‘the lazy one’) in 1894 by Rayleigh and Ramsay,² and the realisation of the monoatomic and unreactive nature of its homologues, it was long believed that group 18 elements cannot form chemical compounds. And the very concept of the stable ‘octet valence configuration’, so vital to chemistry, was born.³ ‘Nothing can force a noble gas (Ng) atom into a chemical bonding’ said this new law of nature. But human nature loves challenges. Led by intuition and qualitative considerations, von Antropoff^{4a,b} and Pauling^{4c} have foreseen that heavier Ng’s might, in fact, be chemically awakened in powerfully oxidizing conditions while entering the oxide or fluoride environment. Yet nearly forty years were to pass since the apposite predictions saw confirmation in the breakthrough-making 1962 discovery of the first Xe compound.^{5,6} In 1989 Xe has completely lost traces of its nobility and inertness when it was turned into metal by use of ultra-high pressure.⁷

About half a thousand compounds of Ng’s have been synthesized since 1962.⁸ Due to the above mentioned historical reasons and for the purpose of this short essay, we would like draw here the line between ‘usual’ and ‘unusual’ compounds. By ‘usual’ or ‘classical’, I refer to those compounds predicted by Pauling, *etc.* so long ago. They contain fluoride, oxide and related ligands (such as SbF₆[−], TeOF₅[−], IO₂F₄[−], WOF₄, *etc.*) and contain Xe at oxidation states +2, +4, +6, +8 (Fig. 1), or Kr^{II} in fluoride environment; chemistry of ‘classical’ Ng compounds—also undergoing violent progress⁹—has been reviewed elsewhere^{10–12} and only rarely will be mentioned here.¹³ Whatever goes beyond that (and *any* chemical bonding involving Ar) will be treated as ‘atypical’, and described from a chemical perspective to a greater detail, with particular emphasis on chemistry of Xe.

2 The known Ng–element bonds

2.1 The first ‘unusual’ Ng–nonmetal bonds

Encouraged by fast enriching spectrum of the Xe–F and Xe–O compounds, several groups have tried to break another

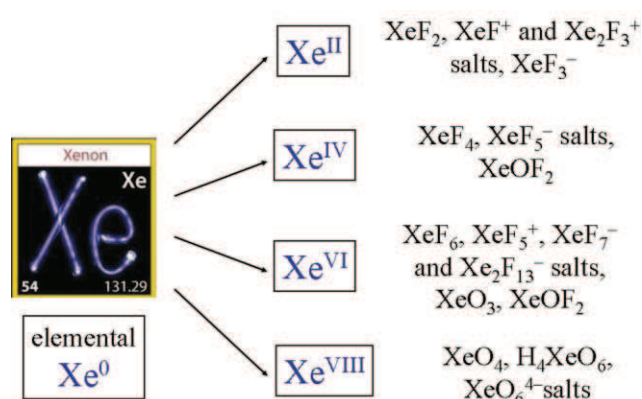


Fig. 1 Classical chemistry of Xe involving connections to F and O ligands at various oxidation states of a “noble” gas.

paradigm, and to extend bonding to Xe beyond the two most electronegative elements.

The first genuine Xe–N bond saw the daylight in 1974, with the discovery of $(\text{F}-\text{Xe}^{\text{II}})[-\text{N}(\text{SO}_2\text{F})_2]$. This new white compound is isolable in gram quantities and is stable to decomposition up to $+70\text{ }^\circ\text{C}$ (Table 1)! This synthesis paved the road for further developments but these went uphill; during the next 25 years about twenty other compounds have been made in chemists’ flasks (including related $\text{Xe}^{\text{II}}[\text{N}(\text{SO}_2\text{F})_2]_2$, $(\text{RCN}-\text{XeF}^+)(\text{AsF}_6^-)$ where $\text{R} = \text{H}, \text{Me}$, derivatives of perfluorinated pyridine, perfluoroalkyls, trifluorotriazine *etc.*),¹⁴ $\text{Xe}[\text{N}(\text{SO}_2\text{R})_2]_2(2,6\text{-F}_2\text{C}_6\text{H}_3^-)$ where $\text{R} = \text{F}, \text{CF}_3$,¹⁵ and $[\text{F}_3\text{SN}-\text{XeF}][\text{AsF}_6]$.¹⁶ Compounds of $[-(\text{NH})-\text{TeF}_5]$ and related anions¹⁷ have also been made, while some others were suggested as short-lived reaction

intermediates.¹⁸ All of them were less thermally stable than the native $\text{F}-\text{Xe}^{\text{II}}-\text{N}(\text{SO}_2\text{F})_2$.

As time passed by and the knowledge of researchers accumulated, the first examples of the unstable $\text{Xe}^{\text{VI}}-\text{N}$ and $\text{Xe}^{\text{VIII}}-\text{N}$ bonds were delivered.¹⁹ Finally, Kr has also been linked to N (and to O), but only below $-60\text{ }^\circ\text{C}$ (for O: $-90\text{ }^\circ\text{C}$) in the BrF_5 (for O: SO_2ClF) solvent.^{20,21}

It was also quite difficult to get compounds which have real Xe–C bonds. The precedents, $[(\text{F}_5\text{C}_6)\text{Xe}^+][\text{B}(\text{C}_6\text{H}_5)_3\text{F}^-]$ and $[(\text{F}_5\text{C}_6)\text{Xe}^+][\text{B}(\text{C}_6\text{H}_5)_3\text{F}_3^-]$ were synthesized as late as 1988 as colorless solids, and their solutions in acetonitrile proved to be stable at $\sim 0\text{ }^\circ\text{C}$.²² Soon the preparation method was extended and modified, and new synthetic paths have been invented yielding more related aryl derivatives, the compounds of (partially or entirely fluorinated) unsaturated hydrocarbon groups (*i.e.* alkenyl²³ and alkynyl),²⁴ and even the first compound with the simultaneous Xe–C and Xe–N bonds.²⁵ $[(\text{F}_5\text{C}_6)\text{Xe}^+](\text{AsF}_6^-)$, which is so thermally stable that it decomposes rapidly only well above its melting temperature ($T_m = 102\text{ }^\circ\text{C}$), has become an important reagent in the emerging organoxenon chemistry.²⁶ It took one decade to synthesize the important siblings $(\text{F}_5\text{C}_6)\text{XeF}$, $\text{Xe}(\text{C}_6\text{F}_5)_2$ and $\{[(\text{F}_5\text{C}_6)\text{Xe}]_2\text{F}^+\}(\text{AsF}_6^-)$.²⁷ The electrochemistry of organoxenon(II) derivatives has been explored,²⁸ and even the first organoxenon(IV) compounds have been prepared ($[(\text{F}_5\text{C}_6)\text{Xe}^{\text{IV}}\text{F}_2^+](\text{BF}_4^-)$ and $\text{Xe}^{\text{IV}}\text{F}_4(\text{CN}^-)$).²⁹

The formation of the $\text{Xe}^{\text{II}}-\text{Cl}$ bond (an analogue of the well-known $\text{Xe}^{\text{II}}-\text{F}$ bond) at temperatures close to ambient, was first seen in 1997.³⁰ This new bond was brought to life in two novel crystalline species, $(\text{F}_5\text{C}_6)\text{XeCl}$ and $\{[(\text{F}_5\text{C}_6)\text{Xe}]_2\text{Cl}^+\}(\text{AsF}_6^-)$, which showed reasonable kinetic stability at ambient temperature. Since then only one more

Table 1 Chemical formula and ranking of the thermal decomposition temperature, T_{dec} , of selected compounds which exhibit the Xe–E bonds (E = N, C, Cl)

Chemical formula	$T_{\text{dec}}/^\circ\text{C}$	Comments
$\text{F}-\text{Xe}^{\text{II}}-\text{N}(\text{SO}_2\text{F})_2$	70	Bulk solid
$(\text{MeCN}-\text{XeF}^+)(\text{AsF}_6^-)$	>-10	Solution in anhydrous HF
$\text{Xe}[\text{N}(\text{SO}_2\text{F})_2]_2$	>-40	Solution in SO_2ClF
$[(\text{F}_5\text{C}_6)\text{Xe}][\text{N}(\text{SO}_2\text{F})_2]$	155	Bulk solid
$[(\text{F}_5\text{C}_6)\text{Xe}][\text{N}(\text{SO}_2\text{CF}_3)_2]$	120	Bulk solid
$[(\text{F}_5\text{C}_6)\text{Xe}(\text{NC}_5\text{H}_3\text{F}_2-2,6)^+](\text{AsF}_6^-)$	<20	Solution in MeCN
$[(\text{F}_5\text{C}_6)\text{Xe}(\text{NC}-\text{CH}_3)^+](\text{F}_2\text{B}(\text{C}_6\text{F}_5)^-)$	14	Bulk solid
$[(\text{F}_5\text{C}_6)\text{Xe}^+](\text{AsF}_6^-)$	>130	Bulk solid; fast decomp. $> 180\text{ }^\circ\text{C}$
$[2,6\text{-}(\text{F}_2\text{H}_3\text{C}_6)\text{Xe}^+](\text{BF}_4^-)$	130	Bulk solid
$[2,6\text{-}(\text{F}_2\text{H}_3\text{C}_6)\text{Xe}^+][\text{C}(\text{SO}_2\text{F})_3]$	113	Bulk solid
$[(\text{F}_5\text{C}_6)\text{Xe}^+](^-\text{OOC}-\text{C}_6\text{F}_5)$	85	Bulk solid
$[(\text{F}_5\text{C}_6)\text{Xe}^+][\text{B}(\text{C}_6\text{H}_5)_3\text{F}_3^-]$	<35	Solution in MeCN
$[(\text{F}_5\text{C}_6)\text{Xe}^+](\text{BF}_4^-)$	>25	Solution in anhydrous HF
$[(\text{F}_5\text{C}_6)\text{Xe}^+](\text{BF}_4^-)$	>25	Solution in anhydrous HF
$(\text{F}_5\text{C}_6)_2\text{Xe}$	20	Bulk solid, explosive decomposition
$[(\text{CF}_3\text{C}=\text{C})\text{Xe}^+](\text{BF}_4^-)$	20	Stable for at least 2–3 h
$[(\text{F}_5\text{C}_6)\text{Xe}^+](\text{HF}_2^-)$	<20	Solution in MeCN
$[(\text{F}_5\text{C}_6)\text{Xe}^+][\text{B}(\text{C}_6\text{H}_5)_3\text{F}^-]$	>0	Solution in MeCN
$[(4\text{-ClH}_4\text{C}_6)\text{Xe}^+](\text{BF}_4^-)$	>-4	Bulk solid
$[(\text{F}_5\text{C}_6)\text{Xe}^{\text{IV}}\text{F}_2^+](\text{BF}_4^-)$	>-20	Bulk solid
$(\text{F}_5\text{C}_6)\text{XeF}$	<-78	Solution in CH_2Cl_2
$(\text{F}_5\text{C}_6)\text{Xe}(\text{CN})$	<-78	Solution in CH_2Cl_2
$\{[(\text{F}_5\text{C}_6)\text{Xe}]_2\text{Cl}^+\}(\text{AsF}_6^-)$	100	Bulk solid
$(\text{F}_5\text{C}_6)\text{XeCl}$	36	Bulk solid, decomposition with melting
$(\text{XeCl}^+)(\text{Sb}_2\text{F}_{11}^-)$	-20	Bulk solid, decomposition with melting

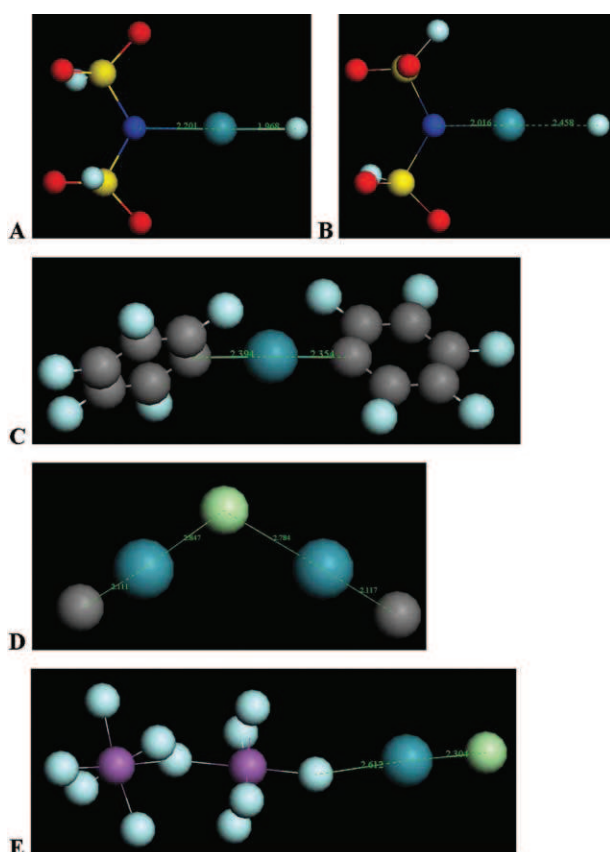


Fig. 2 Structures of: (A) $\text{F-Xe}^{\text{II}}-\text{N}(\text{SO}_2\text{F})_2$; (B) $\text{Xe}^{\text{II}}-\text{N}(\text{SO}_2\text{F})_2(\text{Sb}_3\text{F}_{16})$; (C) $\text{Xe}(\text{C}_6\text{F}_5)_2$; (D) $\{[(\text{F}_5\text{C}_6)\text{Xe}]_2\text{Cl}\}(\text{AsF}_6^-)$; (E) $(\text{XeCl}^+)(\text{Sb}_2\text{F}_{11}^-)$. Xe – blue, F – light blue, Cl – green, C – black, N – dark blue, S – yellow, O – red. Molecular units, extracted from full crystal structures, are shown here, except for (D) where only one C atom from each benzene ring is shown.

compound, $(\text{XeCl}^+)(\text{Sb}_2\text{F}_{11}^-)$,³¹ has been added to the list of compounds isolable ‘in the flask’. The chemistry of the Xe–Cl bond thus remains largely unexplored.

Summarizing this section, we note that close to a hundred organoxenon, Xe–N and Xe–Cl compounds are known up to date.³² Xenon chemistry finally ‘went out from the cold’,³³ and started flourishing.

2.2 Where are the bonds

Despite the 1974–2006 successes of xenon chemistry, only ~15% of all known solids containing short Xe–C, Xe–N and Xe–Cl contacts have been structurally characterized. Selected structures are shown in Fig. 2.

Xe^{II} is isoelectronic to I^{I} . Not surprisingly, XeF_2 is isostructural with the linear symmetric IF_2^- anion (present for example in its Cs^+ salt), and all Xe^{II} compounds show two-coordinated Xe in an $\text{E}^1\cdots\text{Xe}\cdots\text{E}^2$ unit ($\text{E}^1, \text{E}^2 = \text{Lewis base}$) with its bond angle close to $180^\circ (\pm 10^\circ)$. Covalent Xe–C bond lengths vary from 2.08 to 2.39 Å, the Xe–N contacts are at 2.02–2.20 Å, while the Xe–Cl bonds are 2.31–2.85 Å long.

Even in the very limited set of experimental data, a clear trend can be perceived, calling for an obvious generalization (Table 2 and Fig. 3).³⁴ It is clear from Table 2, that for a given $\text{E}^1\cdots\text{Ng}\cdots\text{E}^2$ set of elements (for example: $\text{Ng} = \text{Xe}$, $\text{E}^1 = \text{N}$, $\text{E}^2 = \text{F}$), a relationship always holds: when R^1 becomes longer, R^2 becomes shorter, and *vice versa*. Some will attribute it to the varying basicity of one of molecule’s counterions, using the following reasoning: since the $(\text{Sb}_3\text{F}_{16}^-)$ ion is much less basic than F^- , the $\text{Xe}^{\text{II}}\cdots\text{F}$ contact must be longer in the $(\text{Sb}_3\text{F}_{16}^-)\cdots\text{Xe}^{\text{II}}-\text{N}(\text{SO}_2\text{F})_2$ derivative than in the $(\text{F}^-)\cdots\text{Xe}^{\text{II}}-\text{N}(\text{SO}_2\text{F})_2$ one. In turn, the Xe^{II} center must be more powerful Lewis acid in the former compound, and therefore it is ligated by the $^-\text{N}(\text{SO}_2\text{F})_2$ base at shorter separation than that found for the latter species.

