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Serendipitous Formation of a Cerium(IV)-Mercury(II) Separated Ion Coordination Polymer#

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We dedicate this paper to the late Prof. Dr. Rudolf Hoppe on the occasion of the 100th anniversary of his birth date in recognition of his pivotal role in solid state chemistry.

Trivalent cerium tris-*tert*-butoxide, "$[Ce(OtBu)_3]$", was synthesised *in situ* and treated with excess $HgCl_2$. After reaction, colourless crystals were identified amongst excess $HgCl_2$. Analysis by X-ray crystallography revealed the formation of an unusual ion separated coordination polymer consisting of two $[Ce^{IV}(OtBu)_3(thf)_3]^+$ ions and a di-anionic chloridomercurate(II) two dimensional sheet $[Hg_8Cl_{18}]^{2-}$, giving the overall formula $[\{Ce(OtBu)_3(thf)_3\}_2\{Hg_8Cl_{18}\}]_\infty$ (**1**).

Introduction

Although known for many years prior,[1–4] it was only after their optimised synthesis[5–6] and structural elucidation[6] that the chemistry of tetravalent cerium alkoxides flourished. Of these alkoxides, the *tert*-butoxide derivative held a crucial role in underpinning the chemistry of the cerium(IV) ion.[7–13] Typically synthesised by either salt metathesis[6,10,14–15] or protonolysis protocols[16–17] from cerium(IV) starting materials, hetero- or homoleptic *tert*-butoxide complexes such as $[Ce_2(OtBu)_8]$,[18] $[Ce(OtBu)_4(solv)_2]$ (solv = THF or Py)),[7,11, 19] $[Ce(OtBu)_3(NO_3)(thf)]$,[10] or $[Ce\{N(SiMe_3)_2\}_2(OtBu)_2]$,[20] have been used in complex synthesis,[7,9,15,19,21] catalysis,[9,12–13] or as precursors to the thin film deposition of ceria (CeO_2),[11,16] which is of particular interest considering ceria is a prominent catalyst used under a variety of circumstances,[22–25] such as in automotive catalytic converters.[26]

Although a significant improvement on the original publication,[6] the synthesis of "$[Ce(OtBu)_4]$" derivatives from ceric ammonium nitrate (CAN) based salt metathesis protocols still holds synthetic difficulties,[27] which are aggravated by its tendency to undergo decomposition to mixed oxidation state cerium(III/IV) oxide species.[16,27] More recent studies however have utilised tetravalent cerium silylamides[16–17] as protonolysis precursors, where upon treatment with stoichiometric amounts of HO*t*Bu enables facile access to a cerium(IV) *tert*-butoxide complex. For instance, homoleptic $[Ce(N(SiHMe_2)_2)_4]$ can be treated with HO*t*Bu giving $[Ce(OtBu)_4(py)_4]$ in good yield.[17] Yet, despite the cleaner synthetic route provided by the silylamides and greater applicability of such cerium(IV) starting materials,[28–30] obtaining these silylamide precursors in sufficient quantity and purity can be difficult.[17,20,30] Considering cerium(IV) *tert*-butoxide complexes can be obtained through oxidation of trivalent cerium precursors,[7,32] with strong oxidants such as peroxides,[32] 1,2-benzoquinone,[32] or iodine,[7] and as trivalent "$[Ce(OtBu)_3]$" can be readily almost quantitatively prepared *in situ* from a salt metathesis reaction between cerium(III) chloride and K(O*t*Bu),[31] it was envisioned that an *in situ* synthesis of "$[Ce(OtBu)_3]$" followed by immediate oxidation (by $HgCl_2$) could provide an alternative one-pot synthesis to $[Ce(OtBu)_4(thf)_2]$.

Herein we report the *in situ* formation of "$[Ce(OtBu)_3]$" followed by oxidation with excess $HgCl_2$. After reaction workup, colourless crystals were located within the excess $HgCl_2$ and analysed by X-ray crystallography revealing the formation of a highly unusual ionic coordination polymer containing two tetravalent $[Ce(OtBu)_3(thf)_3]^+$ cations and a di-anionic chloridomercurate(II) $\{Hg_8Cl_{18}\}^{2-}$ two dimensional sheet, $[\{Ce(OtBu)_3(thf)_3\}_2\{Hg_8Cl_{18}\}]_\infty$ (**1**).

Results and Discussion

"$[Ce(OtBu)_3]$" was prepared *in situ* by stirring $CeCl_3(thf)_2$ (synthesised by a literature procedure)[33] and K(O*t*Bu) in *n*-hexane with heating (Scheme 1 i). Upon filtration and evaporation to dryness the resulting white powder ("$[Ce(OtBu)_3(thf)_x]$") was dissolved in Et_2O, and a large excess of $HgCl_2$ was added (Scheme 1 ii). $HgCl_2$ was chosen as the oxidant due to its slight-solubility in ether and the reduction product (either Hg_2Cl_2 or Hg^0) is poorly soluble and unlikely to engage in additional chemistry. After addition of $HgCl_2$, the reaction mixture was heated at reflux for 3–4 hours. Upon cooling, a yellow supernatant and a colourless precipitate formed. The supernatant was decanted, and, colourless crystals were identified amongst the colourless precipitate. The crystals diffracted poorly, but

