

Coordination chemistry of furfurylsilylamides

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The syntheses and crystal structures of three new furfurylamides are described, tetrameric lithium furfurylamide (**1**), dimeric magnesium furfurylamide (**2**), and dimeric dimethylaluminiumfurfurylamide (**3**). The compounds were characterized by ^1H -, ^{13}C -, ^{29}Si - and ^7Li - NMR spectroscopy and by X-ray crystallography.

Introduction

The well known reactions of organyl compounds of Group 1, 2 and 13 metals with amines leads to oligomeric or polymeric ring and cage structured amides.^{1–3} Amides displaying low aggregation are of special interest to correlate their reactivity with structural features, and volatile compounds of lithium-, magnesium- and aluminium-amides are considered as suitable precursors for CVD techniques to achieve ceramic composite materials.⁴ Therefore, a huge number of ligand systems have been investigated to achieve low coordinated amides of these elements.⁵

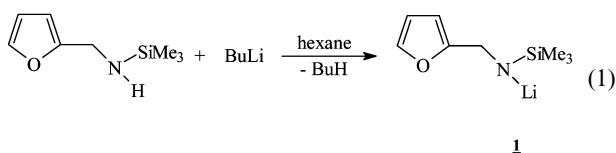
Since the high ionicity of metal–oxygen or metal–nitrogen bonds in alkoxides or amides of Group 1, 2 and 13 elements normally leads to the formation of highly aggregated systems,⁶ either bulky substituents or chelating ligands are used to reduce the formation of oligomeric or polymeric structures.⁷ With this strategy, low coordinated⁸ as well as monomeric magnesium- and aluminium-amides^{9–11} can be achieved.^{12–14}

Furfurylamine was used in this study as a bidentate ligand system to characterize the coordinative effects in the corresponding lithium-, magnesium- and aluminium-amides. The coordinative influence of other heteroaromatic ring systems (e.g. pyridine, bipyridine, etc.) with metal centers has already been widely studied. The furane ligand is a heteroaromatic counterpart to THF and of comparable size. It should also enable a coordinative saturation of metal centers in amides as it is a common feature for THF and other heteroaromatic compounds.¹⁵

Results and discussion

Synthesis of *N*-lithium-*N*-trimethylsilylfurfurylamide (**1**)

To a solution of *N*-trimethylsilylfurfurylamine in hexane a stoichiometric amount of butyllithium was added leading to the straightforward formation of the amide according to eqn. (1). During the addition of the butyllithium, the colorless solution of the furfurylamine turns deep red.



After the reaction was completed, a ^{29}Si -NMR spectrum of the solution showed a single peak at -1.94 ppm (starting material: 4.69 ppm). Two resonances at 0.05 and -1.10 ppm are present in the ^7Li -NMR spectrum indicating two different coordination

sites for lithium atoms in solution. No significant peak shift occurred in the ^{29}Si - and ^7Li -NMR spectra on heating the hexane solution of **1** up to 333 K. The ^{13}C -NMR spectrum of **1** in C_6D_6 reveals only one set of signals for the silylated furfurylamine ligand. Deep red colored single crystals suitable for X-ray structure determination precipitated from a hexane solution after cooling to -18 °C.

X-Ray structure determination of *N*-lithium-*N*-trimethylsilylfurfurylamide (**1**)

The amide **1** crystallizes in the orthorhombic system, space group *Pbca*, and the molecular structure is depicted in Fig. 1.

