



Structural characterization of the 1-metallo-2-*t*-butyl-1,2-dihydropyridyl rubidium and caesium complexes

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ABSTRACT

With recent reports of alkali metal amides used in homogeneous catalytic chemistry where the reactivity down group one is dependent on the metal identity, esoteric rubidium and caesium amides are finding new admirers amongst chemists who usually study lithium, sodium, and potassium utility amides. Here, as a forerunner to their exploitation in catalysis, we report the X-ray crystallographic and NMR solution structures of the 1-metallo-2-*t*-butyl-1,2-dihydropyridyl (DHP) complexes of rubidium and caesium, thereby completing the homologous alkali metal series. Crystallized as monosolvated $\{[\text{Rb}(\text{tBuDHP})\cdot\text{THF}]_2\}_\infty$ and hemisolvated $\{[\text{Cs}(\text{tBuDHP})]_2\cdot\text{THF}\}_\infty$, both form spectacular supramolecular structures. While each shares a plethora of metallo- π -contacts with the DHP anion, their subunits differ. The former dimerizes in a 'slipped' fashion via interactions between the symmetrically-equivalent Rb centres and the π -system of the adjacent DHP ring, but the latter has distinct Cs centres within its dinuclear subunit, with one Cs engaging in σ -bonding to two *t*BuDHP anions, whereas the other Cs binds in a more side-on fashion to the π -system of the ring.

1. Introduction

The nucleophilic 1,2-addition of organometallic compounds to pyridine [1,2] has long been recognized as an efficient way of functionalizing this highly important aromatic heterocycle, that has played a prominent role in organic chemistry [3–5] since its discovery in Scotland in the mid-19th century by Anderson [6,7]. This functionalization process occurs in two steps, first the addition of the M–C or M–N bond across the 1,2-position of the pyridine substrate, thus breaking its aromaticity and forming a 1-metallo-1,2-dihydropyridyl (DHP) intermediate; followed by elimination of M–H to reform the aromatic species such that one α -proton has been replaced by the organic arm. In practice this is often achieved in a one-pot synthesis, since excess pyridine solvent will act as an MH acceptor [8], and aqueous work-up will quench the putative leftover MH, whether it be free or as part of an alternative dihydropyridyl complex (Scheme 1).

Recently, we reported that utilizing alkyllithium reagents with stoichiometric pyridine in hexane solvent rather than the norm of neat pyridine allowed isolation and crystallographic characterization of the intermediate 1-lithio-2-alkyl-1,2-dihydropyridyl complexes [9,10] and that the heavier alkali-metals sodium and potassium could replace

lithium by transmetalation reactions with MOtBu ($\text{M} = \text{Na}$ or K , Scheme 2) [11]. With respect to crystallographic verification of other main group organometallics undergoing 1,2-addition to pyridines, Hill has successfully trapped the addition product using the chelate-supported alkyl magnesium complex $(^{\text{Dipp}}\text{nacnac})\text{Mg}n\text{Bu}$ as the organometallic reagent [12], while Hevia trapped a dihydropyridyl complex from $(^{\text{Dipp}}\text{nacnac})\text{MgTMP}$ ($\text{TMP} = 2,2,6,6\text{-tetramethylpiperidide}$) formed via the α -deprotonation of pyridine followed by addition of the putative pyridyl anion to a second equivalent of pyridine [13]. From the *p*-block, Budzelaar witnessed 1,2-addition of Et_3Al to a pyridine diimine [14] and Zhang, Zheng and Dub demonstrated 1,2-addition of $i\text{Bu}_3\text{Al}$ to terpyridine [15], while Nikonov recently reported a family of aluminium DHP complexes generated from an Al(I) synthon, a ketone and pyridine [16].

Our desire to incorporate alkali-metal DHPs into a family of bimetallic ate complexes via co-complexation resulted in our recent disclosure of a similar synthetic methodology to that of Na/K DHP for the synthesis of the heavier rubidium and caesium dihydropyridyls [17], though their molecular structures remained elusive. Since the DHP anion provides opportunities for both σ - (via the formally anionic N atom) and π -bonding (via the conjugated aza-diene double bond system of the formerly aromatic ring), we were keen to probe the Rb/Cs DHP

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relationship as a consequence of three primary motivations. First, there has been an abundance of recent studies involving heavier alkali-metal amides such as a contacted solvation-free ion-pair caesium amide with remarkably no Cs-N interaction in the crystal [18], a LiHMDS/CsCl one-pot methodology for functionalization of arylmethane substrates [19], and examples of Cs(HMDS) catalyzed selective benzylic deuterations [20] and alkene transfer hydrogenations [21]. Furthermore, recently there has been growing interest in the bonding of aromatic-functionalized ligands to alkali-metals within the context of stabilizing highly reactive sub-valent aluminium centres [22–29]. Finally, the ability of these DHP anions to operate as either amide bases or as soluble sources of otherwise insoluble MH gives these complexes flexible potential in the field of main group (towards more sustainable) catalysis [30,31]. We have now successfully surmounted this challenge and report the solid-state and solution structures of these heavyweight alkali metal complexes herein. Though four-membered (MN)₂ rings (M = Rb, Cs) feature in both structures, their propagation patterns are significantly different in part due to the unequal level of THF solvation (two or one THF ligand/s per dimeric ring, respectively).

