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Synthetic and Reactivity Studies of Hetero-tri-anionic Sodium Zincates

Javier Francos,³ Alan R. Kennedy² and Charles T. O’Hara*⁴

The synthesis and characterisation of several sodium zincate complexes is reported. The all-alkyl monomeric sodium zincate (PMEDTA)·Na(µ-CH₃SiMe₃)Zn[µ-C₄H₉]₂, is prepared by combining an equimolar quantity of Bu₂Zn, BuNa and PMDETA (N,N',N''-pentamethyldiethylenetriamine). A similar approach was used to prepare and isolate the unusual dimeric zincate [(PMEDTA)·Na(µ-TMP)(µ-CH₃SiMe₃)]. When an equimolar mixture of BuNa, Bu₂Zn and TMP[H] (2,2,6,6-tetramethylpiperidine) are combined in hexane, the hetero-tri-leptic TMP[H]-solvated zincate (TMP[H]Na(µ-TMP)[µ-C₄H₉]Zn[µ-C₄H₉]Zn[µ-C₄H₉]Bu) 4 was forthcoming. Complex 4 can also be prepared using a rational approach [i.e., utilising two molar equivalents of TMP[H]]. When TMEDA is reacted with an equimolar mixture of BuNa, Bu₂Zn and TMP[H], the monomeric sodium zincate (TMEDA)Na(µ-TMP)[µ-C₄H₉]Zn[µ-C₄H₉]Bu 5 was obtained – this complex is structurally similar to the synthetically useful relation TMEDA·Na(µ-TMP)[µ-C₄H₉]Zn[µ-C₄H₉]Bu 1. By changing the sodium reagent used in the synthesis of 5, it was possible to prepare (TMEDA)Na(µ-TMP)[µ-Me₃SiCH₂]Zn[µ-C₄H₉]Bu 6. By reacting 5 with cis-DMP[H] (cis-2,6-dimethylpiperidine), the zincate could thermodynamically function as an amide base, to give the transamination product (TMEDA)Na(µ-cis-DMP)[µ-C₄H₉]Zn[µ-C₄H₉]Bu 7, although no crystals could be grown. However, when HMDS[H] (1,1,1,3,3,3-hexamethyldisilazane) or PEA[H] ([(+)-bis(R)-(1-phenylethyl)amine] is reacted with 5, crystalline (TMEDA)Na(µ-HMDS)[µ-C₄H₉]Zn[µ-C₄H₉]Bu 8 or (TMEDA)Na(µ-PEA)[µ-C₄H₉]Zn[µ-C₄H₉]Bu 9 are isolated respectively. With PNA[H] (N-phenyl-naphthalen-1-amine) the reaction took a different course and resulted in the formation of the dimeric sodium amide complex [(TMEDA)Na(PNA)] 10. When reacted with benzene, it appears that a TMEDA-free variant of 5 functions thermodynamically as an ‘Bu base to yield the previously reported (TMEDA)Na(µ-TMP)[µ-BuZn(µ-C₄H₉)Zn(µ-C₄H₉)]Na(TMEDA) 11. Finally when reacted with TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl), 5 undergoes a single electron transfer reaction to form (TMEDA)Na(µ-TMP)[µ-TEMPO]Zn[µ-C₄H₉]Bu 12.

Sodium zincate 1, can act as a powerful base, regioselectively deprotonating arenes, heterocycles, and metalloccenes.³⁷-⁴⁰ It can also act as a source of a t-butyl group, where the zincate formally adds across ketones in an unusual 1,6-manner.⁴¹, ⁴² We also discovered that 1 can undergo single electron transfer (SET) with the stable oxy-radical TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl and chalcone (PhCO=CHPh).⁴³ In this work, the synthesis of TMP-zincates is probed and a series of hetero-tri-leptic zincates (i.e., species that contain three different anionic ligands) is prepared. Finally, the reactivity of a prototypical zincate towards deprotonation, addition, SET and amide exchange reactions is studied.

Introduction

Since the turn of the millennium, alkali metal ate complexes (where an alkali metal organometallic reagent is combined with another less polar organometallic reagent) have come to the fore in synthetic chemistry.¹-⁶ This interest is primarily due to the fact that mixed metal species can often perform chemistry, which is unobtainable by the monometallic constituent parts, or it can be utilized at more user-friendly reaction temperatures and in the presence of donor solvents or reactive functional groups. TMP-ate complexes (where TMP is 2,2,6,6-tetramethylpiperidine), particular magnesiate and zincate reagents⁵-⁻³⁰ are amongst the most widely studied. Focusing on TMP-zincate systems, several donor-solvated heterobimetallic formulations have been crystallographically-characterized including (TMEDA)-Li(µ-TMP)[µ-C₄H₉]Zn[µ-C₄H₉]₃,³¹ (TMEDA)-Li(µ-TMP)Zn(Me)₂,³² (THF)-Li(µ-TMP)Zn(µ-C₄H₉)[µ-C₄H₉]Bu)₃,³³ and most pertinent to this study (TMEDA)-Na(µ-TMP)[µ-CH₃SiMe₃]Zn(CH₂SiMe₃)₃⁶ and most pertinent to this study (TMEDA)-Na(µ-TMP)[µ-C₄H₉]Zn(µ-C₄H₉)Bu) 1.³⁷

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Received 00th January 20xx
Accepted 00th January 20xx
DOI: 10.1039/x0xx00000x
www.rsc.org/

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J. Name., 2013, 00, 1-3 | 1
Results and Discussion

