

Synthesis and crystal structure of trimeric sodium 2,2,6,6-tetramethylpiperidide (NaTMP)

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Abstract

The title compound has been synthesised in powder form by two distinct methods: namely by sodiation of the parent amine 2,2,6,6-tetramethylpiperidine with *n*-butylsodium in a hydrocarbon solvent or by transmetallation from lithium 2,2,6,6-tetramethylpiperidide through the action of sodium *t*-butoxide in hexane solution. An alternative crystalline specimen suitable for X-ray crystallographic study was grown from a solution which additionally contained *n,s*-dibutylmagnesium. This study reveals a trimeric molecule of C_{3h} symmetry, its salient feature being a strictly planar (NaN)₃ ring. The sterically encumbered amide anions are separated by large N–Na–N bond angles of 143.76(6)°, the bonding in which is slightly asymmetrical (Na–N bond lengths: 2.307(2) and 2.362(2) Å). Discussion focuses on the contrast between the tetrameric ring arrangement of the lithium congener, which was reported several years ago. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium 2,2,6,6-tetramethylpiperidide (LiTMP) was one of the first bulky lithium amides to be characterised by X-ray diffraction with its crystal structure being reported in 1983 [1]. This revealed tetrameric association in the form of a cyclic (NLi)₄ planar ring with near-linear N–Li–N edges (Fig. 1). A decade later TMEDA (*N,N,N',N'*-tetramethylethylenediamine) was found to open this structure and cut it in half by chelating the terminal Li centre in the open dimer [(LiTMP)₂·TMEDA] [2], which shed light on the possible aggregated intermediates involved in classical aldol reactions. LiTMP is a useful deprotonating agent both on its own [3] and when coupled to potassium *t*-butoxide. This couple can smoothly metallate isoprene [4] illustrating the low tendency of LiTMP to add across multiple bond systems. Recently the Strathclyde group has utilised LiTMP in the preparation of the ‘inverse

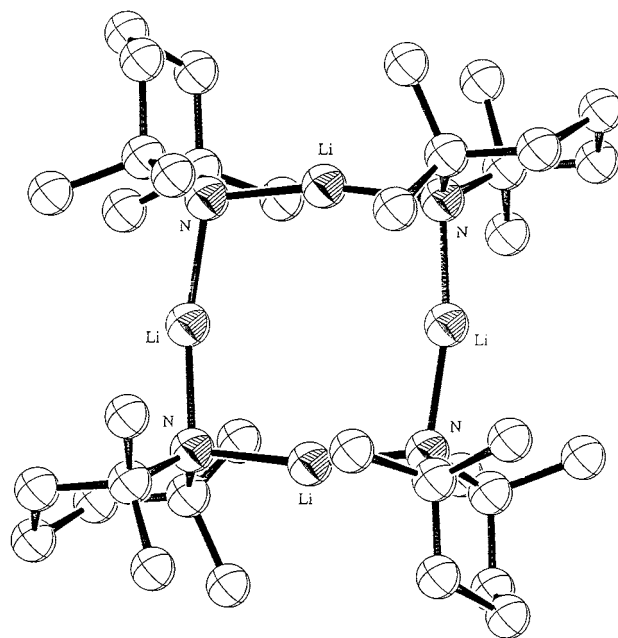


Fig. 1. Molecular structure of (LiTMP)₄.

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‘crown ether’ complex $[\text{Li}_2\text{Mg}_2(\text{TMP})_4(\text{O})]$, an eight-membered 2+ charged macrocyclic ring structure with a 2- charged oxide core [5]. This work has also been extended to sodium through the synthesis and characterisation of the larger twelve-membered macrocyclic complexes $[\text{Na}_4\text{Mg}_2(\text{TMP})_6(\text{C}_6\text{H}_3\text{Me})]$ and $[\text{Na}_4\text{Mg}_2(\text{TMP})_6(\text{C}_6\text{H}_4)]$ [6], which have arene-based dianionic cores. During the course of these mixed-metal studies the Strathclyde group has inadvertently crystallised the homonuclear sodium compound NaTMP (**1**). The fact that examples of unsolvated sodium amide structures are rare prompted us to determine the crystal structure of **1**. Having submitted a paper based on this structural determination, it was brought to our attention at the refereeing stage that the Sussex group had previously communicated this structure in a conference poster abstract [7]. We have therefore decided to pool our results and to present them herein. The structure of **1** provides an interesting comparison with that of the aforementioned LiTMP.