The lithium amide **1** displays a tetrameric aggregation in the solid state. The individual tetramer cluster is chiral and there

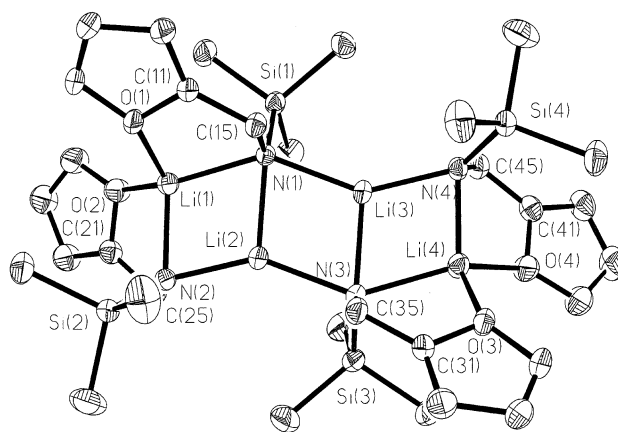


Fig. 1 Molecular structure of tetrameric *N*-lithium-*N*-trimethylsilylfurfurylamide (**1**)₄. Thermal ellipsoids are shown at a 25% probability level and hydrogen atoms are omitted for clarity. Selected atom distances (Å) and bond angles (°): N(1)–Li(1) 2.122(4), N(1)–Li(2) 2.115(4), N(1)–Li(3) 2.098(4), N(2)–Li(1) 1.983(4), N(2)–Li(2) 1.982(4), N(3)–Li(2) 2.128(4), N(3)–Li(3) 2.118(4), N(3)–Li(4) 2.135(4), N(4)–Li(3) 1.970(4), N(4)–Li(4) 1.995(4), O(1)–Li(1) 1.950(4), O(2)–Li(1) 2.042(4), O(3)–Li(4) 1.995(5), O(4)–Li(4) 2.015(4), Li(1)–Li(2) 2.446(5), Li(2)–Li(3) 2.493(5), Li(3)–Li(4) 2.438(5); Li(2)–N(1)–Li(1) 70.50(15), Li(3)–N(1)–Li(1) 142.17(17), Li(3)–N(1)–Li(2) 72.57(15), Li(2)–N(2)–Li(1) 76.15(17), Li(2)–N(3)–Li(4) 140.86(18), Li(3)–N(3)–Li(2) 71.91(15), Li(3)–N(3)–Li(4) 69.96(15), Li(3)–N(4)–Li(4) 75.87(17), N(2)–Li(1)–N(1) 106.50(18), O(2)–Li(1)–N(1) 136.6(2), N(2)–Li(1)–O(2) 88.59(17), O(1)–Li(1)–O(2) 116.25(19), O(1)–Li(1)–N(2) 124.6(2), O(1)–Li(1)–N(1) 88.58(17), N(2)–Li(2)–N(1) 106.79(18), N(2)–Li(2)–N(3) 146.4(2), N(1)–Li(2)–N(3) 106.79(17), N(4)–Li(3)–N(1) 144.3(2), N(4)–Li(3)–N(3) 107.83(18), N(1)–Li(3)–N(3) 107.82(18), N(4)–Li(4)–N(3) 106.25(18), N(4)–Li(4)–O(4) 89.03(18), O(4)–Li(4)–N(3) 139.6(2), O(3)–Li(4)–O(4) 112.1(2), O(3)–Li(4)–N(3) 88.07(17), O(3)–Li(4)–N(4) 127.7(2).

are eight tetramer units present per unit cell resembling four pairs of enantiomers. The individual tetramer reveals a C_2 pseudosymmetry (axis perpendicular to the intersection of the centers N(1)N(3) and Li(2)Li(3)).

The structure of a tetramer unit of the amide **1** resembles a ladder type arrangement of lithium and nitrogen atoms in three four membered Li–N rings (Fig. 1). This kind of aggregation is quite a common feature in lithium-amides, -phosphides and other Group 1 and 2 compounds.^{1–3,6,16,17}

In the structure of (**1**)₄, two kinds of lithium center can be distinguished. The terminal lithium atoms Li(1) and Li(4) of the tetramer (**1**)₄ show a fourfold coordination geometry of the lithium atoms by two oxygen atoms of the furfuryl ligand and two nitrogen atoms respectively resembling a distorted tetrahedral coordination geometry (Li–O distances: 1.950(4)–2.042(4) Å), whereas the lithium atoms Li(2) and Li(3) of the central Li–N ring are only threefold coordinated by nitrogen atoms and reveal a planar coordination geometry regarding the adjacent nitrogen centers (the sum of the N–Li–N angles is 360° for both Li centers)