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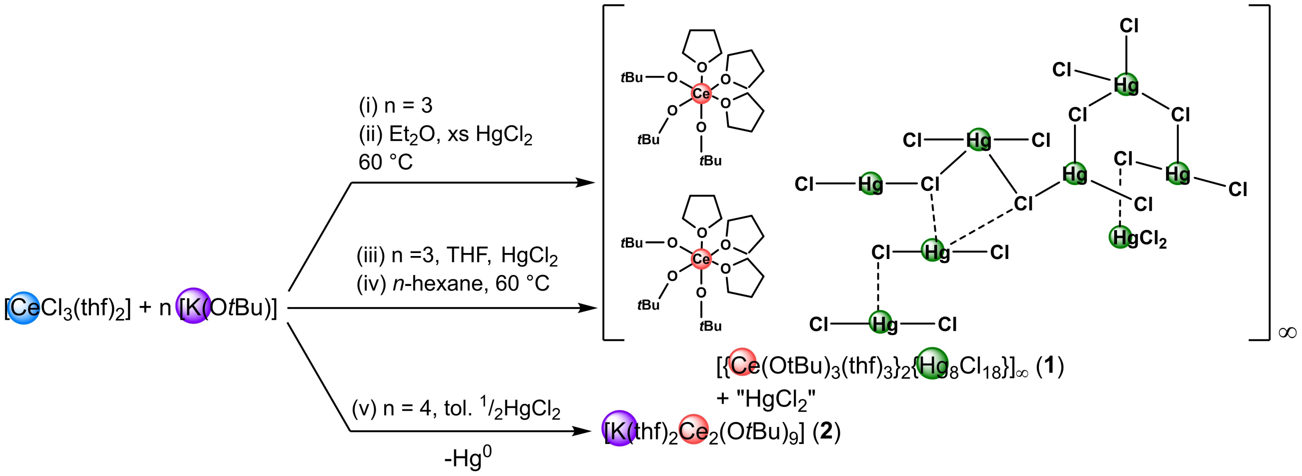

Scheme 1. *In situ* preparation of "$[Ce(OtBu)_3]$" and oxidation by $HgCl_2$ forming either $[\{Ce(OtBu)_3(thf)_3\}_2\{Hg_8Cl_{18}\}]_\infty$ (**1**) or $[K(thf)_2Ce_2(OtBu)_9]$ (**2**). (i) −3 KCl, 60 °C, *n*-hexane, overnight. (ii) Et_2O, ~3–4 hours, reflux. iii) – 3 KCl, ~3–4 h, $HgCl_2$ addition and filtration. (iv) *n*-hexane, 60 °C, precipitation of $HgCl_2$ and crystallisation of **1**. v) – 3 KCl, stirred for one hour. Note: extensive bonding network of the $[Hg_8Cl_{18}]^{2-}$ is not shown.

single crystal X-ray diffraction at the Australian Synchrotron permitted structural elucidation, revealing the formation of an ionic coordination polymer, which consists ed of with a long inter-connected di-anionic $\{Hg_8Cl_{18}\}^{2-}$ sheet with two separated monomeric tris-*tert*-butoxidocerium(IV) cations, giving the overall formula $[\{Ce(OtBu)_3(thf)_3\}_2\{Hg_8Cl_{18}\}]_\infty$ (**1**, Scheme 1).

Due to the colourless nature of **1**, it could not be readily separated from residual $HgCl_2$ by hand picking, making additional characterisation difficult. However, it could be repeatedly detected (by single crystal analysis) when the oxidation of "$[Ce(OtBu)_3]$" was performed with an excess of $HgCl_2$. When $HgCl_2$ was added to the *in situ* synthesis of "$[Ce(OtBu)_3]$" in THF, followed by filtration and concentration, addition of n-hexane caused additional precipitation (likely $HgCl_2/Hg_2Cl_2$), the mixture was heated and filtered followed by slow cooling, producing a fine microcrystalline colourless powder, where crystalline **1** was again identified amongst excess $HgCl_2$. The presence of $HgCl_2$ was determined by an elemental analysis of the resulting white powder/crystalline mixture which gave low C and H values, suggesting the persistence of $HgCl_2$. Although oxidation of cerium became apparent through structural elucidation (see X-ray crystallographic discussion), no observable formation of Hg^0 occurred.

When the synthesis and oxidation of "$[Ce(OtBu)_3]$" was performed with a stoichiometric amount of $HgCl_2$ and in the presence of an additional equivalent of K(O*t*Bu) in toluene, Hg^0 was deposited on the Schlenk flask amongst a colourless precipitate. After filtration and concentration, one very large crystal of $[K(thf)_2Ce_2(OtBu)_9]$ (**2**) formed from the yellow/green solution (Scheme 1) comprising 10% of the yield. The identity of **2** was determined by unit cell comparison with the literature data [14].

