[8] Crystal data for **5**: $C_{25}H_{37}Cl_3N_4Ru$; $M_r = 601.02$; monoclinic; space group $P2_1/n$ (No. 14); $a = 9.8856(1)$, $b = 17.3298(4)$, $c = 16.5954(3)$ Å; $\beta = 94.3395(12)^\circ$; $V = 2834.90(9)$ Å$^3$; $Z = 4$; $F(000) = 1240$; $\rho_{\text{calcd}} = 1.408\ \text{g cm}^{-3}$; $\mu(\text{Mo}_{K\alpha}) = 8.6\ \text{cm}^{-1}$ (crystal size: $0.15 \times 0.10 \times 0.02$ mm); $T = 193$ K; $\lambda$ $(\text{Mo}_{K\alpha}) = 0.71073$ Å; detector: Kappa CCD (Nonius); 9603 data measured ($4.6^\circ < \theta < 25.1^\circ$), unique data = 4911; 3894 observed data $[I > 2.0\sigma(I)]$; hydrogens refined ($U_{\text{iso}}$); $N_{\text{ref}} = 4911$, $N_{\text{par}} = 446$; $R_I = 0.049$, $wR_2 = 0.081$, $GOF = 1.021$; $w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 1.3899P]$ with $P = (F_o^2 + 2F_c^2)/3$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101497 ; copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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# The Stability of the Oxidation State +4 in Group 14 Compounds from Carbon to Element 114[**]

Michael Seth, Knut Faegri, and Peter Schwerdtfeger[*]

*Dedicated to Professor Warren R. Roper*
*on the occasion of his 60th birthday*

With the recent production of the transactinide isotopes $^{269}(110)$, $^{271}(110)$, $^{273}(110)$, $^{272}(111)$, and $^{277}(112)$,[1, 2] the synthesis of the next superheavy elements 113 and 114 in the near future seems to be feasible.[3] For elements with a lifetime in the second range, atom-at-a-time chemistry can give valuable insight into their chemical behavior,[4, 5] and very recently experiments have been carried out on element 106 (seaborgium) by Schädel et al. at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt.[6] Macroscopic and microscopic calculations predict an island of nuclear stability near nuclear charge $Z = 114$ and neutron number $N = 180$ with an $\alpha$-decay half-life of 12 h.[7] However, it is unlikely that such a large neutron number can be achieved with current nuclear fusion techniques. Quantum-chemical calculations are therefore presently the only way to accurately predict the physical and chemical behavior of superheavy elements.[8, 9]

Gas-phase transactinide chemistry is generally carried out in high oxidation states because the resulting volatility allows separation from the other nuclides. By comparison with the known chemistry of the Group 14 elements, the most likely oxidation states of element 114 (eka-lead) are +2 and +4. Grant and Pyper predicted heats of formation for di- and tetravalent compounds of element 114 empirically with Dirac–Fock data.[10] This study suggests a rather low stability of the oxidation state +4, in agreement with the general trend of decreasing stability of the higher oxidation state on going to the heavier main group elements (often termed the inert pair effect).[11] However, high-level relativistic calculations are necessary to decide whether a compound like $(114)F_4$ is thermodynamically stable.

We carried out spin–orbit coupled relativistic pseudopotential calculations for the hydrides, chlorides, and fluorides of element 114 [$(114)X_2$ and $(114)X_4$ (X = H, F, Cl)], as well as four-component Dirac–Fock (DF) calculations for element 114 and the hydrides $(114)H_2$ and $(114)H_4$.[12–16] The nonrelativistic and spin–orbit coupled relativistic pseudopotentials were obtained by a multielectron fitting procedure to calculated numerical (Hartree–Fock) HF and DF data. Electron correlation was included at the coupled cluster level CCSD(T) and at the second-order Møller–Plesset level (MP2). If accurate dissociation energies were not known for the lighter Group 14 homologues Pb, Ge, and Sn, these were determined by ab initio calculations with the pseudopotentials and basis sets of Stoll et al.[17] Optimization of the structures at the MP2 level led to $T_d$ symmetry for $(114)X_4$ and $C_{2v}$ symmetry for $(114)X_2$. Single-point CCSD(T) calculations were carried out with the optimized MP2 geometries. All relativistic calculations for $CH_2$ and $CH_4$ were carried out by using the nonrelativistic optimized geometry.[18, 19]

