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Excellent reagents for transferring their heterocalix[4]arene ligand to f-block organometallic complexes, lithium, sodium and potassium trans-calix[2]benzene[2]pyrrolides have been found to adopt a fascinating series of structures in their own right.

Whilst following the recent seminal breakthroughs in f-block elements literature,¹ the contributions of trans-calix[2]benzene[2]-pyrrole, H₂L⁶⁻, in its doubly deprotonated ligand form (L⁶⁻)²⁻, caught our eye. Introduced by Sessler et al.² as one of a series of heterocalix[4]arene hybrids, (L⁶⁻)²⁻ is made up of four aromatic rings of alternate pyrrolide and arene units that connect via dimethylmethane linkers. Possessing interrupted conjugation, the ligand is blessed with conformational and coordinative flexibility that renders it effective at supporting a range of organometallic lanthanide and actinide complexes. These include uranium[III and IV], samarium[III] and thorium[IV] complexes and most recently organoneptunium[IV] complexes.³ Characterisation of these complexes especially via single crystal X-ray crystallography, a particularly noteworthy feat for the technologically challenging radiotoxic organoneptunium(IV) complexes, have uncovered an assortment of trans-calix[2]benzene[2]pyrrolide σ and π bonding modes, typically mono or bis(κ¹-areneide) coordinations, bis(κ²-pyrrolyl) coordination, bis(κ⁵-pyrrolyl) sandwiching and bis(κ⁶-arene) sandwiching.

Alkali metal reagents play an important if somewhat understated role in this emerging organometallic chemistry of f-block elements. For example, potassium intermediate K₂(L⁶⁻) reacted with SmCl₃(thf)₃ to generate the corresponding Sm⁴⁺Cl(L⁶⁻), where L adopts a σ, π bonding mode with the pyrrolide N atoms σ-bonded to Sm, which occupies a bis(κ⁶-arene) π-pocket. Lithium intermediate, Li₂(L⁶⁻), made by reaction of H₂L⁶ with LiHMDS⁴ [HMDS = 1,1,3,3,3-hexamethyldisilazide; also known as bis(trimethylsilyl)amide] in toluene solution, was used to convert U₁ to dinuclear U⁶⁺[L⁶⁻], with one U in a bis(κ⁵-pyrrolyl) pocket and the second U in a bis(κ⁶-arene) pocket.¹⁴ Moreover, alkali metals can be incorporated into actinide products as seen in K[Th₂(N(SiMe₃)₂)₂](L⁶⁻)₁⁶, synthesised by reaction of Th⁴⁺Cl₂(L⁶⁻) with excess KHMSDs. Here, aside from substituting Cl ligands by the silylamide, the K occupies the bis(arene) pocket of the macrocycle but interestingly also facilitates double C–H metallation of the aryl groups by the Th⁴⁺ centre.

Recently, theoretical investigations by Schreckenbach, Pan et al.⁴ have put the alkali metal (Li, Na and K) derivatives of the trans-calix[2]benzene[2]pyrrolide ligand in the spotlight for accessing low-valent uranium and transuranium complexes. Surprisingly, these important alkali metal intermediates AM₄(L⁶⁻) have not been studied in their own right. Knowing that the structures of alkali metal compounds can have a profound influence on the outcome of reactions,⁵ we set out this study to isolate and characterize these intermediates and where possible to resolve their structures. As outlined here, the results obtained for the congenic series of AM = Li, Na, K are remarkable.

In previous work potassium and lithium derivatives of trans-calix[2]benzene[2]pyrrole were generated in situ by treating the free ligand with potassium hydride⁶ or lithium HMDS⁷ respectively. Adapting this procedure, a set of the alkali metal macrocycles was accessed by reaction of the free ligand with an appropriate metal-lating agent, namely either nBuLi, NaHMDS or KHMSDs (Scheme 1). Crystallisation of the solvated potassium complex [K₂(L⁶⁻)(thf)₃]₁, 1, was accomplished in neat thf solution. Initially obtained as a white solid, crystals of [Li₂(L⁶⁻)(thf)₂], 2, suitable for X-ray analysis, were secured via slow diffusion of n-hexane into a tetrahydrofurran solution of 2. The distinction between thf-rich [Na₂(L⁶⁻)(thf)]₃, 3 and its thf-poor variant [Na₂(L⁶⁻)(thf)]₅, 4 came about by diffusing n-hexane into a tetrahydrofuran solution of the latter but growing the former from an all thf solution,⁶ while thf-free [Na₂(L⁶⁻)]₅, 5 was obtained by performing the sodiation reaction in neat methylcyclohexane.