Table 2 Chemical formula and the lengths, R^1 and R^2 , of two hypervalent Xe–E bonds ($\text{E} = \text{N}, \text{C}, \text{Cl}, \text{F}$) and of two hypervalent Kr–F bonds observed in several compounds of these Ng’s.

Formula	$\text{R}^1/\text{Å}$	$\text{R}^2/\text{Å}$	Comment
$\text{F-Kr}^{\text{II}}-\text{F}$	Kr–F: 1.894	Kr–F: 1.894	Symmetric
$(\text{Kr}_2\text{F}_3^+)(\text{SbF}_6^-)\cdot\text{KrF}_2$	Kr–F: 1.805	Kr–F: 2.041	
$(\text{Kr}_2\text{F}_3^+)(\text{SbF}_6^-)\cdot\text{KrF}_2$	Kr–F: 1.799	Kr–F: 2.065	
$(\text{F-Kr}^{\text{II}})(\text{BiF}_6)$	Kr–F: 1.775	Kr–F: 2.090	
$(\text{F-Kr}^{\text{II}})(\text{AsF}_6)$	Kr–F: 1.765	Kr–F: 2.131	
$(\text{F-Kr}^{\text{II}})(\text{SbF}_6)$	Kr–F: 1.765	Kr–F: 2.140	
$(\text{F-Kr}^{\text{II}})(\text{AuF}_6)$	Kr–F: 1.751	Kr–F: 2.161	
$(\text{Sb}_3\text{F}_{16}^-)\text{-Xe}^{\text{II}}-\text{N}(\text{SO}_2\text{F})_2$	Xe–N: 2.020	Xe–F: 2.457	
$\text{F-Xe}^{\text{II}}-\text{N}(\text{SO}_2\text{F})_2$	Xe–N: 2.200	Xe–F: 1.967	
$[(\text{F}_5\text{C}_6)\text{Xe}^{\text{II}}(\text{NCMe})](\text{F}_2\text{B}(\text{C}_6\text{F}_5)^-)$	Xe–N: 2.681	Xe–C: 2.092	
$[(\text{F}_5\text{C}_6)\text{Xe}(\text{NC}_5\text{H}_3\text{F}_2-2,6)^+](\text{AsF}_6^-)$	Xe–N: 2.694	Xe–C: 2.087	
$[(\text{F}_5\text{C}_6)\text{Xe}^{\text{II}}](\text{AsF}_6)$	Xe–C: 2.079	Xe–F: 2.714	
$[(\text{F}_5\text{C}_6)\text{Xe}^{\text{II}}](\text{AsF}_6)$	Xe–C: 2.082	Xe–F: 2.672	
$[(2,6-\text{F}_2\text{H}_3\text{C}_6)\text{Xe}^{\text{II}}](\text{BF}_4^-)$	Xe–C: 2.090	Xe–F: 2.793	
$[(\text{F}_5\text{C}_6)\text{Xe}(\text{NC}_5\text{H}_3\text{F}_2-2,6)^+](\text{AsF}_6^-)$	Xe–C: 2.087	Xe–N: 2.694	
$[(\text{F}_5\text{C}_6)\text{Xe}^{\text{II}}(\text{NCMe})](\text{F}_2\text{B}(\text{C}_6\text{F}_5)^-)$	Xe–C: 2.092	Xe–N: 2.681	
$\{[(\text{F}_5\text{C}_6)\text{Xe}]_2\text{Cl}\}(\text{AsF}_6^-)$	Xe–C: 2.111	Xe–Cl: 2.847	
$\{[(\text{F}_5\text{C}_6)\text{Xe}]_2\text{Cl}\}(\text{AsF}_6^-)$	Xe–C: 2.116	Xe–Cl: 2.784	
$(\text{F}_5\text{C}_6)_2\text{Xe}^{\text{II}}$	Xe–C: 2.350	Xe–C: 2.394	Close to symmetric
$[(2,6-\text{F}_2\text{H}_3\text{C}_6)\text{Xe}^{\text{II}}](^-\text{OSO}_2\text{CF}_3)$	Xe–C: 2.079	Xe–O: 2.687	
	Xe–C: 2.092	Xe–O: 2.829	
$(\text{XeCl}^+)(\text{Sb}_2\text{F}_{11}^-)$	Xe–Cl: 2.309	Xe–F: 2.644	
XeCl_2	Xe–Cl: 2.542	Xe–Cl: 2.542	Symmetric (theor. result for solid) ¹⁴⁵
$\{[(\text{F}_5\text{C}_6)\text{Xe}]_2\text{Cl}\}(\text{AsF}_6^-)$	Xe–Cl: 2.784	Xe–C: 2.116	
$\{[(\text{F}_5\text{C}_6)\text{Xe}]_2\text{Cl}\}(\text{AsF}_6^-)$	Xe–Cl: 2.847	Xe–C: 2.111	

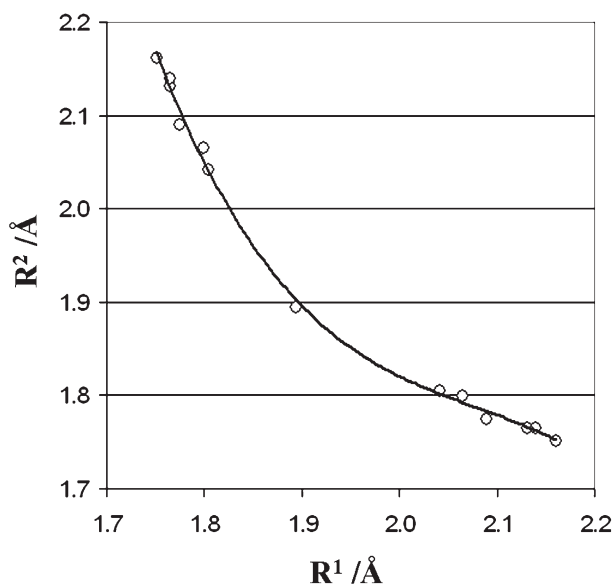


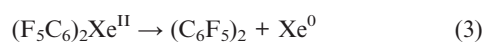
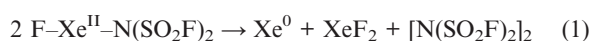
Fig. 3 Illustration of the nature of a hypervalent bond: the experimental R^1 vs. R^2 dependence for several $F^- \cdots Kr^{II} \cdots F^-$ species.

Others will argue that such asymmetric (long–short) bonding pattern is typical for any hypervalent (here: four-electron–three-center) bonding;³⁵ it is seen even in a purely fluoride environment for Kr^{II} (compare Fig. 2) and of course for Xe^{II} , as well as for many other related species.³⁶ Notably, the hypervalent $E \cdots Xe-C$, $E \cdots Xe-N$ and $E \cdots Xe-Cl$ groupings also obey this general relationship.

Coming back to structures: Xe^{IV} resembles I^{III} (or Br^{III}) and Te^{II} (or Se^{II}), and these species usually appear in a square-planar coordination, as seen for $Xe^{IV}F_4$, $Br^{III}F_4^-$ ion or $L_2Se^{II}Cl_2$ (L = tetrahydrothiophene). Distorted square-planar coordination of Xe^{IV} is also likely to be the case for $[(F_5C_6)Xe^{IV}F_2^+](F_3B^-)$. A very rare planar pentacoordinated geometry Xe^{IV} is presumably adopted by Xe^{IV} in the $F_4Xe(CN^-)$ anion. These are the only organoxenon(IV) compounds synthesized so far.

2.3 Combatting against auto–redox reactions

The chemistry of nonmetal–Xe connections is fascinating but quite difficult to do. There are many reactions possible which may hinder formation and limit stability of $Xe-N$, $Xe-C$, $Xe-Cl$ and related bonds, and, indeed, unwanted redox processes are a major headache of researchers of Xe chemistry. Some such processes are illustrated in eqn (1)–(3) for three prototypical $Xe-N$, $Xe-Cl$ and $Xe-C$ compounds:



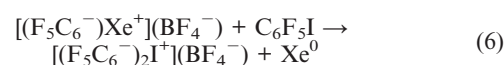
If one considers the limiting ionic Lewis formulas of the native Xe^{II} compounds, in which both ligands are negatively charged, then processes described by eqn (1)–(3) are nothing but ‘simple’ redox reactions: Xe^{II} is (partially or completely)

reduced in a (formally) $2e^-$ process, while two nonmetal–based ligands L^- are oxidized in two $1e^-$ processes, and then they form the $L-L$ bond. Thus stability of nonmetal–Xe bonds is essentially governed by the electron transfer reactions, just as in the case of hydrides,³⁷ oxides, and many other families of compounds with high oxidation states of chemical elements. In practice, these and similar reactions are most troublesome in the synthesis of new compounds, forcing chemists to carry out their preparations at relatively low temperatures, down to $-70^\circ C$; once prepared, the $Xe-N$, $Xe-C$ and $Xe-Cl$ bonds may be quite stable kinetically and thermally (Table 1).

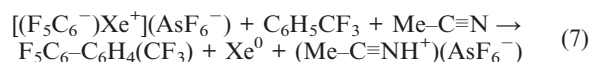
The occurrence of redox reactions analogous to those of eqn (1)–(3) (and the natural preference of Xe^{II} for only two coordinating Lewis bases) results in an *inherent* instability of Xe bonds to elements that are any less electronegative than those discussed above, such as Si, P, As, S, Se, Br and I. Here, a spontaneous depopulation of the nonmetal’s orbital (lone pair) takes place; electrons are transferred for good to Xe^{II} . Compounds which contain bonds between the above-mentioned elements and Xe, have never been prepared in large amounts in a chemist’s flask (despite numerous attempts...), and their existence is limited to low concentrations of molecules embedded in the noble gas matrices, at very low temperatures. We will describe this exotic chemistry in the present contribution, but first let us show several representative examples of old reaction types for new compounds.

2.4 Exploring new chemistry

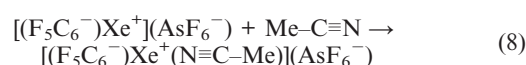
It turns out that when an additional reducing agent (like metallic mercury or C_6F_5I , which are poor reducers, indeed) or an oxidizing one (like I_2) are added to selected organoxenon species, electron-transfer reactions proceed even easier at very low temperatures (sometimes vigorously even below $-80^\circ C$!) (eqn (4) and (5)), and with nearly quantitative yields:



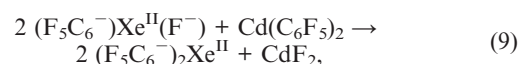
More complex redox reactions (eqn (7)), are also possible:



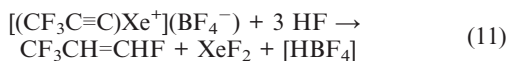
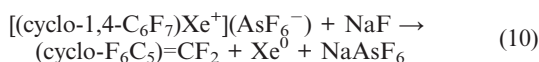
The majority of reactions involving Xe –nonmetal compounds exemplify a ‘simple’ Lewis acid–base chemistry (eqn (8)):



including metathetic reactions (eqn (9)):



but sometimes they may take much less expected course, like in the following group-transfer and hydrogenation reactions (eqn (10) and (11)):



New chemistry (and particularly when it's originating from the formation of *new types of chemical bonds*) is always great experience...!

2.5 Is white stable? *i.e.* prospect for colourful compounds

All Xe–C and Xe–N compounds synthesized so far are white or (seldomly) slightly yellowish. This indicates that the first allowed electronic transition corresponds to UV or deep violet radiation, and thus requires at least 3 eV. Only $(\text{XeCl}^+)(\text{Sb}_2\text{F}_{11}^-)$ and $[\text{F}_5\text{TeN}(\text{H})\text{Xe}][\text{AsF}_6]^{38}$ break this monotony: they are orange, so should absorb in the blue (~2.5 to 2.9 eV). Taking into account the products of the thermal decomposition reactions for a variety of Xe–C and Xe–N compounds, and applying chemical intuition to redox reactions, one might anticipate that the lowest energy electronic transition corresponds to the vertical (nonmetal-to-Xe or Lewis base-to-acid) charge-transfer (CT) excitation. Such an electronic transition would thus be a herald of the ‘full’ redox reaction which takes place if the temperature is raised.

However, analysis of the electronic structure of Xe^{II} derivatives (exemplified here by the quite stable, colourless XeF_2 , Fig. 4 and Table 3) suggests that situation is more complex. Calculations show three spin-forbidden transitions to the triplet states and two transitions to singlet states (the longer wavelength one is symmetry-forbidden) in the photon energy range from 0 to 6 eV. Thus, XeF_2 does not get the chance for colour: the first allowed transition is at 5.64 eV. Nevertheless, the lowest energy transition to $^3\Pi_g$ is at energy as small as 3.56 eV. This indicates that:

- thermal decomposition of XeF_2 to Xe and F_2 may occur through the bending of an isolated molecule (π_u mode), through the coupling between HOMO–1 (π_g^*) and LUMO (σ_u^*);

- the white color of XeF_2 is delusive, as the only potentially colour-providing spin- and symmetry-allowed transition is well above the lowest energy excitation (the one which may be activated thermally, leading to decomposition).

Table 3 List of the lowest energy electronic excitations for the isolated XeF_2 molecule in its $^1\Sigma_g$ ground state (B3LYP-TD results). The transition energy, E , and oscillator strength, f , are shown, along with the predominant orbital contribution to the transition. All transitions to triplet states are spin-forbidden (provided that heavy-atom effects are neglected), and many transitions to singlet states are symmetry-forbidden. HOMO and HOMO–1 of XeF_2 are π_u , HOMO–2 is σ_g , while HOMO–3 and HOMO–4 are π_g ; LUMO is σ_u .

E/eV	f	Excited state	Orbitals contributing	E/eV	f	Excited state	Orbitals contributing
4.33	0	$^1\Pi_g$	$\pi_u \rightarrow \sigma_u^*$	3.56	0	$^3\Pi_g$	$\pi_u \rightarrow \sigma_u^*$
5.64	0.006	$^1\Pi_u$	$\pi_g \rightarrow \sigma_u^*$	3.78	0	$^3\Sigma_u$	$\sigma_g \rightarrow \sigma_u^*$
7.28	0	$^1\Pi_g$	$\pi_u \rightarrow \sigma_u^*$	5.00	0	$^3\Pi_u$	$\pi_g \rightarrow \sigma_u^*$
7.73	0.786	$^1\Sigma_u$	$\sigma_g \rightarrow \sigma_u^*$	6.40	0	$^3\Pi_g$	$\sigma_g \rightarrow \sigma_u^*$

^a Deeper occupier π_u orbitals are involved.

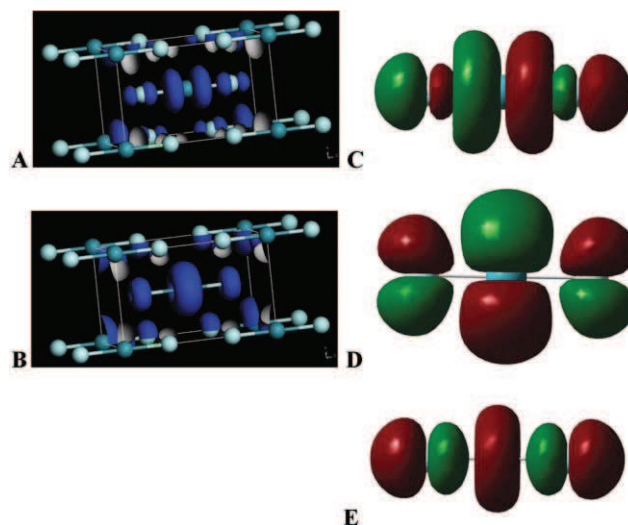


Fig. 4 Electron density integrated over (A) the first unoccupied, (B) the uppermost occupied, band of solid XeF_2 (cell with $Z = 2$), which correspond, respectively, to (C) σ_u^* LUMO and (D) π_u^* HOMO of an isolated XeF_2 molecule. Note, HOMO is doubly degenerate, and only one orbital is shown here. (E) σ_g HOMO–2 of XeF_2 molecule. Note, HOMO–2 is more F- and less Xe-based than LUMO, therefore the allowed HOMO–2 \rightarrow LUMO ($\sigma_g \rightarrow \sigma_u^*$) electronic excitation has F-to-Xe charge transfer character. DFT calculations for solid and molecular XeF_2 .

