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Is the chemistry of lawrencium peculiar?†

Wen-Hua Xu\textsuperscript{ab} and Pekka Pyynkö\textsuperscript{*b}

It is explicitly verified that the atomic 7p\textsuperscript{1} ground-state configuration of Lr originates from relativistic effects. Without relativity one has 6d\textsuperscript{1}. All three ionization potentials IP\textsubscript{1–3} of Lr resemble those of Lu. Simple model studies on mono- and trihydrides, monocarbonyls or trichlorides suggest no major chemical differences between Lr and the lanthanides.

1 Introduction

The periodic table is about chemistry. The group is related to the number of valence electrons and the period is related to the number of nodes in the radial functions of these electrons. In lawrencium, \textsuperscript{103}Lr, counting the filled 5f shell as the ‘core’, there are three valence electrons. It had been debated for some time, whether they are 7s\textsuperscript{2}6d\textsuperscript{1} or 7s\textsuperscript{2}7p\textsuperscript{1/2}\textsuperscript{1}, until both an experiment\textsuperscript{1} and also the latest calculations supported the latter alternative. That 7p\textsuperscript{1} atomic ground state was first surmised by Brewer\textsuperscript{2} and first calculated by Desclaux and Fricke.\textsuperscript{3} Large MCDF calculations by Zou and Froese Fischer\textsuperscript{4} support the 5d\textsuperscript{1} and 7p\textsuperscript{1} ground states for Lu and Lr, respectively, and yield very different oscillator strengths. For Lr, however, they are not yet experimentally confirmed.

This does not yet settle the question on the chemical behaviour. If all three valence electrons are formally ionized away, in an Lr\textsuperscript{3+} compound, lawrencium clearly belongs to Group 3 in Period 7, and nothing unexpected has happened in its chemistry.

The three first ionization potentials of Lr are compared with those of La–Lu in Fig. 1. They are quite similar, especially with Lu. Therefore the ionic chemistry of Lr could be expected to be similar to that of the lanthanides.

Experimentally this is what happened, see Brüchle \textit{et al.},\textsuperscript{7} Hoffman \textit{et al.},\textsuperscript{8} and Scherer \textit{et al.},\textsuperscript{9} all in 1988. Brüchle and Hoffman found that Lr\textsuperscript{3+} had a similar elution behaviour to the latter Ln\textsuperscript{3+} and Scherer found no evidence for a possible reduction to lower oxidation states than Lr\textsuperscript{3+} in aqueous solutions.

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cp02706g
solution. Recently, in reductive surroundings, all the divalent lanthanide oxidation states Ln(II) have also been obtained. These divalent lanthanide, Ln(II), compounds are mostly 5d\(^2\). No such experiments exist on Lr.

Calculations suggest that the free-atom Lr(II) and Lr(III) are 7s\(^2\) and 7s\(^1\), respectively, in contrast to the quoted 5d\(^2\) for Ln(II) in compounds.\(^{10}\) The stabilisation of the 7s shell in Group 3 destabilizes the Pb(IV) state in PbO\(_2\), thereby explaining most of where the 6s shell favours the divalent Pb(II) state in PbO or PbSO\(_4\), respectively. Similarly, for lead, the relativistic stabilization of the \(Z\) of valence s shells down the same column increases as oxidation states in Periods 5 and 6. One possibility considered relativistic stabilization of an ns shell leads to different main group elements.\(^{5,6,11}\) In addition to thallium, having the main oxidation states In(III) and Tl(I), contributes to the chemical difference between indium and thallium.\(^{4}\)

**2 Atomic results**

We first verify the relativistic origin of the ground-state change from 6d\(^1\) to 7p\(^1\), see Table S1 in the ESL.\(^{\dagger}\) Compared with the non-relativistic results, Dirac–Fock (DF) shifts down the relative energy of \((n + 1)\ ^2\)P to \(n\ ^2\)D by nearly 3 eV, and changes the ground state configuration. The relativistic effect is so large that already DF-level evidence makes sense. MCDF results were reported by Fritzsch et al.\(^{13}\)

The calculated orbital energies for Tl and Lr atoms are shown in Fig. 2. It is seen that the relativistic stabilization of the Tl 6s shell is substantial, making its energy comparable to the ligand orbital energy (here H). In contrast, the Lr 7s orbital energy is small, despite a larger \(Z\).

![DF orbital energies of In, Tl and Lr](image)

**Fig. 2** The calculated relativistic (R) and non-relativistic (NR) Dirac–Fock orbital energies of neutral In, Tl and Lr atoms. For lawrencium, the electron configuration 7s\(^6\)6d\(^1\) is assumed. Values from Desclaux.\(^{15}\)

Does the atomic ground state matter in chemistry? As seen in Fig. 2, the valence orbital energies of the electropositive element Lr are small and hence in compounds these electrons, whether 7s, 6d or 7p, will largely go away, anyway. Group 13 is more electronegative\(^{14}\) than Group 3.

