

Synthesis and structure of alkaline earth metal diazasulphinates and triazasulphites¹

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Abstract

The syntheses and solid state structures of $(\text{THF}_n\text{M}\{(\text{NSiMe}_3)_2\text{SPh}\}_2]$ ($\text{M} = \text{Ca}$, **1**; $\text{M} = \text{Sr}$, **2**; $\text{M} = \text{Ba}$, **3**) and $(\text{THF}_n\text{M}\{(\text{NSiMe}_3)_2\text{SN}(\text{SiMe}_3)_2\}_2]$ ($\text{M} = \text{Mg}$, $n = 0$, **4**; $\text{M} = \text{Sr}$, $n = 1$, **5**) are presented. Although the $(\text{Me}_3\text{Si})_2\text{NS}(\text{NSiMe}_3)_2^-$ anion resembles to a large extent the structural features of the $\text{PhS}(\text{NSiMe}_3)_2^-$ anion, careful examination of structural parameters reveals marginal differences in their coordination to alkaline earth metal dications. Above all, bonding to the metals is predominantly ionic, but the nature of the small covalent contribution differs in both anionic systems. Strictly planar SN_2M four-membered rings in **1**, **2** and **3** indicate exclusively σ -bonding of the $\text{PhS}(\text{Me}_3\text{SiN})_2^-$ anion towards the alkaline earth metal. The SN_2 moiety of the $(\text{Me}_3\text{Si})_2\text{NS}(\text{NSiMe}_3)_2^-$ anion seems to be more π electron rich. The metal is not located in the plane of the N–S–N chelating ligand, but is displaced from the plane towards the sulphur atom to interact with the π electron density. This effect is caused neither by the steric demand of the ligand nor by packing effects but is induced by the different electronic nature of the ligand. Structural comparisons to related systems substantiate these findings. The size and polarizability of barium, in particular, enables this metal to interact with the non-directed π electron density of the SN_2 fragment. © 1998 Elsevier Science S.A.

1. Introduction

Recently, alkaline earth metal chemistry has attracted increasing interest of both synthetically (for reviews see Ref. [1]) and theoretically [2] oriented chemists. Since alkaline earth metals have been shown to be a fundamental component of materials like high temperature superconductors, volatile and soluble complexes of these metals, required in the CVD [3] or sol-gel (for review see Ref. [4]) processes, are synthesized and examined in great number and variety. Furthermore, the structural features of alkaline earth metal complexes are vigorously discussed [5]. Among others, the discussion of the bent structures of MX_2 molecules ($\text{M} =$ alkaline earth metal; $\text{X} =$ halides, hydrides, mono or bidentate organic ligands) has led to an extension of the VSEPR model [6].

Complexes of Group 2 and Group 12 metals with sulphur-containing ligands, like the systems reported

here, are promising precursors for II–VI semiconducting materials in the sol-gel as well as the CVD process. The $(\text{NSiMe}_3)_2\text{SPh}^-$ anion is an easily accessible [7], well-examined and versatile building block in transition and Main Group metal chemistry [8]. In contrast, the $(\text{NSiMe}_3)_2\text{SN}(\text{SiMe}_3)_2^-$ anion is a new ligand, which is formally derived from the triazasulphite. Nevertheless, its coordination features resemble those of the $(\text{NSiMe}_3)_2\text{SPh}^-$ anion. Both anions are chelating bidentate monoanions, with the negative charge delocalized over the N–S–N backbone. They provide sufficient bulk to prevent the alkaline earth metal complexes from aggregation. The trimethylsilyl and phenyl groups in the periphery of the complexes, together with donating THF molecules, maintain sufficient solubility of all complexes even in apolar hydrocarbons. Thus, syntheses and further reactions in homogeneous phase are facilitated.

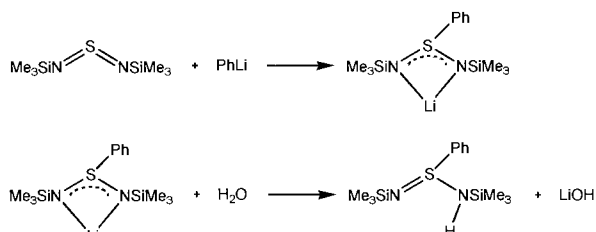
2. Results and discussion

2.1. Preparation of **1**–**3**

Formally, the *N,N'*-bis(trimethylsilyl)-aminoiminophenylsulphine is derived from the phenylsulphinic acid

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¹ Dedicated to Professor Ken Wade, the protagonist of boron chemistry and mentor of Main Group chemistry, on the occasion of his 65th birthday.



Scheme 1. Synthesis of *N,N'*-bis(trimethylsilyl)-aminoiminophenylsulphine.

by isoelectronic substitution of the oxygen atoms by NR-groups. It can easily be obtained in the addition reaction of phenyllithium to bis(trimethylsilyl)sulphur-diimide [9] and subsequent hydrolysis with an equimolar amount of water (Scheme 1).

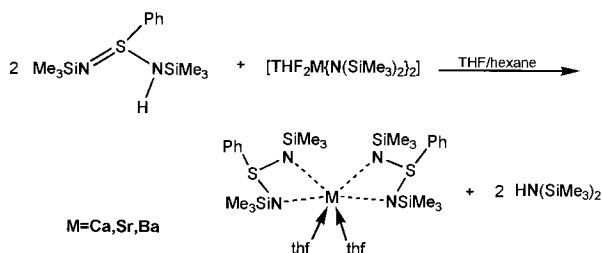
The chemically active sites in *N,N'*-bis(trimethylsilyl)-aminoiminophenylsulphine are (i) the lone pair at the sulphur atom, (ii) the Si–N and S–N bonds which are easily cleaved and (iii) the acidic NH function. The latter can easily be deprotonated by strong bases like the alkaline earth metal bis[bis(trimethylsilyl)amides] [10]. The use of these amides in deprotonation reactions provides general access to alkaline earth metal complexes.

After 2 h stirring of *N,N'*-bis(trimethylsilyl)-aminoiminophenylsulphine and alkaline earth metal bis[bis(trimethylsilyl)amide] in hexane a white precipitate is obtained. Crystallization from THF–hexane (1:1) yields the pure alkaline earth metal complexes (Scheme 2).