For Kr^{II} compounds, of course, the F^- -to- Kr^{II} charge transfer process occurs much more easily than for Xe^{II} (and even in the fluoride environment): yet KrF_2 is still colourless.³⁹ Lack of colour is premonitory here, as it warns of the presence of an ‘invisible’ singlet \rightarrow triplet transition at the low energy of 2.9 eV. This excitation testifies to a significant fragility of the thermodynamically unstable KrF_2 .

Fortunately, the large energies of the *vertical* CT transitions indicate that *barriers* for the Xe–nonmetal bond rupture (in a redox fashion) are not as small as one might think. Indeed, as we have seen from Table 1, some Xe–nonmetal compounds are surprisingly kinetically stable. Hypothetically new bonds of even less electronegative elements to Xe might treat our eye to a palette of colors, but they will be more unstable thermally—and difficult to synthesize. Despite this danger—and as long as events reside in the imaginative minds and skillful hands of an excellent pedigree of synthetic fluorine chemists—compounds containing new Xe–nonmetal bonds, such as Xe–Br, Xe–S, Xe–P, Xe–Si, are just a matter of time.⁴⁰

2.6 Still more new bonds as it gets colder

You want to play even more exotic bond creation games? Then you must first freeze your building blocks well enough. For a low temperature is often a prerequisite for success... This simple indication has been long used by this part of the chemical community, which prefers ultracold noble gas matrices over flasks, and laser photolysis over a smelly synthetic kitchen. Additional advantages of matrix synthesis are that it only seldom leads to many side-products, and that product molecules may be isolated from one another; but even if several different products are simultaneously formed, they may still be identified quite easily by *in-situ* IR spectroscopy supplemented by quantum mechanical calculations. The major disadvantage of matrix synthesis is, however, that it is more difficult to utilize the newly-formed product for subsequent reactions, so a big part of the fun is lost.

Despite this disadvantage, matrix synthesis has several times outdistanced 'bulk synthesis' in the race for new Ng-element bonds.⁴¹ In 1995, in their pioneering work, a Finnish group reported the formation of HXeX (X = Cl, Br, I, H) and of HKrCl.⁴² Impressive as these Ng-containing molecules are, they only hinted at what was yet to come. During the next decade several known bonds (Xe–O, Xe–N, Xe–C, Xe–Cl, Kr–F, Kr–O) were achieved in many new small molecules, and a total of nine new bonds were formed, including Xe–H, Xe–Br,

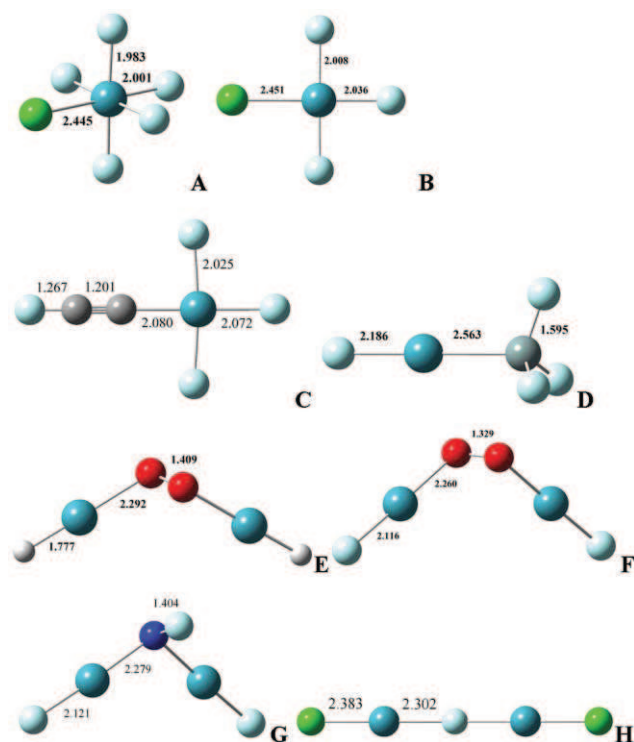


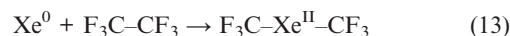
Fig. 5 The calculated structures of: (A) $\text{Xe}^{\text{VI}}\text{F}_5\text{Cl}$ in C_{4v} symmetry; (B) $\text{Xe}^{\text{IV}}\text{F}_3\text{Cl}$ in C_{2v} symmetry; (C) $\text{Xe}^{\text{IV}}\text{F}_3(\text{C}_2\text{F})$ in C_{2v} symmetry; (D) $\text{FXe}^{\text{II}}\text{SiF}_3$ in C_{3v} symmetry; (E) $\text{HXe}^{\text{II}}\text{OOXe}^{\text{II}}\text{H}$ in C_2 symmetry; (F) $\text{FXe}^{\text{II}}\text{OOXe}^{\text{II}}\text{F}$ in C_2 symmetry; note, the O–O bond is shorter than for $\text{HXe}^{\text{II}}\text{OOXe}^{\text{II}}\text{H}$; (G) $\text{FXe}^{\text{II}}(\text{NF})\text{Xe}^{\text{II}}\text{F}$ in C_s symmetry; (H) $\text{ClXe}^{\text{II}}\text{FXe}^{\text{II}}\text{Cl}^+$ in D_{2h} symmetry.¹⁴⁶ Most of these compounds (A–G) are predicted to be unstable thermodynamically with respect to the substrates (eqn (12)–(17)), but they are genuine minima on the PES's. Calculated bond lengths are given in Å.

Xe–I, Xe–S, Kr–H, Kr–Cl, Kr–C.⁴³ Even Ar was forced into two new types of connections (Ar–H and Ar–F) in the unique FArH molecule.⁴⁴ With this discovery another noble gas has been conquered at the dusk of the old millennium.⁴⁵

This surfeit of completely new chemical connections has completely overturned our traditional view of Group 18 elements; it might have overwhelmed the public, which has seen people striving for 30 years to develop classical chemistry of Xe and Kr. New bonds also required more detailed understanding; insight into their nature was gained in numerous theoretical studies.⁴⁶

Some of new molecules may be considered as products of insertion of Ng atoms into common single bonds of quite stable molecules; for example, HXeOH^{47} may be viewed as a product of Xe's insertion in the O–H bond of water, $\text{HXe-C}\equiv\text{CH}^{48}$ into the C–H bond of acetylene, HXe-Br into the H–Br bond of hydrogen bromide *etc.* By analogy, $\text{FXeC}_6\text{F}_5^{49}$ might constitute the product of a smart photochemical reaction between Xe and C_6F_6 , but as far as we know, a similar reaction has never been attempted.

As the noble gas saga continues, even more unstable bonds (Xe–Se, Xe–Te, Xe–P, Xe–As, Xe–Si,⁵⁰ Xe–Ge, Xe–B, Kr–Br, Kr–Si, Kr–S, Ar–Cl *etc.*), if preparable, still await discovery. But, we think that there are still more challenges than just formation of the new bonds. We have here in mind the following specific reactions:



The first two reactions would lead to unprecedented alkyl and dialkyl derivatives of Xe^{II} . The next one would yield the first alkynyl Xe^{IV} compound (Fig. 5(c)). Eqn (15) and (16) in turn describe formation of the tetravalent and hexavalent Xe embedded in a mixed fluoride/non-fluoride environment (Fig. 5(a),(b)),⁵¹ while eqn (17) proposes the creation of the first binuclear peroxide derivatives of Xe (Fig. 5(e),(f)).⁵² Obviously, eqn (12)–(17) might be infinitely modified and extended to derivatives of C, N, S, Cl *etc.* Notably, studies of the thermal stability of the reaction products (on warming of the matrix) would show how realistic is the prospect of obtaining these and related species in larger quantities 'in the flask'.

2.7 A Xe atom is just a Lewis base

So far we have discussed compounds of Xe and Kr in their positive oxidation states, predominantly those of divalent Ng

elements. In all these connections Ng was bound to nonmetal(s). But could a (formally neutral) atom of a Ng element form a strong chemical bond?

A naked Xe⁰ atom is isoelectronic to I⁻, Te²⁻ and Bi³⁻; these anions are well known from a variety of inorganic connections. All have octet electronic structure (5s²5p⁶) and may formally act as Lewis bases. But there are two important quantitative differences which makes Xe⁰ qualitatively apart from the other ligands: (i) Xe atom carries no negative charge, so that most of the electrostatic stabilization on interaction with cations is lost, and (ii) its lone pairs are firmly contracted and lie very low in the energy scale (*i.e.* the ionization potential is high), which makes interactions with many cations very weak. So, telluride and iodide anions are very polarizable, easily ionizable and *very soft*, and they may be oxidized easily, while the Xe atom is *harder*, and it gets oxidized only by aggressive F^{0•} (from photochemical splitting of F₂).

The first hints that Xe *can*, however, bind to strong Lewis acids (positively charged metal centers) were obtained in 1992, and then in 1994, when XeM(CO)₅ (M = Cr, Mo, W) and XeBe^{II}O were observed.⁵³ The case of XeBe^{II}O is pretty straightforward: a coordinatively unsaturated Be^{II} cation exposes its empty (sp) hybrid, and it is ready to bind whatever Lewis base you provide.⁵⁴ So it will bind a Xe atom, too, and the binding energy is surprisingly high, over 0.3 eV. Many still say it is just an anomalous large dispersive interaction but it is probably fair to describe it as a weak chemical bond.⁵⁵

So matters rested till early 2000 when further confirmation was obtained that Ng atoms may bind firmly to Lewis acids at sufficiently low temperatures. In a series of landmark papers,⁵⁶ following their accidental discovery of ArAgCl, researchers from Vancouver showed that in supersonic jets of argon, Ng binds to isolated MX molecules (where M = Cu, Ag and Au, X = F, Cl, Br), and the binding energy was estimated to be as large as 0.25 eV for the Ar...AgF derivative.^{57,58} The work started from the most inert element (Ar) of the Ar...Kr...Xe set, and Kr and Xe were conquered in the following steps (2000–2004). To date, most of the molecules in the NgMX series (where M = Cu, Ag and Au, X = F, Cl, and Br, Ng = Ar, Kr, Xe) have been synthesized, and their fundamental properties measured and calculated.⁵⁹ The XeAuF molecule, synthesized only recently⁶⁰ (recollect: the inherently unstable Au^IF wasn't synthesized until as late as 1994⁶¹), has proved to be most strongly bound of all the complexes, and the Xe–Au^I bond energy was estimated to exceed 1 eV.⁶² No doubts may exist any longer on the genuine 'chemical bond' nature of this twin-noble connection.⁶³

But this was not the end of miracles, since the year 2000 was an excellent for Ng chemistry, as 1999 was for red wine. In the autumn of 2000—unexpectedly to the entire noble gas and fluorine community—the first isolable compound containing an Xe–metal bond entered the stage. It is black, its solutions in HF are deep red–black, and it has the most weird formula [Au^{II}Xe₄](Sb₂F₁₁)₂.⁶⁴ This species contains two rarities: a genuine divalent gold (which is very susceptible to disproportionation, and elsewhere known in less than ten complex fluorides) and Xe atoms acting as Lewis bases. Not just one but four Xe atoms coordinate the Jahn–Teller Au^{II} d⁹ center in a more-or-less square-planar fashion (Fig. 6)! This—admittedly

accidental—discovery opened the door to further developments. At the moment there are seven compounds of this kind known, and all but one of them contain gold (in the oxidation states I, II or III), the seventh containing mercury instead. These are: *cis*- and *trans*-[Au^{II}Xe₂](Sb₂F₁₁)₂, [(Au^{II}Xe)₂F](SbF₆)₃, [Au^{III}FXe₂](Sb₂F₁₁)(SbF₆) and [(F₃As)Au^IXe](Sb₂F₁₁).⁶⁵ They were synthesized in superacidic conditions (anhydrous HF/SbF₅) and they decompose with loss of gaseous Xe either below or only slightly above room temperature. The only compound of Hg has formula [Hg^{II}Xe](Sb₂F₁₁)(SbF₆), and it has been achieved *via* a direct solid state/gas reaction in a glass ampoule at 60 °C. In this compound Xe is so weakly bonded to Hg^{II} that when [Hg^{II}Xe](Sb₂F₁₁)(SbF₆) is immersed in anhydrous HF (and this 'superacidic' solvent is a poor base, indeed!), HF easily substitutes Xe as a ligand.⁶⁶

Crystal structures reveal the presence of regular Au–Xe bonds with lengths of 2.61 Å (for Au^I), 2.65–2.78 Å (for Au^{II}) and down to 2.59–2.62 Å (for smaller Au^{III}). These values are slightly larger than the one of 2.54 Å seen in the XeAuF molecule in the supersonic jets, but still well below the sum of the van der Waals radius of Xe⁰ and cationic radius of Au^I (2.95 Å). The single Hg–Xe contact is at 2.77 Å. In all these compounds Xe is attached to Au or Hg as a *terminal* ligand.

The reader will find other examples confirming strong affinity of Xe to Au and Hg in Sections 3.3, 3.6 and 3.10.

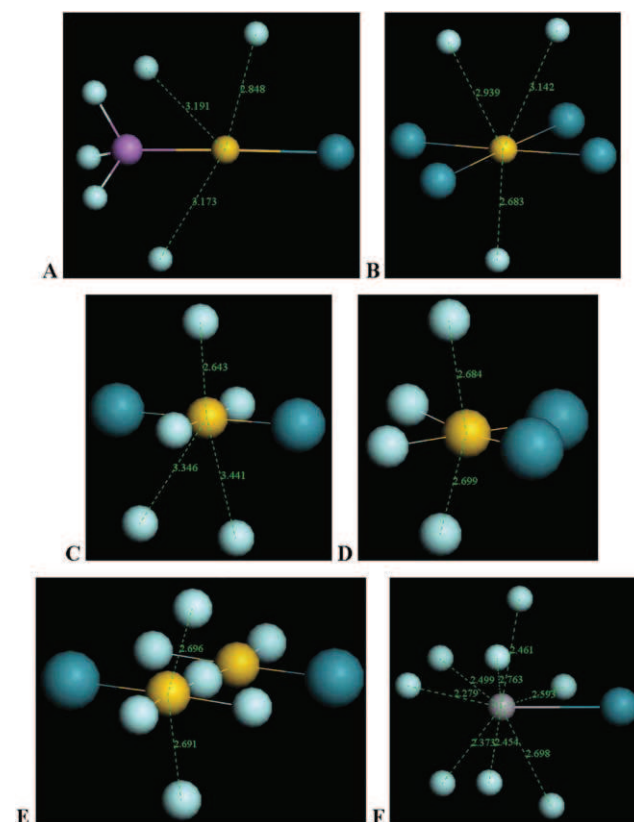


Fig. 6 The local coordination of Au and of Hg in three different compounds with the Xe ligand: (A) (F₃As–Au)(Sb₂F₁₁); (B) the triclinic form of (AuXe₄)(Sb₂F₁₁)₂; (C) *trans*-(AuXe₂)(SbF₆)₂; (D) *cis*-(AuXe₂)(Sb₂F₁₁)₂; (E) [(AuXe₂)₂F](SbF₆)₃; (F) (HgXe)(Sb₃F₁₇); Selected secondary contacts are shown (values in Å).

2.8 Why does Xe bind so strongly to selected cations

Noble gases gave us the ‘octet rule’, and its violations (‘hypervalence’), and it is clear that Seppelt’s compounds do not bend the octet rule (at least if one considers the number of electrons surrounding the Xe atom). Nothing is also weird about $\text{Xe}^0\text{-Au}^+\text{-F}^-$ and XeAuOH^{67} for they are isoelectronic with the known $\text{I}^-\text{-Hg}^{2+}\text{-F}^-$,⁶⁸ $\text{I}^-\text{-Tl}^{3+}\text{-O}^{2-}$,⁶⁹ and with hypothetical $\text{I}^-\text{-Pb}^{3+}\text{-N}^{3-}$ or $\text{Te}^{2-}\text{-Tl}^{3+}\text{-F}^-$. In all these compounds the negative charge on I^- or Te^{2-} ligand is reduced by interaction with cations, and similar depopulation happens to Xe in its connections; Xe attains partial positive charge *via* a σ bonding to the empty orbitals of a metal center. What is different here, however, is that a Xe atom can easily turn fully neutral, forget coulombic forces, and escape from the coordination sphere of a metal. All this happens without any *major* rearrangement of the electronic density, *i.e.* formally speaking, no redox reaction occurs. Evolution of Xe is additionally stimulated by the beneficial translational entropy term for gaseous Xe, which is pretty large at 298 K, over 0.5 eV atom^{-1} .