Table 1 compares the atomic properties of element 114 calculated at the CCSD(T) level with experimental data for Pb. The ground state of element 114 is best described by *jj* coupling ($J = 0$). The MCDF calculations show that admixtures from $p_{3/2}$ orbitals are small. The coefficients of the configuration state wavefunctions are 0.9957 for the $p_{1/2}^2$ configuration (cf. the nonrelativistic limit of $+\sqrt{2/3}$) and $-0.0929$ for the $p_{3/2}^2$ configuration (nonrelativistic limit $-\sqrt{1/3}$). Hence, the ground-state configuration is a closed-shell system. However, in agreeement with the other Group 14 elements, we use the term symbol $^3P_0$ in the following, even though the $^1S_0$ contribution is important in the $J = 0$ ground state of element 114. At the CCSD(T) level of theory the electron affinity of element 114 is zero (Figure 1a), that is, element 114 cannot accomodate an extra

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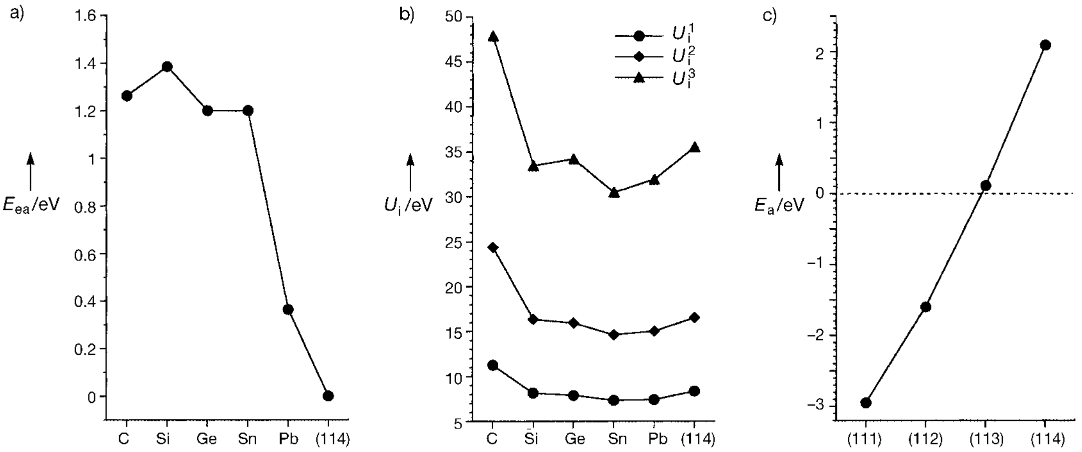

Figure 1. Trends in electron affinities $E_{ea}$ (a) and ionization potentials $U_i$ (b) for the Group 14 elements. c) Excitation energies $E_a$ for the isoelectonic series (111), $(112)^+$, $(113)^{2+}$, and $(114)^{3+}$. For C to Pb, experimental values were taken from refs. [24, 25].

Table 1. Electron affinities $E_{ea}$, ionization potentials $U_i$, and electronic excitation energies $E_a$ for element 114 and Pb. For element 114 DFC CCSD(T) results were used, and for Pb experimental values were taken from ref. [24]. All values are given in eV.

