# Exploiting a substituted dihydrotriazinide as a novel bulky ligand: synthesis and crystal structure of a rubidium complex with an unprecedented tetrameric cyclic core

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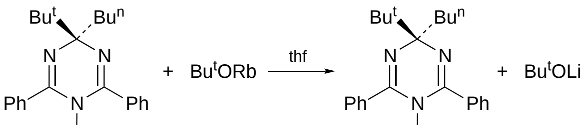
**A metal exchange reaction between the alkoxide Bu$^t$ORb and a dihydrotriazinidolithium complex in tetrahydrofuran (thf) has yielded the first reported triazinidorubidium species, in the bis(thf) solvate of 4-*n*-butyl-4-*tert*-butyl-2,6-diphenyl-1,4-dihydro-*s*-triazinido-1-rubidium, which exists as a unique cyclic tetramer in the solid state having an unprecedented sixteen-membered (NCNRb)$_4$ ring core.**

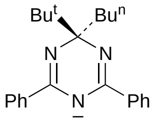
We introduced the dihydrotriazinide **1** in 1993 with a view to shedding light on the intermediate steps involved in alkyllithium-induced cyclotrimerisation reactions of aromatic nitriles.[1] More recently our focus has shifted towards developing this anion as a novel, sterically-encumbered ligand on account of its interesting combination of features. These include (*i*) three heteroatom (N) binding sites; (*ii*) two sterically-flexible Ph sidearms available for π and/or agostic bonding; (*iii*) a bulky, branched [Bu$^n$(Bu$^t$)C] tail, and (*iv*) the possibility of inducing chirality at the saturated ring C atom by metallating only one adjacent N site. **1** made an immediate impact in this role through its participation in the metal derivative, **3**, which established a new type of structure formally designated a 'potassium potassate'.[2] In attempting to extend this work to other metals, we have succeeded in synthesising a rubidium complex employing **1** as a ligand, the surprising structure of which provides the basis for this communication. Structural information on air-sensitive Rb compounds[3] is meagre in comparison to the mountain of data available on lighter alkali-metal congeners (particularly those of lithium[4]), reflecting the lower stability of the former and the greater handling difficulties that this presents. Hitherto only two tetrameric Rb complexes have been reported, as most other aggregates have polymeric constitutions. Moreover, both tetramers, [(Bu$^t$ORb)$_4$][5] and [(Me$_3$SiORb)$_4$],[6] display cubane-based architectures. This background serves to put the novelty of the new complex **2** into perspective, as it, in contrast, adopts an unprecedented cyclic, sixteen-membered (NCNRb)$_4$ ring arrangement. Furthermore, its tetrameric constitution also sets it apart from all other known dihydrotriazinidoalkali-metal structures, which exist as monomers, dimers or polymers.[7]



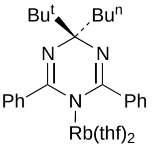
**Scheme 1**

Scheme 1 shows the simple metal exchange strategy used in the synthesis of **2** (anhydrous and anaerobic conditions were employed throughout). Upon isolation the colourless/pale yellow crystals of **2** were taken directly from the mother-liquor and coated in an inert oil prior to undergoing an X-ray diffraction examination. Characterisation of air- and moisture-sensitive **2** was completed by elemental analyses and a $^1$H NMR spectroscopic study.†

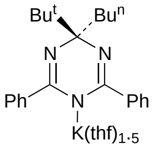
Anion–cation contacts [N(1)–Rb(1) 2.978(3)Å] alternate with longer dative N(2A)–Rb(1) ones [3.033(3)Å] to make up the cyclic tetramer within the crystal structure of **2** (Fig. 1).‡ The molecule possesses tetragonal ($S_4$ or $\bar{4}$) symmetry. With respect to its N centres, the dihydrotriazinide assumes a bis-monodentate, bridging role leaving the N(3) centre unligated. Dimensions within the C$_3$N$_3$ ring show that there is a degree of π-delocalisation about the N(2)C(2)N(1)C(1)N(3) fragment, such that the structural formula of **2** as written represents only one possible mesomeric form, though the dominant one. The C$_3$N$_3$ ring is essentially planar (root mean square deviation