2. Results and discussion

NaTMP is easy to prepare in powder form. It can be made directly from the parent amine TMPH in hexane or pentane solution when *n*-butylsodium is employed as the metallating reagent. Alternatively, LiTMP can be converted to its sodium congener on treatment with sodium *t*-butoxide in hexane solution. The latter transmetalation method appears to be the one of choice as yields approaching 90% are obtainable. This air- and moisture-sensitive but non-pyrophoric powder is essentially insoluble in hydrocarbon solvents, and only sparingly soluble in arene solvents. However, it is soluble enough to enable both ^1H - and ^{13}C -NMR spectra to be recorded in benzene- d_6 solution. A notable feature of these spectra is the observation of two distinct CH_3 resonances. This contrasts with the one such resonance observed in a DMSO- d_6 solution, in which **1** is significantly more soluble. The arene solution is more representative of pure (unsolvated) NaTMP, and is therefore more likely to resemble the solid state molecular structure (see below). Accordingly, the distinct CH_3 resonances can be assigned to axial and equatorial groups within the chair arrangement of the TMP ligand. In strongly solvating DMSO, a lower aggregated solvate is almost certainly formed. A large single crystal of **1** suitable for an X-ray crystallographic examination was obtained from a solution containing *n*-butylsodium, *n,s*-dibutylmagnesium and TMPH in a 1:1:3 molar ratio in hexane/heptane solution. The additional presence of the magnesium reagent appears to enhance the hydrocarbon solubility of the in situ generated NaTMP. The Strathclyde group carried out this reaction with the specific aim of identifying the nature of

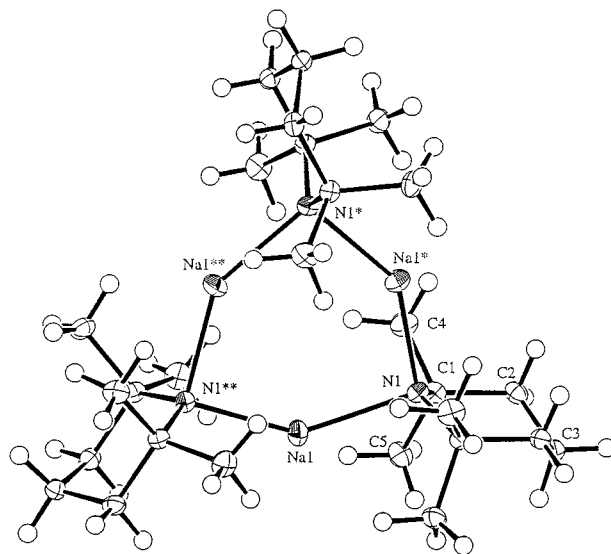


Fig. 2. Molecular structure of **1** showing atom labelling scheme.

the intermediate to the aforementioned $[\text{Na}_4\text{Mg}_2(\text{TMP})_6(\text{C}_6\text{H}_3\text{Me})]$ and $[\text{Na}_4\text{Mg}_2(\text{TMP})_6(\text{C}_6\text{H}_4)]$ complexes prior to the arene (toluene and benzene, respectively) addition stage. So far this aim was not realised, though studies are still ongoing. The Sussex group on the other hand grew suitable single crystals by filtering a hot benzene suspension of **1** and leaving the filtrate aside for several days at ambient temperature.

Fig. 2 shows the labelled molecular structure of **1** as determined by the X-ray crystallographic studies (for brevity only the data from one study is given; the other data are in close agreement). A side view clearly showing the horizontal mirror plane which runs through the $\gamma\text{C}\cdots\text{N}$ vector of the TMP ligand and the $(\text{NaN})_3$ plane, is given in Fig. 3 (the molecule belongs to the point group C_{3h}). Selected bond lengths and bond angles within the structure are listed in Table 1. Trimeric aggregation is observed, built around a (crystallographically imposed) strictly planar $(\text{NaN})_3$ ring. There is a twofold, near-linear ($143.76(6)^\circ$) coordination at Na,