As has been shown in papers, intuitively one would be inclined to (chem)draw the structure of the potassium intermediate with

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been found in the bis(n-pyrrolyl) pocket, drawing comparisons to the pyrrolyl N atoms as reflected by their short lengths (mean K1–N, 2.88 Å; mean K2–N 3.20 Å). In fact, reflecting the distinct coordination environment to that of the Na metal centres, which fall into two distinct types. Na1 and Na3 occupy the bridging bis(benzene) type whilst the Na2 and Na4 centres make intermolecular Na(N)8 ring runs through the structure. Measuring from H...H nuclei the “hole” in the ring is approximately 125 Å3, whereas Na2 and Na4 occupy the bridging bis(n-pyrrolyl) units with a corresponding mean Na–N length of 2.40 Å.

Turning to the intermediate-sized alkali metal sodium, we crystallised the tris(thf) solvate [Na2(LAr)3(thf)]3, which bears a resemblance to the tris(thf) solvated potassium congener 1. The main distinction is that the smaller size of sodium leads to reduced hapticities of the bis(benzene) and bis(pyrrole) rings with its two distinct Na centres, the primary Li (N × 1; O × 2) coordination sphere in 2 is essentially planar (sum of bond angles, 359.62°), though there are two exceedingly long interactions with C(Me) atoms of the dimethylmethane linkers [Li1–C7, 2.727(3); Li1–C16, 2.815(3) Å].

Having crystallised variations of the sodium macrocycle containing different amounts of coordinated thf, we pondered whether crystals of the thf-free version could be obtained. This was achieved by performing the dideprotonative metallation reaction in a methylecyclohexane medium. An X-ray crystallographic determination revealed a remarkably eye-catching tetrameric, octanuclear structure [Na3(LAr)4], 5 (Fig. 2b). As highlighted in Fig. 2b, a 16-atom [NaNa3] ring runs through the structure. Measuring from H nuclei to H nuclei the “hole” in the ring is approximately 125 Å3, but given the van der Waals radii of an H approaches 1 Å that reduces the hole size to about 27 Å3, approximately the size of a water molecule. There are four crystallographically distinct Na centres, which fall into two distinct types. Na1 and Na3 occupy the bis(n-benzene) pocket and form bonds of predominate σ character to the pyrrolyl N atoms as reflected by their short lengths (mean Na–N, 2.40 Å); whereas Na2 and Na4 occupy the bridging bis(n-pyrrolyl) units with a corresponding mean Na–N length
of 2.62 Å. The contacts between Na1 and Na3 with their respective bis[η3-arene] cavities are in the range 2.707(2)–2.968(2) Å. The chameleonic character of sodium to switch from primarily a σ-bonded stance to a π-bonded stance with a NH-deprotonated pyrrole ligand has previously been observed in a series of sodium pyrrolylzinicate structures.10

In addition, compounds 1–5 were successfully characterised by 1H and 13C NMR spectroscopy either in [D₈]thf or C₆D₆/[D₈]thf solutions (see ESI† for full details). All of them are distinguished by the absence of the pyrrolyl NH resonance and the presence of corresponding signals for the macrocyclic framework. 2 exhibits a characteristic broad singlet at 7.94 ppm in the 1H NMR spectrum for the aromatic H flanked by the two CMe₂ groups; whereas this H resonates as a triplet in the range 6.69–6.93 ppm for 1 and 3–5. This situation reflects the distinction between the transoid conformation of the aryl units of the macrocycle in its Li salt form 2 and the alternative cisoid arrangement in the heavier K and Na congeners 1 and 3–5. For all of them, a singlet in the range 5.73–6.08 ppm is found for the pyrrolyl moiety in the 1H NMR spectra.

In conclusion, prior to this work the structures of alkali metal derivatives of the dideprotonated trans-calix[2]benzene[2]pyrrole ligand were concealed since these compounds had only been studied as in situ transfer agents in organometallic lanthanide and actinide chemistry. Here, their isolation and structural characterisation have uncovered a surprisingly diverse range of novel structures from dinuclear monomers, to octanuclear tetramers through to chain polymers.

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Notes and references

6 Mirroring this situation, a second thf-poor variant of 1 was also obtained by diffusion of n-hexane into a thf solution. This complex is included in the ESI† for brevity.