Syntheses and NMR Spectroscopic Characterization of sodium zinicates 2-6

The first objective of this study was to probe further the synthesis of TMP-sodium zinicates. As mentioned in the introduction, previous work has focused on the synthesis and reactivity of 1.37 Sodium zinicate 1 is formed via co-complexation of a 1:1 stoichiometric mixture of NaTMP (itself preformed via a reaction between tBuNa and TMPH), tBu2Zn and TMEDA. In this work, a 1:1 mixture of the alkyl reagents tBuNa and tBu2Zn was studied. On addition of freshly prepared hexane solution of tBu2Zn to the white suspension of tBuNa in hexane, surprisingly immediate dissolution occurred. 1H NMR spectroscopic analysis of this mixture in a cyc-C6D12 solution, revealed the expected n- and tert-butyl resonances. Relying on these data, it was not immediately obvious that co-complexation had occurred as the chemical shift associated with the tBu group was identical to that of tBu2Zn (1.09 ppm); however, there is an tBu CH2 resonance at ~0.79 ppm (integrating to two H atoms, with respect to 18 for the tBu H atoms). A perfect solution was obtained, suggesting that the insoluble monometallic starting material tBuNa (or indeed the potential metathetical product, tBuNa) was not present in the mixture. Unfortunately, all attempts to obtain suitable X-ray quality crystals from this mixture were unsuccessful. Therefore, in an effort to shed some structural insight into the complexation of sodium and zinc alkyl reagents, we exchanged the potential metathetical product, tBuNa for (trimethylsilylmethyl)sodium (Me3SiCH2Na).45, 46 The trimethylsilylmethyl anion was chosen as it aids stability (due to the lack of B-hydrogen atoms), solubility and is known to crystallize well when it is a component of s-block metal complexes.45-53 Unfortunately, again no crystalline material was forthcoming so a donor ligand was introduced [namely the tridentate amine PMDETA ([N,N’,N”]-pentamethyldiethylenetriamine)]. When a 1:1 mixture of Me3SiCH2Na, tBu2Zn and PMDETA was combined in hydrocarbon solution a white solid formed, which was easily dissolved by gentle heating. Storing this solution at ~28 °C resulted in the formation of colourless crystals (in 61% non-optimized yield). X-ray diffraction analysis (vide infra) revealed the formation of the all-alkyl monomeric zincate (PMDETA)Na[μ-CH2SiMe3]Zn2Bu2 (Scheme 1). A similar approach was ultimately used to prepare and isolate the dimeric [[PMDETA]Na[μ-tBu2Zn]Bu2]2 3. NMR spectroscopic analysis of cyc-C6D12 solutions of crystalline 2 and 3 at 300K appeared to confirm the three different anions in each of the complexes were present in a 1:1:1 ratio, and that only one type of each was present, therefore suggesting that no ligand scrambling was occurring.

The next step in this study, was to ascertain the reactivity of a hydrocarbon solution of the donor-free variant of 3 [i.e., ‘Na(tBu)Zn(tBu)’] with the secondary amine TMP(H). In this reaction, an equimolar mixture of tBuNa and tBu2Zn in hexane was stirred for 30 minutes (Scheme 2). One equivalent of TMP(H) was then added via syringe, before allowing the solution to stir for 1 hour, before cooling to ~28°C. This resulted in the crystallization of the hetero-tri-lectic TMP(H)-solvated zincate (TMPH)Na[μ-TMP][μ-tBu]Zn(tBu) 4 in 66% yield [based on TMP(H) consumption]. The incorporation of TMP(H) as a donor ligand is unusual but has been observed previously in a sodium-magnesium ferrocenophane complex.54 Complex 4 may be viewed as a precursor to a bis(TMP) zinicate; however, thus far we have not been able to activate the relatively acidic amino-NH by heating aliphatic hydrocarbon or arene solutions of 4. Complex 4 can also be prepared rationally by introducing two equivalents of TMP(H) to the sodium-zinc tris(alkyl) mixture.

When TMEDA is added to a 1:1:1 mixture of tBuNa, tBu2Zn and TMP(H) in hexane, a white precipitate which was easily dissolved by gentle heating, and subsequent cooling at ~28°C yielded crystals of (TMEDA)Na[μ-TMP][μ-tBu]Zn(tBu) 5 in good yield (60%). Following a similar procedure, when TMEDA is added to a 1:1:1 mixture of Me3SiCH2Na, tBu2Zn and TMP(H), gently heated, and cooled to ~28°C crystals of (TMEDA)Na[μ-TMP][μ-Me3SiCH2]Zn(tBu) 6 (Scheme 3) deposited in good yield (61%). The NMR spectroscopic data for 5 and 6 in cyc-C6D12 solution (Table 1) show the expected 1:1:1 ratio of anionic ligands and that the respective donor ligand remains attached to the metal at 300 K. At this juncture, the incorporation of other amines [i.e., other than TMP(H)] into the zinicates was investigated.
The first alternative amine which was examined was 2,6-cis-dimethylpiperidine, cis-DMP(H). This amine has recently been used to prepare ate reagents which have been utilized in deprotonation reactions. From a synthetic-viability viewpoint, it is considerably less expensive than TMP(H). When it was used in place of TMP(H) (i.e., in the synthesis of 5) it was expected that a zincate with empirical formula (TMEDA) Na(μ-cis-DMP)(μ-²Bu)Zn³Bu 7 could be isolated (Scheme 4). However, no high quality crystalline material could be obtained. NMR spectroscopic data revealed that signal for a cis-DMP, ²Bu, TMEDA and ³Bu ligands were all evident. Table 1 contains a summary of the NMR spectroscopic data for the alkyl ligands present in 2-7. These data suggest that the respective 1H and 13C NMR spectroscopic resonances for the ZnCH₂ and the Zn³Bu groups in 5 and 7 have similar chemical shifts (−0.42 vs −0.40; 1.05 vs 1.01; 16.6 vs 15.9; 34.0 vs 34.1), providing evidence that a similar structural framework exists when either cis-DMP or TMP is employed. Complex 5 can be viewed as a closely related, tri-heteroleptic mimic of 1, as such it was decided to explore the reactivity of 5 with a host of important organic substrates which are known to react with 1.