The nitrogen atoms N(1) and N(3) of the central Li–N ring are fivefold coordinated with three contacts each to a lithium center (Li(1), Li(2), Li(3) for N(1) and Li(2), Li(3), Li(4) for N(3)). The Li–N distances involving the pentacoordinated nitrogen centers range from 2.098(4) to 2.135(4) Å. The terminal nitrogen centers N(2) and N(4) are tetracoordinated with two significantly shorter Li–N distances in the range of 1.970(4) to 1.995(4) Å.

The Li–Li contacts are in a narrow range between 2.438(5) and 2.493(5) Å, but the contacts of the terminal Li–N–rings are slightly shorter (Li(1)–Li(2) 2.446(5), Li(3)–Li(4) 2.438(5) Å) than the contacts of the central ring (Li(2)–Li(3) 2.493(5) Å).

The Li–N–Li angles at the pentacoordinated nitrogen Atoms N(1) and N(3) are quite similar in all Li–N rings ranging from 69.96(15) to 72.57(15)°, whereas the Li–N–Li angles at the tetracoordinated nitrogen atoms N(2) and N(4) are slightly enlarged (76.15(17)° at N(2) and 75.87(17)° at N(4)). The Li–N core fragment set up by the atoms Li(1) to Li(4) and N(1) to N(4), respectively, is almost planar. The interplanar angle between the ring Li(1)–N(1)–Li(2)–N(2) and the central ring Li(2)–N(1)–Li(3)–N(3) is quite small (5.8°), and the angle between the latter plane to the terminal Li(3)–N(3)–Li(4)–N(4) ring is 6.3° and thus of similar magnitude. The interplanar angles of the both terminal rings add up to a value of 12.1°. This slightly bent geometry of the Li–N core structure can be explained by the steric demand of the silyl groups on the atoms N(1) and N(3), which are both directed to one side.

The NMR data for compound **1** in solution are in accordance with the solid state structure, indicating that the molecule is more symmetric in solution than in the solid state (identical Me₃Si– groups in solution, two different types of lithium atoms). A ring opening of the furane system by butyllithium, as reported for a double metalated chelating amide containing thiophene groups,¹⁸ could not be observed.

Instead of the tetrameric structure of the lithium amide, dimeric units also would have been feasible with a threefold coordination sphere at the lithium centers achieved by two nitrogen atoms and the oxygen atom of the furfuryl ligand according to Fig. 2. This is not the case, as indicated by the

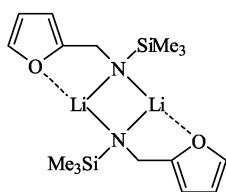
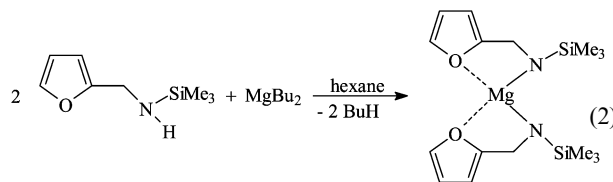


Fig. 2 Coordination of a dimer species of **1**.

crystal structure and the high temperature NMR data. The formation of a tetramer structure with Li–O contacts involving only the terminal lithium atoms Li(1) and Li(4) instead of all lithium atoms can be attributed to the shielding of the lithium centers Li(2) and Li(3) by the silyl groups.

Synthesis of magnesium bis(*N*-trimethylsilylfurfuryl)amide (**2**)

The magnesium amide **2** was prepared by reaction of a heptane solution of dibutylmagnesium with two equivalents of the silylated furfurylamine according to eqn. (2):



2

After addition of the magnesium organyl, the ²⁹Si-NMR spectrum of the solution exhibits two peaks at 7.67 and –1.16 ppm, indicating a complete reaction. A solution of the neat magnesium amide **2** in C₆D₆ shows the same ²⁹Si-NMR resonances.

