

CHAPTER 2

RELATIVISTIC EFFECTS AND THE CHEMISTRY OF THE HEAVIER MAIN GROUP ELEMENTS

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Abstract: This chapter reviews possible experimental aspects of relativistic effects in heavier Main Group elements and their compounds. Attention is focused on the sixth, seventh and eighth Period elements, for which the relativistic contribution to their physical and chemical properties is significant. Superheavy elements through $Z = 120$ are also discussed. This review may increase interest of theoreticians in chemistry-oriented problems that require use of relativistic methods of quantum chemistry.

Keywords: Relativistic effects, Sixth, seventh and eight periodic elements, Superheavy elements

2.1. BACKGROUND

2.1.1. Introduction to Relativistic Effects

The theory of relativistic effects in Chemistry is discussed in detail elsewhere [1–9]. A simple introduction will be given here. Einstein's Theory of Special Relativity states that the mass of any moving object changes as its velocity changes:

$$m = m_0[1 - (v/c)^2]^{-1/2} \quad (2-1)$$

where m_0 is the mass at zero velocity. Under ordinary conditions, the term $(v/c)^2$ is so small that any relativistic effects would be insignificant. However, if v becomes sufficiently large, the ratio m/m_0 becomes appreciably larger than unity.

The Bohr model for a hydrogen-like species (a one-electron cation of general formula ${}_Z A^{(Z-1)+}$) will illustrate this. According to this model, the electron would obey the following equations for its velocity, energy, and its orbital radius [10]:

$$v = (2\pi e^2/nh)Z \quad (2-2)$$

$$E = -(2\pi^2 e^4/n^2 h^2)mZ^2 \quad (2-3)$$

$$r = Ze^2/mv^2 \quad (2-4)$$

where n is a quantum number, e is the charge on the electron, h is Planck's constant and Z is the atomic number of the nucleus. Equation (2-2) enables the calculation of the electron velocity for any element. Substituting this calculated velocity into Eq. (2-1) gives the ratio m_r/m_0 , where m_r is the *relativistic mass* for the electron. Calculated values of this ratio for the ground state ($n = 1$) of selected elements are shown in Table 2-1.

Elements of the first three periods show ratio changes of less than 1%; corresponding ratios for elements in the Fourth Period vary from 0.9% to 3.6%. For the Fifth Period elements, the ratios show changes of ca. 8%. Only for the Sixth and Seventh Period elements does this ratio exceed 10%; these elements show the greatest relativistic effects. Energy changes resulting from replacement of m_0 by m_r increase as Z increases (Eq. (2-3)). Since the orbit radius is inversely proportional to m (Eq. (2-4)), it will *decrease* as Z increases. It has been proposed that relativistic effects might even depend on higher powers of Z , especially for the heaviest elements [11].

The figures in Table 2-1 suggest a steady increase for m_r/m_0 across each given period. More exact calculations indicate otherwise [12]. Across the Sixth Period, the relativistic radius for the 6s orbital slowly decreases between Cs and Ir, then

Table 2-1 Calculated m/m_0 values for the electron in $E^{(Z-1)+}$ ions of groups 1, 2, 11-18

Group 1	Group 2	Group 11	Group 12
H 1.000027			
Li 1.00024	Be 1.00042		
Na 1.0032	Mg 1.0038		
K 1.0092	Ca 1.011	Cu 1.023	Zn 1.025
Rb 1.038	Sr 1.041	Ag 1.064	Cd 1.067
Cs 1.091	Ba 1.095	Au 1.22	Hg 1.23
Fr 1.29	Ra 1.30	Rg 1.69	112 1.72
119 1.99	120 2.05		
Group 13	Group 14	Group 15	Group 16
B 1.00067	C 1.00095	N 1.0013	O 1.001
Al 1.0045	Si 1.0052	P 1.0060	S 1.0068
Ga 1.026	Ge 1.028	As 1.030	Se 1.032
In 1.070	Sn 1.073	Sb 1.077	Te 1.080
Tl 1.24	Pb 1.25	Bi 1.25	Po 1.26
113 1.75	114 1.79	115 1.82	116 1.86
Group 17	Group 18		
	He 1.00011		
F 1.0021	Ne 1.0027		
Cl 1.007	Ar 1.0087		
Br 1.034	Kr 1.036		
I 1.084	Xe 1.087		
At 1.27	Rn 1.28		
117 1.90	118 1.95		

drops sharply, passes through a minimum at Au, and subsequently increases from Au to Rn. This has become known as the “Group 11 maximum” [13]. A similar trend also occurs for the following period, although there the maximum occurs at element 112 (“eka-mercury”) [13].

2.1.2. Intraatomic Changes

2.1.2.1. Orbital Energies

s-orbitals decrease substantially in energy when relativistic effects are considered; p-orbitals also decrease, but to a lesser extent. This enhances their nuclear shielding effect, causing d- and f-orbitals to increase in energy. As a result, energy differences among orbitals change, often drastically, for the heavier elements, compared to what might be expected by extrapolation from their lighter congeners.

2.1.2.2. Subshell Splittings

As a result of spin-orbit interaction, subshells with $l > 0$ will split into two subgroups of $l - 1/2$ and $l + 1/2$, the former being lower in energy. Figure 2-1 shows this for the 5d, 6s and 6p subshells. The energies for these various splittings depend on the specific element, and increase as Z increases.

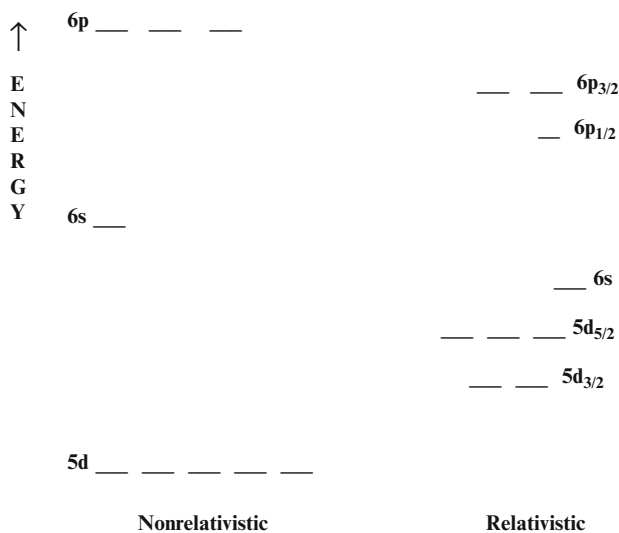


Figure 2-1. Relativistic and nonrelativistic energy level diagrams for the 5d, 6s and 6p sublevels of sixth period elements (Reproduced from [1] with permission from *Journal of Chemical Education*. Copyright ©2005 Division of Chemical Education Inc)

2.1.2.3. *Radial Changes*

If a relativistic mass is calculated and used to calculate the radius of the electron's orbit, the resulting value will decrease. Since relativistic effects are strongest for s orbitals, these will shrink the most. Such shrinkage is termed the *orbital contraction* [5, 6, 8, 9]. This causes changes in bond lengths and other inter-atomic separations.

2.1.3. **Chemical Effects**

All physical and chemical properties ultimately depend on the energies and spatial distributions of electrons in the atoms involved. For heavier elements, the relativistic effect approach must be used to give accurate descriptions for such properties.

Physical properties (bond lengths, transition energies, polarizations, etc.) have been extensively investigated for their relativistic alterations. The two best known macroscopic examples are the low melting point of mercury [4] and the unusual color of gold [8]. Other examples are discussed elsewhere in this volume.