![Scheme 4. Synthesis of cis-DMP zincate 7.](image)

Table 1. 1H and 13C NMR chemical shifts (ppm) of ²BuZn, NaZn⁴Bu⁵Bu, NaZn⁴Bu(CH₂SiMe₃) and zincates (2-7) performed in cyclo-C₆H₁₂ at 293 K (400 MHz).

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<th>Compound</th>
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<th>δ(13C)</th>
<th>δ³Bu</th>
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<tr>
<td>²Bu⁵BuNaZn</td>
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</tr>
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</table>

Exploring the synthetic utility of sodium zincate 5

The remainder of the synthetic work in this paper focuses on the reactivity of 5. Firstly, by treating a hexane solution of ²BuZn, NaZn⁴Bu⁵Bu, NaZn⁴Bu(CH₂SiMe₃) and zincates (2-7) performed in cyclo-C₆H₁₂ at 293 K (400 MHz). The addition of excess TMEDA, in an attempt to drive 8 to a solvent-separated system failed; hence, it seems clear that the structural difference observed between 8 and ([(TMEDA)Na⁺][Zn(²Bu)₂(HMDS)])⁻⁵⁸ is due to the steric difference between the ³Bu⁴Bu arrangement versus the ³Bu⁴Bu one. When 5 is reacted with an equimolar quantity of the chiral secondary amine (⁺)-bis[(R)-1-phenylethyl]amine [PEA(H)] in hexane solution, again the zincate formally acts as an amido base to yield (TMEDA)Na(µ-PEA)(µ-²Bu)Zn³Bu 9 (that can be isolated as colourless crystals in a 48% yield) and TMP(H).

![Scheme 5. Transamination reaction of 5 with HMDS(H) or PEA(H) to produce 8 or 9 respectively.](image)

Complex 5 was also reacted with one molar equivalent of N-phenylnaphthalen-1-amine [PNA(H)] in hexane. Due to solubility issues (which were not encountered in any of the previously discussed reactions), it seemed clear that the reaction had taken a different/unexpected route. The yellow precipitate which was obtained could not be dissolved in hexane and was only partially soluble in benzene or toluene solution. ¹H NMR spectroscopic analysis of a C₆D₆ solution of this solid only revealed resonances corresponding to the H atoms of a PNA ligand and TMEDA, in a 3:4 ratio. Addition of THF to a benzene solution of the solid, followed by gentle warming produced homogeneity. Crystalization at ambient temperature, yielded yellow crystals of the TMEDA-solvated sodium amide [(TMEDA)Na⁺][PNA]⁻⁴⁰ (Scheme 6). The unexpected synthesis of this sodium-only product, suggests that a zincate redistribution is taking place when PNA(H) is involved. Stoichiometrically, it would be expected that the zinc-containing by-product from this reaction could be: (i) ³Bu⁴BuZn [with loss of TMP(H)]; (ii) ³BuZn(TM) [with loss of...
Undoubtedly, one of the most important synthetic functions of 1 has been its use as a regioselective base. Thermodynamically, it has mainly been demonstrated to function as an alkyl base with ultimate loss of "Bu-H (sec-butane), although synthetic and computational studies have shown that it actually functions in a two-step manner, where an amido group kinetically acts as an amide base (generating an all C₂ primary nature) and a tertiary nature) would occur. When an equimolecular mixture of "BuNa, "Bu-Zn, TMPH, TMEDA and TEMPO is reacted in hexane, a pink solution is obtained immediately but unfortunately no crystalline material was obtained at low temperatures. At this point, the reaction ratio was changes to 2:1 in terms of TEMPO to "Bu. After stirring for two hours, then storing at -28°C, X-ray quality crystals of (TMEDA)Na(["Bu-TEMPO])Zn"Bu 12 were produced, showing that 5 has as expected, formally lost its "Bu ligand producing s-butane and isobutene (Scheme 8).

Scheme 8. Synthesis of (TEMPO) zincate (12).

Single Crystal X-ray Diffraction Studies

Compound 2 crystallizes in the space group P 2₁/n (Figure 1) as a cocrystal with (PMEDTA)Na(["Bu-SiMe₃])Zn"Bu. The two complexes share a (disordered) site in the crystal with the site occupancy factor of 2 refining to 84.1(4)%. The disorder means that the accuracy of the model is lower than normal. However, it can be said that the sodium zincate 2 is monomeric, and the
Zn atom is surrounded by three alkyl groups [comprised of two tert-butyl groups and one (trimethylsilyl)ethyl group]. The Zn adopts a distorted trigonal planar environment [range of angles and total, 114.4(3)-124.0(2)°; and 359.7° respectively]. This is in keeping with other sodium zinicates where the environment of the Zn atoms changes from linear in 1-Bu2Zn to trigonal planar.36, 37, 55 The sodium atom has a distorted tetrahedral geometry, and is surrounded by the three nitrogen atoms of the PMDETA [range of N-Na-N angles 76.69(18)-112.4(2)°] and the anionic carbon atom of the (trimethylsilyl)ethyl group. For the bridging CH2 group, the Na-C11 distance is 2.686(6) Å and is similar to those observed in related zinicates.36, 37, 55 There is also a much longer distance interaction between Na1 and a methyl group of the disordered butyl ligand (> 3.00 Å). This can perhaps be considered as an agostic-type interaction.