Why is Lr, like other lanthanides and actinides, so electropositive? A broad-brush explanation could be that they all belong to Group 3 and the electronegativities in the Periodic table increase from left to right (from Group 1 to Group 18), probably due to increasing partial screening by the fellow valence electrons.

**3 Molecular results**

**3.1 Hydrides**

We first consider the simple hydride models and calculate the reaction energy, \(\Delta E\) for the model reaction

\[
\text{MH}_3 \rightarrow \text{MH} + \text{H}_2
\]

for M = Lr, Lu, In and Tl. As seen in Table 1, this \(\Delta E\) is negative for thallium which clearly prefers to be Tl(II), and positive for the other four metals, which prefer being M(III), including Lr(III), Tl(I) is an example of the relativistic 6s\(^2\) inert pair.

The structural parameters are given in Table 2.

**3.2 Monocarbonyls**

We then compare LrCO with the series LnCO, Ln = La–Lu, studied both experimentally and theoretically by Xu et al.\(^{19}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symmetry</th>
<th>Bond length (Å)</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LrH</td>
<td>Linear</td>
<td>1.895</td>
<td></td>
</tr>
<tr>
<td>LrH</td>
<td>Linear</td>
<td>1.960</td>
<td></td>
</tr>
<tr>
<td>LrH(_2)</td>
<td>C(_{2v})</td>
<td>1.915</td>
<td>113.5</td>
</tr>
<tr>
<td>LrH(_2)</td>
<td>C(_{2v})</td>
<td>1.954</td>
<td>110.6</td>
</tr>
<tr>
<td>LrH(_3)</td>
<td>C(_{3v})</td>
<td>2.015</td>
<td>117.5</td>
</tr>
<tr>
<td>LrH(_3)</td>
<td>C(_{3v})</td>
<td>1.921</td>
<td>112</td>
</tr>
<tr>
<td>LrH(_2)</td>
<td>C(_{2v})</td>
<td>1.940</td>
<td>107</td>
</tr>
<tr>
<td>LrHCO</td>
<td>Linear</td>
<td>2.297</td>
<td>(Lu–C), 1.167</td>
</tr>
<tr>
<td>LrCO</td>
<td>Linear</td>
<td>2.384</td>
<td>(Lu–C), 1.169</td>
</tr>
<tr>
<td>LuCl(_3)</td>
<td>D(_{3h})</td>
<td>2.394</td>
<td>120</td>
</tr>
<tr>
<td>LuCl(_3)</td>
<td>C(_{2v})</td>
<td>2.424</td>
<td>113</td>
</tr>
<tr>
<td>([C(<em>{2p}),Lr](</em>{2}))</td>
<td>Linear</td>
<td>2.635(^{16})</td>
<td></td>
</tr>
<tr>
<td>([C(<em>{2p}),Lu](</em>{2}))</td>
<td>Linear</td>
<td>2.697(^{12})</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Ref. 17. \(^{b}\) Ref. 10. \(^{c}\) Shortest M–C.

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Table 3 | Population analysis of LrH, LrH$_2$, LrH$_3$, LuCO and LrCO. P: projection analysis; M: Mulliken population. G: Four-component Hamiltonian with the DZ Gaussian basis set; S: two-component Hamiltonian with the DZ Slater basis set.

<table>
<thead>
<tr>
<th>Mol.</th>
<th>Type</th>
<th>Functional</th>
</tr>
</thead>
<tbody>
<tr>
<td>LuH</td>
<td>P, G</td>
<td>PBE</td>
</tr>
<tr>
<td>LrH</td>
<td>P, G</td>
<td>PBE</td>
</tr>
<tr>
<td>LrH$_2$</td>
<td>P, G</td>
<td>PBE</td>
</tr>
<tr>
<td>LrH$_3$</td>
<td>P, G</td>
<td>CAMB3LYP</td>
</tr>
<tr>
<td>LuCO</td>
<td>M, S</td>
<td>PBE</td>
</tr>
<tr>
<td>LrCO</td>
<td>M, S</td>
<td>PBE</td>
</tr>
</tbody>
</table>

Valence population

| LuH  | H 1s(1.26) | H 1s(1.26) |
| LrH  | H 1s(1.34) | H 1s(1.34) |
| LrH$_2$ | H 1s(1.30) | H 1s(1.30) |
| LrH$_3$ | H 1s(1.34) | H 1s(1.34) |
| LuCO | H 1s(1.34) | H 1s(1.34) |
| LrCO | H 1s(1.36) | H 1s(1.36) |

Periodic table. At the CCSD(T) level, LrCO is 1.0 eV below Lr + CO, while LuCO is 0.77 eV below Lu + CO. The attempts to produce LuCO$^{19}$ nevertheless failed.