So, can one easily calculate the strength of the Xe–metal bond in a quantum mechanical calculation? Is this just a plain acid–base interaction, where a high acidic strength of the cationic center (often inversely proportional to the cation’s size) is crucial for strong interaction? The variety of molecules synthesized so far in matrices (where the Xe–Au^I bond proves to be the strongest, and the Xe–Cu^I one is much weaker), and the difficulties of getting isolable compounds beyond the scarce connections of heavy metals (Au, Hg), tell us that there must be more to it than that.

The sparkling advances in Ng–metal chemistry have stimulated theoretical chemists to examine Xe–metal bonding. And a relatively simple picture has been obtained. Even *prior* to the discovery of $[\text{Au}^{\text{II}}\text{Xe}_4](\text{Sb}_2\text{F}_{11})_2$ and of XeAuF , Pykkö *et al.* argued that Xe^0 may form very strong bonds to Au^{I} (in AuXe^+ , AuXe_2^+ and other species), with $\text{Au}^{\text{I}}\text{-Xe}$ bond energies being as large as 0.9–1.3 eV.⁷⁰ And at least 50% of the binding energy is provided by relativistic effects: contraction of an empty 6s orbital, and the better exposure of a more diffuse 5d valence set.⁷¹ The presence of the relativistic 6s orbital of Au is essential for the appreciable acid–base interaction between Au cations and neutral Xe to take place. Note that the first ionization potentials of Xe^0 and of Au^0 are not far from each other (12.14 and 9.23 eV, respectively). Provisionally adopting the Koopmans theorem, we might argue that the energies of the half-filled 6s orbital of Au and of the filled 6p orbital of Xe are close to each other. The match must be even better if the empty s orbital belongs to the positively charged (cationic) Au center; recollect, the most stable Au–Xe compounds are seen for divalent gold, Au^{II} . Thus, to a reasonable degree of approximation, the $\text{Au}^{\text{I}}\text{-Xe}$ interaction is guided by old good criterion of the sufficient match of energy and of spatial extent of interacting orbitals (provided these are *relativistically* determined orbitals in one’s calculations).

So it seems that in the rich world of chemical misalliances similarities continue to attract: hard Xe^{2+} still prefers hard F^- , soft Xe^0 adores softer Au^{2+} , while noble sticks to noble... And we sense that we will soon see more ‘cold’ Ng-containing

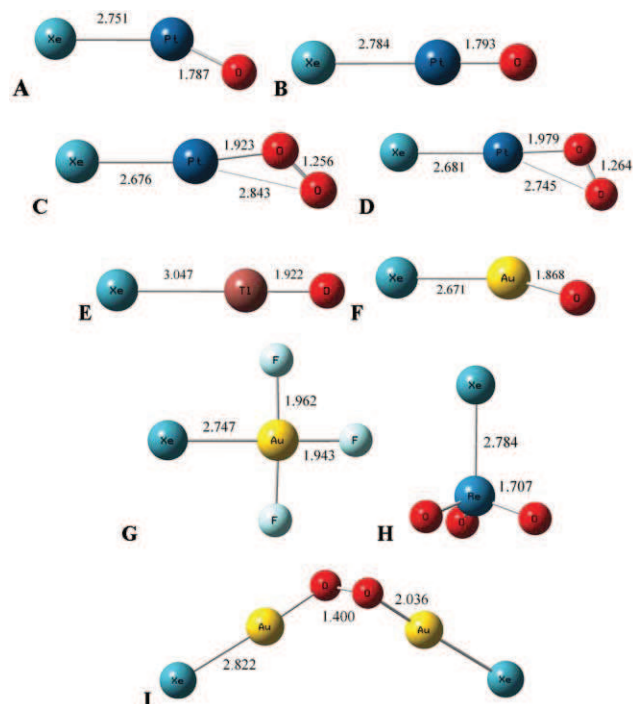


Fig. 7 The calculated molecular structures of novel hypothetical species: (A) $^1\text{XePt}^{\text{II}}\text{O}$ in C_s symmetry; the metal–Xe stretching mode, ν , is at 113 cm^{-1} ; (B) $^3\text{XePt}^{\text{II}}\text{O}$ (C_{2v}), $\nu = 105 \text{ cm}^{-1}$; (C) $^1\text{XePt}^{\text{II}}\text{O}_2$, $\nu = 124 \text{ cm}^{-1}$; (D) $^3\text{XePt}^{\text{II}}\text{O}_2$, $\nu = 123 \text{ cm}^{-1}$; (E) $\text{XeTl}^{\text{III}}\text{O}^+$ (C_{2v}), $\nu = 92 \text{ cm}^{-1}$; (F) $\text{XeAu}^{\text{III}}\text{O}^+$ (C_{2v}), $\nu = 147 \text{ cm}^{-1}$; (G) $\text{XeAu}^{\text{III}}\text{F}_3$ (C_{2v}), $\nu = 120 \text{ cm}^{-1}$; (H) $\text{XeRe}^{\text{VII}}\text{O}_3^+$ (C_{3v}), $\nu = 136 \text{ cm}^{-1}$; (I) $\text{XeAu}^{\text{I}}(\text{O}_2^{2-})\text{Au}^{\text{I}}\text{Xe}$ (C_2), $\nu = 87$ and 90 cm^{-1} .¹⁴⁷ Calculated bond lengths in Å are shown. All these compounds are bound (*i.e.* local minima) in the DFT/relativistic pseudopotential calculations, but most likely the M–Xe interaction is slightly underestimated. Correct assessment of their thermodynamic and kinetic stability requires use of more advanced methods explicitly including electronic correlation and relativistic effects.

molecules, like ones similar to NgAuF (for example $\text{NgM}^{\text{II}}\text{O}$ or $\text{NgM}^{\text{II}}\text{O}_2$, where $M = \text{Hg}, \text{Pd}, \text{Pt}$ (Fig. 7); NgMF_3 , NgMN or NgMO^+ , where $M = \text{Tl}, \text{Rh}, \text{Ir}, \text{Au}, \text{Ac}$), NgMOF_2 , Ng_2MO_2 and $\text{NgMO}(\text{O}_2^{2-})$ ($M = \text{Pb}, \text{Hf}, \text{Th}$), NgMF_5 and NgMO_2F ($M = \text{Bi}, \text{Ta}, \text{Pa}$), NgMO_3 ($M = \text{Te}, \text{W}, \text{U}$), NgMO_3^+ ($M = \text{I}, \text{Re}, \text{Pu}$), pretty exotic ones as $\text{Xe-Au}^{\text{I}}(\text{O}_2^{2-})\text{-Au}^{\text{I}}\text{-Xe}$ (Fig. 7), and more. A range of new compounds ‘in the flask’ will also be obtained, the number of cations expanded, and maybe even an isolable coordination compound of Kr ligand will be synthesized by solvent-free techniques—despite all difficulties which await experimental chemists on the way.

2.9 XeF_2 as a ligand to naked metal cations

Any lone pair is good for interaction with an empty orbital, the problem is just how strong the interaction may be. A nearly naked F^- ion, though itself a rarity (as in NMe_4F), is a pretty strong base. When F^- anion is coordinated to a powerful Lewis acid, say to BF_3 in BF_4^- , its potential for the secondary acid–base interactions is of course diminished (BF_4^- is considered a ‘weakly coordinating anion’). But when fluoride anions are firmly bound to the enormously electron-deficient

Xe^{II} in a neutral XeF₂ molecule, this secondary basicity is even more drastically reduced: the fluoride lone pairs become very contracted and lie deep down in the energy scale. Their basicity is then weak, and an appropriate strong Lewis acid is needed for a substantial interaction.⁷²

The coincidental formation of Ag(XeF₂)₂(AsF₆)⁷³ first achieved in 1991 (in the course of systematic attempts to oxidize Xe with Ag^I), has corroborated this general idea. The cationic Ag^I center is nearly ‘naked’ in Ag(AsF₆), as AsF₅ is a potent superacid—this makes the Ag^I cation here far and away a stronger acid than in Ag^IF. Ag(XeF₂)₂(AsF₆) is a colourless solid, where the Ag^I center is eight-fold coordinated by F atoms: four of these (at 2.466 Å) come from XeF₂, four others (at 2.732 Å) from AsF₆[−] (Fig. 8).⁷⁴ The Ag^I⋯FXeF interaction cannot be very strong, as (i) the Xe–F bond lengths (1.979 Å) resemble those found in the XeF₂ crystal (2.00 Å),⁷⁵ and (ii) crystals decompose in vacuum at a room temperature, losing XeF₂. Thus, Ag(XeF₂)₂(AsF₆) might well be called an ‘adduct’ by some.⁷⁶

Ag(XeF₂)₂(AsF₆) has been harbinger of a whole family of salts, including homologic Ag(XeF₂)₂(PF₆), made over a decade later; it can be prepared in anhydrous HF directly from its components:⁷⁷

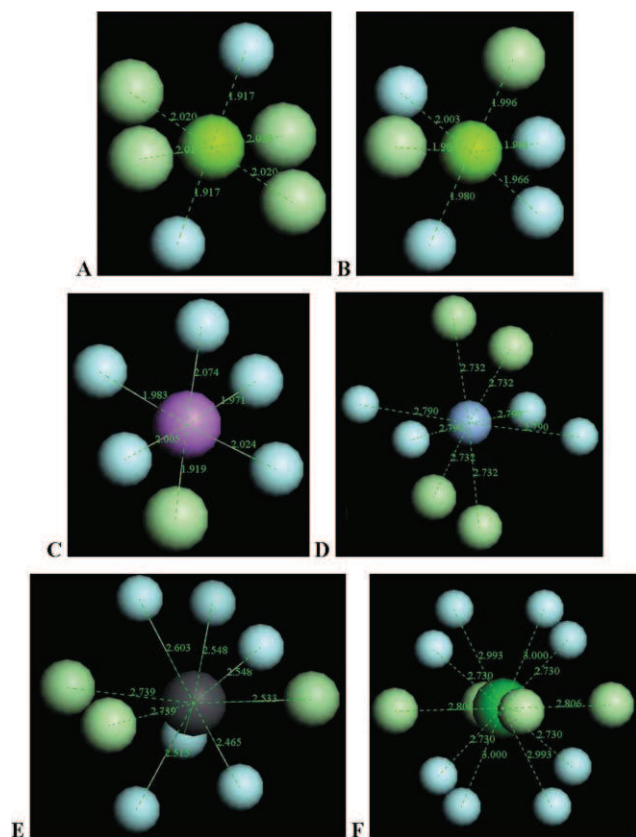
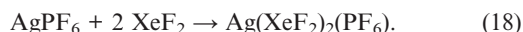


Fig. 8 The local coordination of metal centers in six different compounds with the XeF₂ ligand: (A) Mg(XeF₂)₂(AsF₆)₂; (B) Mg(XeF₂)₄(AsF₆)₂; (C) Li(XeF₂)₃(AsF₆); (D) Ag(XeF₂)₂(AsF₆); (E) Pb(XeF₂)₃(AsF₆)₂; (F) Ba(XeF₂)₅(SbF₆)₂. F atoms coming from MF₆[−] counterion are light green, those coming from XeF₂ are in light blue.

Here, XeF₂ ligand coordinates Ag^I in a similar fashion as in Ag(XeF₂)₂(AsF₆), but now Xe is forced into more asymmetric hypervalent bonding (Xe–F bond lengths are 1.983 and 2.040 Å). As the Ag⋯FPF₅[−] distance is now 2.859 Å, F atoms of XeF₂'s may coordinate Ag^I even more strongly than for the fluoroarsenate salt, with four Ag⋯FXeF contacts at 2.405 Å. This compound is more stable thermally, and it may be melted at 144 °C without a preceding loss of XeF₂! Interestingly, synthesis has failed of analogous MF₆[−] derivatives where M = Sb, Nb and Ta, proving that balance of the ligands' basicities is subtle.

In 1991, Bartlett's Ag(XeF₂)₂(AsF₆) set the stage, but for the next nine years it seemed like it would be a lone stranger. This prompted Žemva and co-workers to systematically investigate connections between XeF₂ and various salts of Group 2, Group 12, lanthanide elements and Group 1 (2000–2006).⁷⁸ Soon it turned out that number of XeF₂ molecules entering the adduct's formula may be as large as 3 (for example in M(XeF₂)₃(AsF₆)₂, where M = Pb, Sr, in Ln(XeF₂)₃(AsF₆)₃, where Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, in Ln(XeF₂)₃(BiF₆)₃, where Ln = La, Nd), 3 (for example in Ba(XeF₂)₄(AsF₆)₂·XeF₂),⁷⁹ 4.5 (in Ca₂(XeF₂)₉(AsF₆)₄) or even 5 (in Cd(XeF₂)₅(SbF₆)₂).⁸⁰ For some of these compounds the thermal stability exceeds that noted for the parent Ag(XeF₂)₂(AsF₆). These and related compounds (Table 4) are yet another testimony to the true ‘renaissance in Ng chemistry’ occurring right now.⁸¹

As mentioned above, an unusual thing about these compounds is that number of ligands per metal cation is quite large (recollect, both XeF₂ and MF₆[−] may still act as bridging ligands to more than one metal center!). The total number of ligands may be as large as 3 per Ag^I, Li^I or Cd^{II} cation, 4 per Mg^{II}, 4½ per Ca^{II}, 5 per Pb^{II} and Sr^{II}, 5½ or 6 per Ln^{III}, 6 per Mg^{II}, 6½ per Ca^{II}, and 7 per Cd^{II}! In some cases this leads to rare coordination numbers for a given metal cation: 8 for Ag^I, 9 for Ca^{II} or for the small Ho³⁺ cation, 12 for Ba^{II}. These CN's are larger than those typically seen in pure binary fluorides (6 for Ag^I, 8 for Ca^{II}, Ho³⁺ and Ba^{II}).

The metal–ligand polyhedra (resulting from coordination of XeF₂ and MF₆[−] ligands to metal centers) only exceptionally are isolated from one another (like for Mg(XeF₂)₄(AsF₆)₂). Typically they interconnect into larger ensembles, using as linkers either XeF₂ alone (Ca(XeF₂)₄(AsF₆)₂), or MF₆[−] alone (Mg(XeF₂)₂(AsF₆)₂), or simultaneously both XeF₂ and MF₆[−] ligands (Pb(XeF₂)₃(AsF₆)₂). The (formal) dimensionality of the network may be 1D (chains, for Cd(XeF₂)₄(AsF₆)₂ or

Table 4 List of compounds with XeF₂ as a ligand, for which the crystal structure has been determined. The coordination number (CN) of central metal cation is listed

Compound	CN	Compound	CN
Mg(XeF ₂) ₂ (AsF ₆) ₂	6	Mg(XeF ₂) ₄ (AsF ₆) ₂	6
Li(XeF ₂) ₃ (AsF ₆)	6	Cd ₂ (XeF ₂) ₁₀ (SbF ₆) ₄	7, 8
Ag(XeF ₂) ₂ (PF ₆)	8	Ag(XeF ₂) ₂ (AsF ₆)	8
Cd(XeF ₂) ₄ (AsF ₆) ₂	8	Ca(XeF ₂) ₄ (AsF ₆) ₂	8
Cd(XeF ₂) ₁ (BF ₄) ₂	8	Nd(XeF ₂) _{2.5} (AsF ₆) ₃	9
Sr(XeF ₂) ₃ (AsF ₆) ₂	9	Pb(XeF ₂) ₃ (AsF ₆) ₂	9
Ca(XeF ₂) _{2.5} (AsF ₆) ₂	9	Ca ₂ (XeF ₂) ₉ (AsF ₆) ₄	8, 9
Ln(XeF ₂) ₃ (BiF ₆) ₃ (Ln = La, Nd)	9 ?	Ba(XeF ₂) ₄ (AsF ₆) ₂ ·XeF ₂	12

double-chains, for $\text{Nd}(\text{XeF}_2)_{2.5}(\text{AsF}_6)_3$, 2D (for $\text{Ca}(\text{XeF}_2)_4(\text{AsF}_6)_2$) or 3D (for $\text{Ba}(\text{XeF}_2)_4(\text{AsF}_6)_2 \cdot \text{XeF}_2$). A great variety of structures is delivered by these seemingly uninteresting and usually colourless compounds.