![Molecular structure of 2. Complex 2 is a mix of bridging tert-butyl (a) and bridging silyl (b) ligand (approximately 15% silyl). Hydrogen atoms and disorder in tert-butyl groups are omitted for clarity (30% ellipsoid probability). Selected bond lengths for 2 (Å) and angles (°): Na1-N1 2.471(3), Na1-N2 2.463(3), Na1-N3 2.453(3), Na1-C14 2.754(3), Na1-C10 2.769(3), Zn1-C14 2.060(3), 2.036(3), Zn1-C18 2.058(3), Na3-Na1-N12 122.84(9), Na2-Na1-N12 74.43(9), N3-Na1-N12 76.37(9), N3-Na1-C14 91.89(9), N2-Na1-C14 160.98(10), N1-Na1-C14 100.60(9), N3-Na1-C10 107.24(10), N3-Na1-C10 107.46(10), N1-Na1-C10 124.62(11), C14-Na1-C10 99.26(10), C18-Na1-C14 119.75(11), C11-Zn1-C14 118.63(11), C11-Zn1-C18 121.01(11), C11-C14-Na1 144.43(13), C11-C10-Na1 167.2(3).](image)

Compound 3 crystallizes in the $P\ 2_1/n$ space group. (Figure 2). Unlike the conventional bimetallic zincate motif which is prominent (including for 2), 3 is a tetranuclear disodium dizinc complex in which one tert-butyl group (from 1) has been replaced by a TMP ligand. Both metal cations adopt distorted trigonal planar motifs (sum of angles around Na1 and Zn, 359.9 and 360.0° respectively). Na1 is bound to a TMP and a $n$-butyl anion, and its coordination sphere is completed by a TMP(H) molecule. Zn1 is bound to three different anions, namely a TMP, $n$-butyl and tert-butyl. As expected the Na-Namide bond [Na1-N1, 2.3587(15) Å] is significantly shorter than the Na-Namine bond [Na1-N2, 2.4536(16) Å]; and the Zn-terminal bond [Zn1-C15, 2.0363(18) Å] is slightly shorter than the Zn-bridging bond [Zn1-C10, 2.0710(17) Å].

![Molecular structure of 3. Hydrogen atoms and disorder in tert-butyl groups are omitted for clarity (30% ellipsoid probability). Selected bond lengths (Å) and angles (°): Na1-N1 2.3587(15), Na1-N2 2.4536(16), Na1-N3 2.490(16), Na1-C14 2.686(6), Na1-C18 2.058(3), Na3-Na1-C11 122.84(9), Na2-Na1-C11 74.43(9), Na3-Na1-C11 76.37(9), Na3-Na1-C14 91.89(9), Na2-Na1-C14 160.98(10), N1-Na1-C14 100.60(9), N3-Na1-C10 107.24(10), N3-Na1-C10 107.46(10), N1-Na1-C10 124.62(11), C14-Na1-C10 99.26(10), C18-Na1-C14 119.75(11), C11-Zn1-C14 118.63(11), C11-Zn1-C18 121.01(11), C11-C14-Na1 144.43(13), C11-C10-Na1 167.2(3).](image)

Figure 1. Molecular structure of 2. Complex 2 is a mix of bridging tert-butyl (a) and bridging silyl (b) ligand (approximately 15% silyl). Hydrogen atoms are omitted for clarity (30% ellipsoid probability). Selected bond lengths for 2 (Å) and angles (°): Na1-N2 2.426(6), Na1-N1 2.437(5), Na1-N3 2.491(6), Na1-C11 2.686(6), Na1-C12 2.56(4), Zn1-C11 2.060(6), Si1-C11 1.836(6), Zn1-C15 2.052(6), N2-Na1-N11 2.042(6), N2-Na1-N13 3.56(2), N1-Na1-C11 99.70(18), N3-Na1-C11 173.5(2), Zn1-C11-Na1 76.69(18), Zn1-C15-Na1 121.3(3), C15-Zn1-C11 124.0(2), C11-Zn1-C19 114.3(3).

Figure 2. Molecular structure of 3. Hydrogen atoms and disorder in tert-butyl groups are omitted for clarity (30% ellipsoid probability). Selected bond lengths (Å) and angles (°): Na1-N1 2.471(3), Na1-N2 2.463(3), Na1-N3 2.453(3), Na1-C14 2.754(3), Na1-C10 2.769(3), Zn1-C14 2.060(3), Zn1-C18 2.058(3), Na3-Na1-N12 122.84(9), Na2-Na1-N12 74.43(9), N3-Na1-N12 76.37(9), N3-Na1-C14 91.89(9), N2-Na1-C14 160.98(10), N1-Na1-C14 100.60(9), N3-Na1-C10 107.24(10), N3-Na1-C10 107.46(10), N1-Na1-C10 124.62(11), C14-Na1-C10 99.26(10), C18-Na1-C14 119.75(11), C11-Zn1-C14 118.63(11), C11-Zn1-C18 121.01(11), C11-C14-Na1 144.43(13), C11-C10-Na1 167.2(3).