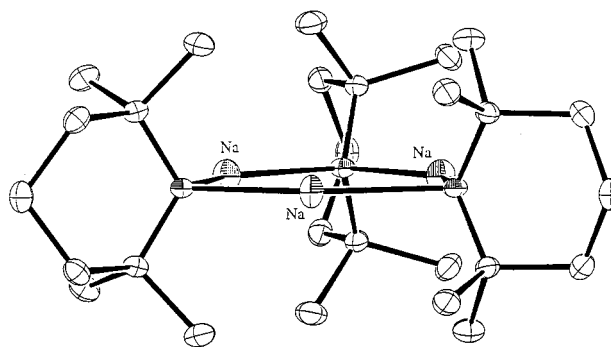


Fig. 3. Alternative side view of **1**. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **1**^a

Na–N(1)	2.362(2)	Na–N(1)**	2.307(2)
N(1)–C(1)	1.475(1)	C(1)–C(2)	1.545(2)
C(1)–C(4)	1.531(2)	C(1)–C(5)	1.554(2)
C(2)–C(3)	1.522(2)		
Na–N(1)–Na*	96.24(6)	Na–N(1)–C(1)	105.55(8)
Na*–N(1)–C(1)	114.46(7)	C(1)–N(1)–C(1) [†]	117.3(1)
N(1)–C(1)–C(2)	113.1(1)	N(1)–C(1)–C(4)	107.1(1)
N(1)–C(1)–C(5)	114.9(1)	C(2)–C(1)–C(4)	107.4(1)
C(2)–C(1)–C(5)	107.70(10)	C(4)–C(1)–C(5)	106.1(1)
C(1)–C(2)–C(3)	112.1(1)	C(2)–C(3)–C(2) [†]	109.0(1)

^a Symmetry transformation used to generate primed atoms: ** = 1–y, x–y, z, * = 1–x+y, 1–x, z, [†] = x, y, 3/2–z.

and fourfold, distorted tetrahedral (mean bond angle, 108.93°) coordination at N. The TMP ligands are arranged in a chair conformation with symmetry-equivalent \propto C/ \propto C* atoms each carrying an axial and an equatorial Me group.

Turning to dimensions, the Na–N ring bonding is asymmetrical (mean length, 2.334; difference, 0.055 Å). Only one unsolvated sodium amide trimer is available for comparison with **1**. Two different groups, those of Driess and Nöth, have recently independently reported [8,9] the crystal structure of the hexamethyldisilazide [$\{\text{NaN}(\text{SiMe}_3)_2\}_3$] (here labelled **2A** and **2B**, respectively), a trimeric polymorph of a compound previously found to exist as a polymeric chain arrangement [10]. The cyclic structures of **2A** and **2B** are less symmetrical than that of **1**, deviating markedly from idealised D_{3h} symmetry because their (NaN)₃ rings are slightly distorted from planarity. As a result they contain six distinct Na–N bond lengths (ranges: 2.364–2.404 and 2.358–2.394 Å, respectively; mean values 2.381 and 2.378 Å, respectively). With regard to interligand repulsions, the marginally shorter Na–N bonds in **1** are offset by larger, more obtuse N–Na–N bond angles (143.76(6)°) than those in **2A** (range 136.85–142.77, mean 139.70°) and **2B** (range 137.6–141.8, mean 139.73°). Concomitantly **1** has smaller Na–N–Na bond angles (96.24(6) cf. mean values 100.07 and 99.97°, respectively). In **1** the largest tetrahedral distortion subtended at N occurs at the C1–N1–C1[†] bond angle (117.3(1)°), primarily to alleviate transannular Me \cdots Me strain. Free from the constraints of a ring system, the corresponding Si–N–Si bond angles in **2A** and **2B** open even wider (mean values, 125.3 and 125.6°, respectively). With a low formal coordination number of 2 for Na, one tends to look for secondary interactions that could possibly relieve this coordinative unsaturation. In **1** this appears to be fulfilled through several Na \cdots C contacts (Na* \cdots C4/C4[†], 3.031(1); Na \cdots C5/C5[†], 3.101(2); Na \cdots C1/C1[†], 3.102(1); Na \cdots C3^{††}, 3.203(2); Na* \cdots C1/C1[†], 3.211(1)), associated Na \cdots H(C) contacts may also contribute. The importance of these agostic-type inter-

actions [11] is difficult to quantify; however, using **2A** as a benchmark where four Na \cdots C contacts shorter than 3.0 Å are observed (i.e. 2.86, 2.94, 2.96 and 2.99 Å), they seem less significant individually, though collectively they probably contribute to the overall stability of **1**.