Structural discussion

Polymeric **1** crystallises in the monoclinic space group $P2_1/c$ with two cerium atoms and part of the chloridomercurate(II) sheet $\{Hg_8Cl_{18}\}^{2-}$ occupying the asymmetric unit (Figure 1). The coordination sphere of the cerium atoms in **1** are each saturated by three coordinating thf ligands and three coordinating anionic *tert*-butoxide ligands giving an overall coordination number of six and a distorted octahedral stereochemistry. The ligands are *fac*-arranged around the cerium atom, a known arrangement for cerium complexes,[34–36] with two examples concerning aryloxide ligands, namely $[Ce(OAr)_3(thf)_3]$ ($Ar = 2\text{-}tBuC_6H_4$, or $2,6\text{-}iPrC_6H_3$).[37] In **1** there is a large difference between the Ce–O bond lengths of the anionic *tert*-butoxide oxygen atoms ($Ce_{(atoms\ 1\&2)}$–$O_{(atoms\ \ 1\text{-}3,7\text{-}9)}$: average: 2.06 Å, range: 2.038(12)–2.069(12) Å), and the neutral thf ligands ($Ce_{(atoms\ 1\&2)}$–$O_{(atoms\ 4\text{-}6,\ 10\text{-}12)}$: average: 2.48 Å, range: 2.470(11)-2.491(12) Å), as is expected due the anionic nature of the *tert*-butoxide. The tetravalent oxidation state of the cerium atoms in **1** can be confirmed by comparisons with other 6-coordinate cerium(IV) *tert*-butoxide complexes, where the bond lengths in **1** are shorter than those in: $[Ce(OtBu)_2(saflen)]$ (saflen = a ferrocene functionalised salen Schiff base, Ce–O: 2.085(3) and 2.087(3) Å),[9] $[Na_2(dme)_2Ce(OtBu)_6]$ (Ce–O: 2.136(4) and 2.146(4)),[6] $[Ce_2(OtBu)_4(C_5Me_5)]$ (Ce–O: 2.116(6) and 2.124(6) Å),[38] and the more sterically congested $[Ce(OtBu)_4(py)_2]$ system ($Ce–O_{average}$: 2.10 Å, range: 2.066(5)–2.122(4) Å).[14] Indeed, the Ce–(O*t*Bu) bond lengths in **1** are closer to those in the five coordinate homoleptic system $[Ce_2(OtBu)_8]$ ($Ce–O_{average}$: 2.06 Å, range: 2.058(3)–2.065(3) Å)[14] despite the difference in coordination number, presumably owing to the positive charge on the present complex. Interestingly, the Ce–O*t*Bu bond lengths in **1** are also comparable to those observed within the ten coordinate *tris*-Cp derivatives $[Ce(X)_3(OtBu)]$ ($X = C_5H_5$, Ce–O: 2.045(6);[10] $X = C_5H_4(SiMe_3)$, Ce–O: 2.071(1)),[39] despite the difference in coordination number (Ce(IV) CN = 6 (ionic radius 0.87 Å), CN = 10 (ionic radius 1.07 Å)),[40] likely owing to the preferential coordination of the *tert*-butoxide over the Cp ligands. For further comparison, the Ce–O bond lengths observed in trivalent derivatives are longer than in **1**, for instance $[Ce_4(OtBu)_{12}]$ (average: 2.12 Å, range: 2.141(14)–2.172(13) Å), or in the aryloxide $[Ce(OAr)_3(thf)_3]$ examples ($OAr = 2\text{-}tBuC_6H_4$, Ce–OAr:

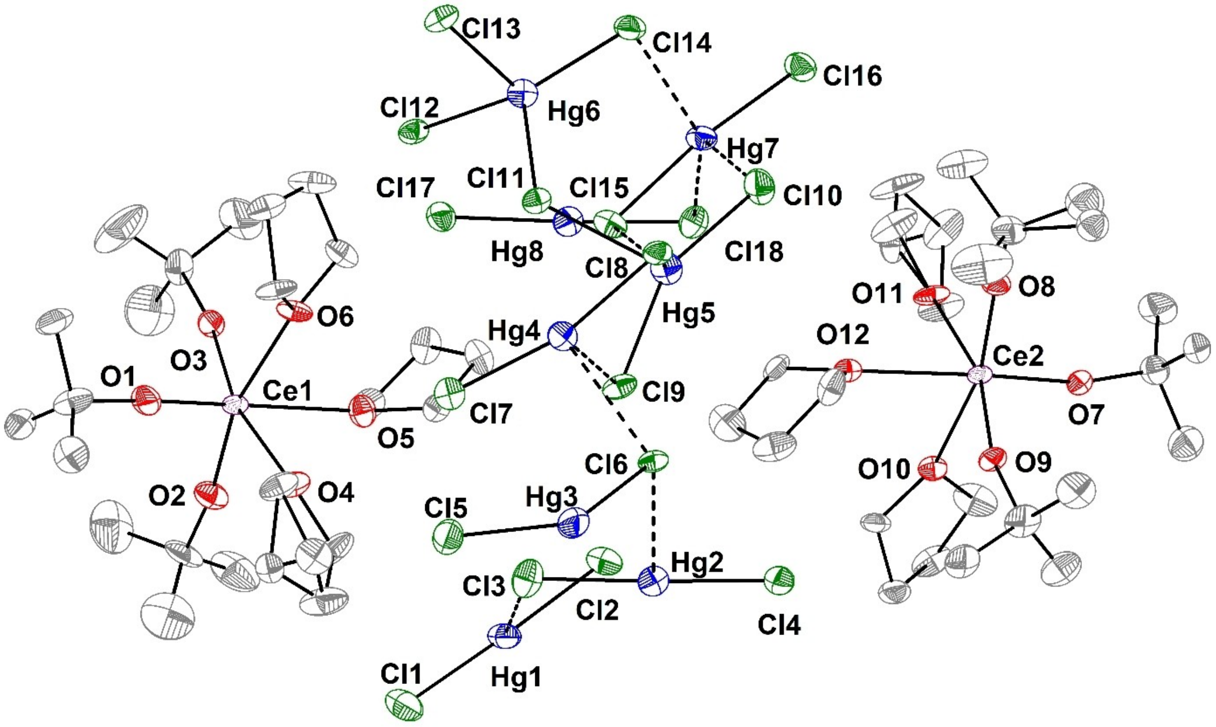

Figure 1. Asymmetric unit of $[\{Ce(OtBu)_3(thf)_3\}_2\{Hg_8Cl_{18}\}]_\infty$ (**1**). Ellipsoids shown at 50 % probability, hydrogen atoms were removed for clarity. Selected bond lengths (Å) and angles concerning Ce(1) environment in **1**: Ce1–O1: 2.064(13), Ce1–O2: 2.050(13), Ce1–O3: 2.038(12), Ce1–O4: 2.473(12), Ce1–O5: 2.474(13), Ce1–O6: 2.470(11), O1–Ce1–O2: 101.9(6), O1–Ce1–O3: 102.0(5), O1–Ce1–O4: 85.9(5), O1–Ce1–O5 : 162.7(5), O1–Ce1–O6: 87.8(5), O2–Ce1–O3: 100.0(5), O2–Ce1–O4: 90.0(5), O2–Ce1–O5: 88.0(5), O2–Ce1–O6: 165.5(5), O3–Ce1–O4: 165.5(5), O3–Ce1–O5: 90.1(5), O3–Ce1–O6: 88.4(5), O4–Ce1–O5: 89.8(4), O4–Ce1–O6: 79.8(4), O5–Ce1–O6: 80.1(4).

2.224(4), Ce–O_{thf}: 2.558(5); OAr = 2,6-*i*PrC_6H_3, Ce–OAr: 2.23 Å, range: 2.216(4)–2.248(4); Ce–O_{thf}: 2.62, range 2.599(5)-2.652(5) Å)[37] being in line with the difference in ionic radii between Ce(III) and Ce(IV) (0.14 Å).[40] Nevertheless, the saturated coordination sphere around the cerium cations restricts any interaction with the "$Hg_8Cl_{18}^{2-}$" sheet generating the ion pair structure.

The coordination environment of the chloridomercurate(II) sheet is complicated, and for easier interpretation, it is separated over Figures 2–4. The $Hg_8Cl_{18}^{2-}$ fragment consists of two components, one concerning Hg atoms Hg3–Hg6, (which connect at C12/Cl13 to the next Hg3–Hg6 unit, Figure 2) which makes one dimension of the polymer. The second component (Hg atoms Hg1, Hg2, Hg7, and Hg8), develops the second dimension through both strong and weak interactions with the chloride atoms of the first component. In Figures 2–4, there are both solid and dashed bonding lines between Hg and Cl, a solid line indicates a bond length that falls below the sum of the ionic radii of both Hg and Cl (2.83 Å),[40] whereas dashed lines represent Hg–Cl distances that fall within the sum of the Van der Waals radii of Cl and Hg (3.48 Å with a commonly accepted conservative value of 1.73 Å[41a] which has recently been supported by a calculated 1.75 Å.[41b] The value 3.83 Å from a more generous estimate[41c] is not used. The dual coordination behaviour of mercury has been elucidated by Grdenic[41d] with many known chloridomercury(II) complexes featuring a near linear Cl–Hg–Cl unit with Hg–Cl bond lengths of *ca*, 2.29 Å which corresponds to the sum of the Hg and Cl covalent radii.[41d] This is also a feature of the present structure for Hg1,2,4,5,7,8 (Figure 2).

The coordination environment of the eight mercury atoms is shown in Figure 2 and the selected Cl–Hg–Cl bond angles show the irregularity of the coordination environments. Each mercury atom is five-coordinate except for Hg6 which is four coordinate (Figure 3). Six (Hg ions 1,2,4,5,7, and 8) have Cl–Hg–Cl units in which the Hg–Cl bond lengths are near the sum of the covalent radii of Hg and Cl (*ca.* 2.29 Å)[41d] and the arrangement is near linear (153.1(2)–176.41(19)°; without Hg4 and Hg5: 170.8(2)–176.41(19)°). Hg5 has an additional Cl atom within the sum of their ionic radii (2.83 Å) thereby accounting for the greater deviation from linearity of the two shortest Hg–Cl bonds. Hg3 has three chloride ligands within this limit but only one near the sum of the covalent radii as does Hg6, but in the latter case, all four chloride ligands are within the sum of the ionic radii (2.353(5)-2.657(6) Å). With four short Hg–Cl bond-lengths, it may be considered that both additional chloride ions converting 8x $HgCl_2$ into the anionic $[Hg_8Cl_{18}]^{2-}$ sheet are located on Hg6.