2.2. Crystal structures of 1, 2 and 3

Crystals, suitable for X-ray structure analysis, are obtained within a few hours by crystallization from THF–hexane. The colourless blocks lose THF upon heating to about 150 °C to give a white amorphous powder.

The already known magnesium complex [11] contains two monoanionic $(\text{NSiMe}_3)_2\text{SPh}^-$ ligands and one coordinating THF molecule, resulting in a trigonal bipyramidal coordination polyhedron of the metal centre. The three isostructural complexes reported here



Scheme 2. Syntheses of $[\text{THF}_2\text{M}(\text{NSiMe}_3)_2\text{SPh}]_2$ complexes.

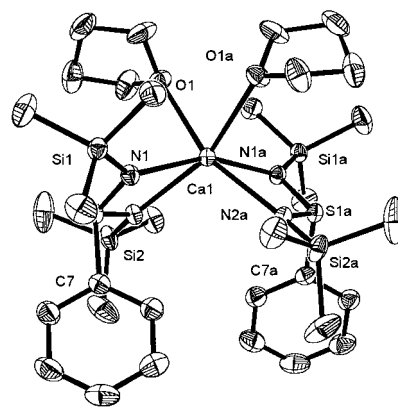


Fig. 1. The structure of $[\text{THF}_2\text{Ca}((\text{NSiMe}_3)_2\text{SPh})_2]$ (**1**) in the solid state; anisotropic displacement parameters are depicted at the 50% probability level.

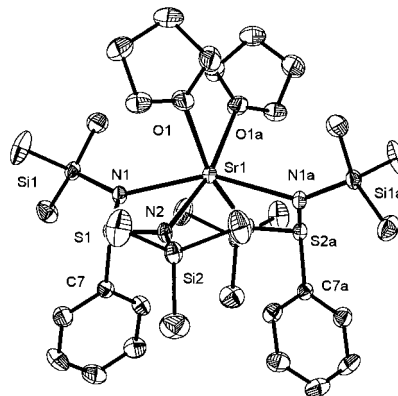


Fig. 2. The structure of $[\text{THF}_2\text{Sr}((\text{NSiMe}_3)_2\text{SPh})_2]$ (**2**) in the solid state; anisotropic displacement parameters are depicted at the 50% probability level.

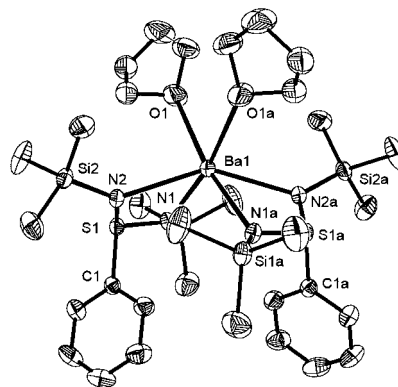


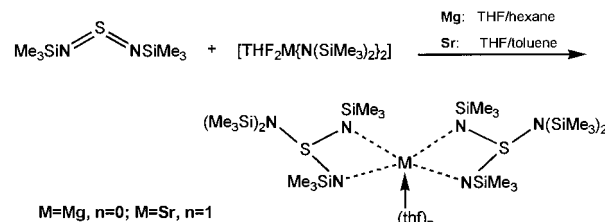
Fig. 3. The structure of $[\text{THF}_2\text{Ba}((\text{NSiMe}_3)_2\text{SPh})_2]$ (**3**) in the solid state; anisotropic displacement parameters are depicted at the 50% probability level.

Table 1
Selected bond lengths (pm) and angles (deg) of 1–5

Compound	1	2	3	4	5
M–N1	242.9(1)	257.4(3)	272.8(2)	205.9(3)	259.1(4)
M–N2	244.1(1)	257.2(3)	271.9(2)	206.4(2)	252.6(4)
M–N3				205.4(2)	255.5(4)
M–N4				206.0(3)	252.1(4)
M–O1	246.3(1)	259.4(3)	276.4(2)		257.1(3)
S1–N1	160.6(1)	160.4(3)	160.4(2)	161.3(2)	159.9(4)
S1–N2	160.6(1)	160.4(3)	159.8(2)	160.8(2)	159.1(4)
S2–N3				161.6(2)	160.6(4)
S2–N4				160.7(2)	159.7(4)
S1–N5				170.6(2)	175.5(4)
S2–N6				170.0(2)	173.8(4)
N1–S1–N2	102.64(7)	103.1(2)	103.3(1)	98.6(1)	102.0(2)
N3–S2–N4				98.3(1)	102.0(2)
S1–N1–Si1	120.23(8)	121.2(2)	122.8(1)	121.4(2)	123.2(2)
S1–N2–Si2	118.66(8)	121.2(2)	123.0(1)	121.3(1)	123.0(2)
S2–N3–Si3				121.1(1)	120.5(2)
S2–N4–Si4				121.4(1)	122.5(2)

provide enough room to accommodate one additional THF molecule. This implies a distorted octahedral coordination at the dicationic metal centre (Figs. 1–3). The ligand adopts a very rigid coordination behaviour, which is indicated by the constant S–N (160 pm) and N...N (251 pm) distances in the alkaline earth metal complexes (Table 1). Obviously, the negative charge is completely delocalized over the N–S–N system. In the above-mentioned magnesium complex the N...N distance in the ligand is about 3 pm shorter.

The increase of the M–N and M–O distances progresses simultaneously with the increasing dicationic radius [12] in the group of the alkaline earth metals from magnesium to barium (Table 2). In each complex the two anionic ligands are coordinated to the same hemisphere of the metal centre, leaving the THF donor molecules coordinated to the other hemisphere. This implies an axial/equatorial coordination of nitrogen atoms in the two chelating ligands. A diequatorial coordination would result in a geometry where the N–S–N units of both ligands are arranged transoid to the metal centre. This would involve an eclipsed conformation of the nitrogen-bonded trimethylsilyl groups which is un-



Scheme 3. Syntheses of $[\text{THF}_n \text{M}\{(\text{NSiMe}_3)_2 \text{SN}(\text{SiMe}_3)_2\}_2]$ complexes.

favourable due to steric hindrance. While a similar cisoid coordination of the ligands was observed in the octahedral complexes of $\text{Ph}_2\text{P}(\text{NSiMe}_3)_2^-$ [13], some octahedral $\text{PhC}(\text{NSiMe}_3)_2^-$ complexes of alkaline earth metals (Mg [14], Ca [15], Sr [16], Ba [17]) show a diequatorial coordination, with the nitrogen-bonded trimethylsilyl groups almost eclipsed to each other. It seems noteworthy that the phenyl groups of the two $\text{PhS}(\text{NSiMe}_3)_2^-$ anions show a cisoid arrangement as well. Despite the absence of π stacking effects or other long range interactions, the phenyl substituents always point to the same side of the metal. An orientation to opposite sides with respect to each other was not observed in any case.