A monomeric species in solution should lead to only one resonance in the ²⁹Si-NMR spectrum (the magnesium amide **2** depicted in eqn. (2) should reveal at least a symmetry close to C_2 leading to two identical silyl groups in solution). Thus, the resulting shifts indicate a higher aggregation of **2**. The peak shifts can be interpreted as silyl groups on tri- and tetra-coordinated nitrogen atoms because comparable ²⁹Si-NMR shifts have been observed in other dimeric magnesium silylamides.¹⁹ The ¹H- and ¹³C-NMR spectra of **2** in C₆D₆ also exhibit two sets of signals for the silylated furfurylamine ligand.

The observed ²⁹Si-NMR signal splitting does not change with temperature on heating a hexane solution of **2** to 333 K indicating a stable cluster in solution.

An interesting effect occurs when THF is added to the hexane solution. In this case, the previously existing signals at 7.67 and –1.16 ppm vanish and only one resonance at –3.80 ppm is present in the ²⁹Si-NMR spectrum indicating two identical Me₃Si– groups and a change in coordination. This peak shift is in accordance with the assumption of a monomeric species of **2** with THF coordinated at the metal center (Fig. 3).

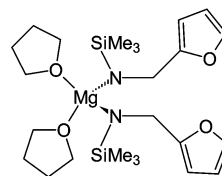


Fig. 3 Coordination of THF leading to a monomer of **2**.

In this case, the stronger donor solvent THF (compared to the furan system) is able to change the coordination geometry of the magnesium atoms. Assuming a tetrahedral environment at the magnesium atoms, a coordination of **2** as depicted in Fig. 3 is possible.

Single crystals of **2** suitable for a crystal structure determination could be obtained from a hexane solution after cooling to –18 °C.

X-Ray structure determination of magnesium bis(*N*-trimethylsilylfurfuryl)amide (**2**)

The crystals belong to the triclinic system and space group $P\bar{1}$. The crystal structure of **2** is depicted in Fig. 4.