2. Materials & methods

Solid unsolvated M(*t*BuDHP) was prepared according to literature methods [17]. Single crystals of {[Rb(*t*BuDHP)·THF]₂}_∞ (1) and {[Cs(*t*BuDHP)]₂·THF}_∞ (2) suitable for X-ray diffraction (XRD) analysis were grown from a THF solution layered with hexane at 248 K.

Crystallographic data for both complexes were collected on an Oxford Diffraction instrument using Cu-K_α radiation ($\lambda = 1.54184 \text{ \AA}$) at 100 K. Structures were solved using OLEX2, while refinement was carried out on F² against all independent reflections by the full-matrix least-squares method by the Gauss-Newton algorithm using OLEX2 [32]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Selected crystallographic and refinement details can be found in Table S11.

¹H and ¹³C NMR spectra were recorded in THF-*d*₈ on a Bruker AV400 MHz spectrometer operating at 400.13, and 100.62 MHz, respectively. ¹H DOSY measurements were recorded on a Bruker AV400 spectrometer operating at 400.13 MHz, using the pulse program dstepp3s.

3. Results & discussion

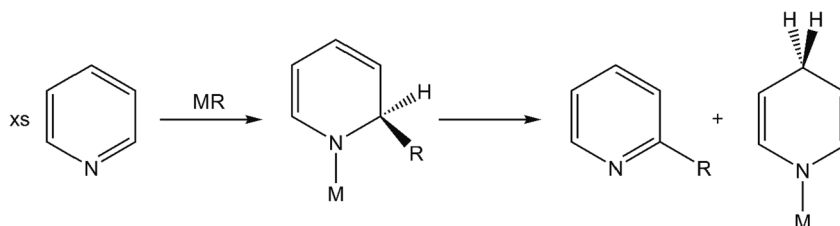
3.1. Solid-state structures

Single crystals suitable for XRD analyses were obtained by generating unsolvated M(*t*BuDHP) by transmetalation from Li(*t*BuDHP) and MOAm (Am = amyl, isopentyl, -C(CH₃)₂CH₂CH₃) according to Scheme 3 [17] and recrystallizing these powders from THF layered with hexane; or by salt metathesis upon reacting Li(*t*BuDHP) directly with the metal fluorides MF in THF at 273 K for 15 h. The XRD analyses confirmed that these complexes are monosolvate {[Rb(*t*BuDHP)·THF]₂}_∞ (1) and hemisolvate {[Cs(*t*BuDHP)]₂·THF}_∞ (2) respectively.

In the rubidium complex 1 each metal centre is solvated by a single THF molecule resulting in an empirical formula of Rb(*t*BuDHP)·THF, with this unit dimerizing to give centrosymmetric units of [Rb(*t*BuDHP)·THF]₂ (Fig. 1). Such a dimeric four-membered ring motif is well-known