| Property | Transition | (114) | Pb |
|---|---|---|---|
| $E_{ea}$ | $(n-1)d^{10}ns^2np_{1/2}^2(^3P_0) \rightarrow (n-1)d^{10}ns^2np_{1/2}^2np_{3/2}^1(^2P_{3/2})$ | 0.00 | 0.36 |
| $U_i^1$ | $(n-1)d^{10}ns^2np_{1/2}^2(^3P_0) \rightarrow (n-1)d^{10}ns^2np_{1/2}^1(^2P_{1/2})$ | 8.36 | 7.42 |
| $U_i^2$ | $(n-1)d^{10}ns^2np_{1/2}^2(^2P_{1/2}) \rightarrow (n-1)d^{10}ns^2(^1S_0)$ | 16.55 | 15.03 |
| $U_i^3$ | $(n-1)d^{10}ns^2(^1S_0) \rightarrow (n-1)d^{10}ns^1(^2S_{1/2})$ | 35.52 | 31.93 |
| $E_a$ | $(n-1)d^{10}ns^2np_{1/2}^1(^2P_{1/2}) \rightarrow (n-1)d^{10}ns^2np_{3/2}^1(^2P_{3/2})$ | 4.77 | 1.75 |
| $E_a$ | $(n-1)d^{10}ns^1(^2S_{1/2}) \rightarrow (n-1)d_{3/2}^4(n-1)d_{5/2}^3ns^2(^2D_{5/2})$ | 2.09 | 12.55 |

electron. More accurate calculations may reveal a very small positive electron affinity, but adding more diffuse p and d functions to the basis set did not change our result. The zero electron affinity is due to the large spin–orbit splitting of the 7p level, as shown by the $7p_{1/2}/7p_{3/2}$ splitting of 4.77 eV in $(114)^+$ (Table 1). This results in a relativistically destabilized $7p_{3/2}$ level (diffuse $7p_{3/2}$ orbital) and a relativistically stabilized $7p_{1/2}$ level, as the comparison with the atomic data of Pb show.[26] One can therefore conclude that element 114 is chemically inert. The first three ionization potentials for all Group 14 atoms are shown in Figure 1 b. The plot shows that element 114 has larger 7p and 7s ionization potentials than Si, Ge, Sn, and Pb but is certainly not more inert than carbon. Of the elements shown in Figure 1 b, carbon has the highest ionization potential. The suitability of ionization potentials for discussing trends in chemical reactivity along a series of elements is questionable,[11] and accurate molecular calculations are preferable for estimating the thermodynamic stability of compounds of element 114.

The decomposition reactions (1) and (2) were used as the basis for discussing the stability of the oxidation states +4 and +2. The decomposition energies of reaction (1) for X = H is

$$MX_4 \rightarrow MX_2 + X_2 \quad (1)$$

$$MX_2 \rightarrow M + X_2 \quad (2)$$

$M = C, Si, Ge, Sn, Pb, (114)$

shown in Figure 2 at the (uncorrelated) Dirac-Fock-Coulomb (DFC) and HF levels of theory. As pointed out before for the lighter Group 13 and 14 compounds,[11, 19] the instability of the higher oxidation state +4 increases monotonically with increasing size of the Group 14 element, and for the heavier elements this effect is amplified by relativistic effects. In contrast to the ionization potentials (Figure 1 b) a pronounced zigzag trend is not observed. The inert pair effect is therefore a natural periodic trend which is intensified by relativistic effects. The DFC calculations suggest that $(114)H_4$ is thermodynamically highly unstable. This trend does not change significantly if electron correlation is included (Figure 2). However, more electronegative ligands such as fluorine might stabilize the oxidation state +4.