It is interesting to compare these unsolvated sodium amide systems with their lithium congeners. Unsolvated lithium hexamethyldisilazide [$\{\text{LiN}(\text{SiMe}_3)_2\}_3$] [12,13] is a cyclic trimer like **2A** and **2B**. On the other hand, as mentioned in the introduction, LiTMP is not a cyclic trimer like NaTMP, but a cyclic tetramer. This higher oligomerisation can be attributed to the greater steric requirements of the TMP ligand versus the hexamethyldisilazide ligand. Replacing Na by the smaller Li in the TMP system results in a 14% (mean) contraction of the metal–N bond length (i.e. Li–N bond length in LiTMP is 2.00 Å). Consequently, the steric crowding of the TMP ligands would significantly increase in LiTMP were it to retain the trimeric ring structure of NaTMP. Therefore, one might expect that LiTMP would prefer to adopt a lower dimeric ring structure in view of the larger coordination arc (exocyclic Li–N–Li bond angles) it can offer to the TMP ligand. However, this would be counterbalanced by increased transannular strain as some methyl groups from the TMP ligand would project towards (and possibly overhang) the face of the (LiN)₂ ring (this situation can be clearly seen for NaTMP in Fig. 2, though the view exaggerates the extent of overhanging). Three related structures indirectly lend support to this idea. First, as already mentioned, LiTMP fails to form a closed dimeric ring structure when solvated by a single TMEDA ligand; its preferred open dimeric arrangement circumvents the problem of transannular strain. Secondly, when one TMP ligand is replaced by a monoatomic anion as in the heterodimer [LiBr·LiTMP·(THF)₃] [14], a closed-ring structure is allowed due to a significant reduction in transannular strain and the expansion in size of the (LiBrLiN) ring compared to a (LiN)₂ ring. Thirdly, lessening steric effects by substituting two H atoms for two Me groups as in the 2,6-dimethylpiperidide (DMP) complex [$\{(\text{LiDMP})_2\cdot\text{TMEDA}\}_\infty$] [15] also allows a closed-ring dimer to exist, which in this case is linked into polymeric chains by Li–TMEDA–Li bridges. Therefore LiTMP opts for the higher tetrameric ring arrangement instead of the dimeric one. As a regular octagon would not offer wide enough N–Li–N bond angles (i.e. 135°) for adequate separation of adjacent TMP ligands, a more square-like (LiN)₄ ring is adopted (mean bond angles: at Li, 168.5; at N, 101.5°). Transannular Me \cdots Me repulsions are of diminished importance in this structure compared to that in a hypothetical dimer due to the significant size distinction between the eight-membered (LiN)₄ face and a four-membered (LiN)₂ face. Finally, the similarity between the crystal

structures of LiTMP and LDA (lithium diisopropylamide) [16] is worthy of comment, since it has not been discussed previously. The latter amide possesses the same infrastructure as the former with near-linear N–Li–N units (mean bond angle, 176.0°) which join perpendicularly (mean Li–N–Li bond angle, 108.9°). However, the greater steric demands of the diisopropylamide ligand force adjacent N–Li–N units to twist out of planarity to form an open, infinite helical arrangement (with four units per helix turn) rather than a closed-ring tetramer.

3. Conclusions

NaTMP has been synthesised and crystallographically characterised. Its molecular structure consists of a (NaN)₃ planar trimeric ring with *C*_{3h} symmetry. This contrasts with the tetrameric ring structure of LiTMP. The preference for lower aggregation can be rationalised in terms of the longer Na–N bonds (compared to Li–N bonds) which are accompanied by the less wide N–Na–N bond angles (compared to N–Li–N bond angles).

4. Experimental

Reactions were performed under a protective inert atmosphere of argon using standard Schlenk-line techniques. Elemental analyses were determined on a Perkin–Elmer 2400 elemental analyser; sodium analysis was carried out by atomic absorption on a PU 9100 Philips spectrometer.