XeF_2 is not the only Ng fluoride which forms adducts with metal fluorides. There is experimental evidence that KrF_2 may also serve as a ligand in various fluoroarsenate connections. Also, very recently, the very first adduct with XeF_4 (a very poor Lewis base), $\text{Mg}(\text{XeF}_4)(\text{AsF}_6)_2$, has been isolated.⁸⁰ XeF_6 , however, has problems in forming similar adducts, due to its significant Lewis basicity. Specifically, XeF_6 most frequently detaches a fluoride anion and forms XeF_5^+ or $\text{Xe}_2\text{F}_{11}^+$ salts. Use of large cations, such as Cs^+ , Rb^+ or Tl^+ (provided no Ti^{3+} forms) might help to solve this problem, but it has never been tested.⁸²

2.10 Brief stop for a summary: preferences of Xe for the chemical bond formation

The preferences of Xe for chemical bond formation are summarized using the Grand Periodic Table of Chemical Elements (Fig. 9(A)). Other known connections of Xe (not described here in detail), such as Xe_2^+ ,⁸³ $(\text{OUC})\text{Xe}_4$,⁸⁴ FXeBF_2 ,⁸⁵ OScXe_5^+ ,⁸⁶ PtNg , PtNg_2 and PdNg_2 ,⁸⁷ $\text{XeM}(\text{CO})$ ($\text{M} = \text{Ni}, \text{Co}$), and $\text{XeM}(\text{N}_2)$ ($\text{M} = \text{Ni}$),⁸⁸ NgMO ($\text{M} = \text{Cr} \cdots \text{Xe}$),

$\text{Ng} = \text{Ar} \cdots \text{Xe}$),⁸⁹ organometallic complexes of Re and Xe,⁹⁰ and XeTi_2 ,⁹¹ have also been considered in this figure. Affinity of XeF_2 to act as a ligand towards 'naked' metal cations has been summarized in Fig. 9(B). ($\text{Cr}^{\text{IV}}\text{F}_4$)(XeF_2)—known since 1992⁹²—and $(\text{Cr}^{\text{IV}}\text{F}_4)_2(\text{XeF}_2)$ ⁹³ have also been taken into account.

For compounds of Xe^{II} the importance of the classical 'diagonal line' within the p-block of the Periodic Table, is prevalent in Fig. 9(A). Any nonmetallic element which has its first ionization potential smaller than that of Xe (1070 kJ mol⁻¹, like I, S, P, Si, B *etc.*) meets problems when forming bonds to Xe^{II} ; such compounds are unstable at ambient temperature conditions due to the ease of redox reactions, but often achievable in matrices. For connections of Xe^0 with metals, importance of the relativistic stabilization is evident (Fig. 9(A)).

Fig. 10 gives a timeline for the synthesis of compounds containing new Ng–element bonds.

The list of people primarily responsible for these fascinating developments is very long. Taking the risk of omitting someone, we would like to specifically mention the laboratories of Hermann J. Frohn (Duisburg-Essen, Germany), Dieter Naumann (Cologne, Germany), Gary J. Schrobilgen (McMaster, Canada), Konrad Seppelt (Berlin, Germany),

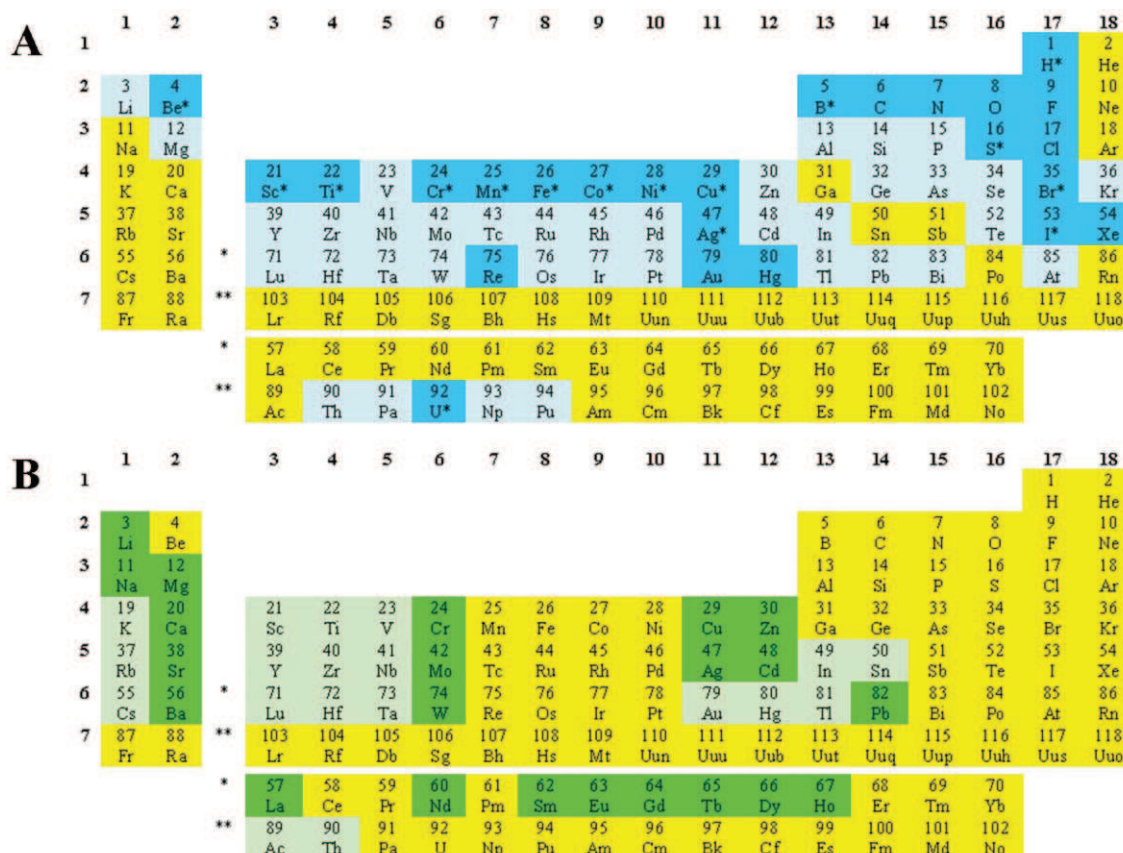


Fig. 9 (A) Preferences of Xe for chemical bond formation are shown in blue; element–Xe bonds detected only at low temperatures in the noble gas matrices or in supersonic jets, are marked with an asterisk at the element symbol. Light blue areas indicate regions where the Xe–element bonding could possibly be extended in the near future. (B) In green are shown elements whose 'naked' cations show affinity to the XeF_2 ligand. Light green fields mark elements where the XeF_2 –element interactions could possibly be detected in the coming years.

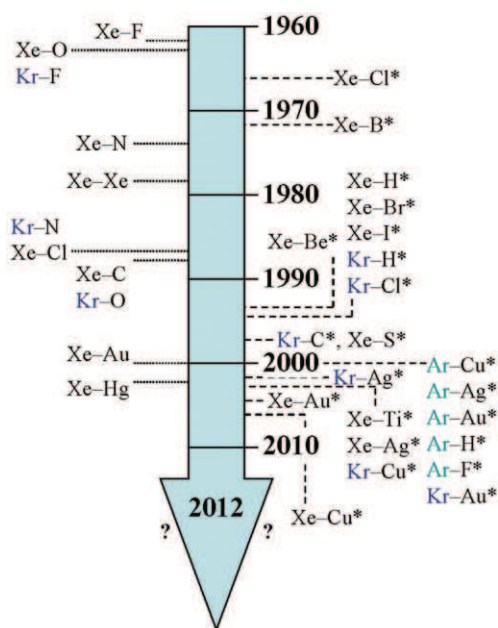


Fig. 10 The year of discovery of every new Ng–element bond (Ng = Xe, Kr, Ar) is shown along a time arrow; bonds detected only at low temperatures in noble gas matrices or in the supersonic Ng jets are marked with an asterisk. In 2012 the semicentennial will be celebrated for the discovery of the very first Ng compound.

Michael C. L. Gerry (Vancouver, Canada), Markku Räsänen (Helsinki, Finland) and Lester Andrews (Virginia, USA) (Fig. 11). Particular credit should also be given to Boris Žemva (Slovenia, Ljubljana), who has greatly advanced chemistry of XeF₂ as a ligand to naked metal cations in anhydrous HF, also studied by Neil Bartlett (Berkeley, USA), and John H. Holloway (Leicester, UK).⁹⁴ We pay special tribute to two theoreticians: Pekka Pyykkö (Helsinki, Finland), who predicted the existence of the strongly bound Au–Xe species, and to Benny J. Gerber (Irvine, US) who pointed out the stability of HArF, *before* these species were actually synthesized in the laboratories. Many young researchers, MSc students, PhD students and postdocs, have advanced this research field, working under guidance of their older colleagues.

Chemistry might have had its highs and lows during the last 200 years, but it seems that a relatively young noble gas chemistry has got only the highs. Much, so much has happened in the Ng chemistry during the last five decades; what else still awaits us around the corner...?

3 The bonds to come

3.1 Going in new directions: prediction of novel species

The advent of the ‘new chemistry’ of Ng’s has inspired many to search for even more unusual interatomic connections. Of course, this is easiest done *in silico*, as monetary costs are then relatively low, risk of explosion of inherently unstable molecules is eliminated,⁹⁵ and technical obstacles to unleashing one’s imagination virtually disappear. But there are also several interesting experimental reports on new species.



Fig. 11 Leaders of the laboratories predominantly responsible for the emerging Ng chemistry. (A) Hermann J. Frohn; (B) Dieter Naumann; (C) Gary J. Schrobilgen; (D) Konrad Seppelt; (E) Michael C. L. Gerry; (F) Markku Räsänen; (G) Boris Žemva; (H) Neil Bartlett; (I) Lester Andrews; (J) John H. Holloway; (K) Pekka Pyykkö; (L) Benny J. Gerber.

Theoretical and experimental research now goes in the following exciting directions:

(i) ability of the lightest Ng’s (He, Ne) for kinetically stable bonding has been estimated, and the results are encouraging; aside from the predicted OBHe⁺, SBHe⁺ and Al³⁺⋯He cations,^{96,54b} a range of neutral species like HHeF,⁹⁷ SBeHe,^{54b} XN = BeNg where X = F, OH, Ng = He⋯Ar,⁹⁸ and (H₃B)OBeHe⁹⁹ have been hypothesized; none of these species, except for He-solvated Al³⁺, has been observed so far in experiment;

(ii) triple bonds between Ar and N (in NgN³⁺) and between heavier Ng’s (Ar, Kr, Xe, Rn) and N (in O₃NgN³⁺), have been theorized;¹⁰⁰

(iii) obvious extensions of the chemistry of Ar and Kr have been analyzed, as exemplified by HArCl,^{46e} FNgSiF₃ where Ng = Ar, Kr,^{50d,e} and many more;

(iv) properties of linear Xe^{II}₂H₃⁺ (analogous to the well known fluoride derivative, which is bent on central F),¹⁰¹ XeH₂,¹⁰² and of many organoxenon derivatives¹⁰³ have been calculated;

(v) Xe-C_n where n = 2, 3, 5, 7, 9,^{104,105} have been discovered, and the issue of stability of a hypothetical 1D polymer (-Xe-C₂-),¹⁰⁶ was immediately addressed,¹⁰⁷

(vi) using the isoelectronic analogy between C₂ and BN, as the yet unknown and quite strongly bound species Xe-BN, Xe-NB, HXeNBH and HXeBNH¹⁰⁸ have been considered;

(vii) the suggestion that Xe might form an alloy with Fe or Pt has not been supported by theoretical calculations and experiments up to 150 GPa;¹⁰⁹ also, the ability of Xe to substitute Si in high-pressure modifications of quartz has been tested experimentally;¹¹⁰

(viii) significant involvement of Xe's empty d orbitals in bonding at high pressures has been postulated;¹¹¹ this might open new avenues for Xe's interaction with selected transition metals under megabar pressures.

We are by no means less courageous than other researchers, and we would like to propose here a selection of novel molecular and extended compounds of Xe. Several such attempts, based on a blend of chemically reasonable Lewis structures, chemical intuition and DFT calculations, will be discussed in the forthcoming sections.

3.2 Perchlorates, permanganates, nitrates

We begin our exploration with as yet unsynthesized connections of Xe^{II}, namely its nitrate, perchlorate and permanganate salts.

In Fig. 12 we show the DFT-optimized structures of Xe^{II}(NO₃)₂ (C₂), Xe^{II}(ClO₄)₂ (C₁) and Xe^{II}(MnO₄)₂ (C₂). All three molecules are local minima on the potential energy surfaces, as indicated by the absence of imaginary vibrational modes.¹¹² The Xe^{II}-O separation is in the 2.21–2.29 Å range, which may be compared with the value calculated for HXe^{II}OH (2.238 Å).

The Xe^{II}L₂ compounds where L = NO₃⁻, ClO₄⁻, MnO₄⁻, are 'classical' in the sense that Xe is bound to O atom, in a similar fashion as it does in HXe^{II}OH. Other hypothetical compositions of this type include FXe^{II}L where L = NO₃⁻, VO₃⁻, PaO₃⁻, ClO₄⁻, BrO₄⁻, MnO₄⁻, etc. These molecules are simply salts of the XeF⁺ cation with the anions of strong acids, similar to the known FXeOSO₂F. Supposedly, the complexity of these molecules excludes their facile formation in the noble gas matrices; it remains an open question if these molecules could form in condensed phases, and form at low temperatures *via* methathetic ligand-exchange reactions utilizing the known compounds of Xe^{II}.

3.3 What about peroxides?

The peroxide dianion (O₂²⁻), a derivative of hydrogen peroxide H₂O₂, is frequently found in chemical compounds. O₂²⁻ may be considered as an oxidized form of oxide (2 O₂²⁻) or as a reduced form of oxygen (O₂). Indeed, stability of peroxide connections of various metals may be limited by two¹¹³ processes, as outlined in eqn (19) for a peroxide of a divalent metal, M^{II}:

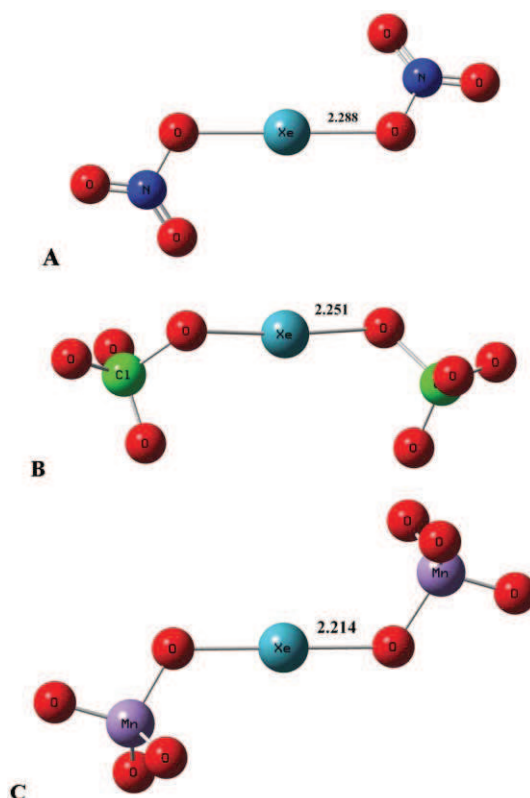
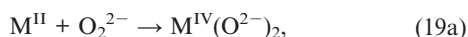


Fig. 12 The DFT-optimized structures of: (A) Xe^{II}(NO₃)₂, with the softest torsional vibration at 7 cm⁻¹, (B) Xe^{II}(ClO₄)₂, 20 cm⁻¹ and (C) Xe^{II}(MnO₄)₂, 13 cm⁻¹.

If M = Ba, the tetravalent core Ba^{IV} state is of course unaccessible, and the stability of BaO₂ is limited only by evolution of gaseous O₂ (eqn (19b)). But if M = Pb, intermolecular charge transfer readily occurs for a hypothetical Pb^{II}(O₂) thus leading to well known Pb^{IV}O₂ (eqn (19a)). For other metals, one or both processes may be operative.