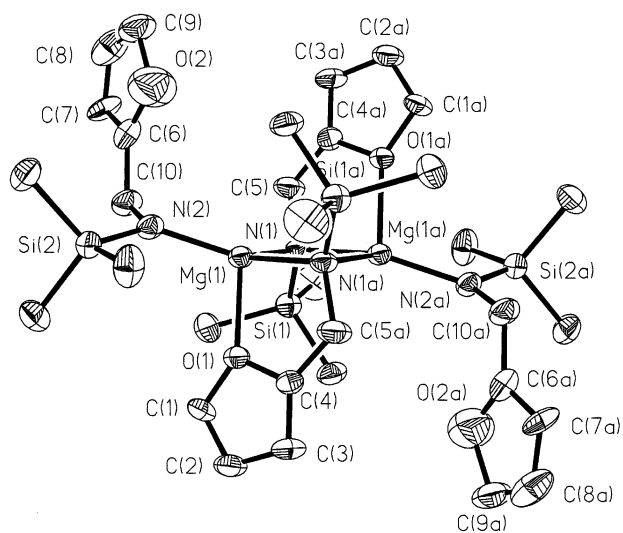


Fig. 4 Molecular structure of dimeric magnesium bis(*N*-trimethylsilylfurfuryl)amide (**2**). Thermal ellipsoids are shown at a 25% probability level and hydrogen atoms are omitted for clarity. Selected atom distances (Å) and bond angles (°): Mg(1)–N(1) 2.134(4), Mg(1)–N(2) 1.971(5), Mg(1)–O(1) 2.129(4), Mg(1)–N(1a) 2.129(4), Si(1)–N(1) 1.738(4), C(5)–N(1) 1.498(6), N(1)–Mg(1a) 2.129(4), Si(2)–N(2) 1.693(5), C(10)–N(2) 1.479(7), Mg(1)–Mg(1a) 2.934(4); N(2)–Mg(1)–N(1) 119.04(18), N(2)–Mg(1)–O(1) 106.61(17), N(1)–Mg(1)–O(1) 106.71(16), N(1)–Mg(1)–N(1a) 93.02(16), N(2)–Mg(1)–N(1) 141.98(19), N(1a)–Mg(1)–O(1) 80.31(15), Si(1)–N(1)–Mg(1) 115.8(2), C(5)–N(1)–Mg(1) 108.0(4), C(5)–N(1)–Si(1) 113.0(3), C(5)–N(1)–Mg(1a) 111.8(3), Si(1)–N(1)–Mg(1a) 118.3(2), Mg(1)–N(1)–Mg(1a) 86.98(16), C(10)–N(2)–Si(2) 114.4(4), C(10)–N(2)–Mg(1) 121.4(4), Si(2)–N(2)–Mg(1) 122.8(2), N(2)–Mg(1)–Mg(1a) 157.63(16).

The magnesium amide **2** is a dimer in the solid state and two dimers are present per unit cell. The individual dimers exhibit almost equal structural data. An individual centrosymmetric dimer is built up by bridging and exocyclic nitrogen atoms leading to a three- and four-fold coordination sphere at the nitrogen atoms N(1) and N(2), respectively. The magnesium atoms are fourfold coordinated by three nitrogen atoms and one oxygen atom from a furfuryl ligand of the bridging amide unit leading to a distorted tetrahedral environment at the Mg centers.

The Mg–N bond lengths of the four membered Mg–N ring are almost equal (Mg(1)–N(1) 2.134(4), Mg(1)–N(1a) 2.129(4) Å), whereas the Mg(1)–N(2) distance to the tricoordinate exocyclic nitrogen atom is 1.971(5) Å. The Mg(1)–O(1) distance from the magnesium center to the furan oxygen atom is 2.129(4) Å and in a similar range to the Mg(1)–N(1) distance. Although the magnesium centers are tetracoordinated, there is only a small deviation from a planar coordination of the Mg centers by the nitrogen atoms N(1), N(1a) and N(2), as indicated by the sum of the corresponding N–Mg–N angles of 354°. This clearly indicates the weak donor effect of the oxygen atom of the furfuryl ligand. The Mg(1a)–Mg(1)–N(2) angle is slightly bent (157.63(16)°), whereas the O–Mg–N angles display a significant distortion from an ideal tetrahedral coordination sphere (N(2)–Mg(1)–O(1) 106.61(17), N(1)–Mg(1)–O(1) 106.71(16), N(1a)–Mg(1)–O(1) 80.31(15), N(2)–Mg(1)–N(1a) 141.98(19)°). The coordination sphere of the exocyclic nitrogen atom N(2) is planar as indicated by the sum of the N–Mg–N angles of 359°. The distance of the magnesium centers is 2.934(3) Å. Other donor solvent free amides of bivalent metals reveal an almost planar N–Mg–Mg' angle for the Mg₂N₂ core structure.

An interesting feature of the structure of **2** is the fact that only the oxygen atoms of the bridging furfurylamide ligands are interacting as chelating ligands resulting in a fourfold coordination sphere at the magnesium atoms. The observed structure of the magnesium amide **2** still shows the typical features of other donor free dimeric magnesium amides, and

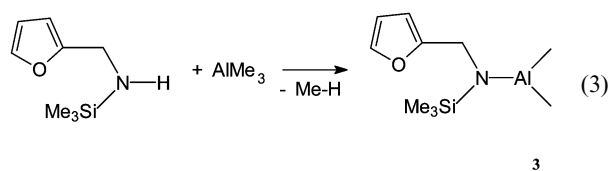
only small deviations from the planar coordination sphere at the magnesium centers are induced by the weak interaction of the furfuryl ligand.