The increasing S–N–Si angle with increasing radius of the metal centre proves the decreasing steric hindrance between the ligands in the complex. The more they are separated because of the increasing radius of the dication the more the angles relax ($119.2(1)^\circ$ in Mg to $122.9(1)^\circ$ in Ba, Table 2).

2.3. Preparation of 4 and 5

Various compounds containing an $\text{S}^{\text{IV}}(\text{NR})_3$ unit have already been synthesized in different reactions: most of them show the $\text{S}^{\text{IV}}(\text{NR})_3$ unit as a dianion [18]. In the compounds reported here, one of the amide functions of the $\text{S}^{\text{IV}}(\text{NR})_3$ ($\text{R} = \text{SiMe}_3$) is protected by an additional trimethylsilyl group, which prevents this nitrogen atom from coordination to any metal. Comparison of triaza-sulphuric acid $\text{H}_2\text{S}(\text{NR})_3$ to its isoelectronic oxygen analogue is very elucidative. Similar to the sulphurous

Table 2
Geometric features of 1–3, average distances (pm) and angles (deg)

Compound	$[\text{THFMg}\{(\text{NSiMe}_3)_2 \text{SPh}\}_2]$ [11]	1	2	3
Metal	Mg	Ca	Sr	Ba
Dicationic radius	78	106	127	143
M–N	210.3(2)eq./218.2(2)ax.	243.5(1)	257.3(3)	271.4(2)
M–O	207.4(2)	246.3(1)	259.4(3)	276.4(2)
N...N	247.6	250.7	251.3	251.1
S–N–Si	119.2(1)	119.4(1)	121.2(2)	122.9(1)

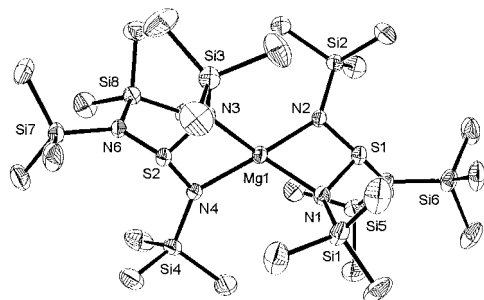


Fig. 4. The structure of $[\text{Mg}\{(\text{NSiMe}_3)_2\text{SN}(\text{SiMe}_3)_2\}_2]$ (**4**) in the solid state; anisotropic displacement parameters are depicted at the 50% probability level.

acid H_2SO_3 , which is not a stable substance, up to now the free triazsulphuric acid could not be proved to exist at all. Thus the deprotonation of the acid by alkaline earth metal amides, in a reaction similar to that shown above, is not feasible. Nevertheless, the syntheses of the complexes **4** and **5** can be achieved by a straightforward nucleophilic addition reaction of alkaline earth metal bis[bis(trimethylsilyl)amide] to the double bond of bis(trimethylsilyl)sulphurdiimide (Scheme 3).

2.4. Crystal structures of **4** and **5**

Although crystals of **4** were grown from THF–hexane at 0°C , the monomeric structure shows no THF molecule in the coordination sphere of the magnesium dication in addition to the two monoanionic N,N,N',N'' tetrakis(trimethylsilyl)triazsulphite moieties (Fig. 4). Obviously, the bis(trimethylsilyl)amide unit provides more steric strain than the phenyl group in the related $[\text{THFMg}\{(\text{NSiMe}_3)_2\text{SPh}\}_2]$ complex [11].

The four coordinating nitrogen atoms display a distorted tetrahedral geometry at the central magnesium dication. Like in the $\text{PhS}(\text{NSiMe}_3)_2^-$ ligand, the negative charge in the $(\text{NSiMe}_3)_2\text{SN}(\text{SiMe}_3)_2^-$ ligand is completely delocalized over the chelating N–S–N unit ($\text{S}-\text{N}_{(\text{av.})}$: 161 pm). The $\text{S}-\text{N}_{(\text{SiMe}_3)_2}$ distance

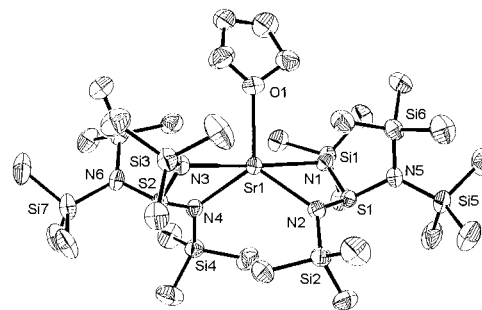


Fig. 5. The structure of $[\text{THFSr}\{(\text{NSiMe}_3)_2\text{SN}(\text{SiMe}_3)_2\}_2]$ (**5**) in the solid state; anisotropic displacement parameters are depicted at the 50% probability level.

(170.3(2) pm, Table 3) is within the range of a standard S–N single bond length (169 pm) [19]. The four independent Mg–N distances are equal within estimated standard deviations (205.9(3) pm) and correspond to those in the comparable complex of $\text{Ph}_2\text{P}(\text{NSiMe}_3)_2^-$ (207.5 pm) [13].

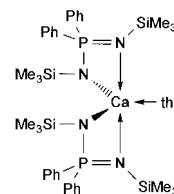
Crystals of **5** were obtained by crystallization from THF–toluene at 0°C . Coordination of one donating THF molecule leads to a distorted trigonal bipyramidal coordination made up of the four ligand nitrogen atoms and the oxygen atom of the THF molecule around the strontium centre (Fig. 5).