Chemical properties also are changed by relativistic effects. The best known example is the so-called Inert Pair Effect [1, 8]. This term was originally coined to describe the reluctance of Sixth Period elements (Hg-Rn) to use the 6s electrons in bonding, and remains the most common example of relativistic effects mentioned in general textbooks. Other species affected are mentioned either slightly or not at all; species such as intermetallic compounds, semiconductors, metal clusters etc.

The Sixth Period elements can be studied directly (with difficulty for Po, At and Rn) and effects of relativity measured. For the superheavy elements, where actual chemical studies are few and where relativistic effects are expected to be strong, theoretical studies of such effects can be used to predict physical and/or chemical properties, providing guidelines for future investigation.

For the purposes of this article the "heavier Main Group elements" are those of the Sixth and Seventh Periods. Pt and Au (along with their heavier congeners Ds and Rg) are not Main Group elements, but are included in this article because their strong and well-studied relativistic properties provide a convenient starting point for comparison discussion.

2.2. **SIXTH PERIOD ELEMENTS**

2.2.1. **s-Block Elements**

2.2.1.1. *Cesium*

Cesium behaves like a typical Group I metal, and examples of relativistic effects are few. Like Na, K, and Rb, Cs forms an alkali anion Cs^- [14]. One paper reports that triatomic Cs_3^{3-} may form in solid lattices of certain cesides [15].

2.2.1.2. Barium

In the intermetallic compound Ba_2Pt [16], one of the two 6s electrons of barium is transferred to platinum while the other remains in the barium band, indicative of the increased stability of the 6s subshell. Experimentally observed polarizabilities of both Ba and Ba_2 agreed well with calculated relativistic values [17].

2.2.2. d-Block Elements

2.2.2.1. Introduction

These elements show the strongest relativistic effects in the Sixth Period. All three metals can use both d-electrons and s-electrons in their bonding. The color of gold, unique among the elements, arises from elevated energies of the 5d electrons, shifting those wavelengths required for their excitation to into the visible region of the electromagnetic spectrum [3, 8]. The liquidity of mercury at ordinary temperatures, unusual among metals, results from relativistically lowered energy of the 6s electrons, weakening Hg-Hg interatomic attractions [4].

2.2.2.2. Platinum $\{5d_{3/2}^4 5d_{5/2}^5 6s^1\}$

General The electron configuration of platinum differs from the $4d^{10}$ configuration of its lighter congener palladium and reflects relativistic changes in both the energies of the 6s subshell and the $5d_{5/2}$ spinor. This in turn leads to substantial differences in their chemistries.

Platinide Ions Addition of two electrons to a platinum atom forms the platinide anion Pt^{2-} found in the salt Cs_2Pt [14, 18]. This deep red solid adopts the Ni_2In structure with each Pt atom surrounded by nine Cs atoms in a tricapped trigonal prism [18]. Band structure investigations gave results consistent with an ionic formulation [16, 18].

The ion Pt_2^{2-} would be the first member of an isoelectronic series that continues with Au_2 and Hg_2^{2+} . BaPt did not contain this ion, but formed chains having Pt-Pt bonds [18, 19]. Charge transfer studies indicated that each barium atom transferred only one electron to the platinum; the compound was described as “the first example of a Zintl-phase where the polyatomic structure is established by a transition element” [19]. Ba_3Pt_2 contained Pt-Pt dumbbells in the solid state [19], while Ba_2Pt has a CdCl_2 structure with isolated platinide ions and has been proposed to have a charge assignment $(\text{Ba}^{2+})_2\text{Pt}^{2-} \bullet 2e^-$ [16]. Electrochemical and X-ray photoelectron spectroscopy investigations have confirmed the formation of negative oxidation states for platinum [20].

Higher Oxidation States Common oxidation states for Pt are +2 and +4. The +6 state is found in platinum hexafluoride, PtF_6 , which earned a niche in chemical history as the first species to form a dioxygenyl salt, $\text{O}_2^+ \text{PtF}_6^-$ [21] and a xenon compound $\text{Xe}^+ \text{PtF}_6^-$ [22]. The ground state structure of PtF_6 [23, 24]

has a regular octahedral structure and a closed-shell ground state. This compound has a high electron affinity (ca 7 eV) [25], and forms both PtF_6^- and PtF_6^{2-} ions. The latter has had its detachment spectrum studied by a relativistic approach [26]. No Pd(VI) compounds have been reported; apparently there is not enough relativistic destabilization of its 4d electrons to allow their oxidation.

Platinum pentafluoride is a deep-red solid that disproportionates readily upon heating [27]:



Theoretical studies indicated that platinum octafluoride, PtF_8 , would be unstable towards loss of F_2 [27].

Laser ablation of atomic platinum in an Ar- O_2 mixture at 10 K gave evidence for the formation of PtO_3 with D_{3h} symmetry [28]. Theoretical calculations indicate that Pt atoms should be able to combine with noble gas atoms to form species of formula Ng-Pt-Ng in the gas phase or in a matrix [29].

Platinum Clusters Investigation of $\{\text{Pt}(\text{CO})(\text{AuR})_8\}^{2+}$ (R = triphenylphosphine) indicated that 5d orbitals from both Pt and Au contributed to the HOMO [30]. Similar studies on effects of mixed Au-Pt species (e.g. PtAu^+) in the dehydrogenation of methane revealed that the HOMO formed primarily from gold and showed enhanced interaction with the LUMO σ^* of methane, when compared to the corresponding interaction for Pt^+ [31]. Ionization spectroscopy showed that bond energies of Pt_2 and Pt_2^+ were 3.14 and 3.26 eV respectively [32], indicating significant 5d contributions to these Pt-Pt bonds.

2.2.2.3. Gold $\{5d^{10}6s^1\}$

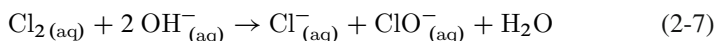
General The roles of relativistic effects in the properties of gold have been extensively reported [2, 3, 6, 8, 16, 33]. These effects expand the chemistry of gold well beyond “normal” limits for Group 11 elements (the “Coinage Metals”) and give a remarkably rich chemistry to a “noble metal.”

Auride Salts and Au–Au Bonds The outer shell configuration of gold predicts an oxidation state of +1, also found for other Group 11 elements. However, enhanced stability of the 6s orbital allows formation of both *auride* anion, Au^- , and the molecule Au_2 . Comparable species are known for the alkali metals, but *alkalide* compounds require stabilizing ligands for isolation [34]. The silver counterpart, *argentide* ion, Ag^- has been prepared by electrochemistry in liquid ammonia solution [35]. Yellow CsAu dissolved readily in liquid ammonia; however, slow removal of solvent resulted in crystallization of an intensely blue solid $\text{CsAu} \bullet \text{NH}_3$ [33, 36]. The presence of auride anion as a distinct entity has been verified by various techniques, including ^{197}Au Mössbauer spectroscopy [16]. A colorless salt $(\text{Me}_4\text{N})^+ \text{Au}^-$ {Me = methyl} was prepared from CsAu by ion exchange and was isostructural with the corresponding bromide [16]. Auride ion has been suggested to be an analog of halide ions [16]. Two examples of this analogy:

1. Gold undergoes disproportionation in base:



This compares to:



The product was described as “intergrowths of slabs corresponding to the binary aurides and to the ternary aurates(I)” [37]. The presence of two different oxidation states of gold was verified by ^{197}Au Mössbauer spectroscopy [16]. The electronic structure of auride ion has been studied [38].