According to the dimeric structure of **2** in the solid state, the two peaks in the ²⁹Si-NMR spectrum can be attributed to the terminal silylamide group (–1.16 ppm) and to the tetra-coordinated nitrogen atoms of the silylamide bridging two Mg centers (7.66 ppm). Thus, the dimeric structure of **2** is also retained in solution.

The addition of the stronger donor solvent THF to a benzene or hexane solution of **2** leads to a cleavage of the dimeric species to a monomer as indicated by the signal shift towards high field in the ²⁹Si-NMR spectrum.

Synthesis of dimethylaluminum-*N*-trimethylsilylfurfurylamide (**3**)

The reaction of *N*-trimethylsilylfurfurylamine with one equivalent of trimethylaluminum in hexane leads to the straightforward formation of the amide **3** according to eqn. (3):



A resonance at 13.24 ppm can be observed in the ²⁹Si-NMR spectrum of a hexane solution of **3** indicating only one type of silyl group in solution. The peak shift is in the range of bridging silylamide groups. The ²⁷Al-NMR spectrum of **3** reveals a signal at 174.3 ppm, indicating a dimer structure with tetra-coordinated aluminum atoms.²⁰ The amide **3** can be distilled in vacuum at 150 °C. Light orange colored single crystals suitable for X-ray structure determination could be obtained from a hexane solution of **3** at ambient temperature.

X-Ray structure determination of dimethylaluminum-*N*-trimethylsilylfurfurylamide (**3**)

The crystals belong to the monoclinic system and space group *P2(1)/c*. The crystal structure determination reveals the formation of a centrosymmetric dimer of **3** in the solid state. There are two dimers present per unit cell correlated by the crystal symmetry. The structure of an individual dimer is shown in Fig. 5.

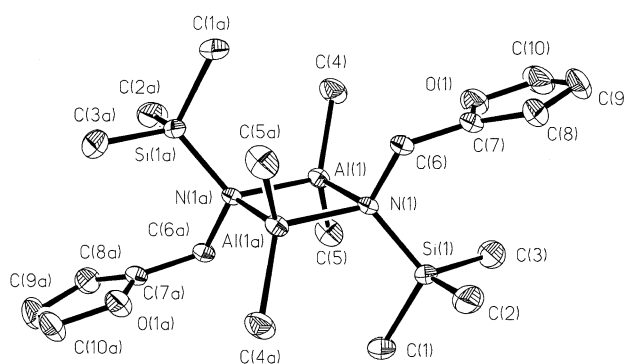


Fig. 5 Molecular structure of dimeric dimethylaluminum-*N*-trimethylsilylfurfurylamide (**3**)₂. Thermal ellipsoids are shown at a 25% probability level and hydrogen atoms are omitted for clarity. Selected atom distances (Å) and bond angles (°): Al(1)–N(1) 1.971(2), Al(1)–N(1a) 2.025(2), Al(1)–C(4) 1.973(3), Al(1)–C(5) 1.967(3), N(1)–C(6) 1.526(3), C(6)–C(7) 1.483(4), Si(1)–N(1) 1.749(2), Al(1)–Al(1a) 2.826(16); Al(1)–N(1)–Al(1a) 90.03(9), N(1)–Al(1)–N(1a) 89.97(9), C(6)–N(1)–Al(1) 112.89(16), Si(1)–N(1)–Al(1) 118.41(12), C(7)–C(6)–N(1) 118.5(2), C(5)–Al(1)–C(4) 109.00(16), C(5)–Al(1)–N(1) 115.07(14), C(4)–Al(1)–N(1) 115.54(13), C(5)–Al(1)–N(1a) 110.29(12), C(4)–Al(1)–N(1a) 116.00(13), C(6)–N(1)–Si(1) 111.24(16).