The overall polymeric nature of the di-anionic $Hg_8Cl_{18}^{2-}$ sheet is indeed interesting. As the sheet spreads across the 2 dimensions (Figure 4), two cerium counter cations fill open pockets in the network (Figure 4, a), with one cerium atom resting above the plane of mercury and chlorine atoms, and

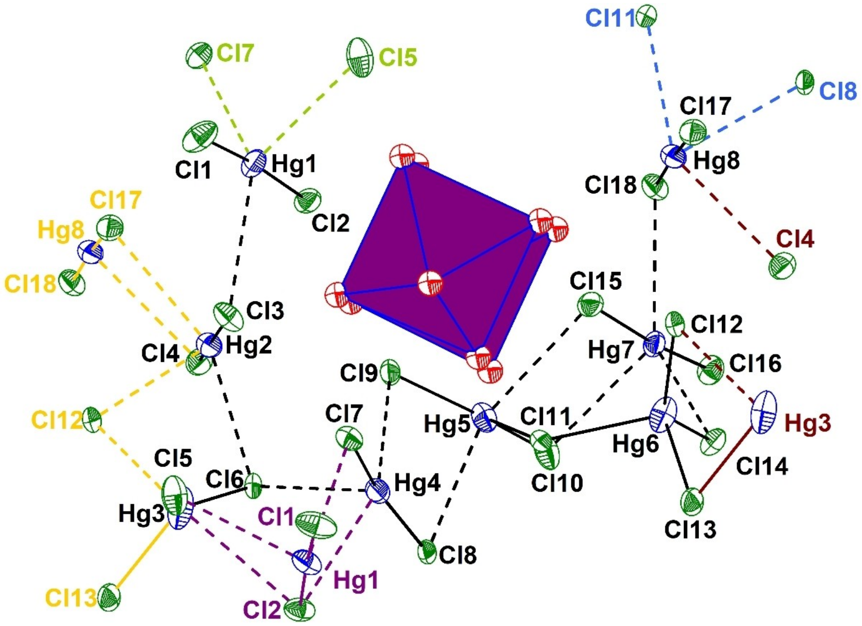

Figure 2. Asymmetric unit (bonds displayed as black), of the chloridomercurate(II) sheet (with two eclipsed cerium cations indicated as the purple polyhedra) showing the linear component (Hg3-6) which connects at C12/C13, to the next Hg3-6 sequence, and the bridging Hg atoms to five different units (each colour represents a different Hg_8Cl_{18} sheet). Full bonds indicate bond lengths within the sum of ionic radii of Hg and Cl (2.83 Å), dashed bonds indicate bonds longer than 2.83 Å but within the sum of the Van der Waals radii for Hg and Cl (3.48 Å). Selected bond lengths (Å, for Hg separated segmentation see Figure 3): Segment a: **Hg1–Cl1: 2.280(6)**, **Hg1–Cl2: 2.300(5)**, Hg1–Cl3: 3.225(3), Hg1–Cl5^1: 3.099(6), Hg1–Cl7^1: 3.033(6); Segment b: **Hg2–Cl3: 2.291(5)**, **Hg2–Cl4: 2.297(5)**, Hg2–Cl6: 3.091(5), Hg2–Cl12^2: 3.034(5), Hg2–Cl17^2: 3.199(5); Segment c: **Hg3–Cl5: 2.338(6)**, Hg3–Cl6: 2.403(5), Hg3–Cl2^3: 3.323(5), Hg3–Cl12^2: 2.916(5), Hg3–Cl13^2: 2.597(5); Segment d: Hg4–Cl6: 2.904(4), Hg4–Cl7: **2.308(5)**, **Hg4–Cl8: 2.304(4)**, Hg4–Cl9: 2.983(6), Hg4–Cl2^3: 3.188(6); Segment e: Hg5–Cl8: 3.166(5), **Hg5–Cl9: 2.341**, **Hg5–Cl10: 2.301(5)**, Hg5–Cl11: 2.707(4), Hg5–Cl15: 3.199(5); Segment f: Hg6–Cl11: 2.581(4), Hg6–C12: 2.455(4), Hg6–Cl13: 2.657(6), **Hg6–Cl14: 2.353(5)**; Segment g: Hg7–Cl10: 3.136(6), Hg7–Cl14: 2.877(6), **Hg7–Cl15: 2.310(5)**, **Hg7–Cl16: 2.291(5)**, Hg7–Cl18: 3.290(5), Segment h: **Hg8–Cl17: 2.314(5)**, **Hg8–Cl18: 2.285(5)**. Hg8–Cl4^4: 3.211(5), f Hg8–Cl8: 3.261(5), Hg8–Cl11: 2.996(4). Note: between atoms Hg8–Cl15: a contact was observed at 3.497(5), as this lies on the border of a potential bond it was not included in the diagram as a solid or dashed line.

one below (Figure 4, b). A view from the c axis of the crystal lattice, highlights how the sheet of mercury and chlorine atoms weaves in between the cerium cations.