2. Auride ion shows hydrogen bonding:

$\{\text{Rb}([\text{18crown-6})(\text{NH}_3)_3\}^+ \{\text{Au}\bullet\text{NH}_3\}^-$, when studied by X-ray crystallography, was found to have a Au–H distance of 258 pm, comparable to corresponding H–Br and H–I hydrogen-bond distances of 249 and 272 pm [39].

Hydrolysis of the model species $\text{Au}(\text{OH}_2)^+$, when compared to the hydrolysis of analogous Cu(I) and Ag(I) species, showed marked relativistic effects [40]. Inclusion of relativistic corrections for AuCN increased the bond order of the Au–C bond [41, 42]. Au_2 showed a dissociation energy of 2.34 eV [3] (= 225.8 kJ/mol), making it considerably more stable than Ag_2 [43] or the corresponding alkali metal dimers. The Au–Au bond length was shortened by some 35 pm by inclusion of relativistic effects [3].

Unusual Gold Compounds Au(III) compounds with oxygen and the halogens are well known, and less reactive than Cu(III) or Ag(III) analogs. Gold pentafluoride, Au_2F_{10} [44], is a powerful oxidizing agent and readily forms AuF_6^- salts, including $[\text{O}_2]^+ [\text{AuF}_6]^-$. A compound with stoichiometry AuF_7 , stable at room temperature, has been reported [45]. Theoretical studies suggested the formula $\text{AuF}_5 \text{F}_2$ [46]! If verified, this would be the first example of difluorine acting as a Lewis base in a condensed phase [46].

Another surprising class of ionic gold compounds contains Au–Xe cations with $\text{Sb}_2\text{F}_{11}^-$ counterions [47–49]. Examples reported to date are

AuXe_4^{2+} (a square-planar Au(II) derivative), *cis*- AuXe_2^{2+} (also square planar, with bridging fluorides), an unstable *trans*-isomer, the F-bridging species XeAuFAuXe^{3+} [47, 49], and the unusual ion $(\text{F}_3\text{As})\text{AuXe}^+$, containing a linear As–Au–Xe framework [48, 50]. All these show varying degrees of fluoride bridging, contain the unusual Au^{2+} ion, and apparently involve d–d electron pair donation from Xe [49]. Studies on chemical bonds between Au(I) and noble gases indicated an appreciable charge transfer from the noble gas to Au [50–54].

Gold Clusters and Auophilic Interactions Gold has an extensive cluster chemistry, as exemplified by Au_{55} [55] and $\text{Au}_2\text{Te}_{12}^{4-}$ [56]. Gold nanoclusters have

low-symmetry structures due to relativistic effects [57]. In mixed Cu-Au species, pure Au clusters were more stable than mixed clusters when the total number of atoms was less than 12 [58].

Closed-shell interactions have considerably extended the chemistry of gold and other elements. The term “aurophilicity”, originally coined by Schmidbaur [59], describes interactions between filled 5d subshells of adjacent gold atoms [60, 61]. Relativistically enhanced energy of Au(I) 5d electrons makes such interactions comparable in energy to hydrogen bonding [60, 61]. The compound $M(C_6F_5)\{N(H) = CPh_2$ ($M = Ag, Au$), displayed both types of bonding [62]. For the gold species, both types were almost equal in energy; in the silver species, hydrogen bonding was stronger, indicating that ‘argentophilicity’ is weaker than its gold counterpart. Both aurophilic attraction and relativistic effects were predicted to stabilize the cluster species $W@Au_{12}$ [63], a possible analogue to C_{60} . This prediction has been confirmed by experimental observation of $W@Au_{12}$ and its molybdenum counterpart [64]. Investigation indicated strong $6s - 5d_{5/2}$ hybridization in the tungsten cluster, whose structure is icosahedral (overall symmetry I_h) with the tungsten atom surrounded by gold atoms [64]. Gold clusters have been investigated for their role in absorbing and catalyzing the oxidation of carbon monoxide [65, 66].

2.2.2.4. Mercury $\{5d^{10}6s^2\}$

General Unlike gold, the outermost electrons of mercury comprise a completely filled subshell. As Norrby pointed out, gold and mercury are “next-door neighbors in the Periodic Table but have dramatically different properties” [4]. There is an s^2-s^2 interaction [60]; dimeric Hg_2 has a bond length of 363 pm (compared 416 pm for the sum of the van der Waals radii) and a bond energy of 0.0434 eV. The first ionization energy of Hg is higher than most other metals of the Sixth Period (Table 2-2),

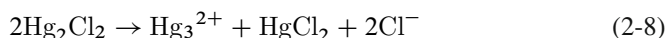
Table 2-2 First ionization energies for fourth, fifth and sixth row elements of groups 8 through 18 (All values are taken from The Elements (Emsley J. ed) Clarendon, Oxford, 2nd edn, 1991 and have units of kJ/mol)

8	9	10	11
Fe 759.3	Co 760.0	Ni 736.7	Cu 745.4
Ru 711	Rh 720	Pd 805	Ag 731.0
Os 840	Ir 880	Pt 870	Au 890.1
12	13	14	15
Zn 745.4	Ga 578.8	Ge 762.1	As 947.0
Cd 867.6	In 558.3	Sn 708.6	Sb 833.7
Hg 1007.0	Tl 589.3	Pb 715.5	Bi 703.2
16	17	18	
Se 940.9	Br 1139.9	Kr 1350.7	
Te 869.2	I 1008.4	Xe 1170.4	
Po 812	At 930	Rn 1037	

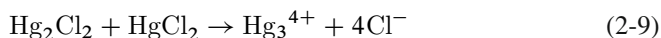
due to relativistic stabilization of the 6s subshell. Consequently, Hg^{2+} ion very electrophilic, and Hg(II) compounds differ in many respects from their Zn and Cd counterparts for this reason. The configuration also suggests that Hg(0) would be less likely to gain electrons to form anionic species than either Pt(0) or Au(0) .

Polyatomic Cations Mercurous ion, Hg_2^{2+} , has been studied theoretically [67–70]. This ion is isoelectronic with Au_2 and Pt_2^{2-} . In the gas phase, it was slightly unstable towards dissociation [70]; however, a large heat of hydration stabilizes it in aqueous solution. The monatomic species Hg^+ formed only under high energy conditions and dimerized in a second-order reaction with a rate constant of $4.0 \times 10^9 \text{ L/mol}\cdot\text{s}$ [68]. Stability of the Hg–Hg bond depended very much on the attached group [70–72]: ligands with electronegativities above 2.5 formed stable compounds, while those below that value caused disproportionation. Pure crystals of mercurous halides needed to be prepared by sublimation [71]. Diorganodimercury compounds have never been isolated because the Hg–Hg bond in such compounds was too weak [69, 70]. Mercurous complexes of formula $[\text{M}_2\text{Hg}_2\text{L}_3](\text{PF}_6)_2$ ($\text{M} = \text{Pt, Pd}$; $\text{L} = 2,9\text{-bis(diphenylphosphino)-1,10-phenanthroline}$) [72] had one mercury atom linked to two N atoms and two Pd(Pt) atoms as well as to the other mercury; spectroscopic evidence indicated that the Hg–Hg unit was spinning rapidly [72].