Population analyses are shown in Tables 3–5. Projection analysis is stable regarding different types of functionals. In this study, Mulliken populations agree well with the projection analysis. There is a high correlation between Lu and Lr electronic configurations in all the hydrides and carbonyls.

The C–O stretching frequencies are 1897 and 1921 cm$^{-1}$ for LrCO and LuCO, respectively. The valence orbitals of LuCO and LrCO are compared in Fig. 3 and found to be very similar. We conclude that although the p populations strongly depend on the method of calculation, Mulliken, NBO (Natural Bond Orbital) or projection, the results for Lu 6p and Lr 7p are closely similar.

Table 4 | Natural electron configurations of LrH, LrH$_3$, LuCO and LrCO. The density matrices are from ZORA1c and PBE calculations. At this level, an NBO was available.

<table>
<thead>
<tr>
<th>Mol.</th>
<th>Natural electron configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>LrH</td>
<td>core$^7$7s(1.92) 6d(0.34) 7p(0.04)</td>
</tr>
<tr>
<td>LrH$_3$</td>
<td>core$^7$7s(0.84) 6d(0.67) 7p(0.01)</td>
</tr>
<tr>
<td>LuCO</td>
<td>core$^7$7s(0.19) 6d(0.56) 6p(0.06)</td>
</tr>
</tbody>
</table>

The density matrices are from ZORA1c and PBE calculations. At this level, an NBO was available. See Table 3 for populations.

3.3 Lawrencium trichloride and a divalent complex

One feature of the bonding in lanthanide chlorides is the pr–dr bond. It is also observed in LrCl$_3$. Note that unlike in D$_{3h}$ LuCl$_3$, the geometry of LrCl$_3$ is C$_{3v}$, with an out-of-plane vibrational frequency of only 48 cm$^{-1}$. For the bonding molecular orbitals, see Fig. 4.

In recent years, one breakthrough in lanthanide chemistry is that divalent complexes were synthesized and characterized for all lanthanides. We now studied an Lr complex with the same ligand as the LrCl$_3$ complex. Experimentally, a potassium atom in a crown ether$^{10}$ functioned as the counterion of [Lr(Cp$_3$)$_3$]$^+$. A stable geometry was found for this complex anion. The electronic structure is similar to that of Lu. The metal configuration is 6d$^1$. Spin–orbit effects were included in the calculation. As seen from Table 3, this LrHOMO is a d$^1$ orbital on Lr.

The structures of all systems are given in the ESI.$^+$

4 Relation to the periodic table

Three different choices can be outlined for the f-element rows:

1. Fourteen-element rows, La–Yb and Ac–No. Put Lu and Lr in Group 3. Chosen by Jensen$^{26}$ and currently Wikipedia.

3. Fifteen-element rows, La–Lu and Ac–Lr. This includes f⁰ among the f⁰ to f¹⁴ series. All elements are mostly trivalent. Their ionic and covalent radii form a continuous series. Now chosen by IUPAC23 and by us. To us the atomic ground state is less important than the chemical bonding, in the systems so far considered.

5 Computational details

The geometries were optimized at the ZORA2c 24 level, DFT (PBE functional25) with TZ2P 26 Slater basis sets. The vibrational frequencies were obtained to confirm the minima. However, [(Cp')3Lr]− was optimized with the TPSSh functional27,28 to compare with the published [(Cp')3Lu]− results. Solvent effects were considered by the COSMO model29 with tetrahydrofuran (THF) parameters. For more details, see the computational part of ref. 10. ADF 201610,31 and Turbomole 7.0232 packages were used. To calculate more accurate energetics, the two-component (2c)-MP233,34 and (2c)-CCSD(T)35 as implemented in Dirac 15.0,36 and CCSD(T) implemented in Molpro 2015.137,38 were employed. The basis sets are Dyall all-electron double zeta39 and ECP from the Stuttgart/Cologne group,40,41 respectively.

6 Conclusion

All three ionization potentials of the lawrencium atom resemble those of the lanthanides, especially lutetium. Despite the different atomic ground states of d¹ and (p*)¹ for Lu and Lr, respectively, their chemical behaviour in the present systems is found to be similar. Nothing prevents one from keeping a fifteen-element trivalent actinide row Ac–Lr, under the trivalent lanthanide row La–Lu. This entirely avoids the issues arising from fourteen-element rows.20,21

Acknowledgements

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References