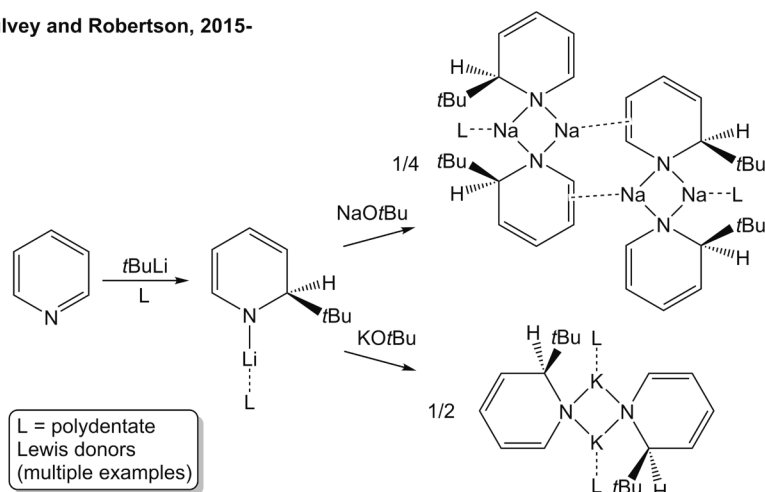
for alkali-metal amide complexes [33], having been seen regularly for both unsolvated [34] and solvated RbN(SiMe₃)₂ [35–38] and related complexes [39], as well as for the TMEDA solvate of the bulkier amide Rb(TMP) [40]. However, unusually in this instance the monomeric units, which contain Rb1-N1 σ interactions [2.875(3)Å], dimerize in a ‘slipped’ fashion via interactions between the large alkali-metal and the π -system of the adjacent dihydropyridyl ring. This relationship is emphasised by the distances between the rubidium cation and the six members of the dihydropyridyl ring (Fig. 2, top left), whereby the four *sp*² hybridized carbon atoms and the anionic nitrogen lie in the range 3.124(3)–3.367(5)Å from Rb; whereas the quaternary carbon is further removed at 3.834(4)Å, suggesting η^5 coordination. These values are similar to those of the Rb- η^5 DHP relationship in bimetallic Rb(*t*BuDHP)(TMP)Al*i*Bu₂ which span the range 3.059(2)–3.351(2)Å for the five atoms in the plane and 3.763(2)Å for the Rb-C (*sp*³) distance [17]. The Rb-N σ interaction forms a Rb-N-C7 angle of 153.2(2)°. In this context, we use this N-C γ unit vector as a proxy for the plane of the ring, as the *sp*³ α -carbon formed upon dearomatization lies out of the plane of the formerly aromatic NC₅ ring by 0.637(4)Å; but the five remaining ring atoms are approximately co-planar (Fig. 2, right). The slipped dimeric units then polymerize via further propagating Rb-DHP π -interactions to an adjacent dimeric unit, giving a sandwich-like feature (Fig. 2, right). The Rb-DHP relationship is perhaps better described as η^2 in this instance, with the Rb-C α [3.302(4)Å] and Rb-C β [3.285(4)Å] interactions considerably shorter than all others which are greater than 3.8 Å (Fig. 2, bottom left). Rb(*t*BuDHP)(TMP)Al*i*Bu₂ also polymerizes as a consequence of Rb forming a sandwich-like structure between *t*BuDHP ligands [17]. Overall, the resulting structure is thus best described as a polymer of dimers of formula {[Rb(*t*BuDHP)·THF]₂}_∞ as depicted in Fig. 3, with no covalent bonds between neighbouring polymeric chains (Fig. S13).

Complex 2 consists of hemisolvated dinuclear asymmetric units (Fig. 4). The two caesium cations lie in different environments, specifically Cs2 forms σ -type bonds to two *t*BuDHP anions [Cs2-N1, 3.122(4); Cs2-N2, 3.046(16)] while Cs1 binds in a more side-on fashion to the π -electron density of the ring. The relationship with the first ring represented by N2 (shaded in yellow in Fig. 4) is best described as η^5 (Cs-C/N distances < 3.6 Å, see Fig. 5, left), similar to that seen in complex 1, where the quaternarized α -C is moved out of the plane of the ring and therefore does not engage with the alkali-metal cation [4.064(10)Å]. This mirrors the Cs-*t*BuDHP relationship in bimetallic PMDETA-Cs(*t*BuDHP)AlMe₃, with the five approximately co-planar atoms residing 3.505(2)–3.648(2)Å from Cs with the sixth, *sp*³ hybridized carbon further away at 4.039(2)Å [41]. The other ring (grey in Fig. 4) engages in a η^2 fashion through the N and C α atoms [Cs1-N1, 3.407(5)Å; Cs1-C9, 3.391(6)Å; Fig. 5, middle]. The π -nature of the interaction is further demonstrated by the Cs-N-C γ angle of 107.9(2)°. A further distinction with Cs2 which is unsolvated, is that Cs1 carries a single THF ligand [Cs1-O1, 3.168(8)Å] hence accounting for the hemi-solvate nature of the complex. Overall, this asymmetric unit can be described then as a ‘caesium caesiate’ where Cs1 represents the cation in the cationic moiety and Cs2 represents the cation in the anionic moiety. These asymmetric units then propagate via an inversion point to form a dimeric ladder unit facilitated by an additional Cs-DHP interaction, whose interaction with Cs is best described as η^2 to the N [3.49(3)Å] and

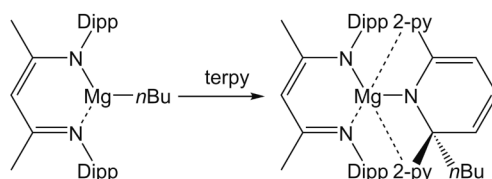


Scheme 1. Functionalization of pyridine through an addition/elimination mechanism using a generic organometallic reagent ‘MR’ (for example LinBu).