Other polyatomic mercury cations (e.g. Hg_3^{2+} , Hg_3^{4+} , Hg_4^{2+}) are also known [73–75]. The linear Hg_3^{2+} cation, formed by disproportionation,



contributed to the photoluminescence of Hg_2Cl_2 , as did Hg_3^{4+} , believed to form by the reaction [73]



Hg_2^{2+} and Hg_3^{2+} both formed complexes with benzene, in which the benzene molecules interacted with mercury atoms at the end of the chain [74]. Both cations also occurred in the three-dimensional framework of $[\text{Hg}_{11}\text{As}_4](\text{GaBr}_4)_4$ [76], and showed large Hg–Hg coupling constants in their crown ether complexes [77]. The triangular cation Hg_3^{4+} formed complexes with bis(diphenylphosphinomethane): each mercury atom was bonded to two other mercury atoms and two phosphorus atoms [78, 79]. Extended structures for mercurous-oxy cations [80] and Hg–P linkages [81] have also been reported.

Higher Oxidation States As with platinum and gold, mercury can lose electrons from its 5d subshell, albeit reluctantly. An early report of trivalent mercury [82] has never been verified and must be considered doubtful. Theoretical attention has been given to HgF_4 and its derivatives [83–86]. In 2007, HgF_4 was finally prepared and

isolated in inert-gas matrices [87]. It has a square-planar structure with a $5d^8$ configuration, making it isoelectronic with AuF_4^{1-} and PtF_4^{2-} . Infrared spectroscopy of HgF_4 in neon showed a peak at 703 cm^{-1} , assigned to the degenerate E_u stretching mode of HgF_4 [87]. Similar experiments involving ZnF_2/F_2 or $HgCl_2/Cl_2$ in Ne matrices gave no evidence for the formation of either ZnF_4 or $HgCl_4$ [87]. Theoretical studies indicated that many potential $Hg(IV)$ complexes would be thermodynamically unstable [88], but might possess a sufficiently high activation energy barrier to enable their detection. Other studies indicate that HgF_3 by itself would probably be unstable [86], but the dimeric molecule Hg_2F_6 or complexes such as HgF_4^- might be more stable.

Both HgH_4 and HgH_6 have been proposed as possible candidates for higher-valence mercury compounds [88]. The isoelectronic species PtD_4^{2-} [89] and AuH_4^- [90, 91] have been reported; they have square-planar $5d^8$ structures.

The involvement of $5d$ electrons in $d_\pi \pi^*$ backbonding in mercury cyanides has been proposed on the basis of their photoelectron spectra [92].

Mercury Clusters and Amalgams Mercury has an extensive cluster chemistry [1, 93]. Polyatomic mercury cations have already been discussed. Anionic clusters have been reported: Na_3Hg contains the square planar species Hg_6^{4--} [93], while electron transfer has been reported for alkaline earth metal-mercury intermetallic compounds [94]. Bonding varies according to whether the clusters are cationic, neutral or anionic [93, 95]: both cationic and anionic clusters show Hg-Hg σ – bonding, while neutral clusters show van der Waal's bonding. Bonding in neutral clusters seems also to depend on the cluster size [1, 95, 96].

2.2.3. p-Block Elements

2.2.3.1. Introduction

For the elements Tl-Rn, $6p$ -electrons become the dominant contributors to bonding, while the $5d$ electrons become part of the core and the $6s$ electrons reacted only under oxidizing conditions. Oxidation states involving $6s$ electrons become increasingly less stable from thallium to astatine, and disappear entirely for radon. Table 2-3 shows examples of compounds for these elements in their most positive oxidation states. The roles of relativistic effects and ligands (especially H and the halogens) has been discussed by Schwerdtfeger [97], who noted a sharp change between Pb and Bi for the oxidizing power of the highest oxidation state. In the elements bismuth through radon, the energy of the $6p_{1/2}$ – $6p_{3/2}$ spinor separation becomes increasingly important in determining oxidation state stability.

Because of their radioactivity, the chemistry of Po, At and Rn is less developed than other Sixth Period elements.

Table 2-3 Some stable compounds for Thallium through Radon in their highest oxidation states (Reproduced from [1] with permission from *Journal of Chemical Education*; copyright ©2005, Division of Chemical Education, Inc.)

Element	Compounds
Tl(III)	TlX ₃ (X = F-Br), TlX ₄ ⁻ , Tl ₂ E ₃ (E = O, S, Se) R ₄ Tl ⁻ , R ₃ Tl, R ₂ Tl ⁺ , C ₆ H ₅ Tl(OAc)
Pb(IV)	PbX ₄ , PbX ₆ ²⁻ (X = F,Cl), PbO ₂ , PbO ₃ ²⁻ , PbO ₈ ⁶⁻ , R ₄ Pb, R ₃ PbA, R ₂ PbA ₂ , C ₆ H ₅ Pb(OAc) ₃ , R ₆ Pb ₂
Bi(V)	BiF ₅ , BiF ₆ ⁻ , BiF ₇ ²⁻ , Bi ₂ O ₅ (?), BiO ₃ ⁻ R ₆ Bi ⁻ , R ₅ Bi, R ₄ Bi ⁺ , Ar ₃ BiA ₂
Po(VI)	PoF ₆ (?), PoO ₃ (?)
At(VII)	AtO ₄ ⁻ (?)
Rn(VIII)	None reported

A – anion, R – alkyl and/or aryl group, Ar – aryl group, (?) – existence uncertain

2.2.3.2. Thallium {6s²6p_{1/2}¹}

General The electron configuration predicts two oxidation states: +1 (“thallous”) and +3 (“thallic”). The +1 state, isoelectronic with Hg(0), is the more stable state, forming numerous salts. Tl⁺ is much the same size of Rb⁺ (ionic radii are 159 and 149 pm respectively), and is quite toxic. Compounds in the +3 state are covalent, and readily reduced to the +1 state. TlI₃ is actually Tl⁺ I₃⁻, but addition of iodide ion produces TlI₄⁻, containing Tl(III). Stable Tl(III) compounds contain bonds to electronegative elements and/or organic groups (Table 2-3).

Thallides Relativistic effect theory predicts that Tl⁻ should be isoelectronic with Pb(0) and have a filled 6p_{1/2} spinor. Both KTI and CsTI are known compounds but do not have monatomic thallide ions; their stoichiometry is actually M₆Tl₆ [98,99]! The Tl₆⁶⁻ octahedra show D_{4h} symmetry due to tetragonal distortion [98]. Other binary alkali metal-thallide compounds have been reported [100,101]. BaTl₃ shows TI-TI interactions involving 6p orbitals [99]. Various anionic Tl clusters have also been reported [98], including the new phase Na₉K₁₆Tl_{25,25}, which contains Tl₉⁹⁻ clusters [102].

Thallium-Thallium Bonds and Heteroatomic Clusters Both the Au₂ molecule and the mercurous ion, Hg₂²⁺, show distinct metal-metal covalent bonds; the corresponding isoelectronic thallium species would be Tl₂⁴⁺. No salts containing such an ion have yet been reported. Halides of the formula TlX₂ are actually mixed-valence species Tl⁺TlX₄⁻ having the NiAs structure [103]. Theoretical studies on E₂X₄ (E = B-Tl; X = H, F-I) indicated that the TI-TI bond would be the weakest in the series [104]. Thallium forms fewer compounds of this type than do other Group 13 elements [104, 105]. The TI-TI bond occurs in the cluster species Tl_{0.8}Sn_{0.6}Mo_{0.7}O₁₁ [106]. Three compounds of formula [(R₃Si)₃Si]₄Tl₂ have been

reported, where R = Me [107], t-Bu [108] or a t-Bu/Ph mixture [109]. All are colored and decompose at 20° [107], 52° [108] and 125° [109] respectively. Tl-Tl bond lengths in these compounds vary from 2.881 to 2.966 Å [107–109].