Table 1 Crystallographic data for compounds (1)₄, (2)₂ and (3)₂

	(1) ₄	(2) ₂	(3) ₂
Formula	C ₈ H ₁₄ LiNOSi	C ₁₆ H ₂₈ MgN ₂ O ₂ Si ₂	C ₁₀ H ₂₀ AlNOSi
FW/g mol ⁻¹	175.23	360.89	225.34
Color, habit	Deep red, plates	Deep red, rhombs	Light orange, plates
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P2(1)/c</i>
<i>a</i> /Å	20.838(4)	11.326(2)	8.000(2)
<i>b</i> /Å	15.254(3)	12.571(3)	17.559(4)
<i>c</i> /Å	26.986(5)	14.982(3)	9.706(2)
<i>a</i> ^o	—	89.43(3)	—
<i>β</i> ^o	—	76.80(3)	99.34(3)
<i>γ</i> ^o	—	89.53(3)	—
<i>V</i> /Å ³	8578(3)	2076.6(7)	1345.3(5)
<i>Z</i>	32	4	4
Crystal dimensions/mm	0.5 × 0.5 × 0.5	0.5 × 0.5 × 0.5	0.5 × 0.5 × 0.5
<i>μ</i> /mm ⁻¹	0.201	0.210	0.214
No. of unique data	50537	5410	1772
No. of data with (<i>I</i> > 2σ(<i>I</i>))	6446	5410	1772
No. of paramaters	445	425	127
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.0430	0.0693	0.0438
<i>wR</i> 2 (all data)	0.1159	0.2055	0.1225

The aluminium and nitrogen atoms are tetracoordinated. The Al centers are coordinated only by two nitrogen atoms and two methyl groups. The oxygen atoms of the furfuryl ligands do not participate in the coordination of the metal centers. The Al–N bond length are 1.971 and 2.025 Å, respectively, and are in the range of other dimeric Al–N compounds. The Al–C distances are almost equal at around 1.97 Å.

The angles of the planar ring formed by two aluminium and nitrogen atoms are 90.03 (Al(1)–N(1)–Al(1a)) and 89.97° (N(1)–Al(1)–N(1a)), respectively. Thus, the Al–N ring is almost a perfect rectangle. The C(4)–Al(1)–C(4) angle of the dimethylaluminium group is 109.00°, the C–Al–N angles are in the range from 110.29 to 115.07°. The C(6)–N(1)–Si(1) angle is 111.24°, and the Si–N–Al angles range from 116.41 to 118.41°.

Conclusion

It could be shown that furfurylamine can act as a chelating ligand system in lithium and magnesium amides, but the donor strength is weaker compared to THF due to the participation of the oxygen atom in the heteroaromatic furan ring system resulting in an sp²-type lone pair orbital, which can act as a dative bond to metal centers. In the structure of the lithium amide (1)₄, all oxygen atoms of all furfuryl ligands are involved in the coordination of the lithium centers, whereas the structure of the magnesium amide (2)₂ shows only a participation of one ligand per metal center in the coordination of the magnesium atoms. The solid state structure of the corresponding aluminium amide (3)₂ reveals no interaction of the oxygen atoms of the ligand with the metal centers. No intermolecular interactions could be observed in the structures of the compounds (1)₄, (2)₂ and (3)₂. It could be shown in the presented structures, that the interaction of the furfurylamine ligand can be considered as strong in the case of the lithium compound (1)₄, weak for the magnesium compound (2)₂, and non-existent for the aluminium compound (3)₂.

Experimental

All reactions were performed using modified Schlenk techniques and a protective atmosphere of argon. Solvents were freshly distilled from Na/K alloy. Butyllithium (1.5 M in hexane), dibutylmagnesium (1 M in heptane), trimethylaluminium (2 M in hexane) and furfurylamine (distilled prior to use) were obtained from commercial suppliers. Although the NMR spectra indicate pure compounds in all cases, the carbon content of the elemental analysis of the amides is in

general lower due to the formation of silicon carbide. NMR spectra were recorded in C₆D₆ solution by using a Bruker ACP 200 spectrometer (TMS, LiCl and AlCl₃ as external standards, ¹H: 200 MHz, ¹³C: 55.0 MHz, ²⁹Si: 39.7 MHz, ⁷Li: 77.7 MHz, ²⁷Al: 52.2 MHz).