Thus, the axial and equatorial M–N distances differ by about 5 pm ($\text{M}-\text{N}(1,3)_{\text{ax.}}$ 257.3(4) and $\text{M}-\text{N}(2,4)_{\text{eq.}}$ 252.4(4) pm on average, Table 3). Despite this fact, there is no remarkable difference in the corresponding S–N distances ($\text{S1}-\text{N1}$: 159.9(4), $\text{S1}-\text{N2}$: 159.1(4), $\text{S2}-\text{N3}$: 160.6(4), $\text{S2}-\text{N4}$: 159.7(4) pm). Obviously, the small differences in M–N distances do not induce S=N partial double bond character in the anion and the negative charge remains completely delocalized in the chelating N–S–N system. The same is valid for the magnesium complex $[\text{THFMg}\{(\text{NSiMe}_3)_2\text{SPh}\}_2]$ [11]. In the related $[\text{THF}_2\text{Ca}\{(\text{NSiMe}_3)_2\text{PPh}_2\}_2]$ complex [13], however, ideal delocalization in the PN_2 unit is precluded (Scheme 4). In the trigonal bipyramidal coordination polyhedron P=N partial double bonds correspond to longer N → M donor bonds in the axial positions. The shorter Ca–N distances of the equatorial positions (239.3 and 239.7 pm) correspond to the longer P–N bonds (164.6 and 166.4 pm), while the shorter

Table 3

Geometric features of **4** and **5**, average distances (pm) and angles (deg)

Compound	4	5
Metal	Mg	Sr
Dicationic radius	78	127
M–N	205.9(3)	252.4(4)eq. 257.3(4)ax.
$\text{S}-\text{N}_{(\text{SiMe}_3)_2}$	173.0(2)	176.3(4)
M–O		257.1(3)
N...N	244.0	248.4
S–N–Si	121.3(2)	122.3(2)
S1...M...S2	162.31(5)	139.56(4)



Scheme 4. The bonding situation in $[\text{THFCa}\{(\text{NSiMe}_3)_2\text{PPh}_2\}_2]$.

P=N bonds (158.9 and 159.0 pm) give rise to longer axial Ca–N distances (255.1 and 254.6 pm).

3. Structural comparison

While the two ligand systems discussed in this work are chemically very different—the first is a derivative of the phenylsulphinic acid and the second a derivative of the sulphurous acid—their properties in alkaline earth metal complexes are very similar. Both are monoanionic systems, with the negative charge delocalized over a chelating N–S–N unit, providing a very constant ‘bite’ (N⋯N distance) and enough steric demand, to prevent aggregation. A closer look to the geometrical features, however, reveals an interesting difference. While in the complexes of *N,N,N',N''* tetrakis(trimethylsilyl)triazasulphite the metal dications leave the plane of the chelating N–S–N system ($\phi = 169^\circ$ for Sr; see Fig. 6), there is no such effect in the complexes of *N,N'*-bis(trimethylsilyl)-aminoimino phenyl sulphine.

The out-of-plane coordination of heavier alkaline earth metal dications was ascertained earlier [13], in particular with the benzamidinates $\text{PhC}(\text{NSiMe}_3)_2^-$ [14–17], the aminoiminodiphenylphosphinates $\text{Ph}_2\text{P}(\text{NSiMe}_3)_2^-$ [13], and the alkaline earth metal carbazoles [20]. In the $[\text{THF}_2\text{M}\{(\text{NSiMe}_3)_2\text{PPh}_2\}_2]$, M = Sr and Ba, the metal is considerably displaced from the plane of the PN_2 -anion ($\phi = 167^\circ$ for Sr), even against steric strain. The same is valid for the sterically not so demanding benzamidinates ($\phi = 172^\circ$ for Sr). The flat anion in the carbazolyl alkaline earth metal complexes tolerates even higher deviation from the plane of the anion ($\phi = 140^\circ$ for Sr), although metal–carbon contacts have not been observed. The carbazoles were regarded as exclusively monohapto σ -bonded without any multihapto π bonding to the metal, although the heavier alkaline earth metals were calculated to prefer multihapto bonding to delocalized electron density [20]. The observed tilt of the strontium atom towards the sulphur atom in **5** may be taken as an indication of increasing metal– π interaction of the $\text{R}_2\text{NS}(\text{NR})_2^-$ moiety. The SN_2 -unit provides both, σ and π electron density because of sp^2 hybridization of the nitrogen

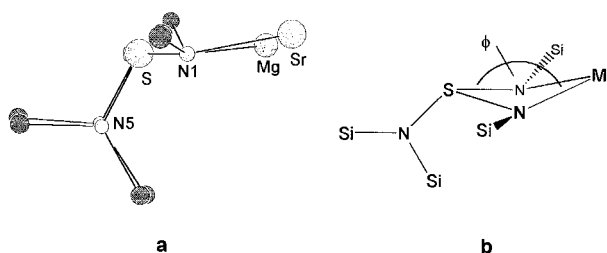
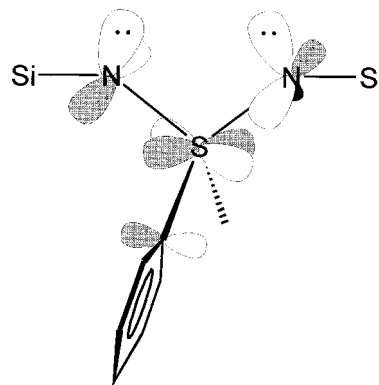


Fig. 6. Out-of-plane arrangement of **4** and **5**.



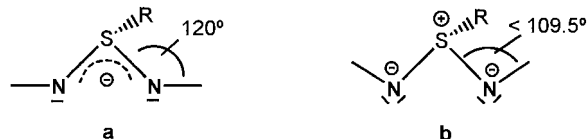
Scheme 5. The electronic structure of the $(\text{NSiMe}_3)_2\text{SPh}$ monoanion.

atoms. Therefore, one always would expect mainly end-on σ bonding of the metal and hardly ever η^3 coordination. However, the soft and easy to polarize metal strontium prefers to interact with the π electron density in **5**.

There remains the question as to why this effect is precluded in the complexes **1–3**. Detailed investigation of the structures reveals the phenyl ring plane to be orthogonal to the SN_2 plane oriented along the N–S–N bisection. This seems to be the sterically most relaxed orientation of the substituent, although the orientation of the phenyl ring orthogonal to the N–S–N bisection is not totally unfavourable, because it is observed in all alkaline metal complexes containing the $\text{PhS}(\text{NSiMe}_3)_2^-$ anion [7,11]. The adjustment of the phenyl ring in **1–3** affects the whole anion electronically (Scheme 5).