2. Tl(I)-Tl(I) interactions have been reported in some pentaorganocyclopentadienylthallium(I) compounds, with Tl-Tl bond lengths exceeding 3.3 Å [110–112]. The bonding appears to be another example of “metallophilic interactions” [60, 112–114]. Larger clusters have been reported, containing covalently bonded Tl atoms with bond lengths around 2.92 Å [109, 115].

A model study of Au(I)-Tl(I) complexes showed that metallophilic attraction occurred and that the charge on Tl was more positive than on Au [116]. In clusters of Tl with coinage metals, Au₁₂Tl₂ was the most stable [117]. Compounds of formula Tl₃Ag₃E₂S₆ (E = As, Sb) showed certain very short Tl-Ag separations, indicating strong metallophilic interactions [118].

2.2.3.3. Lead {6s²6p^{''2}}

General The relativistically stabilized 6p'' spinor is completely filled, causing lead metal to be unreactive; its first ionization energy is higher than that for either Tl or Bi (Table 2-2). Predicted oxidation states are +2 (“plumbous”) and +4 (“plumbic”). Pb(II) compounds tend to be ionic with some covalent character; Pb(IV) compounds are rarer, polar covalent, and usually good oxidizing agents. Pb-Pb bonds are less numerous than for lighter Group 14 elements and occur in organolead compounds or cluster species. The marked difference in stability for Pb(IV) with inorganic versus organic substituents has been discussed by Kaupp and Schleyer [119]. They suggested that bonds to electronegative substituents deplete the 6p-orbitals more than the 6s orbitals, weakening their ability to enter into hybridization.

Plumbides and Some Inorganic Lead Compounds Various anionic lead clusters have been reported [120–123], of which the best known is probably Pb₉⁴⁻. Unlike Pt and Au, but like Hg and Tl, Pb does not form monatomic anions. Relativistic theory suggests that formation of Pb⁴⁻ might not be energetically favorable, since the additional electrons would have to go into the higher energy 6p_{3/2} spinor. Studies on alkali metal-lead alloys indicate that, for Li and Na, the stable compounds nearest in stoichiometry to the 4:1 ratio are Li₂₂Pb₅ and Na₁₅Pb₄ respectively [122].

Plumbane, PbH₄, has been extensively studied [7, 119, 124–127]. Infrared spectra at 3.5 K indicated that it had T_d symmetry [125]. The hydride Pb₂H₄ was also observed, and was assigned a *trans*-ring C_{2h} structure with two-bridging H atoms [125], in contrast to structures for ethylene or its Si and Ge analogs. Plumbane has only a transient existence at 25°, but is stable enough to allow its use in lead analysis by hydride generation [128].

The tetrahaloplumbanes, PbX₄, have also received theoretical investigations [127, 129–131]. Only the fluoride is stable at 25°C; the chloride decomposes slowly at that temperature, while the bromide and iodide have never been reported. Salts containing PbCl₆²⁻ ion have been isolated and are stable at room temperature [132]. This ion has a yellow color, attributed to relativistic stabilization of the a_{1g} LUMO [133]. Solution studies on PbBr₂-Br₂-Br⁻-H₂O systems led to a claim

for both PbBr_4 and PbBr_6^{2-} formation [134, 135], but that claim has not been verified. Advances in scientific techniques make it probable that PbBr_4 and PbI_4 could be formed and identified at low temperatures—probably by matrix trapping—and that the corresponding PbX_6^{2-} salts might be stable enough for detection and/or isolation.

Steric effects from the lone pair on Pb(II) can be diminished by relativistic contraction. In the ternary oxide SnWO_4 , the electron pair on Sn(II) interacts strongly with the 2p orbitals on oxygen, affecting its crystalline structure [136]; the 6s electron pair in PbWO_4 shows a markedly lower interaction.

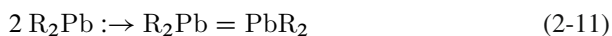
Organolead Compounds Organolead compounds represent the most common examples of stable Pb(IV) derivatives, with, however, considerable variation in their thermal and chemical stability. In a comparative study of bond energies in the series $(\text{CH}_3)_2\text{M}$ ($\text{M} = \text{Au}^-, \text{Hg}, \text{Tl}^+, \text{Pb}^{2+}$), the energy rose from Au to Hg, then decreased from Hg to Tl to Pb [137], due to relativistic effects. The presence of organic groups adds thermal stability to Pb-halogen bonds. For example, all triphenyllead halides are stable solids, melting at temperatures above 140° [138a]; diphenyllead dibromide decomposes above 250° , while the corresponding iodide melts smoothly at 103° . Phenyllead trichloride decomposes below 0° , but the derived salts tetraphenylphosphonium phenyltetrachloroplumbate(IV) and bis(tetramethylammonium phenylpentachloroplumbate(IV) are stable up to 137° and 108° respectively [138a]. Corresponding alkyllead compounds are less stable thermally, but trimethyllead bromide and iodide are both known, and dimethyllead dibromide has been isolated as an unstable white solid [138a]. The highly sterically hindered compound bis {2,4,6-tris[bis(trimethylsilyl)methyl]phenyldibromoplumbane is monomeric in the crystalline state [139], unlike diphenyllead dihalides, which are polymeric as solids.

The previously mentioned series $\text{Pt}_2^{2-} \text{Au}_2, \text{Hg}_2^{2+}, \text{Tl}_2^{4+}$ should continue with Pb_2^{6+} . No such ion has yet been reported; however, the hexaorganodiplumbanes, R_6Pb_2 , containing Pb-Pb bonds, may be considered as derivatives. Hexamethyldiplumbane decomposes slowly at room temperature, while hexaphenyldiplumbane melts at 170° with decomposition [138a]. Pentaphenyl [tris(trimethylsilyl)methyl]diplumbane melts at 143° , but changes from yellow to green at 134° [140]. Cyclotriplumbanes are also known [141, 142], and unusual organolead cluster compounds, containing Pb- C_6H_5 σ -bonds, have been reported [143, 144].

Pb(II) also forms organo derivatives. Plumbylenes, R_2Pb ., usually polymerise to a cycloplumbane [145, 146]



but, if the organic group is sufficiently bulky, a diplumbene can form [145]

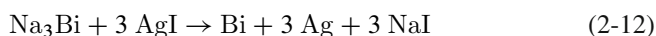


and, for extremely bulky groups, the monomeric plumbylene can actually be isolated [146]. Like Tl(I), Pb(II) can form compounds with cyclopentadiene; $(\eta^5\text{-C}_5\text{H}_5)_2\text{Pb}$ (plumbocene) and numerous derivatives have been reported [147]. Plumbocene is polymeric as a solid but has a monomeric bent structure in the gas phase, reflecting the steric influence of the Pb 6s electrons.

2.2.3.4. Bismuth $\{6s^26p_{1/2}^26p_{3/2}^1\}$

General Decreasing stability of the highest oxidation state for Sixth Period elements continues with bismuth. Table 2-3 shows fewer compounds of Bi(V) than for either Pb(IV) or Tl(III). Inorganic Bi(V) species usually behave as strong oxidizing agents. Organobismuth(V) compounds are the most numerous examples for this oxidation state.