There have been a number of different anionic chloride mercury sheets reported,[42] with several being "$[Hg_xCl_{2x+2}]^{2-}$" ($x \neq 0$) with ammonium based counterions.[43–45] However, there appears to be no similar structure reported (to the best of our knowledge) of a similar $[Hg_8Cl_{18}]^{2-}$ coordination polymer, emphasising the novelty of **1**. As Hg1, Hg2, and Hg8 are the most separated from the residual $[Hg_5Cl_{12}]^{2-}$ of the $[Hg_8Cl_{18}]^{2-}$ asymmetric unit, a search of the Cambridge crystallographic database was performed for $[Hg_5Cl_{12}]^{2-}$ moieties showing a similar coordination as in **1**.[42] Although these examples showed different connectivity to the $[Hg_5Cl_{12}]^{2-}$ fragment in **1**, one compound of interest is $\{[CuL(NO_3)]_2[Hg_5(Cl)_8(\mu_3\text{-}Cl)_2]Cl_2\}$ (L = 1,3,6,10,12,15-hexaazatricyclo[13.3.1.16,10]icosane), which was obtained from treatment of $[CuL(NO_3)_2]$ with $HgCl_2$.[46] In this example the chloridomercury array forms a more ordered grid around the copper cations, likely due to additional coordination of one nitrogen atom from the copper bound ligand to mercury. In addition, another interesting compound has a repeating $[Hg_3Cl_9(H_3L)]\cdot 2H_2O$ unit, where H_3L = tri-cationic *N*,*N*,*N′*,*N′*-tetraethyl-3-oxo-2-(1-pyridin-2-ylmethyl)-2,3-dihydrospiro[isoindole-1,9′-xanthene]-3′,6′-diammonium.[47] In this latter example, all Hg–Cl bonds are within the sum of the ionic radii (range: 2.334(3)–2.739(2) Å), and the chain is connected by four elongated Hg–Cl interactions (3.086(2)–3.3477(19) Å), with a degree of Cl···H interaction with the lattice water molecule.

Conclusion: Mercury dichloride was examined for the ability to oxidise *in situ* prepared cerium(III) *tert*-butoxide as a means to access tetravalent cerium *tert*-butoxides. After work up, small crystals of a highly unusual cerium(IV) chloridomercurate(II) ionic coordination polymer were obtained, namely of $[\{Ce(OtBu)_3(thf)_3\}_2\{Hg_8Cl_{18}\}]_\infty$ (**1**). The formation of **1** was repeatable and only occurred in the presence of excess $HgCl_2$. Although isolation, and purification of **1** proved difficult, its formation is remarkable, and it is a new addition to theclass of complexes containing mercuric chloride chains.

Experimental Section

General considerations: All products were treated as air-sensitive, and were manipulated under an inert atmosphere using glovebox,

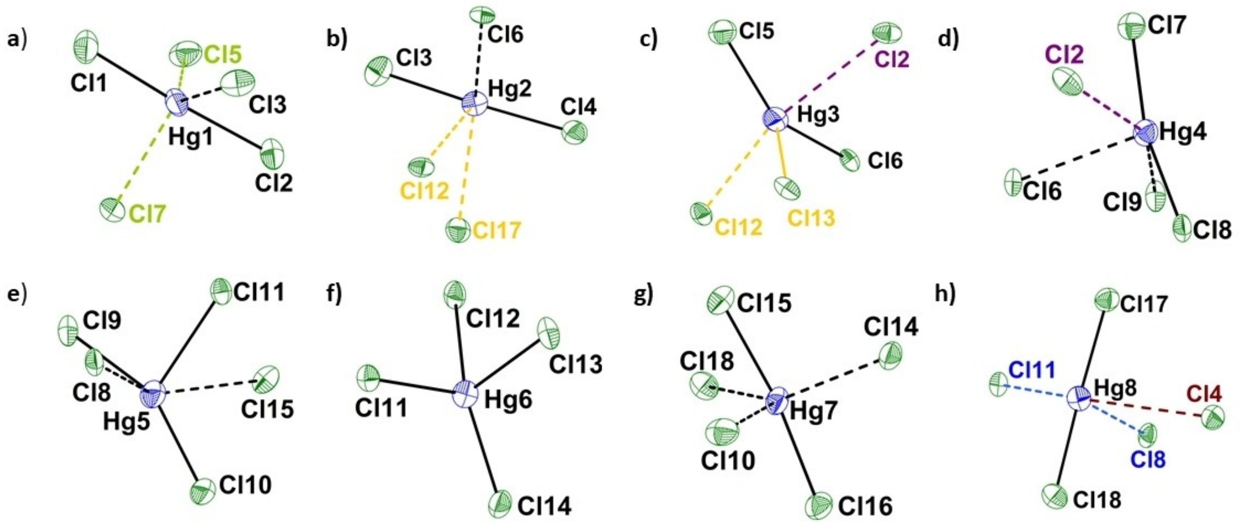

Figure 3. Depiction of each Hg atom in the asymmetric unit (black indicates asymmetric unit atoms, other colours represent a connection to a different $Hg_8Cl_{18}^{2-}$ sheet) Selected angles (°): Segment a: Cl1–Hg1–Cl2: 174.4(2), Cl1–Hg1–Cl3: 93.40(17), Cl3–Hg1–Cl5^{1}: 142.44(13), Cl3–Hg1–Cl7^{1}: 136.51(13), Cl5^{1}–Hg1–Cl7^{1}: 78.21(16); Segment b: Cl3–Hg2–Cl4: 172.02(19), Cl3–Hg2–Cl6: 90.81(16), Cl4–Hg2–Cl6: 93.72(16), Cl3–Hg2–Cl12^{2}: 87.09(16), Cl3–Hg2–Cl17^{2}: 93.82(16), Cl6–Hg2–Cl17^{2}: 157.45(12): Segment c: Cl5–Hg3–Cl6: 139.91(16), Cl12^{2}–Hg3–Cl3: 83.70(15), Cl6–Hg3–Cl13^{2}: 99.70(16), Cl2^{3}–Hg3–Cl5: 82.13(17); Segment d: Cl7–Hg4–Cl8: 165.85(17), Cl6–Hg4–Cl7: 99.38(15), Cl2^{3}–Hg4–C7: 83.96(16); Segment e: Cl9–Hg5–Cl10: 153.1(2), Cl9–Hg5–Cl11: 94.17(15), Cl8–Hg5–Cl9: 85.22(15), Cl9–Hg5–Cl15: 104.47(14), Cl8–Hg5–Cl15: 150.54(13); Segment f: Cl12–Hg6–Cl13: 92.19(17), Cl12–Hg6–Cl14: 134.06(17), Cl11–Hg6–Cl12: 101.66(13); Segment g: Cl15–Hg7–Cl16: 170.8(2), Cl14–Hg7–Cl15: 93.40(17), Cl10–Hg7–Cl15: 84.80(16), Cl18–Hg7–Cl15: 78.09(16), Cl10–Hg7–Cl18: 132.85(15); Segment h: Cl17–Hg8–Cl18: 176.41(19), Cl4^{4}–Hg8–Cl17: 83.95(15), Cl11^{5}–Hg8–Cl17: 90.25(16), Cl8^{5}–Hg8–Cl17: 93.07(15), Cl4^{4}–Hg8–Cl11^{5}: 146.52(12).