Figure 3. Molecular structure of 4. Hydrogen atoms are omitted for clarity (30% ellipsoid probability). Selected bond lengths (Å) and angles (°): Na1-N1 2.3587(15), Na1-N2 2.4536(16), Na1-N3 2.490(16), Na1-C14 2.686(6), Na1-C18 2.058(3), Na3-Na1-C11 122.84(9), Na2-Na1-C11 74.43(9), Na3-Na1-C11 76.37(9), Na3-Na1-C14 91.89(9), Na2-Na1-C14 160.98(10), N1-Na1-C14 100.60(9), N3-Na1-C10 107.24(10), N3-Na1-C10 107.46(10), N1-Na1-C10 124.62(11), C14-Na1-C10 99.26(10), C18-Na1-C14 119.75(11), C11-Zn1-C14 118.63(11), C11-Zn1-C18 121.01(11), C11-C14-Na1 144.43(13), C11-C10-Na1 167.2(3).
Compound 5 crystallizes in the orthorhombic system, Pnma space group, with a crystallographically imposed mirror plane running through the central Zn-N-Na-C ring (Figure 4). It has the same metal–anion framework as 4, but in 5 the Na cation is coordinated to the bidentate ligand TMEDA. Complex 5 is the most apt complex to compare with the well-studied and utilised 1, as they are both TMEDA-solvated bis(alkyl)-TMP sodium zinicates – the only difference between them is that the former contains three different anions (tert-buty1, n-buty1 and TMP) whilst the latter contains two tert-buty1 and a TMP anion. In 1, the Na cation does not formally bond with the anionic C of the 'bridging' t-buty1 anion. Instead it agostically coordinates to an adjacent CH3 group. The consequence of this interaction is that a five-membered Na-N-Zn-C-C ring is obtained. In 5, presumably due to the lower steric demand of \(^{t}\)Bu versus \(^{n}\)Bu the Na cation bonds to the bridging anionic CH2 of the \(^{t}\)Bu ligand, resulting in a four-membered Na-N-Zn-C ring. The internal angles of this irregular trapezoid range from 80.93(5)° (for the N1-Na1-C4 angle) to 106.66(6)° (for the N1-Zn1-C4 angle), whilst the sum of the angles is 360°. The Na-N\(_{\text{TMEDA}}\) distance is 2.3846(13) Å, and as expected is slightly shorter than the Na-N\(_{\text{TMEDA}}\) bond distance (2.505(10) Å). To the best of our knowledge, there appears to be only one other example reported of a completely heteroleptic bisal1kyl-amido zinate in the literature. Reported by Mulvey and co-workers, \(^{2}\) \(^{2}\)Complex 8 containing the HMDS ligand, crystallizes in the orthorhombic system, Pnma space group and again the Zn-N-Na-C ring is coincident upon the crystallographically imposed mirror plane (Figure 6). Unfortunately all the organic groups in 8 are disordered to some extent preventing discussion of the structural parameters. However, as alluded to earlier, 8 has a completely different structure to that found when 1 is reacted with HMDS(H) namely. In this latter reaction the solvent-separated system \(((\text{HMDS})\text{Na})[\text{ZnBu}_2\text{HMDS}]\) is produced. In an attempt to prepare a solvent-separated system akin to this complex, a further equivalent of TMEDA was added; however, only 8 could be isolated.

Complex 9 crystallizes in the monoclinic system, P 21 space group (Figure 7). The asymmetric unit contains two crystallographically independent molecules (Z' = 2). One of these molecules appears to be well ordered, whilst the second has disorder in parts of all of the organic groups. Only geometric parameters for the well-ordered molecule are discussed below. Complex 9 is a monomeric dinuclear sodium...
zincate. The chiral amide bridges between the two metals, and the Na cation’s coordination sphere is completed by bonding to a TMEDA molecule. Rather surprisingly, the Na–CH₂ group interaction is considerably longer than in its achiral congeners [2.968(3) Å], so this structure adopts an essentially open motif. As a consequence, the Na-N₃ terminal amide bond distance [2.344(2) Å] is shorter than the corresponding Na-N₃₃ distances in 2-6. The Zn-N bond do not differ significantly in these complexes and in keeping with the other zincates, the Zn atom is three coordinate and its coordination sphere is completed by bonding to a tert-butyl and a n-butyl ligand.

Complex 12 crystallises in the P-1 space group and it has a bimetallic motif which contains a C, N and O anionic ligand set (Figure 9). The sodium atom adopts a distorted tetrahedral N₃O geometry (sum of angles around Na1, 665.1°), whilst the Zn atom is trigonal planar bonding to TMP, '₄Bu and TEMPO anions. During the synthesis of 12 from 4 and the TEMPO radical, it is evident the TEMPO has been reduced to an anion and a '₄Bu group has been lost (as a radical). The TEMPO N-O bond distance in 12 [1.446(6) Å] is longer than in the free-radical [1.284(8) Å], indicating that reduction has taken place and is comparable to that in other main group TEMPO complexes.²², ⁶³

Finally, when comparing the Zn-C₃bridging, Zn-Cterminal and Zn-amide bond distances for 2-6, 8, 9 and 12, it is clear that there is only a slight but potentially significant variance in the bond distances between the compounds. Notably when TMP is replaced by a less basic amide (e.g., HMDS or PEA) the Zn-C₃bridging and Zn-Cterminal bonds appear to contract, whereas the Zn-Namide elongate. The all alkyl complexes 2 and 3 can be compared with lithium zincates such as (PMDETA)-Li(µ-Me)₂ZnMe.⁶⁷ There is an interesting variance in the mean Zn-C₃bridging and Zn-Cterminal bonds in these complexes. For the sodium containing 2 and 3 the mean Zn-C₃bridging bond distance is 2.059 Å and for (PMDETA)-Li(µ-Me)₂ZnMe it is slightly shorter (2.046 Å). The mean Zn-Cterminal bond distances in 2 and 3 are 2.055 Å whilst that in the lithium zincate is considerably shorter 2.018(2) Å.