Inorganic Bismuth Compounds The “standard” oxidation states for Group 15 elements are -3 , $+3$ and $+5$. Bismuth forms compounds in all three states. The -3 state is found in various bismuthides, such as Na_3Bi . Some reactions for this compound in liquid ammonia have been reported [148]:



These reactions are all consistent with the presence of Bi^{3-} but do not necessarily prove that this ion exists as a monomer in the solid state. In species such as $\text{M}_{11}\text{Bi}_{10}$ ($\text{M} = \text{Sr}, \text{Ba}$) there are Bi^{3-} ions, but also Bi_2^{4-} and Bi_4^{4-} [149]. Apparently, the monomeric anion does exist for Bi, unlike Pb.

Bismuth forms a $+1$ oxidation state by loss of the electron from the $6p_{3/2}$ spinor, but might also form a -1 oxidation state by adding one electron to form the half-filled $6p_{3/2}$ spinor. No compounds for the latter configuration have yet been reported, but it is predicted to have two bound states [150]. Bismuth monohalides BiX contain bismuth clusters [151]. Bi^+ ion does occur in solution [152, 153] and in $\text{Bi}_{10}\text{Hf}_3\text{Cl}_{18}$ [154]. Mixed-valence compounds, such as $\text{BiI}\{\text{which contains both Bi(0) and Bi(II)}\}$, are also known [155]. A compound containing the Bi_2 molecule has been reported [156, 157]

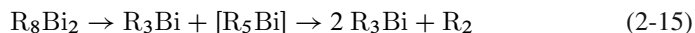
Stable inorganic compounds of Bi(V) contain fluorine or oxygen. The ions BiF_6^- and BiF_7^{2-} have been reported [158]. Other pentahalides are predicted to be unstable towards reductive elimination of halogen [159], but they may be detectable at low temperatures in an inert matrix, and salts containing BiCl_6^- may be isolable.

Bismuth Clusters Unlike thallium and lead, bismuth usually forms cationic clusters [160–162], although some neutral ones are also known [161, 163]. Homoleptic Bi cationic clusters are electrophilic and require weakly basic counterions for stability. Bi_9^{5+} is isoelectronic with Pb_9^{4-} , but the bismuth cluster has a tricapped trigonal prism structure whereas the lead cluster (along with its Group 14 congeners)

has a monocapped square antiprism structure [161]. The electrophilic nature of bismuth clusters appears in the aromatic planar cation $[\text{Fe}(\text{Bi}_5)]^+$ [164]. A mixed Bi-Te cluster cation has been reported [165]. Solid compounds of bismuth with other Group 15 elements show a decrease in the band gap due to the relativistic lowering of the 6s electrons on Bi [166, 167].

Organobismuth Compounds Bismuth forms organo derivatives in both +3 and +5 states. The latter has a restricted range of stability: no Bi(V) derivatives containing only one or two organo ligands are known, and compounds with three organo ligands exist only when the inorganic groups are halogens or oxygen. Tetraaryl-bismuthonium salts, $\text{Ar}_4\text{Bi}^+ \text{X}^-$ have been isolated; tetramethylbismuthonium ion formed from the β -decay of $^{210}\text{Pb}(\text{CH}_3)_4$ [168]. Pentaphenylbismuth and other pentaaryl-bismuth compounds are known [169, 170], and the unstable pentamethyl-bismuth has been reported [169]. Hexaorganobismuthates have also been prepared [169, 171]. The color for pentaaryl-bismuth compounds was attributed to its square pyramidal structure and to lowering of the HOMO-LUMO separation in this structure due to relativistic effects [133, 170]. However, pentamethyl-bismuth has a trigonal bipyramidal structure and also a violet color [169], so other factors may be involved.

No organo compounds containing Bi(V)–Bi(V) bonds have been reported. The ion Bi_2^{8+} , predicted by continuation of the aforementioned dimeric series starting with Pt_2^{2-} , does not yet have any derivatives reported; one might expect any organo derivative of stoichiometry R_8Bi_2 to decompose rapidly under ordinary conditions:



Possibly such a compound may be prepared if the attached groups are very large, as with Tl and Pb. Covalently bonded dibismuth(III) compounds R_4Bi_2 are known [138b, 172], some of which are thermochromic (change color upon melting). Bond angles are close to 90° , indicating that the Bi atoms use p-orbitals for bonding, and that the lone pair is predominantly situated in the 6s orbital. Thermochromic dibismuthines, like their antimony analogues [172], show intermolecular closed-shell interactions in the solid state.

2.2.3.5. Polonium $\{6s^2 6p_{1/2}^2 6p_{3/2}^2\}$

General The chemistry of polonium is more extensive than textbooks indicate [173, 174], although its radioactivity has hampered investigation. α -Polonium is the only elemental allotrope that has a simple cubic structure, attributed to relativistic effects [175]. Declining stability of the highest oxidation state continues: the oxidation state of +6 for Po is has only two examples. The +4 state is the dominant one, and +2 is well represented. Various polonides in the –2 state are also known.

Inorganic Chemistry: Positive Oxidation States The +6 state is currently represented by PoF_6 and PoO_3 , neither of which has been isolated in macroscopic

quantities. A volatile fluoride was reported for the reaction of Po with fluorine, but was not characterized [176]. Calculations indicate that inclusion of relativistic effects should weaken the Po-F bond in PoF_6 [177]. PoI_6 was reported to form and decompose in the vapor phase [178, 179]. Possibly Po(VI) , like other high oxidation states, may be stabilized by anion formation, e.g. PoF_8^{2-} or PoO_6^{6-} .

The +4 state includes numerous characterized compounds similar to tellurium in their chemical behavior. Po(IV) resembles corresponding Zr, Hf and Rf species in forming diketonate complexes [180]. Po(IV) is stable in aqueous solution over a wide pH range, enabling both anion exchange [181] and hydration [182] studies.

The +2 state occurs in various compounds [174a] and is more widespread than the isoelectronic +1 state for bismuth. Most of these compounds are readily oxidized to the +4 state. Tracer work using ^{210}Po indicate that Po^{2+} can be coprecipitated with a variety of M^{+2} salts [183].

While a +3 state has been claimed [173], these claims have never been verified [174a]. The +5 state occurred when ^{222}Rn underwent α -decay in the presence of water vapor or nitrogen dioxide [184]. In the latter case, electron transfer occurred:



From this reaction, the ionization energy of PoO_2 has been estimated as 10.44 ± 0.05 eV [184].

Inorganic Chemistry: Zero or Negative Oxidation States Polonium metal vaporizes as Po_2 molecules [174a, 185], and its partial pressures have been calculated over a wide temperature range [185].

Hydrogen polonide is a volatile molecule, studied for its bonding properties [186, 187]. When water vapor was exposed to ^{210}Po , the levels of volatilized polonium increased sharply due to H_2Po formation [188, 189].

Various metal polonides have been prepared [174a, 190]. PbPo received particular attention because its volatility enabled it to vaporize from a lead-bismuth eutectic coolant in nuclear reactors [191]. Energy band analysis for this compound indicated that it was a semimetal rather than a direct-gap semiconductor [192]. This was also true for ZnPo , CdPo and HgPo , being attributed to relativistic effects [193]. These compounds had a strong ionic character; metal polonides, especially Na_2Po [174a], apparently contain the monomeric Po^{2-} ion. No homoleptic polonium clusters have yet been reported, even though both Bi and Te form clusters.