Schlenk flask, and vacuum line techniques. All solvents were predried by distillation over sodium or sodium/benzophenone, and were further degassed (by freeze pump thaw), prior to use. $HgCl_2$ was purchased from Merck and potassium tert-butoxide was purchased from Sigma-Aldrich – both compounds were dried prior use. $[CeCl_3(thf)_2]$ was synthesised according to literature procedures.[33] The Microanalysis was performed by the elemental analysis service of London Metropolitan University.

Treatment of in situ prepared "[Ce(OtBu)$_3$]" with HgCl$_2$

Method a, oxidation performed in Et$_2$O: $CeCl_3(thf)_2$ (1.05 g, 2.68 mmol), and K(O*t*Bu) (0.88 g, 7.84 mmol), were stirred in *n*-hexane at 60 °C overnight (~16 hours). After filtration from insoluble residues, and evaporation to dryness, the resulting white powder (approximately 0.28 g), was dissolved in minimal Et_2O and excess $HgCl_2$ (0.11 g, 0.41 mmol), was added. Concentration of the reaction mixture, followed by heating (at reflux for several hours, ~3–4 hours), and slowly cooling the sample gave colourless crystals of $[\{Ce(OtBu)_3(thf)_3\}_2\{Hg_8Cl_{18}\}]_\infty$ (**1**, identified by single crystal X-ray crystallography) amongst a colourless precipitate.

Method b, one pot synthesis and oxidation in THF: $CeCl_3(thf)_2$ (1.19 g, 3.04 mmol), and K(O*t*Bu) (0.96 g, 8.55 mmol), were stirred in minimal THF for several hours (~3–4 h) and $HgCl_2$ (0.41 g, 3.04 mmol) was added. The reaction mixture was filtered and concentrated. Addition of *n*-hexane and heating at 60 °C caused the formation of a colourless precipitate with colourless twinned crystals of $[\{Ce(OtBu)_3(thf)_3\}_2\{Hg_8Cl_{18}\}]_\infty$ (**1**), identified by unit cell comparison: monoclinic, *a* = 40.955, *b* = 12.340, *c* = 18.156 Å; α = 90, β = 99.86, γ = 90°, V = 8912 Å^3. The mixture was re-heated, filtered hot, and upon cooling a colourless precipitate and crystalline **1** was obtained (**1** identified by unit cell comparison). A microanalysis was performed on the resulting white powder/crystalline material calcd. % for $C_{48}H_{102}Ce_2Cl_{18}Hg_8O_{12}$ (3394.39 g mol^{-1}): C 16.98, H 3.03; found: C 7.02, H 1.23. These lower C and H values indicate the presence of excess $HgCl_2$: Calcd. (%) for $C_{48}H_{102}Ce_2Cl_{54}Hg_{26}O_{12}$ (8281.21 g mol^{-1}): C 6.96, H 1.24; found: C 7.02, H 1.23, complete loss of THF solvent is unlikely: Calcd. (%) for $C_{24}H_{54}Ce_2Cl_{18}Hg_8O_6$ (2961.74 g mol^{-1}): C 9.73, H 1.84.

Method c, with an additional equivalent of K(OtBu): $CeCl_3(thf)_2$ (0.70 g, 1.79 mmol), and K(O*t*Bu) (0.81 g, 7.22 mmol), were stirred in toluene at 60 °C for one hour and $HgCl_2$ (0.244 g, 0.90 mmol) was added with stirring, resulting in a dark green/yellow solution and formation of Hg^0. Filtration from the insoluble residues and concentration gave one very large yellow crystal of $[K(thf)_2Ce_2(OtBu)_9]$ (**2**), identified by unit cell comparison with the literature (orthorhombic, a = 19.702(4), b = 17.016(4), c = 17.9901(9) Å, α, β, γ = 90 (3), V = 6031.1(19) Å^3; lit. [14]. orthorhombic, a = 17.0121(4), b = 18.0594(4), c = 19.6945(6) Å. V = 6050.7(3) Å^3). Yield 0.10 g (10 %).

X-Ray Crystallography: Complex 1 was separately measured on the MX1[28][29] beamline at the Australian synchrotron. Absorption corrections were completed using SADABS.[30] Data integrations were completed using Blueice,[31] structural solutions were obtained by ShelXT[30] using full matrix least squares methods against *F*^{2} using SHELX2015,[30] within the OLEX 2 graphical interface.[32] Refer to CCDC for full structural details. CCDC data for complex 1 (CCDC 2163479) can be obtained free of charge from the Cambridge Crystallographic Data Centre.