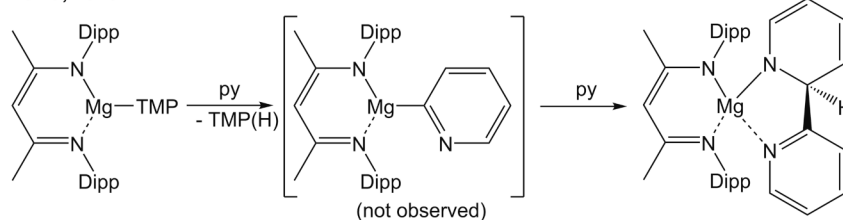
Mulvey and Robertson, 2015-



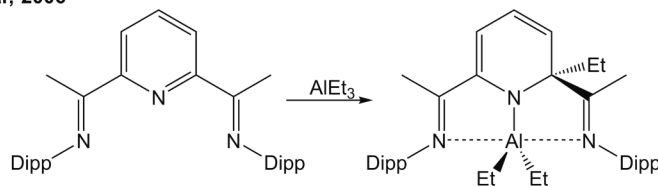
Hill, 2016



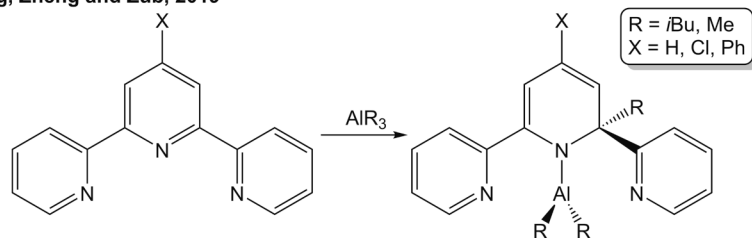
Hevia, 2018



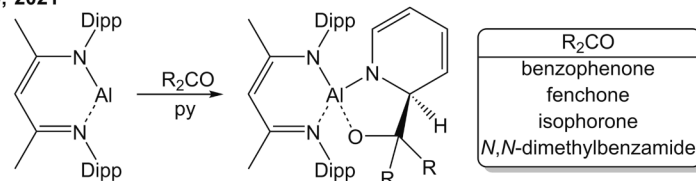
Budzelaar, 2006



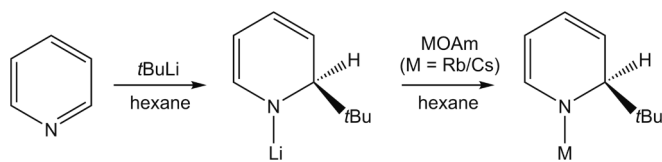
Zhang, Zheng and Zub, 2019



Nikonov, 2021



Scheme 2. Selected crystallographically characterized 1-metallo-1,2-dihydropyridyl complexes of group 1, 2 and 13. Dipp = 2,6-diisopropylphenyl; py = pyridine; terpy = 2,2':6',2''-terpyridine; TMP = 2,2,6,6-tetramethylpiperidide.



Scheme 3. Synthesis of unsolvated Rb and Cs *t*BuDHP complexes.

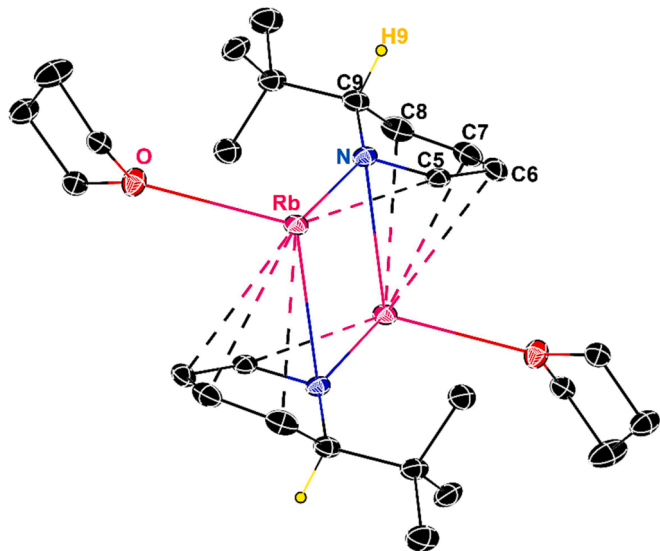


Fig. 1. Section of polymeric structure of **1** showing dimeric arrangement of Rb (*t*BuDHP) units. Thermal ellipsoids are drawn at 30% probability and all hydrogens other than on C9 and disordered component of THF are removed for clarity.

C_{α} [3.321(7)Å] ring atoms (Fig. 6, inset; see Fig. S14 for full details of Cs2-DHP bond distances). While ladder motifs are well documented within alkali-metal amide chemistry [42–48], to the best of our knowledge complex **2** represents the first example of a caesium amide ladder. That said, there are known cubic motifs that could be envisioned