Organopolonium Compounds These compounds have been reviewed [174b]. Organo derivatives are known for both Po(II) and Po(IV) . Arylpolonium(IV) compounds can be formed by β decay of ^{210}Bi precursors [194]



with the product ratio depending on the nature of X. A similar reaction using pentaphenylbismuth gave a mixture of di- and tetraphenylpolonium [194]. The endohedral compound $\text{Po}@C_{60}$ has been prepared and proposed as a candidate for radiotracer and radiopharmaceutical work [195, 196].

Volatilization of polonium is reported to occur through bacterial methylation and release of dimethylpolonide [197, 198].

2.2.3.6. Astatine $\{6s^26p_{1/2}^26p_{3/2}^3\}$

General Astatine is a member of the halogens, and its chemistry is much like iodine [199, 200]. Due to its radioactivity and the short half-lives of its isotopes (^{210}At has the longest $t_{1/2}$: 8.1 h), investigations have been limited. Most recent work has concentrated on the use of ^{211}At (t'' 7.2 h) in radiotherapy [200, 201]. Like the other halogens, astatine would be expected to show oxidation states of -1 , $+1$, $+3$, $+5$ and $+7$. Relativistic effects modify their relative stabilities. The highest oxidation state of $+7$ has not been verified in any detected compound; earlier claims for perastatate ion, AtO_4^- [199] have not been verified. Even the $+5$ state seems to be limited to astatate ion and a few organoastatine compounds [199, 200]. An oxidation state of $+3$ would be predicted from the electron configuration and by extension from Bi(I) and Po(II). Some organo derivatives are known [199, 200]. The molecule AtF_3 has been investigated; the FAtF bond angle increases relative to the corresponding bond angle in IF_3 due to relativistic effects [202, 203].

Two stable states are $+1$ and -1 , corresponding to loss or gain of one electron by the high energy $6p_{3/2}$ spinor. Calculated values for polonium, astatine and radon appear in Table 2-3, showing a steadily increasing gap between the $6p_{1/2}$ and $6p_{3/2}$ spinors [204], which would be expected to enhance the resistance of At in the $+1$ state to oxidation.

Astatides Astatide anion, At^- , resembles iodide anion in its general chemical behavior, although it was not always retained when coprecipitated with iodide [199]. Astatide formed a complex with Hg(II) in aqueous solution; as might be expected, astatide was a softer base than iodide and formed stronger complexes [205]. It also formed complexes with chelated Rh(III) and Ir(III), which might serve as precursors to radiopharmaceuticals [206]. Liquid-liquid extraction experiments showed high separation factors for astatide ion [207].

Hydrogen astatide, HAt , has been extensively studied for its properties [208–211]. Its dissociation energy is 2.52 eV ($\text{HI} = 3.19$ eV) and the molecular dipole moment is 0.22D ($\text{HI} = 0.47$ D) [211]. A value of 0.06D has been calculated, with the negative end on the hydrogen atom, indicating that this molecule should be named astatine hydride [211].

Like iodine, astatine would be expected to form polyhalides; only a few, such as AtI_2^- , have so far been reported [199].

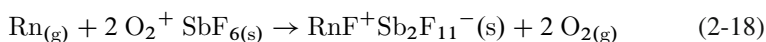
2.2.3.7. Radon $\{6s^26p_{1/2}^26p_{3/2}^4\}$

General Radon, a member of Group 18, is the last element of the Sixth Period; relativistic trends across that Period reach their culmination here. Reported chemical reactions for this element are few [212, 213].

No compounds in the +8 state have been reported or even claimed. RnF_8 is predicted to be unstable towards loss of fluorine [214]. By analogy with Xe, the most likely Rn(VIII) compound to be isolated would probably be Ba_2RnO_6 , the radon analog of barium perxenate.

Two recent studies on RnF_6 [214, 215] indicated that the molecule should be stable to loss of fluorine, and that relativistic effects actually weakened the Rn-F bond! Theoretical calculations indicate that RnF_6 and the isoelectronic ions AtF_6^- and PoF_6^{2-} should have regular octahedral structures because relativistic contraction removes any stereochemical distortion from the 6s electron pair [216]. Chemical species containing Rn(VI), such as RnO_3 and certain derivatives, have been claimed [213], but these claims have not been confirmed. RnF_4 is also predicted to be stable, but has yet to be prepared [214].

Radon(II) and Rn(0) Compounds The +2 oxidation state is the only one for which compounds have been prepared and characterized. This state, isoelectronic with At(I), corresponds to the loss of half the electrons in the $6p_{3/2}$ spinor. RnF_2 and RnF^+ derivatives (e.g. $[RnF^+][SbF_6^-]$) are known [213]; in fact, formation of involatile compounds of this type has been proposed as a method for removing gaseous radon from air [217]:



Trichlorotrifluoroethane solutions of RnF_2 passed through specially prepared columns displaced protons, sodium ion and potassium ion from salts, indicating that Rn can exist as a cation in solution [218].

Radon gas has been predicted to interact with bromide ion [219] and to form a monomeric carbonyl $RnCO$ [220].

2.3. SEVENTH AND EIGHTH PERIOD ELEMENTS

2.3.1. General

All elements in these Period are radioactive. Some have yet to be prepared; others have such short half-lives that their chemical behavior has yet to be investigated. All these elements are predicted to show strong relativistic effects. As of this writing, only francium, radium and element 112 have observed chemical properties. For those elements whose chemistry still remains to be determined, a few selected predictions will be presented.

2.3.2. s-Block Elements

2.3.2.1. Introduction

Francium and radium have only s electrons in their outermost shell. The increased stabilization of these electrons would be expected to alter their properties in comparison to those of the lighter elements. Such alterations do appear, but have not been extensively investigated. Calculated values for electronegativities of the ions Fr^+ and Ra^{2+} show that they increase, relative to those of Cs^+ and Ba^{2+} , rather than decrease as might be expected [221].

2.3.2.2. Francium

The short half-life for this element (the most stable isotope, ^{223}Fr , has $t_{1/2} = 21.8$ min) has hampered chemical investigation. Some selected physical properties have been reported, all of which deviate from the trends for Li through Cs. Ionization energy [222] is higher for Fr than for Cs, as is the electron affinity [223] and the polarizability of the anion [224]. Investigation into alkali metal homo- and heterodiatom molecules showed that the dipole moment for CsFr indicated $\text{Cs}^+ \text{Fr}^-$ polarization [225]; by contrast, other heteroatomic dialkalis have the heavier alkali metal atom at the positive end of the dipole. This reflects a greater relativistic stabilization of the Fr 7s subshell compared to the Cs 6s subshell. Similarly, there was more covalent character in FrO_2 than in the other alkali metal superoxides, attributed to increased interaction between 6p orbitals on Fr and orbitals on oxygen [226]. Potential energy curves and transport coefficients for Fr with the rare gases have been determined spectroscopically [227].

2.3.2.3. Radium

There exists a substantial literature on radium, almost all dealing with its radioactivity, environmental occurrence or use in medical treatment. An investigation into hydrolysis of Ra^{2+} showed that the value for the first hydrolysis constant was the same as for Ba^{2+} , despite the larger size of radium [228]. Studies on both RaF_2 [229] and RaAt_2 [230] indicate that the 6s and 6p orbitals on Ra participate in the bonding, creating a degree of covalency in the bonding. A study of a radium amalgam indicated stronger Ra-Hg interactions than were found in the Ba-Hg system [231].

2.3.3. Superheavy Elements

2.3.3.1. Introduction

Elements having $Z > 103$, are occasionally termed *transactinide elements* or *translawrencium elements*. Much of the work done on these elements is described in a book by Schädel [232], and in two papers [233, 234]. This article will discuss the elements darmstadtium ($Z = 110$) through unbinilium ($Z = 120$). Some theoretical

studies for elements in this series have been reported [235, 236]. At the time of this writing, actual chemical studies have only been reported for ununbium ($Z = 112$).