<table>
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<th>Compound</th>
<th>Zn-Cbridging (Å)</th>
<th>Zn-Cterminal (Å)</th>
<th>Zn-Namide (Å)</th>
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<td>2</td>
<td>2.060(6)</td>
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<td>-</td>
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<tr>
<td>3</td>
<td>2.060(3)</td>
<td>2.058(3)</td>
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<td>9</td>
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<tr>
<td>12</td>
<td>-</td>
<td>1.973(2)</td>
<td>1.9874(18)</td>
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</table>

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Conclusions

In summary, we have reported the synthesis and characterisation of several novel sodium zincate complexes. It has been demonstrated that amino bia(alkyl) heterotetrelpic zincates can be formed, and can undergo a variety of different reactions involving all three of the pendant ligands.

Acknowledgement

We gratefully acknowledge the support of the EPSRC (J001872/1 and L001497/1) for the award of a Career Acceleration Fellowship to C.T.O.H. We also thank Prof. Robert Mulvey and Prof. Eva Hevia (Strathclyde) for thoughtful discussions. Finally, the authors would like to thank Dr Jan Klett and Mrs Caroline Pietranek for early studies involving 5.

General Methods: All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane was dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. ²BuNa was prepared according to the literature procedure. ¹³BuZn was synthesised according to the literature procedure. ¹³TMP(H), cis-DMP(H), and PEA(H) were obtained from Sigma-Aldrich and stored over 4 Å molecular sieves prior to use. TMEDA and HMDS(H) were obtained from Sigma-Aldrich and distilled from CaH₂ and stored over molecular sieves. Other chemicals were obtained from Sigma-Aldrich or Alfa Aesar and were used as supplied. NMR spectra were measured on a Bruker Av400 MHz spectrometer. Correlations between proton and carbon atoms were obtained using COSY and HSQC spectroscopic methods.

Crystal structure determinations: Single-crystal data were measured at 123(2) K on Oxford Diffraction Xcalibur and Gemini instruments. The structures were refined to convergence on F² and against all independent reflections by full-matrix least squares using the SHELXL-97 program. Due to the highly reactive nature of the zincate species, consistent microanalyses could not be obtained.

Synthesis of [(PMEDTA)-Na(µ-CH₂SiMe₃)(µ-²BuZn)Bu] (2): (Me₅SiCH₂)Na (0.11 g, 1 mmol) was suspended in hexane (10 mL) and stirred for 5 minutes. A solution of ²BuZn (1 mL of a solution 1 M in hexane, 1 mmol) was added and the resulting clear solution was stirred for 25 minutes. At this stage PMEDTA (0.14 mL, 1 mmol) was added and stirred for 1 hour, before being placed into a freezer operating at −28 °C to aid crystallisation. A crop of colourless crystals were obtained (0.14 g, 31%). ¹H NMR (400.13 MHz, 298 K, cyc-C₅D₅): −1.36 (2H, s, NaCH₂Zn), 0.02 (9H, s, CH₂SiMe₃), 1.02 (18H, s, CH₂Zn(C₂H₅)), 2.28 (12H, s, N(CH₂)₂, PMEDTA), 2.33 (3H, s, NCH₃, PMEDTA), 2.37-2.40 (4H, m, CH₂, PMEDTA), 2.46-2.47 (4H, m, CH₂, PMEDTA). ¹³C(¹H) NMR (100.62 MHz, 298 K, cyc-C₅D₅): −3.1 (CH₂, CH₂Zn), 3.3 (CH₂, CH₂SiMe₃), 33.5 (CH₂, ZnC(CH₂)), 33.7 (ZnCC(CH₃)), 43.4 (N(CH₂), PMEDTA), 45.4 (N(CH₂), PMEDTA), 54.9 (N(CH₂), PMEDTA), 57.1 (N(CH₂), PMEDTA).

Synthesis of [(PMEDTA)-Na(µ-²Bu)(µ-²BuZn)But] (3): ²BuNa (0.08 g, 1 mmol) was suspended in hexane (10 mL) and stirred for 5 minutes. A solution of ²BuZn (1 mL of a solution 1 M in hexane, 1 mmol) was added and the resulting clear solution was stirred for 25 minutes. At this stage PMEDTA (0.14 mL, 1 mmol) was added, and stirred for one hour. The solution and then placed into the freezer operating at −28 °C to aid crystallisation. Suitable crystals for X-ray diffraction analysis were obtained; however the crystals redissolved at ambient temperature during filtration. NMR analysis of the solution was performed. ¹H NMR (400.13 MHz, 298 K, cyc-C₅D₅): −0.13 (2H, t, ¹JHH = 10.0 Hz, NaCH₂Zn), 0.92 (3H, t, ¹JHH = 7.2 Hz, CH₂Bu), 1.05 (18H, s, CH₂Zn(C₂H₅)), 1.30-1.36 (2H, m, CH₂, Bu), 1.60-1.67 (2H, m, CH₂, Bu), 2.27 (12H, s, N(CH₂)₂, PMEDTA), 2.32 (3H, s, NCH₃, PMEDTA), 2.40-2.42 (4H, m, CH₂, PMEDTA), 2.48-2.94 (4H, m, CH₂, PMEDTA). ¹³C(¹H) NMR (100.62 MHz, 298 K, cyc-C₅D₅): 12.1 (CH₂, ²Bu), 13.6 (CH₃, ²Bu), 30.5 (CH₂, ²Bu), 32.4 (CH₂, ²Bu), 33.6 (CH₂, ZnC(CH₂)), 35.3 (ZnCC(CH₃)), 42.7 (N(CH₂), PMEDTA), 45.4 (N(CH₂), PMEDTA), 55.8 (N(CH₂), PMEDTA), 57.3 (N(CH₂), PMEDTA).