4.1. Direct synthesis of **1**

n-Butylsodium was prepared by a metathesis reaction involving *n*-butyllithium and sodium *t*-butoxide as described in the literature [17]. Washed with hexane, dried under vacuum, and isolated, the freshly prepared sodium reagent (10 mmol) was resuspended in hexane (10 ml), and the mixture was sonicated for 5 min to give a fine cream-coloured dispersion. The amine TMPH (30 mmol) was subsequently added without causing any discernible change to the dispersion. The mixture was then heated to reflux overnight at which stage a pale yellow suspension was obtained. This solid was collected by vacuum filtration and washed with several aliquots of hexane. It was identified as NaTMP (yield, 32%); m.p. (dec.) (yellow to black) from 140°C, melting at 241–242°C; ¹H-NMR (400 MHz, DMSO-*d*₆, 298 K): δ 1.02 (s, 12H, CH₃ × 4), 1.23 (t, 4H, βCH₂ × 2) and 1.56 (m, 2H, γCH₂). ¹H-NMR (500 MHz, benzene-*d*₆, 298 K): δ 1.06 and 1.09 (2 s, 12H, CH₃), 1.21–1.87 (m, 6H). ¹³C{¹H}-

NMR (75.47 MHz, benzene-*d*₆, 298 K) 32.0 (CH₂), 38.27 and 38.59 (CH₃), 42.4 (CH₂) and 52.29 (CN). Anal. Calc. for C₉H₁₈NNa: C, 66.3; H, 11.0; N, 8.6; Na, 14.1. Found: C, 66.2; H, 11.4; N, 8.0; Na, 13.4%. The corresponding reaction between TMPH (44 mmol) and *n*-butylsodium (42 mmol) in pentane (50 ml) at ambient temperature afforded **1** in a significantly greater yield (82%).

4.1.1. Alternative synthesis via transmetalation

Sodium *t*-butoxide (38 mmol) was added to a solution of LiTMP (38 mmol) in hexane (50 ml) and stirred overnight at ambient temperature, which resulted in the formation of a white solid. The solvent was removed by filtration and the collected solid was washed several times with pentane. After drying in vacuo, compound **1** (yield 87%) was obtained as an off-white powder.

4.1.2. Fortuitous synthesis of crystalline **1**

A mixture of freshly prepared *n*-butylsodium (10 mmol) in hexane (10 ml) was sonicated for 5 min to give a fine cream-coloured dispersion. *n,s*-dibutylmagnesium (10 mmol) was then introduced resulting in the formation of a oily, brown precipitate. Addition of TMPH (30 mmol) caused complete dissolution, and the mixture was stirred for 48 h. At this stage the mixture had turned a dark brown colour and a small amount of brown solid was visible. Next the solution was filtered through Celite and the filtrate was cooled in a refrigerator (at +3°C) overnight. This solution deposited a small number of colourless transparent crystals which turned opaque before an X-ray crystallographic examination could be carried out. The solution was subsequently kept for 10 days at ambient temperature by which time a large colourless single crystal had grown. Cut to a suitable size, this crystal was used for the X-ray crystallographic examination and determined to be trimeric (NaTMP)₃.

4.2. Crystal structure determination

A colourless fragment, size 0.60 × 0.40 × 0.25 mm, of [Na(NC₉H₁₈)₃] was found to be hexagonal, *P*6₃/*m*, with *a* = *b* = 10.6455(11), *c* = 14.706(2) Å, *V* = 1443.3(2) Å³ and *Z* = 2. Data were collected on a Rigaku AFC7S diffractometer using Mo–K_α radiation, λ = 0.71069 Å, and the ω–2θ technique to a 2θ_{max} of 55°. No absorption or decay corrections were needed. Of 1650 reflections 1164 were unique, *R*_{int} = 0.032, and 976 observed with *I* ≥ 1.5σ(*I*). The structure was solved by direct methods [18] and refined [19] on *F* with 93 parameters (H atoms isotropic) to converge at *R* = 0.0378 and *R*_w = 0.0574 (molecular structure determined by texsan [19]).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Data Centre, CCDC-116291 for compound **1**.

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