2.3.3.2. Darmstadtium

In a study of MF_6 ($M = Pd, Pt, Ds$), a $10Dq$ value of 34, 625.6 cm^{-1} was predicted for Ds, compared to 29, 471.7 cm^{-1} for Pt [237]. Two reports on DsC [238, 239] and one on $DsCl_4$ [240] support the placement of Ds in Periodic Group 10. Calculations indicate that DsF_6 would have an O_h symmetry [24].

2.3.3.3. Roentgenium

Roentgenium is predicted to have a ground state of $6d^9 7s^2$, compared to the expected $6d^{10} 7s^1$ [241], reflecting enhanced relativistic stabilization of the 7s sub-shell and destabilization of the $6d_{5/2}$ spinor. Theoretical studies indicated that $Rg(I)$ is a “softer” base than $Au(I)$, making it the “softest metal ion” [242]. Studies on Group 11 monohydrides, MH ($M = Cu, Ag, Au, Rg$) indicated that $Au-H$ had a shorter bond length than $Ag-H$, due to relativistic effects, and that $Rg-H$ was shorter still [243]. The dissociation energy for Rg_2 was calculated to be less than the corresponding energy of Au_2 [43]. The $Rg-C$ bond length in $RgCN$ was predicted to be less than the corresponding $Au-C$ bond length [41, 42].

2.3.3.4. Element 112 (Ununbium, Eka-Mercury)

This element has received considerable attention due to an expected strong stabilization of the assumed outer shell configuration $7s^2$, making it less reactive than mercury, and possibly inert [244]. The atomic structure and properties of this element have been calculated and compared to those of mercury [245].

Adsorption/desorption investigations on a gold surface, using the radioisotopes $^{283}112$, ^{185}Hg and ^{219}Rn , showed that element 112 behaved like a metal rather than like a noble gas [246–248]. From these experiments, workers estimated the boiling point of element 112 to be 357^{+112}_{-108} K [248], compared to 629.7 K for Hg and 211.4 K for Rn. Fully relativistic studies on $(112)X$ and HgX ($X = Pd, Cu, Ag, Au$) showed a decrease of 15–20 kJ/mol in bonding for $(112)X$ relative to HgX [249]. This was attributed to decreased contribution of the 7s orbital (compared to the 6s orbital on Hg) due to stronger relativistic effects.

2.3.3.5. Element 113 (Ununtrium, Eka-Thallium)

Calculations on the linkage between element 113 and element 117 indicated that this bond would be weaker than the $Tl-At$ bond and that, when spin-orbit effects were included, element 113 became more electronegative than element 117 [250]. The strong relativistic stabilization of the 7s orbital for this element suggests that the oxidation state of -1 should be more stable than for Tl [251].

2.3.3.6. Element 114 (Ununquadium, Eka-Lead)

Element 114 has attracted attention because its outer shell configuration $7s^27p_{1/2}^2$ should be exceptionally stable, making it less reactive than lead.

Ionization potentials and excitation energies have been calculated for element 114 and its lighter homologs [252]. The +4 oxidation state is expected to be unstable, except possibly for $(114)F_4$ [253]. Ion exchange behavior of Pb in hydrohalic acids was proposed as a homolog for the corresponding behavior of element 114 [254, 255]. A study on mixed metal-metal species indicated that element 114 would form weaker bonds than Pb [256] and would show lower adsorption on surfaces [257]. Density functional theoretical calculations indicate that element 114 would be more electronegative than Pb [258].

2.3.3.7. Element 115 (Ununpentium, Eka-Bismuth)

An early paper on this element [259] predicted that element 115 would have an outer shell configuration analogous to that of Bi, that the oxidation state of +1 would become more important (with a standard reduction potential of -1.5 V), and that the aqueous chemistry of the +3 state would resemble that of Bi^{+3} . Another paper confirmed the importance of the +1 state and suggests cluster compounds might form [162].

2.3.3.8. Element 116 (Ununhexium, Eka-Polonium)

A study of the Group 16 dihalides reported that spin-orbit coupling was so strong in element 116 that its dihalides would be linear rather than bent [260]. The bond angle in $(116)H_2$ was found to be larger than expected, and the authors suggest the possibility of “supervalent” hybridization involving the 8s orbital [261]. Subshell and spinor energy splittings for this element are larger than for polonium (Table 2-4), suggesting that the oxidation states of +2 and -2 may be correspondingly more stable.

Table 2-4 Selected calculated spinor energies (All values taken from [204]. Reproduced [with modifications] from [1] with permission from the *Journal of Chemical Education*; copyright © 2005 by the Division of Chemical Education Inc.)

Element	Calculated energies, eV		
	$np_{3/2}$	$np_{1/2}$	ns
Sixth row	-8.22	-10.98	-22.04
Po	-9.33	-12.80	-25.53
At	-10.45	-14.70	-29.16
Rn			
Seventh row			
(116)	-6.69	-14.67	-27.16

2.3.3.9. *Element 117 (Ununseptium, Eka-Astatine)*

Element 117 has been estimated to have a boiling point of 618 K [262], comparable to that for At(610 K) and considerably higher than for I(457.5 K). As previously mentioned, element 117 became less electronegative than element 113 in the compound (113)(117) [250, 263]. Spin-orbit effects in the molecule H(117) caused the bond to become unusually long and unusually strong [264]. The species (117)₂ has been studied [265].

2.3.3.10. *Element 118 (Ununoctium, Eka-Radon)*

Element 118 has been estimated to have a boiling point of 247 K [262], compared to 211 K for Rn and 166 K for xenon. It may also be the first rare gas with an electron affinity [266]. The compound (118)F₄ is predicted to have a tetrahedral structure rather than a square planar structure [267, 268].

2.3.3.11. *Element 119 (Ununennium, Eka-Francium)*

Calculations predicted that Element 119 would have higher values for the first ionization energy [222] and electron affinity [223] than francium.

2.3.3.12. *Element 120 (Unbinilium, Eka-Radium)*

Little is known of this element. Relativistic trends predict that it is likely to be more covalent, less ionic than radium; a +1 state might be isolable. Vibrational excitations for ²⁹²120 have been reported [269].

2.4. CONCLUSIONS

Advances in chemical theory, combined with great enhancement of computer capabilities during the last 20 years, have resulted in a near-exponential growth in understanding and applications of relativity theory to chemistry. Corresponding advances in experimental techniques have also grown, though more slowly. Compounds that once were considered too unstable to exist can now be prepared and studied; HgF₄ is an example.

The heavier Main Group elements have been somewhat neglected by comparison to their lighter congeners. Growing interest in these elements over recent years has changed that, and there is likely to be a surging growth in this area in coming years. Realization of all the physical properties and chemical systems that can be predicted by relativity theory, plus the ability to apply it, will play a large part in this.

Synthesis of the superheavy elements has spurred development of "single atom techniques" for their chemical investigation, which in turn have been guided by predictions generated from relativity. Very soon the first true compound(s) of element 112 will be reported, with element 114 following soon thereafter. Subsequently, as more stable nuclides from the "Island of Stability" are synthesized, their compounds will also be prepared.

Relativistic effects have a much greater role in the chemistry of Main Group elements than has generally been realized. Hopefully, this article and this volume will do much to correct that lack of awareness.

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