**1**



**2**



**3**

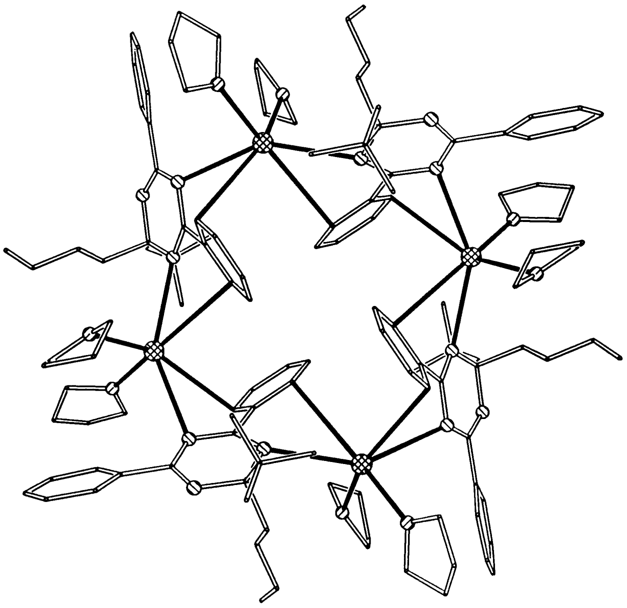


**Fig. 1** The structure of the tetrameric molecule without hydrogen atoms. Selected dimensions (Å and °): Rb(1)–N(1) 2.978(3), Rb(1)–N(2A) 3.033(3), Rb(1)–O(1) 2.824(3), Rb(1)–O(2) 2.811(3), Rb(1)–C(11) 3.352(3), Rb(1)–C(15A) 3.380(3), N(1)–C(1) 1.369(4), N(1)–C(2) 1.362(4), N(2)–C(2) 1.304(4), N(2)–C(3) 1.471(4), N(3)–C(3) 1.481(4), N(3)–C(1) 1.295(4), N(1)–Rb(1)–N(2A) 148.19(7), O(1)–Rb(1)–O(2) 110.00(10), C(11)–Rb(1)–C(15A) 90.17(9); symmetry operator A: $\frac{1}{2}+y$, $\frac{1}{2}-x$, $\frac{1}{2}-z$.

0.017 Å). The coordination sphere of the Rb cation involves opposing sides of two equivalent triazinide ligands (Fig. 2). A pair of thf molecules also bind to Rb. Accompanying these Rb–heteroatom bonds are a number of Rb–C interactions. As is often the case with organometallic derivatives of alkali metals, the coordination number and geometry are not entirely clearly defined, with a range of Rb–C distances and with some close contacts a necessary consequence of others. In this structure, however, one phenyl group on each triazine ring lies between two Rb cations in such an orientation that each *ortho* C atom forms a bond with one metal ion [C(11)–Rb(1) 3.352(3) Å, C(15)–Rb(1B) 3.380(3) Å], giving a primary coordination number of six for Rb. Each Rb cation is thus chelated by one N atom and one phenyl *ortho*-C atom of two triazinide ligands. The disposition of the ligands relative to the cations generates other close Rb–C contacts, notably 3.450(3) Å for C(10) and 3.573(3) Å for C(2), which presumably also contribute to the overall ligand–metal bonding. All other Rb–C distances are > 3.6 Å. The second phenyl group on each triazine is not involved in metal coordination; these four groups occupy positions at the periphery of the structure and form a 'paddle wheel' arrangement. In effect, the thf ligands lie *cis* to each other in view of the relatively small O–Rb–O bond angle [110.12(10)° *cf* 180° in an ideal *trans* situation]. More open, but still well short of being linear, are the N-Rb-N contacts [angle 148.12(7)°] which link the four monomeric fragments together into a cyclic ring. To achieve this ring closure, the Rb cation sits out of the mean planes of both attached $C_3N_3$ rings, by 1.750 and 1.160 Å.

Turning to a comparison of bond dimensions with those in other structures, the N–Rb distances in **2** lie between those of the two asymmetric N–Rb bonds in the amide $[\{[RbN(SiMe_3)_2\cdot 1.5\,dioxane]_2\}_\infty]$ (2.946, 3.141 Å).[8] The C–Rb contact distances in **2** are also typical of those found in structures with delocalised aryl groups, *e.g.* 3.351–3.643 Å in $[(Ph_3CRb\cdot pmdeta)_\infty]$;[9] 3.14–3.57 Å in $[(PhCH_2Rb\cdot pmdeta)_\infty]$.[10]

The cyclic, oligomeric nature of the structure of **2** provides an interesting contrast with the zigzag, polymeric chain arrangement preferred by the potassium counterpart **3**.[2] Given that the precursor to **2**, $[(Bu^tORb)_4]$ is isostructural with $[(Bu^tOK)_4]$,[5] it would not have been unreasonable to assume that **2** and **3** might adopt a common structural motif. However, it is important to recognise that these butoxides are three-dimensional 'stacked-ring' structures, which are not greatly affected by the size differential between the metals (ionic radii: $Rb^+$ 1.52 Å, $K^+$ 1.38 Å). On the other hand, structures with one-dimensional heteroatom–metal connectivities, as in **2** and **3**, can be profoundly affected. In **2** this is manifested in the addition of extra solvent ligands (metal : thf ratio 1 : 2, *cf* 1 : 1.5 in **3**), and in an increased number of metal–ligand interactions (primary coordination number of Rb = 6; *cf.* 4 or 5 for K in **3**).