Due to its valence structure (in particular due to the unfavourable spatial arrangement of two lone pairs on adjacent O atoms), the peroxide anion often meets difficulties in serving as a bidentate ligand at *one* cationic center; more frequently O's are unequally engaged in bonding (in molecular species), or each of them coordinates only one metal center in a polymeric extended structure (*i.e.* each O₂²⁻ is bridging two metal centers). Because of that, and of the more positive oxidation state of O for O₂²⁻ than for O²⁻, the basicity of the lone pair of O atom in O₂²⁻ is smaller than that of O²⁻. Therefore, metal centers coordinated by O₂²⁻ (for example Be^{II}) should be much more exposed to auxiliary ligands than for analogous oxide species, and the former should form shorter and stronger bonding to Xe⁰ than the latter. Unfortunately, to the best of our knowledge, no connections of Ng's containing peroxide anion have been observed so far.¹¹⁴

The potential of peroxide dianion for serving as a counterion in molecular complexes of Xe is illustrated in Fig. 13. Here, we have explored a series of neutral XeBeL complexes, where L = CH₂²⁻, NH₂⁻, O²⁻, and O₂²⁻. Note that the Xe-Be^{II} separation slightly decreases as the basicity of the counterligand decreases in the order: H₂C²⁻ > HN₂⁻ ~ O²⁻ > O₂²⁻.

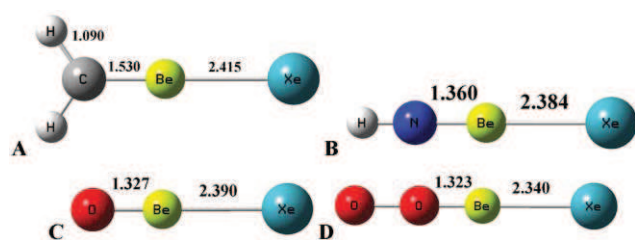


Fig. 13 The potential of the peroxide ion for stabilizing various connections of Xe with metal cations is illustrated, as exemplified by four Be^{II} species: (A) (H₂C²⁻)Be⋯Xe, the force constant for the Be–Xe stretching mode, *f*, is 0.194 [mDyn Å⁻¹]; (B) (HN²⁻)Be⋯Xe, *f* = 0.307; (C) (O²⁻)Be⋯Xe, *f* = 0.460; (D) (O₂²⁻)Be⋯Xe, *f* = 0.456.

A similar trend is seen when comparing oxide and peroxide connections of Pt^{II} (Fig. 6(A)–(D)) and for other model systems (not shown). O₂²⁻ might possibly link two XeAu^I units (as in Fig. 6(I)), and hopefully even bridge two XeF⁺ or XeH⁺ cations (Fig. 7(E) and (F)).

Although O₂²⁻ is more basic than two F⁻ counteranions, we think that chemistry of isolable solids containing Xe connected to transition metal cations (so far limited to fluoride-only environment) might be extended, with some effort, also to molecular peroxides with coordinatively unsaturated metal centers.

3.4 Unusual topological isomers

A chemist asked to assign oxidation states in a XeAuF molecule is likely to formulate it as: Xe⁰ → Au^I–F⁻¹. But imagine another valence isomer, Au⁻¹→Xe^{II}←F⁻¹: here gold would formally serve as a monovalent *auride anion* (pseudohalide isostructural to I⁻)—as found for the Cs⁺Au⁻ *semiconductor*. This idea may seem crazy at first; some might suppose that Au⁻¹–Xe^{II}–F⁻¹ should not survive even as an isolated ‘cold’ molecule, as it contains very strong oxidant (Xe^{II}) linked to very strong reducing agent (Au⁻¹). In other words, that Au⁻¹–Xe^{II}–F⁻¹ might too easily undergo an intramolecular redox reaction with the liberation of Xe^IF and Au⁰, by analogy to I⁻¹–Xe^{II}–H⁻¹ (for IXeH the ionic/neutral curve crossing happens at very short Xe⋯I distance, and excitation of several vibrational modes suffices to dissociate this molecule). However, the chemistry of Au is often surprising, and often more similar to that of H than that of I.¹¹⁵ This auride/hydride analogy gives more hope for existence of Au⁻¹–Xe^{II}–F⁻¹.

Indeed, our DFT calculations (Fig. 14(D)) allowed for the detection of a linear AuXeF as a genuine minimum on the potential energy surface for this triatomic system. Remarkably, the computed Au–Xe bond length is slightly shorter (by ~0.02 Å) than one predicted for the ‘common’ XeAuF isomer. A qualitatively similar result is obtained in MP2/SDD calculations for these species; here the bond length difference exceeds 0.03 Å. This result is interesting, but it requires confirmation in fully relativistic calculations. Fortunately, such calculations have actually been done, and they are described below.¹¹⁶

As predicted by Benkova and Sadlej,¹¹⁷ linear Au⁻¹–Xe^{II}–F⁻¹ is a local minimum, indeed. The equilibrium geometry

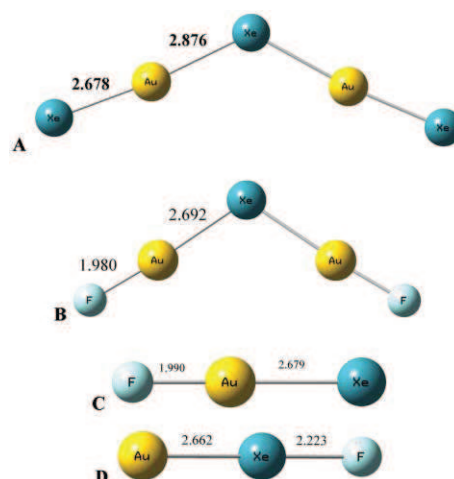


Fig. 14 Illustration of the relative weakness of the bonds formed by a bridging Xe ligand in two hypothetical species with the Au^I⋯Xe⁰⋯Au^I moiety: (A) [XeAu^I⋯Xe⁰⋯Au^IXe]²⁺; (B) FAu^I⋯Xe⁰⋯Au^IF, as compared to (C) the classical FAu^I⋯Xe⁰ with one terminal Xe ligand. Note, the Xe_{bridge}⋯Au contact is 2.88 Å for (A), as compared to 2.68 Å for the terminal Au–Xe bond. (A) and (B) are also interesting in context of possible weak aurophilic interactions. (D) The AuXeF isomer—see section 3.4; note, the Au–Xe bond length is slightly shorter for (D) than for (C).

reveals the surprisingly short Au–Xe bond length of 2.556 Å and the Xe–F bond length of 2.136 Å. The Au–Xe separation is again slightly shorter than that calculated by these authors for the XeAuF isomer (2.564 Å). As the predicted Ng–Au bond length (for NgAuF, Ng = Ar, Kr) is consistently shorter (by ~0.007 Å) than the actual experimental values, one may suppose that the AuXeF isomer will indeed deliver the shortest Au–Xe bond ever observed.

Benkova and Sadlej also predict that AuXeF will be thermodynamically stable towards decomposition to Au, Xe and F radical (by +1.15 eV at the MP2 level) but unstable with respect to AuF and Xe (by –1.67 eV). Anyway, it should exhibit significant kinetic stability, as the calculated harmonic frequencies for the Xe–Au stretching and for the molecule’s bending are ~30% larger than their counterparts calculated for the XeAuF isomer.

The remarkable stability of the isolated AuXeF molecule will certainly be violated when other similar molecules are in its vicinity, thus opening new intermolecular channels for decomposition (dimerization *via* electric dipole/dipole interactions *etc.*). But it might be dramatically enhanced again if external pressure is applied, thus preventing such decomposition. This will be discussed again in section 3.10.

3.5 Xe⁰ as a bridging ligand between two metal centers

In all known compounds of Xe⁰ with transition metals, be these molecules or extended solids, the Xe is attached to a metal cation as a *terminal ligand*. So far Xe has never been seen to bridge two metal centers, and there are sound reasons for it: the M⋯ligand⋯M bridging bonds are always longer, less covalent and weaker than M⋯ligand terminal bonds; they are simply more fragile, and less likely to appear even in Xe-poor systems. All bridging bonds behave this way. The other

obstacle, usually not experienced by typical negatively charged ligands, is that zerovalent Xe shares some electron density with neighbouring cations, and itself becomes *positively* charged. Thus, the $M^{\delta+}\cdots Xe^{\sigma+}\cdots M^{\delta+}$ configuration is not favoured from a purely electrostatics point of view.

Thus, even some ligand-hungry systems, like polymeric MF_5 ($M = Bi, Sb, Nb, Ta, U, Ru$ etc.) and other oxofluoride derivatives with five ligands to a metal cation, like UOF_4 , ReO_2F_3 etc., might form adducts with neutral Xe to create the hexacoordinated metal centers with Xe as a *terminal* ligand. An analogous situation is likely to persist for other strong Lewis acids like AuF_3 : a hypothetical $Au^{III}F_3Xe$ will form isolated AuF_4^- -like units (if the redox reaction leading to Xe^{II} and Au^I does not intrude) without the $Au\cdots Xe\cdots Au$ bridges. The same type of reaction product will presumably appear for Xe attached at very low temperatures to IF_3 , or to BF_3 .

Could, despite these problems, new molecular or extended compounds be crafted which contain $M\cdots Xe\cdots M$ bridges? Simplistic calculations show that careful approach to the Xe-poor systems might help to bring Xe bridges to life in the matrices¹¹⁸ or in molecular jets, as exemplified by $FAu^I\cdots Xe\cdots Au^IF$ (Fig. 14(B)), but there is still the risk of isomerization to $[FAu\cdots FAu\cdots Xe]$. The Xe-rich systems, like $[XeAu^I\cdots Xe\cdots Au^IXe]^{2+}$, come up less strongly bound in calculations (Fig. 14(A)), and should be searched for in the gas phase for they must be very sensitive to (even inherently weak) Lewis bases.

Utilization of external pressure brings better prospect for both terminal ($M\cdots Xe$) and the $M\cdots Xe\cdots M$ bridging bonds. this will be outlined in sections 3.6–3.10.

3.6 Pressure as an independent variable

'Ours is a material(s) world, but remarkably, we are still unable to predict the chemical composition, the crystal structure and the physical properties of most known, and all emerging new materials'.¹¹⁹ It must be honestly admitted that we have very limited knowledge of phase diagrams even for binary connections of chemical elements, as far as the very broad range of achievable temperatures and pressures is considered. The range of attainable pressures now extends to well over 3 Mbar (3 million atmospheres), laser heating can simultaneously provide temperatures above 5000 K. The behaviour of matter at such harsh conditions is usually drastically different from that known to us from the ambient world.¹²⁰

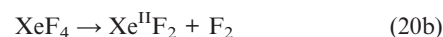
The simplest binary fluorides of Xe, XeF_2 , XeF_4 and XeF_6 have never been exposed to large pressures, largely due to technical problems with strong oxidants inside the diamond anvil cell. What might happen at one or two million atmospheres to, say, XeF_4 ? Let us now see what is delivered by a squeezing-in-computer experiment.¹²¹

Unit cells of XeF_4 at ~ 1 atm (experimental) and at 200 GPa = 2 million atm (computed) are compared in Fig. 15. At ambient pressure Xe^{IV} adopts square planar geometry, and is reluctant to secondary bonding. The coordination number of Xe equals 4, with nearly identical Xe–F bond lengths of 1.900–1.914 Å. The electronic bandgap is *ca.* 3.5 eV, and XeF_4 is colourless. At 200 GPa the Xe–F bonds get shrunk to 1.894 Å, and *eight* new short contacts at 2.297 Å appear. The Xe–F bonds of XeF_4 prove to be extremely incompressible; this may

be traced back to the protective effect of lone pairs on F and on the Xe center, which prevent molecules from being squeezed one into another.¹²²

The shortest F \cdots F distance at 200 GPa is less than 2 Å; the coordination environment of Xe is then 4 + 8. The direct electronic band gap is now as small as 1.7 eV, therefore XeF_4 should be green at this pressure.

But how much would the chemistry of XeF_4 change under high pressure? Consider for example the following reactions:



The first process (autodissociation, eqn (20a)) is forbidden by *ca.* 7.0 eV in the gas phase (value for a non-interacting $Xe^{IV}F_5^-$ anion/ $Xe^{IV}F_3^+$ cation system; electrostatic stabilization will obviously decrease this value for a solid); the second process is not permitted by 0.7 eV; the third reaction is inhibited by a mere 0.2 eV at ambient pressure.¹²³ Albeit these reactions are thermodynamically forbidden at ambient pressure, they might occur at sufficiently large pressures. For example, reaction (20a) is analogous to autodissociation of CO_2 (into CO^{2+} and CO_3^{2-}), which has been observed experimentally at elevated pressure; an analogous process might happen for a compressed XeF_2/XeF_6 mixture, leading to XeF^+ and XeF_7^- ; eqn (20b) resembles a pressure-activated decomposition of thermodynamically unstable CuH , while an analogue of eqn (20c) has been detected for N_2O (*i.e.* disproportionation to N_2^0 and $(N^{III}O^+)(N^VO_3^-)$). The outcome of squeezing XeF_4 is as yet unknown...

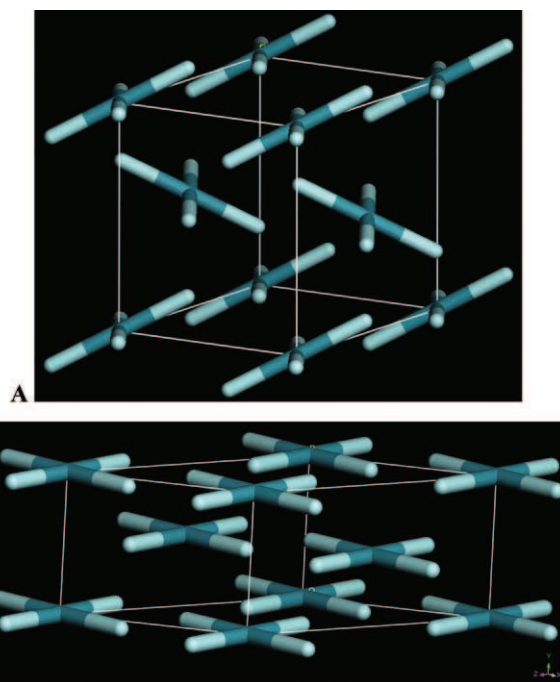


Fig. 15 Comparison of unit cells of XeF_4 (A) at ~ 1 atm (experimental) and (B) at 200 GPa (computed). (A) $a = 5.05$ Å, $b = 5.92$ Å, $c = 5.77$ Å, $\beta = 99.6^\circ$; (B) $a = 4.53$ Å, $b = 3.39$ Å, $c = 6.42$ Å, $\beta = 134.9^\circ$.

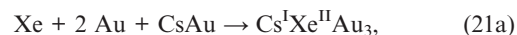
Application of high pressures may be profitable not only for the well known compounds of Xe. As we will see in the forthcoming sections, it also offers an exciting chance for the extension of the Ng–nonmetal and Ng–transition metal chemistry to entirely new elements or structures. Importantly, some of these compounds might form metastable polymorphs upon decompression, not achievable through other routes.

3.7 Metallic alloys of Xe

As Xe is squeezed, it undergoes martensitic transformation from the fcc to the hcp structure and becomes metallic at *ca.* 132–150 GPa. A natural question arises if at these conditions Xe might form alloys with other metallic elements (very few *are not* metallic at 2 Mbar) or compounds. Elements close to Xe in the periodic table with similar energies of valence orbitals, like Te or I, are obvious elements of choice. Due to the strong Pt–Xe, Au–Xe and Hg–Xe interactions discussed in the previous sections, platinum, gold and mercury are interesting options, as well. The XeAu₂ and XePt are two particularly reasonable stoichiometries, which contain Au^{−1} and isoelectronic Pt^{−2}, as far as ionic formulation is enforced.¹²⁴ Such stoichiometries (i) favour natural Xe^{δ+}TM^{σ−} polarization and (ii) utilize the enhanced electron-accepting abilities of the relativistic 6s orbitals of Au and Pt.

As far as simple compounds are concerned, the ability of CsI or BaTe (in which both anions and cations are isoelectronic

with “Xe₂”, and are metallizable at, respectively, 115 GPa¹²⁵ and 200 GPa),¹²⁶ and of CsAu (isostructural to CsI) to form alloys with Xe, are worth theoretical analysis. Xe might also merge into more complex (ternary and higher) systems, as exemplified by eqn (21):



Let us concentrate on the Hg–Xe system. A Hg atom in a sense resembles the Xe atom to the largest extent among all TM atoms; both elements have a closed or quasi-closed shell (at an even-electron configuration), a pretty large HOMO–LUMO gap (*i.e.* they are less polarizable than the neighbouring elements in the same period), and they only weakly interact with other atoms of the same kind (recollect an anomalous property of Hg—it is *liquid* at normal conditions, while all its elemental neighbours are solids).