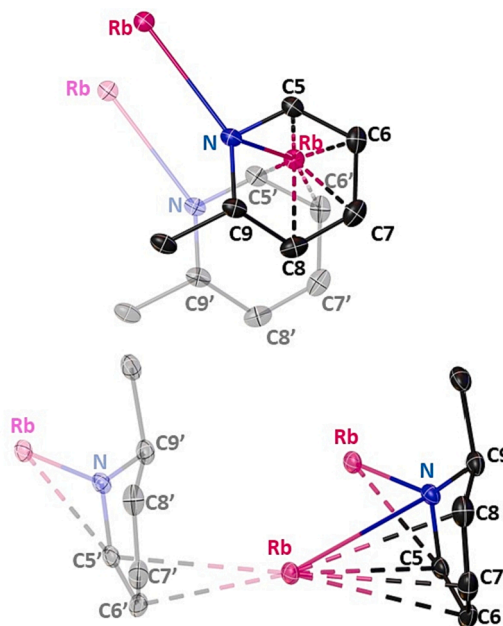
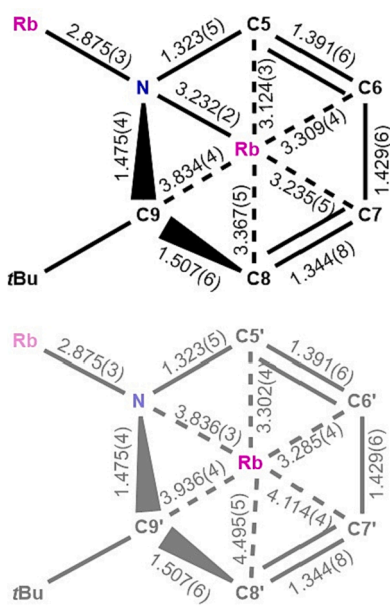


Fig. 2. Summary of interactions between Rb and DHP rings showing the dimerizing interaction (top left) and the polymerizing interaction (bottom left); and a section of the structure showing the sandwich-like interaction of Rb with the DHP rings from above (top right) and from the side (bottom right).

as having derived from the folding of a four-rung ladder as seen in the unsolvated primary amide [CsNHSiMe₃]₄ [49], a feature which is repeated in a family of phosphoraneiminates of formula [CsN=PR₃]₄ [50,51]. Cubane-type structures are also prevalent in alkoxide chemistry such as in [CsOtBu]₄ [52] and [CsOAm]₄ [53], while ladder structures are well documented for related alkali-metal P(SiMe₃)₂ complexes [54–56]. This ladder in **2** is considerably removed though from being cubic as demonstrated by the torsion angle of the ladder side, N1-Cs2-N2A-Cs1A at 169.3(9)°. The additional Cs-DHP interaction which facilitates this dimerization is also η⁵ (Fig. 5, right), with Cs-N/C distances in the range 3.361(7)–3.622(6)Å for the five atoms in the pseudo-plane and 4.171(3)Å for the sp³ hybridized carbon atom. The ladder structures then associate into a polymeric array due to longer-range interactions between the N1 atoms located at the corners of the ladder structure and the corner Cs1 atoms of an adjacent ladder [3.593(5)Å] and also by coordination of Cs2 to the C_β and C_γ of an additional DHP ring [3.421(7) and 3.457(6)Å respectively, Fig. S14]. The relationship between ladders is clearly seen in Fig. S15 (Cs, N and O atoms only) while the extended polymeric structure is displayed in Fig. 6. Two [CsOAr]₄ ladders are linked to one another via an additional [CsOAr]₂ cyclobridge (Ar = *o*-iPrPh) [57], although in this earlier case it is the internal caesium cation of the ladder which forms the bridging link.

3.2. Solution-state characterization

Having determined the solid-state structures of these two alkali-metal dihydropyridyl complexes, we proceeded to study their solution state aggregation via DOSY NMR spectroscopy. The molecular weight in THF-d₈ (MW_{det}) was determined from the ¹H DOSY data via two methods in the presence of adamantane as the inert internal standard and using Stalke's literature method [58–60]. The methods gave values of 514 and 556 gmol⁻¹, respectively, which agree well with the theoretically calculated MW (MW_{cal}) for the monomeric [Rb(*t*BuDHP)(THF)₄] (MW_{cal} = 541, 5 % and 3 % error, respectively; see ESI, Tables S4 and S5). The MW_{det} values for the heaviest member obtained from the ¹H DOSY data (482 and 519 gmol⁻¹) bode well for either a solvated monomeric species [Cs(*t*BuDHP)(THF)₃] (MW_{cal} = 509, 6 % and 2 % error, respectively; see ESI, Tables S9 and S10) or a donor free [Cs(*t*BuDHP)]₂ dimer (MW_{cal} = 538, 4 % and 12 % error, respectively; see