Synthesis of [(TMPH)-Na(µ-²Bu)(µ-²BuZn)But] (4): ²BuNa (0.32 g, 4 mmol) was suspended in hexane (15 mL) and stirred for 5 minutes. A solution of ²BuZn (2 mL of a solution 1 M in hexane, 4 mmol) was added and the resulting clear solution was stirred for 5 minutes. TMP(H) (0.68 mL, 4 mmol) was then introduced and the mixture was stirred at ambient temperature for 10 minutes until all the solid had dissolved. The solution was heated slightly before placed in the freezer at −28 °C, the resulting pale yellow solution deposited a crop of white crystals (0.65 g, 66%; based on TMPH consumption). ¹H NMR (400.13 MHz, 298 K, cyc-C₅D₅): −0.35 - 0.29 (2H, m, CH₂, Bu), 0.91 (3H, t, ¹JHH = 7.2 Hz, Bu), 1.06 (9H, s, CH₂, ZnCC(CH₃)), 1.07-1.20 (12H, s, TMPH), 1.21 (12H, s, TMP), 1.30-1.36 (2H, m, CH₂, Bu), 1.39-1.42 (6H, m, CH₂, Bu and TMP), 1.58-1.74 (8H, m, CH₂, Bu and TMP). ¹³C(¹H) NMR (100.62 MHz, 298 K, cyc-C₅D₅): 13.5 (CH₂, Bu), 16.6 (ZnCH₂Bu), 17.7 (CH₂, TMP), 19.5 (CH₂, TMP), 20.2 (ZnCC(CH₃)), 30.2 (ZnCC(CH₃)), 31.0 (CH₂Bu), 31.5 (CH₂, TMP), 32.2 (CH₂, Bu), 34.1 (CH₂, TMP), 38.2 (CH₂, TMP), 40.0 (CH₂, TMP), 50.5 (N-C, TMP), 52.3 (N-C, TMP).

Synthesis of [(TMEDA)Na(µ-²Bu)(µ-²BuZn)But] (5): ²BuNa (0.16 g, 2 mmol) was suspended in hexane (15 mL) and stirred for 5 minutes. A solution of ²BuZn (2 mL of a solution 1 M in hexane, 2 mmol) was added and the resulting clear solution was stirred for 5 minutes. TMP(H) (0.34 mL, 2 mmol) was then introduced and the mixture was stirred at room temperature for 10 minutes until all the solid had dissolved. At this stage TMPD (0.30 mL, 2 mmol) was added, stirring for 15 minutes and the solution is heated slightly before placed in the freezer at −28 °C, the resulting pale yellow solution deposited a crop of white crystals (0.55 g, 60%). ¹H NMR (400.13 MHz, 298 K, cyc-C₅D₅): −0.43 - 0.39 (2H, m, CH₂, Bu), 0.91 (3H, t, ¹JHH = 6.0 Hz, Bu), 1.05 (12H, s, TMP), 1.14 (9H, s, CH₂, ZnCC(CH₃)), 1.28-1.33 (2H, m, CH₂, Bu), 1.56-1.61 (2H, m, CH₂, Bu), 2.31 (12H, s, N(CH₂)₂, TMEDA), 2.41 (4H, s, NCH₃, TMEDA). ¹³C(¹H) NMR (100.62 MHz, 298 K, cyc-C₅D₅): 13.6 (CH₂, Bu), 16.6 (ZnCC(CH₃)), 19.6 (CH₂, TMP), 20.1 (ZnCC(CH₃)), 31.3 (CH₂, Bu), 32.6 (CH₂, Bu), 34.0 (ZnCC(CH₃)), 34.4
Synthesis of [(TMEDA)−Na(µ-THF)](µ-CH₂SiMe₃)Zn₃Bu (6): A solution of Bu₃Zn (2 mL of a solution 1 M in hexane, 2 mmol) was then introduced and the mixture was stirred at ambient temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.15 mL, 1 mmol) was added, stirring for 15 minutes. One molar equivalent of the amine was then introduced. On addition of this amine an orange solution was obtained which was allowed to stir at ambient temperature for one hour and the solution and then placed into the freezer at −28 °C to aid crystallization. A crop of white crystals were obtained (0.53 g, 48%).

1H NMR (400.13 MHz, 298 K, cyc-C₆D₆): 0.92 (3H, s, CH₃(THF)), 1.05 (9H, s, N(CH₃)₃), 1.28-1.33 (2H, m, CH₂ (THF)), 1.63-1.69 (2H, m, CH₂(Bu)), 2.25 (12H, s, N(CH₃)₃), TMEDA, 57.2 (N(CH₃)₃), 60.4 (N(CH₃)₃), 125.4, 126.1, 127.8 (CH₂, Ar), 146.0 (C₆H₅, Ar).