The p-orbitals of the phenyl ring interact with the same d-orbital of the sulphur atom, which maintains the delocalization of the negative charge in the N–S–N system (Scheme 5). This coupling decreases the π electron density at the SN_2 backbone, but has no effect on the σ electron density, located at the nitrogen atoms. This argumentation is based on the sp^2 hybridization of the nitrogen atoms (Scheme 6a), which is in fact indicated by the S–N–Si angles of about 120° (Table 2). The second resonance form (Scheme 6b), where both nitrogen atoms are negatively charged and sp^3 hybridized, is inadequate to describe the bonding within the anion. Based on the VSEPR model, this should result in S–N–Si angles smaller than the tetrahedral angle (109.5°).

The arrangement of the nitrogen p-orbital of the $(\text{Me}_3\text{Si})_2\text{N}$ groups in **4** and **5**, similar to the phenyl



Scheme 6. sp^2 vs. sp^3 hybridization.

carbon p-orbital in **1–3**, can be assumed; however, in contrast to the electron-withdrawing phenyl group the $(\text{Me}_3\text{Si})_2\text{N}$ group is a π donating group, due to the electron releasing properties of the two silyl groups. Hence the π electron density in the SN_2 backbone is increased rather than decreased. In all known alkaline earth metal benzamidinate complexes the phenyl group bonded to the central carbon atom is oriented orthogonal to the CN_2 plane. In this system the π electron density is not decreased either, and displacement of the heavier alkaline earth metals from the CN_2 plane can be observed.

4. Conclusion

The two systems reported here have been shown to behave very similarly in many respects. Both are bidentate monoanions, with the negative charge delocalized over an N–S–N system, which provides a very constant ‘bite’. The additional substituent at the sulphur atom supplies enough steric demand to prevent the resulting alkaline earth metal complexes from aggregation and, together with the nitrogen-bonded trimethylsilyl groups and additional THF donors, maintains a good solubility even in apolar solvents.

The structural differences are marginal, but nevertheless instructive. While the phenyl-substituted anion in **1–3** provides σ bonding to the metal dications exclusively, the amide-substituted anion in **4** and **5** allows the metal dications to leave the plane of the chelating N–S–N system and interact with its π electron density. This out-of-plane arrangement of **4** and **5** is shown to be valid for the heavy metal dications and demonstrates their preference to interact with π electron density, leading to a multihapto bonding mode. This effect is prevented in complexes **1–3** because of the electronic coupling of the phenyl group. It acts as a π electron acceptor and reduces the π electron density in the SN_2 backbone. In contrast, the $(\text{Me}_3\text{Si})_2\text{N}$ group acts as a π electron donor and leaves the π electron density attractive to the metal. An accurate model, however, cannot be derived from geometric features alone, but needs to be substantiated by high level MO calculations.

5. Experimental section

All manipulations were performed under inert gas atmosphere of dry N_2 with standard Schlenk techniques or in an argon glove box. All solvents were dried over Na–K alloy and distilled prior to use. NMR spectra were obtained in benzene- d_6 as solvent with SiMe_4 as external reference on a Bruker AM 250 or Bruker MSL 400. Mass spectra were recorded on a Finnigan Mat 8230 or Varian Mat CH5 spectrometer. Elemental anal-

yses were performed by the Analytisches Laboratorium des Instituts für Anorganische Chemie der Universität Göttingen.

N,N' -Bis-(trimethylsilyl)-aminophenylsulphinimine [8] and alkaline earth metal bis[bis(trimethylsilyl)amides] [10] were prepared according to known literature procedures.

The alkaline earth metal bis[N,N' -bis(trimethylsilyl)-aminophenylsulphinimides] were obtained using the following general procedure: a solution of alkaline earth metal bis[bis(trimethylsilyl)amide] (0.62 mmol) in 5 ml hexane is added to a solution of N,N' -bis(trimethylsilyl)-aminophenylsulphinimine (1.24 mmol, 0.35 g) in 5 ml hexane and stirred 2 h. After the precipitate has settled, the reaction solution is decanted. Crystallization of the precipitate from THF–hexane gives colourless crystals, suitable for X-ray structure analysis.

5.1. $[\text{THF}_2\text{Ca}\{(\text{NSiMe}_3)_2\text{SPh}\}_2]$ (**1**)

$M = 750.30 \text{ g mol}^{-1}$. Yield: 91%. M.p.: 195 °C. ^1H (C_6D_6): δ 0.29 (s, 36H), 1.30 (m, 8H), 3.56 (m, 8H), 7.02 (m, 4H), 7.14 (m, 2H), 7.82 (m, 4H); ^{29}Si (C_6D_6): δ –3.84; MS (70 eV) m/z : 606 (8% $\text{M}^+ - 2\text{thf}$), 529 (100% $\text{M}^+ - \text{C}_{14}\text{H}_{21}\text{O}_2$), 323 (47% $\text{M}^+ - \text{C}_{20}\text{H}_{39}\text{N}_2\text{O}_2\text{SSi}_2$); Anal. Calcd. (found): C, 51.2 (50.4); H, 8.3 (8.3); N, 7.5 (7.5).

5.2. $[\text{THF}_2\text{Sr}\{(\text{NSiMe}_3)_2\text{SPh}\}_2]$ (**2**)

$M = 798.94 \text{ g mol}^{-1}$. Yield: 87%. M.p.: 157 °C. ^1H (C_6D_6): δ 0.30 (s, 36H), 1.32 (m, 8H), 3.58 (m, 8H), 7.04 (m, 4H), 7.20 (m, 2H), 7.89 (m, 4H); ^{29}Si (C_6D_6): δ –4.04; MS (70 eV) m/z : 654 (7% $\text{M}^+ - 2\text{thf}$), 577 (73% $\text{M}^+ - \text{C}_{14}\text{H}_{21}\text{O}_2$), 371 (100% $\text{M}^+ - \text{C}_{20}\text{H}_{39}\text{N}_2\text{O}_2\text{SSi}_2$); Anal. Calcd. (found): C, 48.1 (47.6); H, 7.8 (7.9); N, 7.0 (7.1).