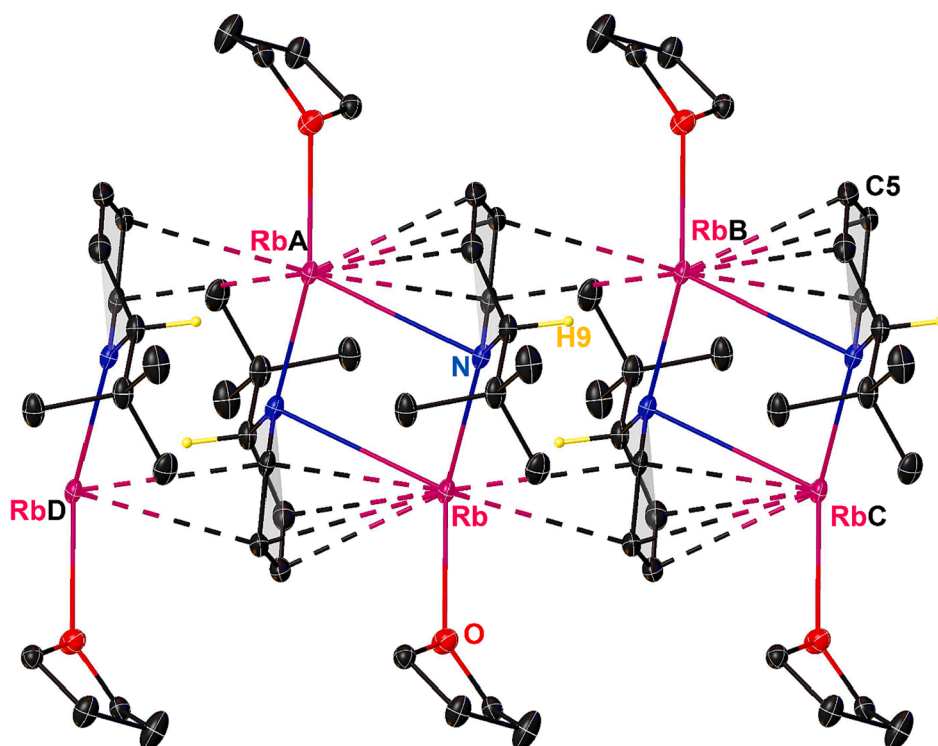


Fig. 3. Polymeric structure of 1. Thermal ellipsoids are drawn at 30 % probability and all hydrogens other than on C9 and disordered component of THF are removed for clarity. Symmetry operations to generate atoms labelled A: $1 - x, 1 - y, 1 - z$; B: $2 - x, 1 - y, 1 - z$; C: $1 + x, +y, +z$; D: $-1 + x, +y, +z$.

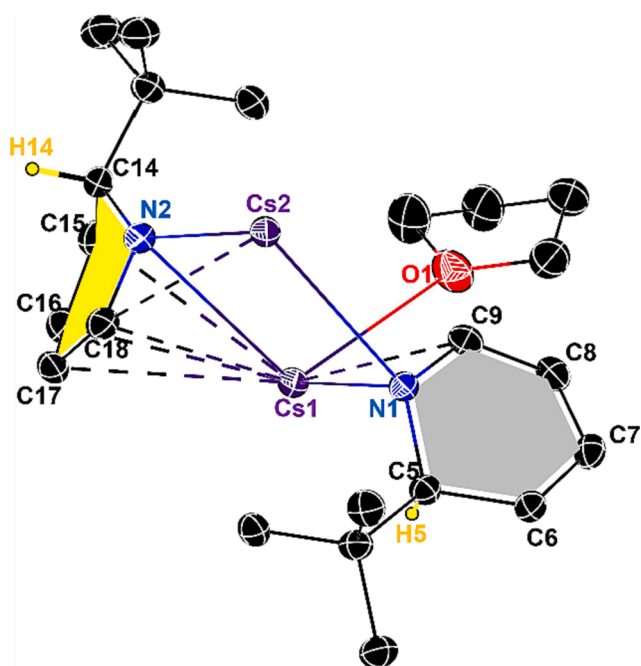


Fig. 4. Section of solid-state structure of 2 showing hemisolvated dinuclear arrangement of Cs(*t*BuDHP) units. Thermal ellipsoids are drawn at 30% probability and all hydrogens other than on C9 and disordered component of THF and yellow DHP ring are removed for clarity.

ESI, Table S8). The occurrence of the latter THF-free dimeric form can be deemed unlikely due to the inability of an individual *t*BuDHP unit to shield the large cationic surface of Cs as evident from the solid-state studies discussed previously where one Cs cation is found to be surrounded by three or more dihydropyridyl units. The solution state

studies thus reveal the likely preference of the softest alkali metal to bind to the π -surface of the DHP ring, thereby leaving less space for coordination of solvent molecules to the cationic sphere (Fig. 7, right). The increase in the number of THF molecules coordinated to smaller Rb is indicative of a more anionic/ σ -type of DHP binding in contrast to its heavier relative (Fig. 7, left). This is not surprising since these alkali metal DHP complexes in the solid state also have more (one), and less (half an equivalent) THF co-ordinated to Rb and Cs in their asymmetric component respectively.

4. Conclusions

This work has structurally defined the THF solvates of the 1-metallo-2-*t*-butyl-1,2-dihydropyridyl rubidium and caesium complexes adding to the previous reports of their lighter lithium, sodium and potassium congeners, to complete the alkali metal dihydropyridyl family. These new structures have brought to light some significant distinctions in their bonding in the solid-state and in solution, where the extent of THF solvation differs in both phases. Ongoing research will address the question, whether these discovered distinctions will influence any noteworthy differences found in their reactivity in synthetic and catalytic applications.