Synthesis of [(TMEDA)−Na(µ-THF)](µ-CH₂SiMe₃)Zn₃Bu (8): A solution of Bu₃Zn (2 mL of a solution 1 M in hexane, 2 mmol) was then introduced and the mixture was stirred at room temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.15 mL, 2 mmol) was added, stirring for 15 minutes. One molar equivalent of the amine was then introduced. On addition of this amine an orange solution was obtained which was allowed to stir at ambient temperature for one hour and the solution and then placed into the freezer at −28 °C to aid crystallization. A crop of white crystals were obtained (0.53 g, 48%).

1H NMR (400.13 MHz, 298 K, cyc-C₆D₆): 0.92 (3H, s, CH₃(THF)), 1.05 (9H, s, N(CH₃)₃), 1.28-1.33 (2H, m, CH₂ (THF)), 1.63-1.69 (2H, m, CH₂(Bu)), 2.25 (12H, s, N(CH₃)₃), TMEDA, 57.2 (N(CH₃)₃), 60.4 (N(CH₃)₃), 125.4, 126.1, 127.8 (CH₂, Ar), 146.0 (C₆H₅, Ar).

Synthesis of [(TMEDA)−Na(µ-THF)](µ-CH₂SiMe₃)Zn₃Bu (7): BuNa (0.16 g, 2 mmol) was suspended in hexane (15 mL) and stirred for 5 minutes. A solution of Bu₃Zn (2 mL of a solution 1 M in hexane, 2 mmol) was then introduced and the mixture was stirred at room temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.15 mL, 2 mmol) was added, stirring for 15 minutes. One molar equivalent of the amine was then introduced. On addition of this amine an orange solution was obtained which was allowed to stir at ambient temperature for one hour and the solution and then placed into the freezer at −28 °C to aid crystallization. A crop of white crystals were obtained (0.53 g, 48%).

1H NMR (400.13 MHz, 298 K, cyc-C₆D₆): 1.05 (9H, s, N(CH₃)₃), 1.28-1.33 (2H, m, CH₂ (THF)), 1.63-1.69 (2H, m, CH₂(Bu)), 2.25 (12H, s, N(CH₃)₃), TMEDA, 57.2 (N(CH₃)₃), 60.4 (N(CH₃)₃), 125.4, 126.1, 127.8 (CH₂, Ar), 146.0 (C₆H₅, Ar).

Synthesis of [(TMEDA)−Na(µ-THF)](µ-CH₂SiMe₃)Zn₃Bu (9): BuNa (0.16 g, 2 mmol) was suspended in hexane (15 mL) and stirred for 5 minutes. A solution of Bu₃Zn (2 mL of a solution 1 M in hexane, 2 mmol) was then introduced and the mixture was stirred at room temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.15 mL, 2 mmol) was added, stirring for 15 minutes. One molar equivalent of the amine was then introduced. On addition of this amine an orange solution was obtained which was allowed to stir at ambient temperature for one hour and the solution and then placed into the freezer at −28 °C to aid crystallization. A crop of white crystals were obtained (0.53 g, 48%).

1H NMR (400.13 MHz, 298 K, cyc-C₆D₆): 1.05 (9H, s, N(CH₃)₃), 1.28-1.33 (2H, m, CH₂ (THF)), 1.63-1.69 (2H, m, CH₂(Bu)), 2.25 (12H, s, N(CH₃)₃), TMEDA, 57.2 (N(CH₃)₃), 60.4 (N(CH₃)₃), 125.4, 126.1, 127.8 (CH₂, Ar), 146.0 (C₆H₅, Ar).

Synthesis of [(TMEDA)−Na(µ-THF)](µ-CH₂SiMe₃)Zn₃Bu (10): BuNa (0.08 g, 1 mmol) was suspended in hexane (10 mL) and stirred for 5 minutes. A solution of Bu₃Zn (1 mL of a solution 1 M in hexane, 1 mmol) was then introduced and the mixture was stirred at room temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.15 mL, 1 mmol) was added, stirring for 15 minutes. One molar equivalent of the amine was then introduced. On addition of this amine a yellow solid was obtained. The solid was filtered via cannula and stored in a glove box. Suitable crystals for X-ray diffraction were obtained by cooling a hot THF-hexane solution of this compound slowly. 1H NMR (400.13 MHz, 298 K, C₆D₆): 1.54 (16H, bs, CH₂ and CH₃, TMEDA), 6.62-6.66 (1H, m, Ar), 7.00-7.05 (m, 3H, Ar), 7.17-7.19 (m, 2H, Ar), 7.25-7.30 (3H, m, Ar), 7.39-7.43 (1H, m, Ar), 7.77-7.79 (1H, d, 3J = 8 Hz, Ar), 8.31-8.33 (1H, m, Ar), 13C NMR (100.62 MHz, 298 K, C₆D₆): 13.5 (CH₃, Bu), 16.8 (CH₃, Bu), 22.6 (ZnC(CH₃)₂), 31.0 (CH₂, Bu), 35.2 (CH₅, Bu), 33.2 (ZnC(CH₃)₂), 34.5 (NCH₃, TMEDA), 57.2 (N(CH₃)₃), 60.4 (N(CH₃)₃), 125.4, 126.1, 127.8 (CH₂, Ar), 146.0 (C₆H₅, Ar).
References


References

57. Cost of TMP(H) and cis-DMP(H) were £4.26 and £0.18 per gram respectively on sigmaaldrich.com on 30/10/2015.
The blue, red and green spheres represent three different anions present within a series of novel hetero-trianionic sodium zincates. The syntheses and structures of the complexes are reported as well as their reactivities with important organic molecules.