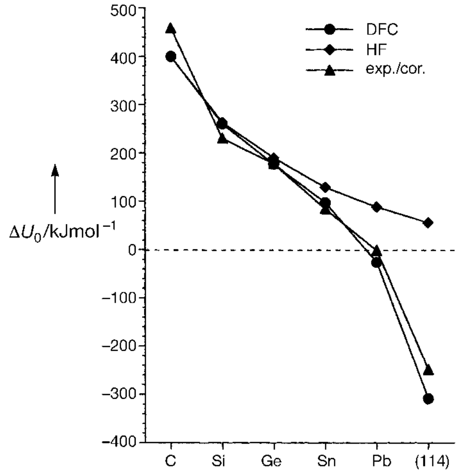

Figure 2. Decomposition energies $\Delta U_0$ of the reaction $MH_4 \rightarrow MH_2 + H_2$ for the hydrides of Group 14. Results from relativistic DFC and nonrelativistic HF calculations (see also ref. [19]). Results of electron-correlated calculations: for C and Si experimental decomposition energies were used,[27] for Ge and Sn calculated pseudopotential MP2 values, for Pb the QCISD(T) values from ref. [11], and for element 114 DFC CCSD(T) results.

Figure 3 shows the results of relativistic spin–orbit coupled pseudopotential calculations for the hydrides, fluorides, and chlorides of lead and element 114. The fluorides and chlorides of element 114 are of interest for future radiochemical experiments. Figure 3 clearly shows a pronounced relativistic

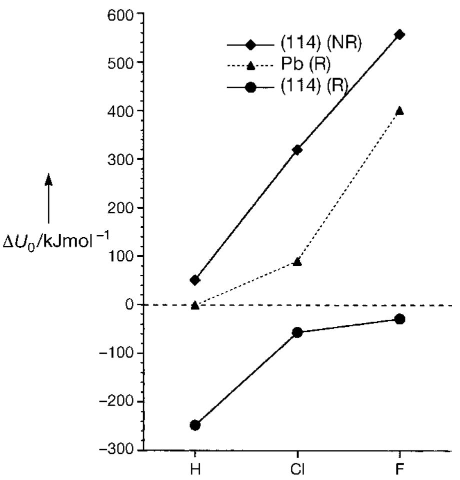

Figure 3. Nonrelativistic (NR) and relativistic (R) decomposition energies $\Delta U_0$ for the reaction $MX_4 \rightarrow MX_2 + X_2$ for the hydrides, fluorides, and chlorides of element 114 and Pb. All results are from CCSD(T) calculations. The results for the decomposition energy of the reaction $PbCl_4 \rightarrow PbCl_2 + Cl_2$ were taken from ref. [28].

destabilization of the oxidation state +4 for element 114, and none of the compounds studied here is thermodynamically stable at this level of theory. However, the calculated structures are local minima according to frequency analyses. Hence, the $(114)X_4$ (X = H, Cl, F) compounds are kinetically stable. More accurate calculations on $(114)F_4$ may eventually reveal a small stability towards decomposition ($\Delta U_0 > 0$), but there is no doubt that element 114 compounds in the oxidation state +4 will have very low thermodynamic stability, and it may therefore be difficult to perform radiochemical experiments for this oxidation state.

The decrease in stability of the high oxidation state of the Group 14 elements is probably not monotonic for the fluorides. Experimental values for $CF_4$ and $SiF_4$[27] and calculated MP2 values for the other fluorides give the following $\Delta U_0$ values for the reaction $MF_4 \rightarrow MF_2 + F_2$: $CF_4$: 745, $SiF_4$: 1022, $GeF_4$: 669, $SnF_4$: 684, $PbF_4$: 401, $(114)F_4$: $-28$ kJ mol$^{-1}$. The $\Delta U_0$ values decrease from Si to element 114, and only carbon does not follow this trend. The experimental values have large errors, and more accurate correlated calculations for the Group 14 halides are necessary for discussing these trends in detail.

Concerning the stability of the oxidation state +2 [Eq. (2)], the fluoride and chloride are stable towards decomposition into element 114 and $X_2$ ($\Delta U_0 = 287$ kJ mol$^{-1}$ for X = F and 114 kJ mol$^{-1}$ for X = Cl at the CCSD(T) level). The hydride $(114)H_2$ is thermodynamically unstable ($\Delta U_0 = -320$ kJ mol$^{-1}$). All compounds are relativistically destabilized. At the nonrelativistic CCSD(T) level, $\Delta U_0 = +39$ kJ mol$^{-1}$ for $(114)H_2$. Hence, the most stable oxidation state for element 114 is +2 and not +4.[10, 29]

The (114)–X bonds are comparable to or slightly longer than those of the corresponding lead compounds. At the MP2 level we obtained 1.75 Å for both $(114)H_4$ and $PbH_4$, in agreement with earlier predictions,[30] and 2.14 Å for $(114)F_4$ and 1.97 Å for $PbF_4$. The bond angles of the $(114)X_2$ species are very similar to those of the corresponding lead compounds.