CRedit authorship contribution statement

Peter A. Macdonald: Investigation, Formal analysis. **Sumanta Banerjee:** Investigation, Formal analysis, Visualization. **Alan R. Kennedy:** Validation, Data curation. **Robert E. Mulvey:** Supervision, Conceptualization, Funding acquisition, Resources, Writing – review & editing. **Stuart D. Robertson:** Supervision, Visualization, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial

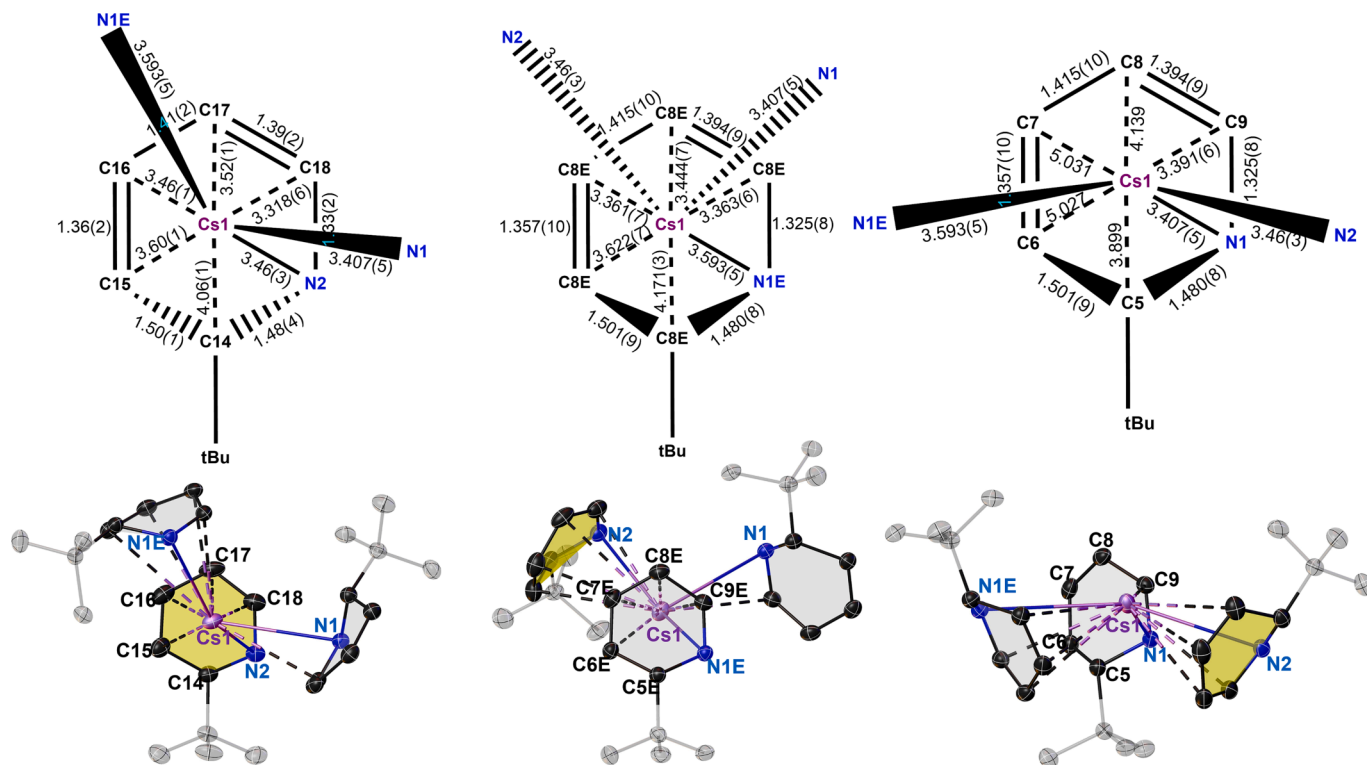


Fig. 5. Summary of interactions between Cs and DHP rings in complex 2. Note that the ring containing N2 is disordered over two positions and all values quoted are for the major component.