Above 45 GPa Hg adopts the hcp structure;¹²⁷ Xe does too, over the whole broad pressure range beyond 70 GPa.¹²⁸ Therefore, the chance exists that these elements might form an hcp alloy at pressures close to or exceeding 70 GPa. Actually, preliminary DFT calculations for HgXe¹²⁹ (Fig. 16) point to something qualitatively different: the novel HgXe binary compound should indeed form at similar pressure of 75 GPa, but the HgXe product prefers the CsCl structure over ordered variants of the hcp arrangement. The HgXe lattice is modestly

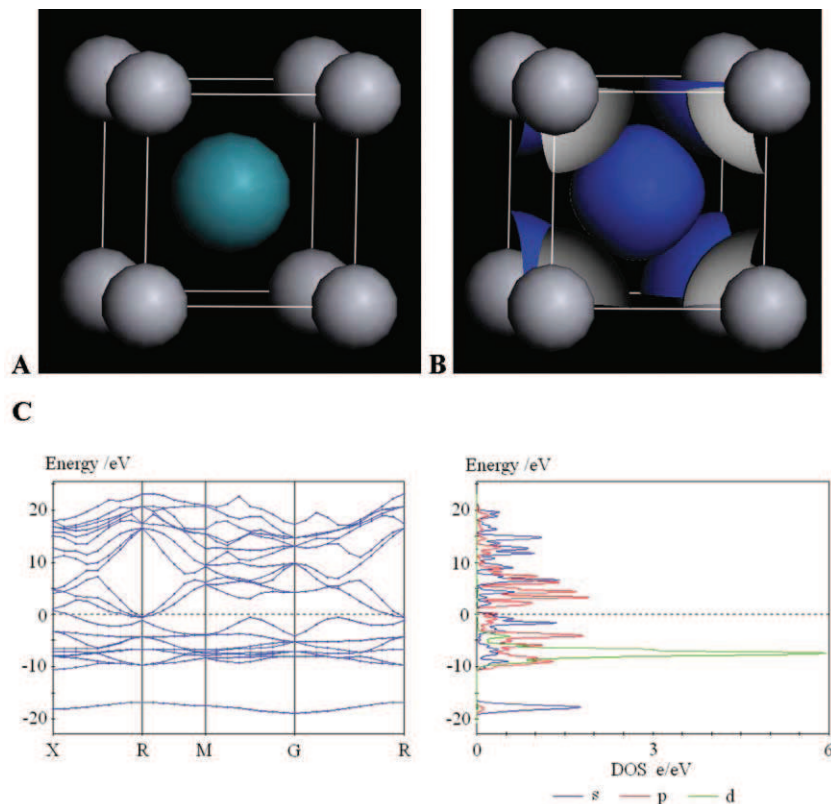


Fig. 16 (A) Unit cell of HgXe at 50 GPa from DFT calculations (the CsCl structure, $a = b = c = 3.49 \text{ \AA}$); Hg – gray, Xe – blue balls. (B) electron density integrated over band No. 10, one of the bands which cross the Fermi level; density isovalue 0.03 e \AA^{-3} ; (C) electronic band structure and density of states of HgXe at 50 GPa.

polarized, with a partial positive charge residing on Xe, and a negative one on Hg. Despite its slightly ionic character, HgXe is metallic even when decompressed to 50 GPa. Electron density at the Fermi level comes mainly from s and p states, and Xe sublattice participates in metallic bonding on a nearly equal footing with Hg (Fig. 16).

Concluding this section we would like to emphasize that Xe is predicted to form a *metallic amalgam* with mercury at pressures as moderate as three fourths of a megabar, although Xe alone is not yet metallic at this pressure. The HgXe compound might be forerunner for a whole family of analogous alloys. It would be interesting to check if the alloy formation of Xe could be extended to the AuTl and PtPb compositions, both isoelectronic to “Hg₂”.

3.8 Reversing of the redox reactions

KrF₂, XeF₂ and other binary fluorides of Xe are relatively unstable; they decompose thermally with the liberation of F₂ and Ng (or in some cases of a lower fluoride). NgX₂ compounds, where Ng = Xe or Kr, and X = Cl, Br, I, have never been isolated. Obviously, in this family of compounds, XeCl₂ would be the least and KrI₂ the most thermodynamically unstable one. But it is a common experience for an inorganic chemist that many species may be oxidized more easily when the pressure of the oxidant is increased. Therefore we think that the synthesis of selected NgX₂ compounds might be targeted at elevated pressure; they could be accessed directly from Ng and elemental halogens, or reactive halogen precursors.

To test the viability of this approach, we have performed DFT calculations for bromine in the *Immm* structure (adopted >80 GPa, with dissociated Br₂ molecules), Xe in the hcp structure (also preferred in this pressure range over fcc), and hypothetical XeBr₂ in its presumed XeF₂ structure (as illustrated in Fig. 17). The XeF₂ structure type might favour formation of XeBr₂; here pressure allows for compression of the (otherwise unstable) Xe–Br bonds and may prevent the Br[−]-to-Xe^{II} electron transfer and the concomitant defragmentation of the molecule. In other words, in full analogy to an ambient pressure reaction involving F₂, also Br₂ might oxidize Xe⁰ to Xe^{II} if the external pressure is sufficiently large.

Indeed, our DFT calculations indicate that at 80 GPa XeBr₂ has enthalpy of formation (from hcp Xe and the elemental phase of Br) of *ca.* −0.4 eV molecule^{−1}. This suggests that XeBr₂ might be formed directly from the elements at pressures lower than 80 GPa, *i.e.* from ccp Xe and Br₂ in its molecular phases.¹³⁰

Describing the crystal structure of XeBr₂ (relaxed back from 80 to 50 GPa) as one analogous to that of molecular XeF₂ would, however, be misleading; it is more fair to say that XeBr₂ is in fact a MoSi₂-type polymer (Fig. 15) with each Xe surrounded by 8 equidistant Br atoms (at 2.933 Å); the XeBr₈ unit propagates in the *a* and *c* crystallographic directions; each Xe forms two more short Xe–Br contacts (at 3.032 Å) along the *c* axis. The XeBr₂ compound is still a narrow-gap semiconductor at 50 GPa, indicating a modest inter-cell orbital overlap.

The anticipated formation pressure of semiconducting (ionic) XeCl₂ should of course be much lower than for

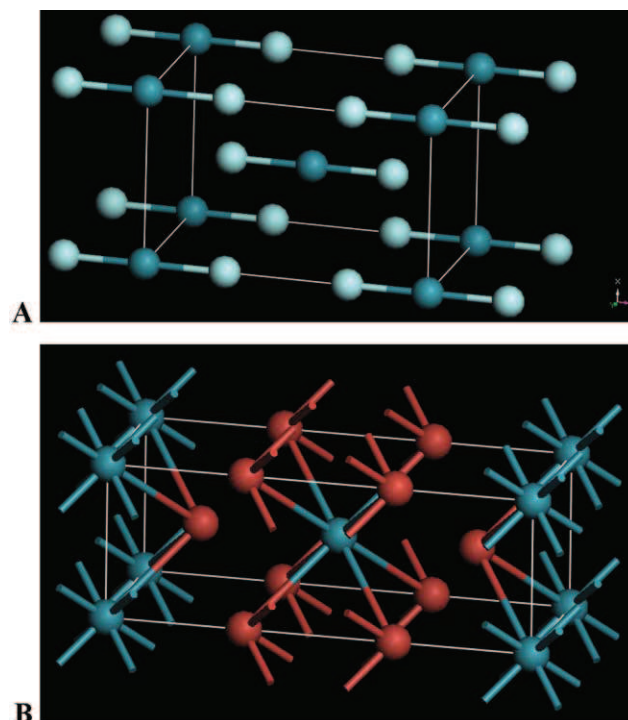


Fig. 17 (A) Unit cell of XeF₂ at ~1 atm (experimental), $a = b = 5.05$ Å, $c = 5.77$ Å; (B) unit cell of XeBr₂ at 50 GPa (computed), $a = b = 3.44$ Å, $c = 9.34$ Å. Xe – dark blue, F – light blue, Br – red-brown balls. Structure of XeBr₂ (closer to MoSi₂-type) may be derived from that of XeF₂ by slightly moving halogen atoms along the crystallographic *c* axis (symmetry is preserved).

XeBr₂ (*i.e.* of the order of ~10 GPa), because Cl₂ is a much stronger oxidant than Br₂, and since Xe^{II}–Cl bonds are known even from the 1 atm world. And maybe even KrCl₂ and XeAu₂ (with its partial Xe^{II}(Au[−])₂ character) might be achieved when the pressure is large enough?

It is an interesting issue whether the novel high-pressure NgX₂ phases would be quenchable, *i.e.* if they could be decompressed to the ambient pressure while remaining metastable. Unfortunately, the XeF₂-type structure of XeBr₂ doesn't seem to support metastability to a great extent: a simple symmetry-preserving Br[⋯]Br pairing distortion within the bromine sublattice may easily result in the electron transfer between the potential energy surfaces of the reactants and of the products, and in the subsequent appearance of the Xe⁰ and Br₂⁰ sublattices.

These promising theoretical results now await being confirmed—or refuted—in experimental studies.

3.9. Forget solvents, just put the squeeze on

As emphasized in section 2.7, all reactions leading to complexes of Au with Xe ligands were realized in anhydrous HF. As HF is still a stronger Lewis base than Kr, attempts to prepare analogous complexes of Kr have failed. Notably, as Au–Xe complexes are on the verge of thermodynamic stability, Seppelt *et al.* have observed that the thermal stability of selected metal–Xe complexes in the HF/SbF₅ solvent may be significantly increased by applying a very modest pressure of

gaseous Xe (10 atm). Obviously, this is an excellent prognostic for synthesizing a very rich spectrum of new Xe compounds at pressures exceeding 1 GPa ($=1 \text{ tonne cm}^{-2} = 10 \text{ thousand atm}$), even in systems where metal cations are not as 'naked' as in, say, $\text{Au}(\text{Sb}_2\text{F}_{11})_2$.

Complete elimination of the anhydrous HF solvent in the high-pressure solid state synthesis opens an exciting possibility to synthesize the first metal–Kr and possibly even metal–Ar bonds. Recollect, the $\text{Xe} \rightarrow \text{Kr}$ substitution costs less than 0.5 eV per metal–Ng bond. Enthalpic effects of this size are usually overcome in the pressure range of 50–100 GPa, which is 3–4 times less than the actual record of static pressures achieved in the laboratory. In such preparative techniques (which up to 50 GPa works even for substantial volumes of reagents, $\sim 1 \text{ cm}^3$), the only Lewis bases which could still compete with Ng come from the counteranions of the parent compounds. It is therefore possible that polymerization (leading to new more compact polymorphs of, for example, $\text{Au}(\text{Sb}_2\text{F}_{11})_2$) will still constitute an obstacle for the attachment of the light Ng atoms (Kr, Ar). An additional difficulty here is that the formation of Ng complexes at room temperature or at lower temperatures may be very slow and difficult to detect in the timescale of experiment. When reagents are firmly compressed, and solvent is not present, one typically pays a price of increased kinetic barriers to reactions. Applying the standard method of laser heating may not help, as it works *against* the formation of the thermally unstable Ng complexes. Therefore, there might be only a very narrow niche of the (p, T) conditions which favours formation of this fascinating class of solids.

No matter how difficult it would be to detect this (p, T) regime, it is certainly worth trying, as a beautiful extension of Xe chemistry to its lighter homologues might be achieved this way.

3.10 Keep electron count, decrease dimensionality

Increasing the oxidation state of an element in binary connections is often connected to the decrease of dimensionality of its compounds. Take for example fluorides of Ru: RuF_3 is a 3D solid, RuF_4 forms puckered sheets and is quasi-2D, RuF_5 is quasi-1D (it is a molecular tetramer *i.e.* finite polymer; the related SbF_5 polymerizes into an infinite 1D chain), while RuF_6 is 0D (isolated molecules forming a molecular crystal). The idea arises to use Xe (a formally zerovalent ligand) to decrease the electronic dimensionality of various solids, while preserving the oxidation state of a metallic element. Deliberate manipulation of electronic dimensionality of an extended network, while preserving the electron count, might be indispensable for achieving desired electric and/or magnetic properties of a solid.

This concept will be illustrated using $\text{Hg}^{\text{II}}\text{F}_2$ as an example. Binary HgF_2 adopts the cubic CaF_2 structure, with eight-coordinated Hg^{II} forming an isotropic three-dimensional fcc network (Fig. 18(A)). Upon attachment of a large Xe ligand Hg^{II} is expected go six-coordinate, forming HgF_2Xe in the tetragonally-distorted RuO_3 structure (Fig. 18(D)).¹³¹ This compound is two-dimensional, as far as the Hg–F sublattice is considered. The progressive attachment of another Xe ligand might allow hypothetical HgF_2Xe_2 (Fig. 18(F)) to

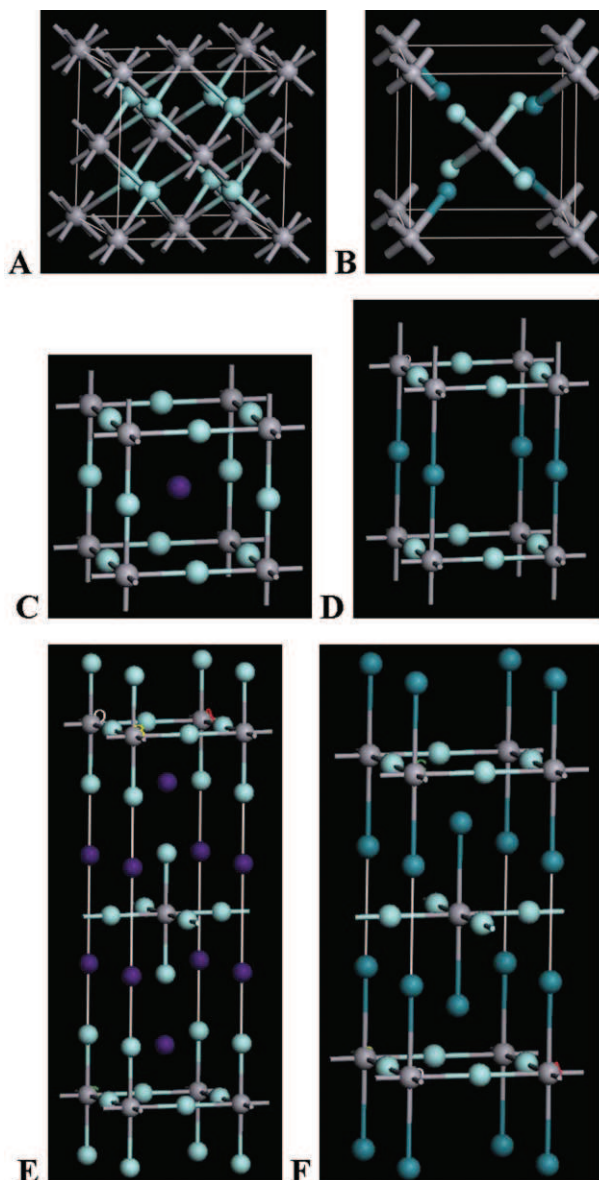


Fig. 18 Unit cells of several known and hypothetical (*) fluorides of Hg at 10 GPa: (A) cubic $\text{Hg}^{\text{II}}\text{F}_2$, $a = b = c = 5.55 \text{ \AA}$; (B) $\text{Hg}^{\text{II}}\text{F}_2\text{Xe}_2^*$ in an ordered variant of the Hg_4Pt structure, $a = b = c = 6.36 \text{ \AA}$; (C) $\text{CsHg}^{\text{II}}\text{F}_3$ perovskite, $a = b = c = 4.50 \text{ \AA}$; (D) $\text{Hg}^{\text{II}}\text{F}_2\text{Xe}^*$, $a = b = 4.27 \text{ \AA}$, $c = 5.87 \text{ \AA}$; (E) $\text{Cs}_2\text{Hg}^{\text{II}}\text{F}_4$ in the K_2NiF_4 structure, $a = b = 4.45 \text{ \AA}$, $c = 14.10 \text{ \AA}$; (F) $\text{Hg}^{\text{II}}\text{F}_2\text{Xe}_2^*$ in the PbF_4 structure, $a = b = 4.70 \text{ \AA}$, $c = 9.87 \text{ \AA}$; Hg – gray, F – light blue, Xe – blue, Cs – violet balls. Known compounds were optimized in their experimental structures for $p = 10 \text{ GPa}$. Note that electronic dimensionality of the Hg–F network has been reduced from three (for HgF_2) to two (for compounds containing Hg–Xe bonds) and that structures (C) and (E) are analogous to, respectively, (B) and (D), with vacancies at the Cs sites.

retain two-dimensionality, by forming a variant of the PbF_4 -type structure (note, this structure type is typical for a *tetravalent*, and not a *divalent* element in the fluoride environment!). Therefore, the entire transformation:



might hopefully be realized at a sufficiently large pressure.