5.3. $[\text{THF}_2\text{Ba}\{(\text{NSiMe}_3)_2\text{SPh}\}_2]$ (**3**)

$M = 848.65 \text{ g mol}^{-1}$. Yield: 73%. M.p.: 145 °C. ^1H (C_6D_6): δ 0.30 (s, 36H), 1.34 (m, 8H), 3.51 (m, 8H), 7.04 (m, 4H), 7.19 (m, 2H), 7.85 (m, 4H); ^{29}Si (C_6D_6): δ –4.46; MS (70 eV) m/z : 627 (18% $\text{M}^+ - 2\text{thf}$), 421 (75% $\text{M}^+ - \text{C}_{20}\text{H}_{39}\text{N}_2\text{O}_2\text{SSi}_2$), 207 (100% $\text{M}^+ - \text{C}_{26}\text{H}_{44}\text{BaN}_2\text{O}_2\text{SSi}_2$); Anal. Calcd. (found): C, 45.3 (44.3); H, 7.4 (7.2); N, 6.6 (6.7).

5.4. $\text{Mg}\{(\text{NSiMe}_3)_2\text{SN}(\text{SiMe}_3)_2\}_2$ (**4**)

A solution of 1.03 g N,N' -bis(trimethylsilyl)sulphurdiimide (5 mmol) in 10 ml hexane is added to a solution of 1.22 g magnesium bis[bis(trimethylsilyl)amide] (2.5 mmol) in 5 ml THF and stirred for 4 h. Crystallization at 0 °C yields 1.56 g (2.1 mmol, 84%) of

Table 4
Crystal data of **1–5** at $T = 153$ K

Compound	1	2	3	4	5
Formula	$C_{32}H_{62}CaN_4O_2S_2Si_4$	$C_{32}H_{62}N_4O_2S_2Si_4Sr$	$C_{32}H_{62}BaN_4O_2S_2Si_4$	$C_{24}H_{72}MgN_6S_2Si_8$	$C_{28}H_{80}N_6OS_2Si_8Sr^*$
Fw	751.42	798.96	848.68	758.03	0.81C ₇ H ₈ · 0.19C ₄ H ₈ O
Crystal size (mm)	0.4 × 0.4 × 0.3	0.3 × 0.2 × 0.2	0.3 × 0.3 × 0.2	0.6 × 0.6 × 0.6	0.4 × 0.3 × 0.2
Space group	$C2/c$	$C2/c$	$C2/c$	$P2_1/c$	$P2_1/c$
<i>a</i> (pm)	1995.1(4)	1919.0(2)	1921.9(2)	1044.3(1)	2403.6(3)
<i>b</i> (pm)	1060.7(2)	1145.2(2)	1151.6(2)	2349.5(3)	1031.9(1)
<i>c</i> (pm)	2140.8(3)	2130.2(4)	2154.7(3)	1964.5(3)	2345.6(4)
β (deg)	112.905(9)	114.00(1)	113.389(9)	100.49(1)	96.260(9)
<i>V</i> (nm ³)	4.173(1)	4.277(1)	4.3769(9)	4.739(1)	5.783(1)
<i>Z</i>	4	4	4	4	4
ρ_c (Mg m ⁻³)	1.196	1.241	1.288	1.062	1.128
μ (mm ⁻¹)	0.397	1.502	1.143	0.350	1.200
<i>F</i> (000)	1624	1696	1768	1656	2112
2 θ -range (deg)	8–50	8–45	8–45	8–45	8–45
No. of reflections measured	3705	2805	4385	7393	7547
No. of unique reflections	3690	2781	2724	6309	7507
No. of restraints	146	107	174	0	381
Refined parameters	238	229	247	394	544
<i>R</i> 1 ($I > 2\sigma(I)$) ^a	0.030	0.040	0.024	0.038	0.047
<i>wR</i> 2 ^b (all data)	0.078	0.092	0.057	0.087	0.104
<i>g</i> ₁ ; <i>g</i> ₂ ^c	0.036; 5.36	0.035; 18.97	0.028; 6.90	0.022; 7.35	0.025; 8.85
Highest difference peak (10 ⁻⁶ e ⁻ pm ⁻³)	0.32	0.41	0.62	0.26	0.37

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

^c $w = 1 / [\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P]$; $P = (F_o^2 + 2F_c^2) / 3$.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm² $\times 10^{-1}$) for **1**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Ca(1)	0	7880(1)	2500	19(1)
S(1)	-48(1)	9195(1)	3771(1)	22(1)
N(1)	-646(1)	8300(1)	3234(1)	23(1)
Si(1)	-1366(1)	7737(1)	3403(1)	24(1)
C(1)	-2032(1)	8978(2)	3393(1)	41(1)
C(2)	-1079(1)	6923(2)	4242(1)	47(1)
C(3)	-1854(1)	6600(2)	2717(1)	34(1)
N(2)	581(1)	9252(1)	3478(1)	22(1)
Si(2)	1411(1)	9883(1)	3980(1)	30(1)
C(4)	1758(1)	9259(3)	4864(1)	63(1)
C(5)	1377(1)	11639(2)	4039(1)	59(1)
C(6)	2068(1)	9481(2)	3588(1)	40(1)
C(7)	-461(1)	10742(2)	3611(1)	24(1)
C(8)	-714(1)	11276(2)	2971(1)	32(1)
C(9)	-1067(1)	12425(2)	2867(1)	41(1)
C(10)	-1164(1)	13034(2)	3397(1)	44(1)
C(11)	-900(1)	12512(2)	4032(1)	44(1)
C(12)	-545(1)	11358(2)	4144(1)	33(1)
O(1)	632(1)	6054(1)	3188(1)	31(1)
C(13)	1330(1)	6101(2)	3742(1)	47(1)
C14a	1105(4)	5946(10)	4339(3)	51(2)
C15a	591(7)	4824(8)	4078(6)	51(2)
C16a	264(10)	4986(17)	3318(7)	45(4)
C14'b	1299(3)	5298(7)	4324(2)	45(1)
C15'b	481(4)	5206(10)	4143(5)	55(2)
C16'b	187(7)	5185(14)	3382(5)	43(3)