$[\{Ce(OtBu)_3(thf)_3\}_2\{Hg_8Cl_{18}\}]_\infty$ (1): $C_{48}H_{102}Ce_2Cl_{18}Hg_8O_{12}$ (*M* = 3394.36 g/mol): monoclinic, space group *P*2$_1$/*c* (no. 14), *a* = 40.512(8) Å, *b* = 12.328(3) Å, *c* = 17.959(4) Å, *β* = 100.68(3)°, *V* = 8814(3) Å^3, *Z* = 4, *T* = 100.15 K, *Dcalc* = 2.558 g/cm^3, 63369 reflections measured (3.06° ≤ 2Θ ≤ 50°), 15412 unique (R_{int} = 0.1022, R_{sigma} = 0.0793) which were used in all calculations. The final R_1 was 0.0726 (> 2sigma(I)) and wR_2 was 0.1729 (all data).

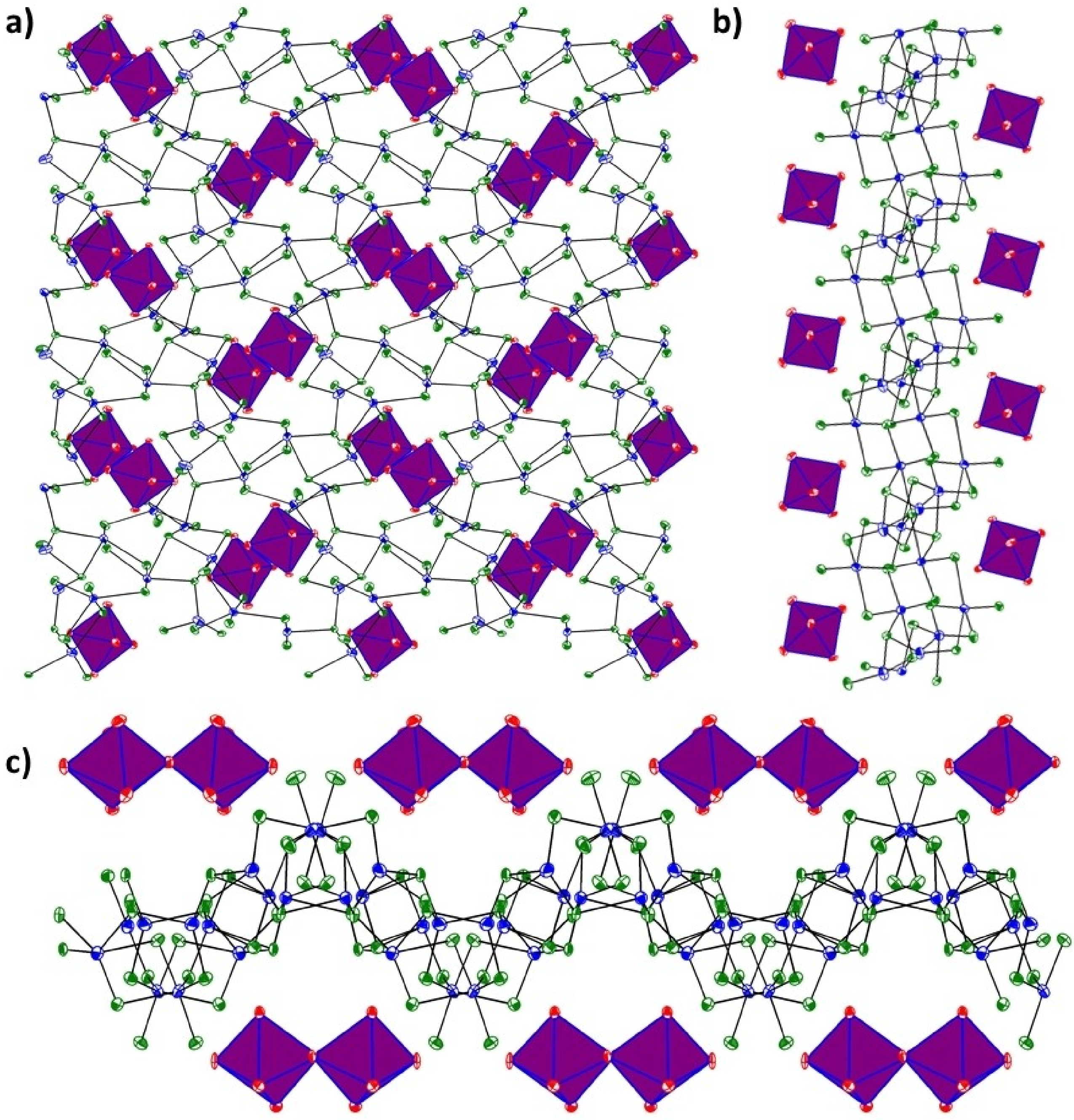

Figure 4. View along the three axes (a) = a axis, b) = b axis, c) = c axis), of the coordination polymer (cerium atoms depicted as polyhedra). For clarity no Hg–Cl bonds are dashed. For c, the two cerium counterions are not connected at the oxygen atoms.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interest

The authors declare no conflict of interest.

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