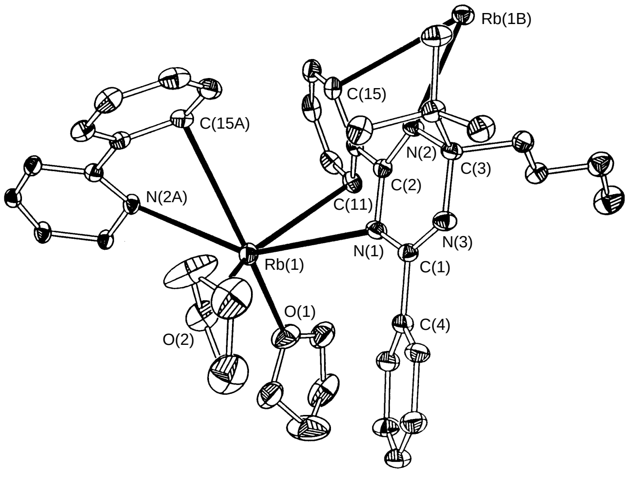


**Fig. 2** Thermal ellipsoid plot at 30% probability, showing the asymmetric unit of **2**, together with one adjacent $PhC_3N_3$ unit to complete the coordination of Rb(1), and the adjacent Rb atom to complete the bonding environment of the triazine ligand. Hydrogen atoms are omitted, and key atoms are labelled.

In conclusion, the special ligating ability of **1** has been further demonstrated by the determination of the crystal structure of a rubidium complex exhibiting a novel cyclic tetrameric arrangement. From this evidence, **1** can be regarded as a novel alternative to conventional bulky nitrogen ligands such as the amide $[(Me_3Si)_2N^-]$. This prospect now calls for a full investigation of the coordination chemistry of **1** with other metal partners.

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## Footnotes

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† Yield (first batch), 28%; mp 70–72 °C. Anal ($C_{31}H_{44}N_3O_2Rb$)C, H, N, Rb. $^1H$ NMR (400 MHz, [$^2H_5$]pyridine) $\delta$ 0.73 (t, $CH_3$ of $Bu^n$), 1.41 (m, $\gamma$-$CH_2$ of $Bu^n$), 1.55 (s, $Bu^t$), 1.67 (m, $CH_2$ of thf), 1.84 (m, $\beta$-$CH_2$ of $Bu^n$), 2.12 (m, $\alpha$-$CH_2$ of $Bu^n$), 3.70 (t, $OCH_2$ of thf), 7.38(t, *p*-Ph), 7.47 (m, *m*-Ph), 8.94 (d, *o*-Ph).

‡ *Crystal data* for **2**: $C_{124}H_{176}N_{12}O_8Rb_4$, $M$ = 2304.6, tetragonal, space group $I\bar{4}$, $a$ = 25.225(2), $c$ = 11.1115(9) Å, $U$ = 7070.3(10) Å$^3$, $Z$ = 2, $D_c$ = 1.083 g cm$^{-3}$, $\mu$ = 1.43 mm$^{-1}$ (Mo-K$\alpha$, $\lambda$ = 0.710 73 Å), $F(000)$ = 2432, $T$ = 160 K. Siemens SMART CCD area-detector diffractometer, crystal size 0.56 × 0.50 × 0.38 mm, $\theta_{max}$ 28.5°, 22406 reflections measured, 8002 unique ($R_{int}$ = 0.0236). Structure solution by direct methods, full-matrix least-squares refinement on $F^2$ with weighting $w^{-1} = \sigma^2(F_o^2) + (0.0683P)^2$, where $P = (2F_c^2 + F_o^2)/3$, anisotropic displacement parameters, riding hydrogen atoms, no absorption correction, extinction parameter $x$ = 0.000 40(16), where $F_c' = F_c/(1 + 0.001\,x\,F_c^2\lambda^3/\sin 2\theta)^{\frac{1}{4}}$, absolute structure parameter = 0.042(7). Final $R_w = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ = 0.1194 for all data, conventional $R$ = 0.0423 on $F$ values of 6506 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S$ = 1.074 on $F^2$ for all data and 339 parameters. Final difference map between +0.70 and −0.41 e Å$^{-3}$. Programs: Siemens SMART and SAINT control and integration software, SHELXTL (G. M. Sheldrick, University of Göttingen, Germany), and local programs. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallogaphic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and reference number 182/488.

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