^a *U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm² $\times 10^{-1}$) for **2**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Sr(1)	0	2092(1)	7500	21(1)
S(1)	50(1)	706(1)	6191(1)	22(1)
N(1)	691(2)	1531(3)	6730(2)	23(1)
Si(1)	1421(1)	2081(1)	6554(1)	25(1)
C(1)	2188(2)	995(4)	6694(2)	42(1)
C(2)	1113(3)	2626(5)	5657(2)	58(2)
C(3)	1825(3)	3322(4)	7150(3)	45(1)
N(2)	-623(2)	740(3)	6455(2)	21(1)
Si(2)	-1541(1)	382(1)	5921(1)	26(1)
C(4)	-2161(2)	1018(5)	6307(2)	49(1)
C(5)	-1834(3)	956(5)	5031(2)	53(1)
C(6)	-1698(3)	-1220(4)	5850(3)	51(1)
C(7)	440(2)	-740(3)	6402(2)	22(1)
C(8)	518(2)	-1395(4)	5889(2)	33(1)
C(9)	825(3)	-2506(4)	6031(2)	42(1)
C(10)	1049(2)	-2964(4)	6677(2)	40(1)
C(11)	969(2)	-2320(4)	7188(2)	37(1)
C(12)	673(2)	-1202(4)	7057(2)	30(1)
O(1)	-584(2)	3842(3)	6681(1)	38(1)
C13a	-787(7)	3736(7)	5954(4)	36(2)
C(14)	-772(4)	4935(4)	5707(3)	63(2)
C(15)	-986(3)	5678(4)	6178(3)	57(1)
C16a	-1071(8)	4791(9)	6674(6)	52(4)
C13'b	-394(15)	3944(17)	6098(8)	47(5)
C16'b	-761(16)	4998(14)	6817(8)	54(6)

^a *U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

colourless crystals, suitable for X-ray structure analysis. $M = 758.03 \text{ g mol}^{-1}$. M.p.: 135°C . ^1H (C_6D_6): δ 0.34 (s, 36H, NSiMe₃), 0.48 (s, 36H, N(SiMe₃)₂).

5.5. [THFSr{(NSiMe₃)₂SN(SiMe₃)₂}]₂ (5)

A solution of 1.03 g *N,N'*-bis(trimethylsilyl)sulphurdiimide (5 mmol) in 10 ml toluol is added to a solution of 1.38 g strontium bis[bis(trimethylsilyl)amide] (2.5 mmol) in 5 ml THF and stirred for 2 h. Crystallization at 0°C yields 1.87 g (2.1 mmol, 84%) of colourless crystals, suitable for X-ray structure analysis. $M = 893.41 \text{ g mol}^{-1}$. M.p.: 127°C . ^1H (C_6D_6): δ 0.34 (s, 36H, NSiMe₃), 0.43 (s, 36H, N(SiMe₃)₂), 1.35 (m, 4H), 3.68 (m, 4H).

5.6. X-ray measurements of 1–5

Crystal data for structures 1–5 are presented in Table 4. Data of all structures were collected at low temperatures (153 K) using oil-coated shock-cooled crystals [21] on an Stoe–Siemens AED using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Semi-empirical absorption correction was applied [22]. The structures were solved by Patterson or direct methods

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for 3

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Ba(1)	5000	2818(1)	7500	27(1)
S(1)	4943(1)	4341(1)	8836(1)	26(1)
C(1)	4560(1)	5790(2)	8614(1)	26(1)
C(2)	4480(2)	6457(3)	9115(2)	37(1)
C(3)	4176(2)	7557(3)	8960(2)	49(1)
C(4)	3958(2)	7979(3)	8316(2)	51(1)
C(5)	4045(2)	7314(3)	7821(2)	47(1)
C(6)	4343(2)	6213(2)	7968(1)	36(1)
Si(1)	6531(1)	4594(1)	9080(1)	31(1)
N(1)	5616(1)	4284(2)	8575(1)	28(1)
C(7)	7116(2)	3892(4)	8676(2)	62(1)
C(8)	6822(2)	4048(4)	9963(2)	56(1)
C(9)	6727(2)	6187(3)	9134(2)	60(1)
Si(2)	3570(1)	2969(1)	8473(1)	31(1)
N(2)	4304(1)	3528(2)	8313(1)	28(1)
C(10)	3221(2)	1693(3)	7905(2)	55(1)
C(11)	3854(2)	2499(4)	9370(2)	65(1)
C(12)	2777(2)	4013(3)	8285(2)	49(1)
O(1)	5564(1)	990(2)	8392(1)	59(1)
C13a	5690(9)	–224(9)	8316(7)	59(4)
C14a	6080(2)	–705(19)	9024(10)	73(6)
C15a	5975(10)	224(16)	9475(7)	54(4)
C16a	5349(9)	908(11)	8967(5)	53(3)
C13' b	6044(7)	65(9)	8413(5)	71(3)
C14' b	6012(14)	–733(13)	8967(8)	78(4)
C15' b	5716(9)	30(10)	9377(6)	64(4)
C16' b	5780(6)	1221(6)	9115(3)	50(2)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 8

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for 4

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Mg(1)	2606(1)	5594(1)	2742(1)	22(1)
S(1)	2767(1)	6549(1)	3526(1)	22(1)
N(1)	1592(2)	6305(1)	2951(1)	25(1)
Si(1)	554(1)	6756(1)	2417(1)	34(1)
C(11)	–184(4)	6332(2)	1644(2)	58(1)
C(12)	1436(4)	7367(2)	2122(2)	53(1)
C(13)	–785(4)	7027(2)	2840(2)	57(1)
N(2)	3764(2)	6026(1)	3540(1)	22(1)
Si(2)	5380(1)	6090(1)	3930(1)	26(1)
C(21)	5621(3)	5938(2)	4871(2)	44(1)
C(22)	6298(3)	5552(2)	3519(2)	43(1)
C(23)	6019(3)	6816(1)	3815(2)	41(1)
N(5)	2236(2)	6559(1)	4297(1)	24(1)
Si(5)	1553(1)	5964(1)	4649(1)	31(1)
C(51)	1996(4)	5268(1)	4310(2)	42(1)
C(52)	2175(4)	5941(2)	5602(2)	49(1)
C(53)	–250(3)	6008(2)	4480(2)	48(1)
Si(6)	2353(1)	7233(1)	4701(1)	35(1)
C(61)	2329(4)	7812(1)	4056(2)	47(1)
C(62)	3860(4)	7297(2)	5363(2)	53(1)
C(63)	921(4)	7348(2)	5125(2)	51(1)
S(2)	2300(1)	4882(1)	1643(1)	22(1)
N(3)	3400(2)	5356(1)	1902(1)	23(1)
Si(3)	4116(1)	5736(1)	1318(1)	31(1)
C(31)	2900(4)	5985(2)	564(2)	55(1)
C(32)	5389(4)	5321(2)	987(2)	62(1)
C(33)	4889(4)	6369(2)	1787(2)	58(1)
N(4)	1550(2)	4909(1)	2288(1)	23(1)
Si(4)	54(1)	4583(1)	2257(1)	31(1)
C(41)	234(4)	3852(2)	2621(2)	57(1)
C(42)	–876(4)	5014(2)	2797(2)	56(1)
C(43)	–893(3)	4537(2)	1359(2)	47(1)
N(6)	3062(2)	4241(1)	1662(1)	23(1)
Si(7)	2731(1)	3865(1)	870(1)	30(1)
C(71)	4270(4)	3589(2)	645(2)	46(1)
C(72)	1949(4)	4334(2)	151(2)	42(1)
C(73)	1623(4)	3254(2)	915(2)	48(1)
Si(8)	4181(1)	3986(1)	2386(1)	27(1)
C(81)	3992(4)	3202(1)	2451(2)	49(1)
C(82)	5883(3)	4146(2)	2300(2)	44(1)
C(83)	3908(3)	4285(2)	3223(2)	37(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