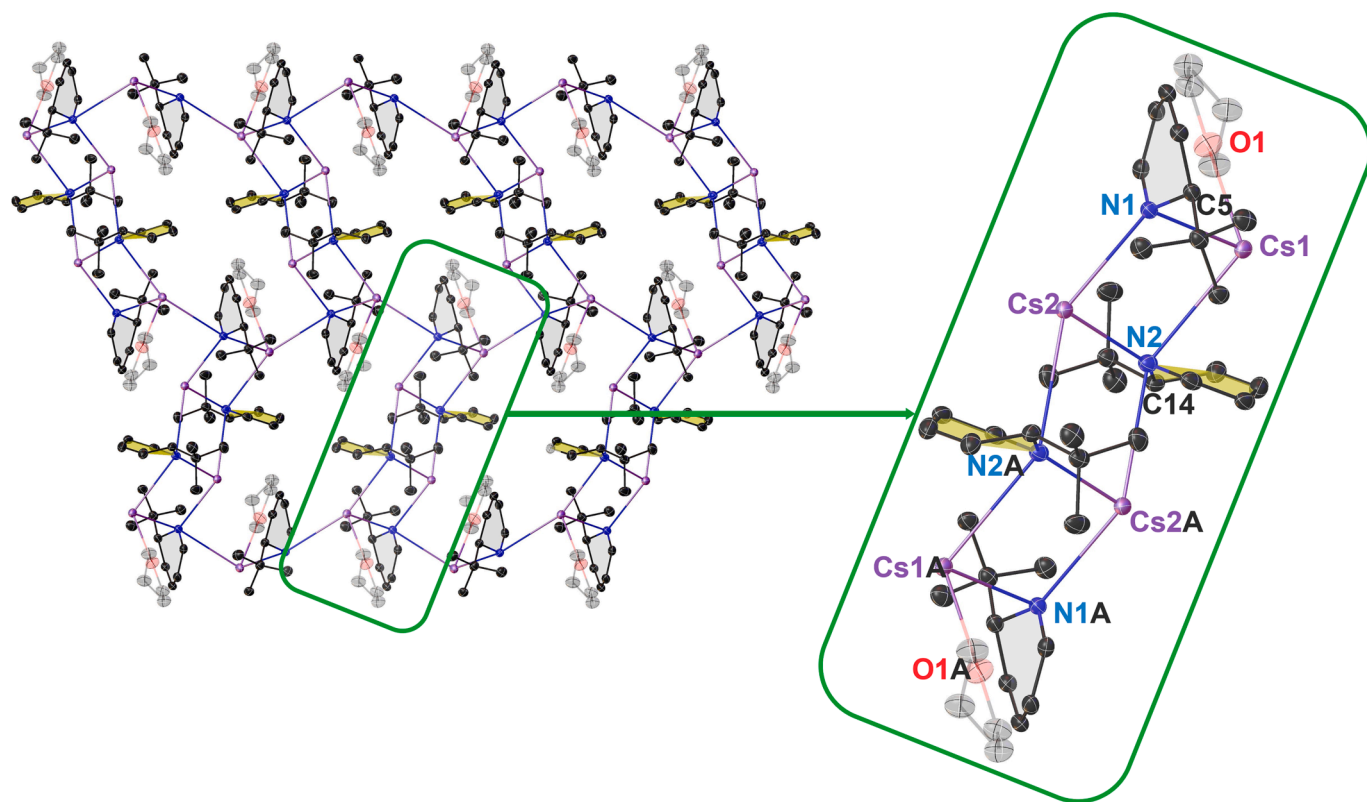


Fig. 6. Dimerization of dinuclear units to form repeating ladder arrangement in complex 2 (inset) and propagation of ladder units to form polymeric structure.

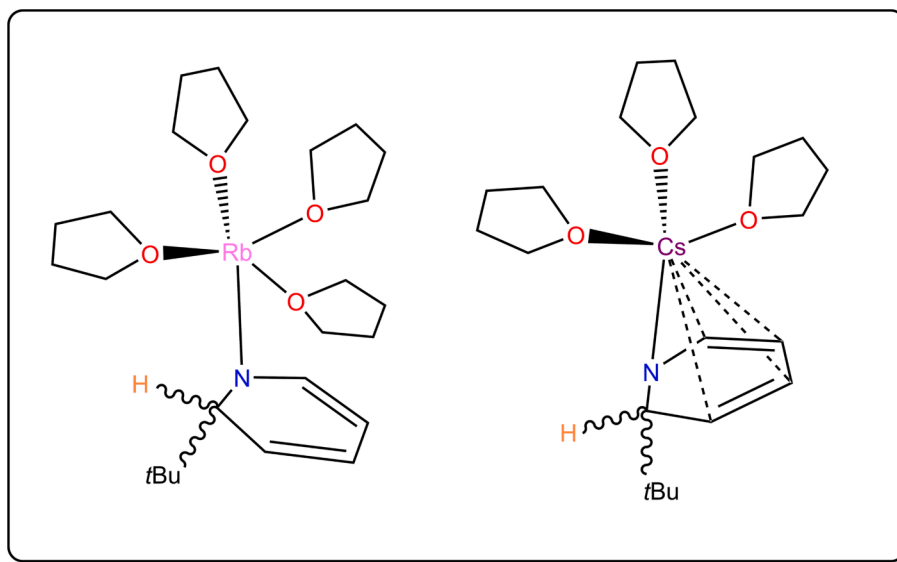


Fig. 7. ChemDraw representation of potential alkali-metal coordination in complexes 1 and 2 in THF solution.

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The supporting data set has been lodged with our institutional repository and the doi <https://doi.org/10.15129/a000f2e0-3683-439b-ab02-d7ff10dc6b76> can now be explicitly quoted.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2023.116302>.

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