Finally, another interesting effect is noteworthy. Figure 1c shows the $6d^{10}7s^1 \rightarrow 6d^4_{3/2}6d^5_{5/2}7s^2$ excitation energies for the isoelectronic series (111), $(112)^+$, $(113)^{2+}$, and $(114)^{3+}$.[31–33] As observed before,[31] element 111 (eka-gold) undergoes a relativistic change in its ground state configuration from $d^{10}s^1$ ($^2S_{1/2}$) to $d^9s^2$ ($^2D_{5/2}$). This is mainly due to the large direct relativistic 7s stabilization and in part due to the indirect relativistic $6d_{5/2}$ expansion. Interestingly, this effect diminishes with increasing nuclear charge along the isoelectronic series, and element 113 is the first element that again exhibits a $^2S_{1/2}$ ground state configuration. This is probably due to stabilization of the 6d orbitals with increasing nuclear charge. The relativistic effect is largest for element 111. This is well known for Group 11 elements and has been termed the Group 11 maximum.[34]

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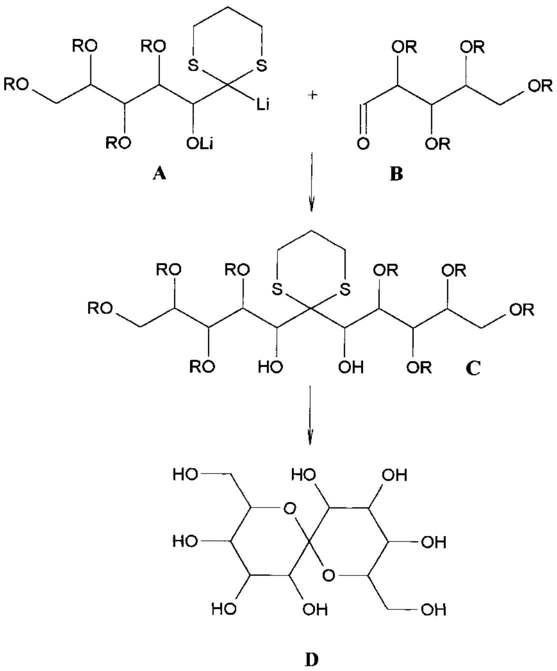
# Perhydroxylated 1,7-Dioxaspiro[5.5]undecanes ("Spiro Sugars"): Synthesis, Stereochemistry, and Structure[**]

Raphael Bextermöller, Hartmut Redlich,*
Klaus Schnieders, Sven Thormählen, and
Roland Fröhlich

*Dedicated to Professor Dieter Seebach*
*on the occasion of his 60th birthday*

Perhydroxylated 1,7-dioxaspiro[5.5]undecanes (**D**; Scheme 1) – a class of compounds which hitherto has not been identified in nature and whose synthesis is reported herein for the first time – can be formally considered as two hexopyranoses joined together by a spiroacetal center ("spiro sugar").[1]



Scheme 1.

In contrast to perhydroxylated derivatives, spiroacetals are widespread in nature and exhibit a broad range of biological activities, and are found, for example, as insect pheromones, antibiotics, and toxins.[2]

In their synthesis from open-chain precursors – the most common route[2] – structural features such as substituents and their relative arrangement in the acyclic compound need to be taken into consideration. This is particularly evident if the relatively well known properties of monosaccharide hexopyranoses are compared to those of the perhydroxylated 1,7-dioxaspiro[5.5]undecanes (spiro sugars).

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