with SHELXS-90 [23]. All structures were refined by full-matrix least squares procedures on F^2 , using SHELXL-93 [24]. All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. In **1** the disordered THF molecule around O1 was refined to a split occupancy of 0.56 and 0.44 respectively using distance and similarity restraints. The disorder of the THF molecules around O1 in **2** (split occupancy of 0.65

Note to Table 9

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 9
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for **5**

	x	y	z	U_{eq}^a
Sr(1)	7350(1)	621(1)	660(1)	34(1)
S(1)	7884(1)	66(1)	-522(1)	30(1)
N(1)	8109(2)	1047(4)	-22(2)	31(1)
Si(1)	8359(1)	2566(1)	-148(1)	35(1)
C(11)	9139(2)	2620(6)	-62(3)	56(2)
C(12)	8100(3)	3633(6)	410(2)	53(2)
C(13)	8107(3)	3249(6)	-870(2)	53(2)
N(2)	7411(2)	-701(4)	-238(2)	31(1)
Si(2)	6926(1)	-1680(2)	-624(1)	39(1)
C(21)	7155(3)	-3405(6)	-627(3)	69(2)
C(22)	6280(2)	-1591(7)	-255(3)	59(2)
C(23)	6776(3)	-1127(7)	-1382(2)	61(2)
N(5)	8427(2)	-1043(4)	-588(2)	34(1)
Si(5)	8632(1)	-1194(2)	-1279(1)	44(1)
C(53)	9413(2)	-1127(7)	-1252(3)	62(2)
C(52)	8352(3)	146(7)	-1763(2)	73(2)
C(51)	8379(3)	-2744(6)	-1629(3)	71(2)
Si(6)	8771(1)	-1846(2)	11(1)	39(1)
C(63)	9009(3)	-3471(6)	-214(3)	61(2)
C(62)	9400(2)	-943(6)	325(2)	50(2)
C(61)	8330(2)	-2174(6)	595(2)	49(2)
S(2)	6150(1)	1059(1)	1106(1)	32(1)
N(3)	6646(2)	124(4)	1371(2)	34(1)
Si(3)	6497(1)	-1365(2)	1653(1)	41(1)
C(33)	7116(3)	-2421(6)	1569(3)	77(2)
C(32)	6395(3)	-1272(7)	2428(2)	70(2)
C(31)	5868(2)	-2176(5)	1267(2)	51(2)
N(4)	6449(2)	1875(4)	647(2)	33(1)
Si(4)	6079(1)	2776(2)	118(1)	41(1)
C(43)	5357(2)	2163(7)	-87(3)	74(2)
C(42)	6037(3)	4518(6)	331(3)	68(2)
C(41)	6481(3)	2700(7)	-518(2)	66(2)
N(6)	6019(2)	2118(4)	1651(2)	38(1)
Si(8)	6543(1)	3027(2)	2051(1)	44(1)
C(81)	6251(3)	4662(6)	2195(3)	63(2)
C(82)	6789(3)	2252(6)	2752(2)	60(2)
C(83)	7173(2)	3335(6)	1672(2)	55(2)
Si(7)	5313(1)	2152(2)	1801(1)	51(1)
C(71)	4929(3)	3594(6)	1472(3)	71(2)
C(72)	5279(3)	2172(7)	2595(3)	78(2)
C(73)	4930(2)	666(6)	1528(3)	68(2)
O(1)	8122(2)	587(4)	1509(2)	51(1)
C(91)	8062(3)	314(7)	2099(2)	66(2)
C92a	8537(6)	1079(18)	2431(7)	65(5)
C93a	8930(7)	1480(18)	1986(9)	67(5)
C94a	8711(6)	710(3)	1449(9)	61(5)
C92' b	8371(8)	1390(2)	2459(9)	62(6)
C93' b	8808(9)	1880(2)	2075(11)	71(7)
C94' b	8702(8)	1050(3)	1530(10)	51(6)
C100a	9758(5)	-2723(11)	1941(4)	93(3)
C101a	9275(2)	-3395(6)	1951(2)	92(3)
C102a	9188(2)	-4554(6)	1652(2)	122(4)
C103a	9596(2)	-5028(6)	1330(2)	144(5)
C104a	10090(2)	-4343(6)	1306(2)	133(4)
C105a	10178(2)	-3184(6)	1604(2)	110(4)
C106a	9844(2)	-1587(6)	2224(2)	131(5)
O2b	9689(2)	-4021(6)	1577(2)	119(7)
C110b	9388(2)	-3708(6)	2106(2)	107(8)
C111b	9387(2)	-2203(6)	2192(2)	100(9)
C112b	10111(2)	-1917(6)	2011(2)	91(8)
C113b	10178(2)	-3184(6)	1604(2)	107(9)

and 0.35) and O1 in **3** (split occupancy of 0.59 and 0.41) were resolved in a similar way. The disordered THF molecule around O1 (split occupancy of 0.57 and 0.43) in **5** was refined as described above. In addition, an uncoordinated solvent molecule is located at an unoccupied lattice position. This was refined to a split occupancy of 81% toluene (C100–C106) and 19% THF (O2, C110, C111, C112, C113).

Selected bond lengths and angles are presented in Table 1, crystal data in Table 4 and fractional coordinates in Tables 5–9. Tables of hydrogen atom coordinates and anisotropic thermal parameters, along with complete lists of bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

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