Some might argue that an identical transformation might be easily achieved by use of the weak CsF base; indeed, CsHgF₃ and Cs₂HgF₄ are known, and they adopt a perovskite¹³² and a K₂NiF₄ structure,¹³³ respectively. However, the bonding nature in these solids is different than one of the HgF₂Xe_n compounds: CsHgF₃ is clearly a 3D material, but □₁HgF₂Xe (where, □ stands for a vacancy) is 2D, as apical Xe⁰ forms much weaker bonding to Hg^{II} than does F⁻. HgF₂Xe₂ is a layered compound, as well, with [HgF₂] sheets sandwiched between puckered [Xe₂] layers.

The as yet unexplored Hg–F–Xe ternary system may offer still more surprises; HgF₂Xe₂ might also adopt an ordered variant of the distorted Hg₄Pt structure (Fig. 18(B)). This compound is best written as (HgXe₄²⁺)(HgF₄²⁻) and is electronically zero-dimensional, with its isolated HgXe₄²⁺ cations and HgF₄²⁻ anions.

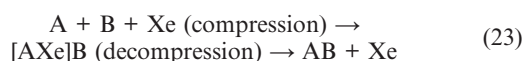
As our calculations show, the attachment of two Xe atoms to HgF₂ with the simultaneous formation of any of the structures considered, is not favoured thermodynamically at pressures up to 10 GPa. However, the molar volume of the K₂NiF₄-like product is smaller (by nearly 6%) than for the HgF₂ and 2 Xe reactants together. This means that formation of the ternary phase should be favoured at elevated pressure (linear tangent method gives estimated value of ~15 GPa). As decreasing the molar volume is a major advantage in achieving a better enthalpic score at elevated pressure, other structure types (with even better packing) may pop out at pressures even smaller than 15 GPa.

A compound with the HgF₂Xe₂ stoichiometry might open a series of novel ternary Xe-containing solids; alternatively, the Xe/HgI₂ phases may be considered as the size of Xe⁰ is similar to that of I⁻ (the HgI₂Xe_n phases would then adopt the compact structure types). Use of metals other than Hg should also be taken into account.

We feel that these theoretical results are very encouraging, and they show hopeful prospects for the high-pressure synthesis of novel compounds with metal–Ng bonds, even those containing Kr and Ar.¹³⁴

3.11 Xe as a mediator of formation reactions of novel chemical compounds

Xenon's ability to form adducts with chemical compounds, described in the sections above, might be utilized for the synthesis of new connections between the elements (*i.e.* such stoichiometries as have not yet been synthesized and are unknown at ambient conditions). Consider a direct reaction of formation of the AB compound from the A and B elements. If AB is kinetically unstable at $p = 1$ atm, and various side reactions may occur, the direct synthesis may be very difficult. In an alternative path, Xe might be used to form an intermediate phase [AXe]B upon compression of reagents. The intermediate phase might subsequently decompose to Xe and the desired AB product upon careful decompression:

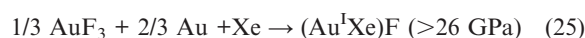


We will now illustrate this exciting prospect utilizing the classical case of a binary gold monofluoride, AuF.¹³⁵

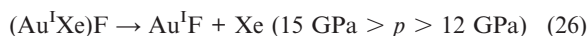
Scarce molecules of Au^IF in the gas phase were first synthesized in 1994 and unequivocally characterized as late as in 2000.¹³⁶ However, binary Au^IF in the solid state is still unknown.¹³⁷ The main reason for this striking lack of stability is in the propensity of Au^IF towards disproportionation into the very stable Au^{III}F₃ and elemental Au. Our preliminary calculations show that this behaviour might be reversed under high pressure. The synthesis of Au^IF (in the CsCl structure, preferred above 12 GPa over various infinite chain structures, Fig. 19):



might indeed take place at pressures larger than 46 GPa. However, if 'inert' Xe is added to the reaction mixture, a novel adduct (Au^IXe)F forms:



at a much smaller pressure of 26 GPa. The (Au^IXe)F compound is predicted to adopt the InOBr structure (Fig. 17), with the infinite chains of AuF stoichiometry, reminiscent of the hypothesised structure of pure Au^IF at 1 atm. Upon subsequent decompression to 15 GPa, this intermediate might decompose to Au^IF (CsCl type, Fig. 19), while releasing Xe:



Reduction by nearly 45% of the pressure necessary for the formation of AuF may seem spectacular; recollect, however, that the Au–Xe interaction has proved very strong in Pyykkö's calculations and in the synthesized Seppelt's compounds.

Summarizing this section, extended phases might be obtained which are simply unknown at ambient pressure. Thus, Xe might act here as an *indispensable mediator* in forming compositions, which cannot be obtained on other paths.

3.12 Unprecedented polymorphs: cage structures, sponges and other 'negative pressure' forms

The ability of Xe to form moderately-bound connections with various compounds at high pressure, might be utilized for synthesis of as yet unknown high-energy polymorphs of these compounds. Let us assume that (i) a compound AB forms

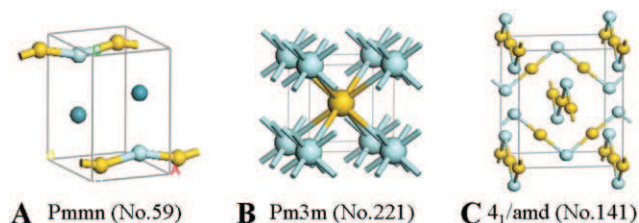


Fig. 19 Illustration of the idea of using Xe for the formation of solid Au^IF (in the AuCl structure) compound *via* synthesis of (A) an [Au^IXe]F intermediate at 26 GPa, its decomposition to (B) Au^IF (in the CsCl structure) upon decompression to 15 GPa, and the formation of the final product (C) at pressures below 12 GPa. Au – yellow, F – light blue, Xe – dark blue balls.

ABXe_n under pressure, (ii) the bonding pattern of the AB subsystem in ABXe_n is different from that in pure AB, and (iii) the new phase is *not* quenchable, *i.e.* it would decompose upon decompression. If decomposition can be realized by smooth extraction of Xe and without definitive collapse of the AB network, a novel polymorph (AB)' will result from decomposition, possibly with an unprecedented bonding topology.

The idea presented above may now be applied to porous structures, *P*, and with the pore size of several Å's (Fig. 20). Of course, such structures are not frequently met at high pressure, as they usually tend to turn into their higher-density siblings, *S*. However, *P* might be greatly stabilized (as compared to *S*) if Xe could be allowed to interact with *P* at high pressure, forming bridges between various metal atoms in *P*, or simply filling in the cages. In such cases, the atomic framework of *P* would be firmly supported. Upon slow decompression, Xe would slowly leave the network, yielding a novel metastable sponge polymorph (unattainable on other routes), and without its transformation to *S*. Preparation of such polymorphs might enrich the set of cage structures such as Prussian Blue type structures, or metal–organic frameworks (MOFs). In this way novel important ultra-lightweight materials (such as the cage Al/Be alloys) might be obtained, their densities being significantly smaller than those of their classical (bulk) counterparts.

The idea described above is nicely exemplified by the known water–xenon clathrate. It will now be illustrated using two more exotic examples, which come from the fields of inorganic and organic chemistry.

The first example is provided by Ag₃N. This compound is extremely explosive at ambient pressure,¹³⁸ due to its susceptibility to decompose to the constituent elements. However, our GGA/PBE calculations show that hypothetical Ag₃N might be stabilized by addition of atomic Xe with the concomitant formation of [Ag₃Xe]N under elevated pressure. This compound would adopt the cubic perovskite CaTiO₃ (*Pm3m*) cage structure (Fig. 20(A)), which—upon decompression—would yield Xe and a cage form of Ag₃N (Cu₃N-type) rather than the

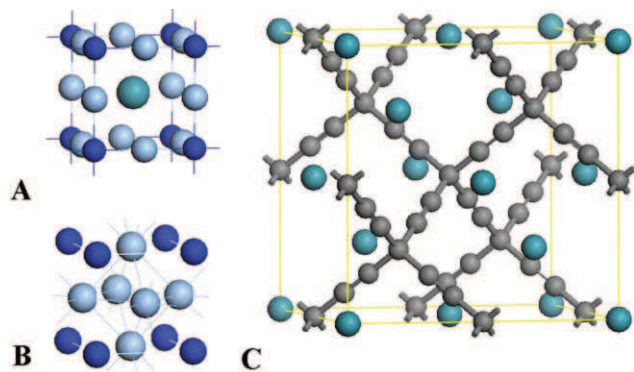


Fig. 20 Two examples of utilizing Xe for the formation of novel cage polymorphs of various elements and compounds. (A) Perovskite structure of [Ag₃Xe]N, formed under elevated pressure; this compound is likely to yield the cage AuCu₃-type structure of Ag₃N upon careful decompression, instead of the compact layered polymorph, (B). Ag – grey, Xe – light blue, N – dark blue balls. (C) Diamond-type sponge polymorph of elemental carbon with empty volumes filled with Xe, with the formula of C₁₀Xe₂. C – dark grey, Xe – light blue balls.

compact layered [(AgN)(Ag₂)] type (with an fcc Ag sublattice, *Pm3m*, Fig. 20(B)).

A hypothetical sponge polymorph of carbon is another interesting case (Fig. 20(C)). Here, the cubic diamond structure is inflated through the insertion between every C–C bond of a –C≡C– linker. The overall formula may be written as {C(C₂)₂} and two such C₅ units enter a primitive cell of this hypothetical solid. Expansion of the diamond lattice results in a remarkable decrease of the density; our DFT calculations predict the specific gravity of this moderate-bandgap (4.5 eV) colourless insulating polymorph of carbon of about 0.88 g cm⁻³, thus this material would float over water.

Synthesis of the above-mentioned ‘negative pressure’ sponge form of carbon has not been successful *via* a classical organic chemistry approach. It would certainly be difficult; our calculations predict that the sponge allotrope is unstable by 1.15 eV per carbon atom with respect to the classical ‘collapsed’ material (graphite).¹³⁹ However, the situation may change dramatically under very high pressure, but only if Xe is present as a stabilizer. Under such conditions, the C₁₀Xe₂ adduct (Fig. 18(C)) might form. Careful and slow decompression of C₁₀Xe₂ might result in the formation of the sponge polymorph, C₁₀. Analogous clathrates, containing iodine-filled Si sponges, have been synthesized at elevated pressure.¹⁴⁰

We summarize this section with the statement that the ‘inert’ Xe reagent might be a remedy to the inherent instability of various fragile cage polymorphs of elements and compounds.

3.13 Prospect for new compounds—summary

As the process of the discovery of new elements is nearly finished by now,¹⁴¹ chemistry is the art of crafting new compounds, of synthesizing entirely novel connections between the known atomic building blocks. There is nothing more essential to our enterprise than making new kinds of bonds, and new compounds which contain a cornucopia of the known bonds—but in previously unknown patterns.

In this work we have summarized recent achievements of Ng chemistry. We have also discussed the emerging directions in this field. In addition we have analyzed perspectives for the synthesis of entirely novel systems with particular emphasis on high-pressure techniques. Our most preliminary, simplistic calculations and chemical intuition have yielded several hypotheses. Specifically, we have predicted the existence of:

- the first alkyl derivatives of Xe^{II}, alkynyl compounds of Xe^{IV}, and mixed fluoride/chloride complexes of Xe^{VI};
- molecular and extended compounds with terminal or bridging peroxide anions in metal-free and metal-containing connections, such as *e.g.* FXe^{II}O₂Xe^{II}F, Xe⋯Pt^{II}(O₂) or XeAu^IO₂Au^IXe;
- complexes of XeF₆ as a ligand with fluoride salts containing large monovalent cations (Cs⁺, Rb⁺);
- molecules and solids containing Xe⁰ atoms as ligands bridging two or more cations;
- the first metallic alloy of Xe, namely HgXe, achievable at pressures lower than 1 Mbar; the difficulty is in achieving this amalgam at a temperature low enough to prevent its decomposition, yet high enough to overcome kinetic barriers to the reaction;

- a range of NgX₂ solids, where Ng = Xe, Kr and X = Cl, Br, I, attainable at elevated pressures;

- novel compounds containing a neutral Xe ligand, notably HgF₂Xe₂, AuFXe⁰ and its unusual AuXe^{II}F isomer;

- metastable sponge polymorphs of chemical elements and compounds, such as Ag₃N and C, stabilized at high pressure in the form of their adducts with Xe (filled sponges).

It would be fascinating if confirmation of these simplistic predictions were achieved in more advanced calculations, and particularly in experiments.

4 Methodology of calculations

The DFT and MP2 calculations using relativistic pseudopotentials have been employed in the past to rationalize^{64,84,142} and predict^{115b} properties of the Xe-containing species. However, they are not meant to predict with enormous accuracy certain absolute molecular properties (geometry, energetics)¹⁴³ but rather (i) illustrate the general concept, (ii) highlight important trends across a series of related systems (such as O₂²⁻ vs. O²⁻, XeAuF vs. AuXeF etc.), (iii) allow for fast screening of a large set of species, (iv) point out exciting new areas for future higher level (fully relativistic) calculations and (v) provide guidance and encouragement to experimentalists. Note that the trends of molecular properties are often much better reproduced than their absolute values, even with fast, low level calculations, because the origin of largest differences between the elements sits in the periodicity of properties of chemical elements (as expressed by Mendeleev's Table) and many errors cancel when comparing same-level calculations for two chemically related species. It is therefore important to realize that all (previously unpublished) calculations presented in this contribution have a preliminary character.

The density functional theory in its present implementation in commercial packages has the well-known deficiency of predicting too small (and even 'negative') bandgaps; in other words, real systems show larger Pearson's hardness than the calculated ones; therefore, the values of pressure at which phase transitions, metallization or decomposition reactions should occur (as derived from the calculations for extended solids), must also be treated as an approximation only.

In most calculations for solids we have used the moderate cutoff of 300 eV, the convergence criterion of 10⁻⁶ eV per atom, the *k*-point mesh corresponding to 0.04 Å⁻¹, and the ultrasoft Vanderbilt pseudopotentials. We have used the Generalized Gradient Approximation (GGA) and the exchange–correlation functional of Perdew–Burke–Ernzerhof (PBE).

The more specific computational details allowing one to repeat the calculations, are given in the endnotes.^{39, 66, 100, 117, 121, 129, 139, 149, 150}

Note added in proof

When this paper was in proof, the author became aware of two important theoretical papers, where the properties of the first chemically bound anionic species containing helium, such as for example FHeO⁻, have been predicted.¹⁵¹ The author

would like to thank Dr Mazej for attracting his attention to these important works.

Acknowledgements

I would like to gratefully acknowledge Prof. Naumann and Prof. Frohn for providing hardcopies of their selected publications, and Prof. Boris Žemva for sharing unpublished results related to Li(XeF₂)₃(AsF₆) and Cd(XeF₂)₅(SbF₆)₂. I also wish to thank Boris, Gary Schrobilgen, Pekka Pyykkö and Mike Gerry for the fast exchange of information. Prof. Andrzej J. Sadlej (Nicolaus Copernicus University, Toruń, Poland) has made available a large set of unpublished computational results for Au–Ng–F molecules. I am greatly indebted to Danny Fredrickson (Stockholm, Sweden), Boris Žemva (Ljubljana, Slovenia), Mike Gerry (Vancouver, Canada), Ji Feng (Cornell, USA), and Lucjan Piela (Warsaw, Poland) for their kind and thoughtful comments on this work.

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- 79 B. Žemva wrote to me in January 2007: "We isolated three coordination compounds of the type Ba(XeF₂)₄(MF₆)₂·XeF₂ with M = Sb, As and Ru. All three compounds are isostructural but only the compound with M = Sb was published till now. The other two will be published together with their NMR data".
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