Synthesis

***N*-Trimethylsilylfurfurylamine.** Furfurylamine 50 ml (0.57 mol) and 86.3 ml (0.62 mol) triethylamine were dissolved in 300 ml benzene. 71.5 ml (0.57 mol) chlorotrimethylsilane were added dropwise to the stirred solution. The reaction mixture was then warmed slightly and a precipitate of triethylammonium chloride formed. After the addition of silane, the mixture was heated for 2 h to reflux. The solid residue was filtered off and the solvent removed *in vacuo*. The remaining liquid was subjected to vacuum distillation; the product distilled off at 37 °C/10⁻² mbar. Yield 69.93 g (0.41 mol; 73%). Anal. C₈H₁₅NOSi, *M* = 169.30 g mol⁻¹: Calc. C, 56.77; H, 8.93; N, 8.27. Found: C, 56.46; H, 9.32; N, 8.27%. NMR (CDCl₃): ¹H: δ -0.02 (Me₃Si, s, 9 H); 0.74 (NH, br, 1 H); 3.80, 3.66 (Ar–CH₂–NH, d, 2 H), 5.98–7.20 (Ar–CH, m, 3 H); ¹³C: δ -0.47 (Me₃Si), 38.75 (Ar–CH₂–NH), 104.51, 109.83 (Ar–C₂–C₃), 140.83 (Ar–C₄), 157.20 (Ar–C₁); ²⁹Si: δ 4.69 (Me₃Si).

***N*-Lithium-*N*-trimethylsilylfurfurylamide (1).** To a solution of 1.21 g (7.13 mmol) *N*-trimethylsilylfurfurylamine in 20 ml hexane 4.57 ml (7.13 mmol) of a 1.5 M butyllithium solution in hexane were added slowly at room temperature. The colorless solution immediately turns deep red while adding the butyllithium. Deep red single crystals could be isolated from the solution after storage at -18 °C. Yield: 0.77 g (4.40 mmol; 62%). Anal. C₈H₁₄NOSiLi, *M* = 175.233 g mol⁻¹: Calc. C, 54.83; H, 8.06; N, 7.99. Found: C, 53.90; H, 8.43; N, 7.52%. NMR (C₆D₆): ¹H: δ 0.11 (Me₃Si, s, 9 H), 4.38 (Ar–CH₂–N, s, 2 H), 5.80–6.98 (Ar–H, m, 3 H); ¹³C: δ 1.72 (Me₃Si), 44.25 (Ar–CH₂–N), 103.43, 112.05, (Ar–C₂–C₃), 139.48 (Ar–C₄), 162.06 (Ar–C₁); ²⁹Si: δ -1.67 (Me₃Si); ⁷Li: δ 0.05, -1.10.

Magnesium bis(*N*-trimethylsilylfurfuryl)amide (2). *N*-Trimethylsilylfurfurylamine 0.53 g (3.10 mmol) was dissolved in 20 ml hexane and 1.55 ml (1.55 mmol) of a 1 M solution of dibutylmagnesium in heptane were added slowly. The solution becomes magenta during the addition of the dibutylmagnesium. The mixture was heated to reflux for 24 h leading to a deep red solution. The completion of the reaction was indicated by a ²⁹Si-NMR of the solution. Storage of the solution at -18 °C led to the formation of deep red crystals, which were

suitable for X-ray structure determination. Yield: 0.40 g (1.11 mmol; 71%). Anal. $C_{16}H_{28}N_2O_2Si_2Mg$, $M = 360.89$ g mol⁻¹; Calc. C, 53.25; H, 7.82; N, 7.76. Found: C, 51.86; H, 7.64; N, 7.53%. NMR (C_6D_6): ¹H: δ 0.03 (Me₃Si, s, 9 H), 0.10 (Me₃Si, s, 9 H), 4.06 (Ar-CH₂-N, s, 2 H), 4.36 (Ar-CH₂-N, s, 2 H), 5.60–7.21 (Ar-CH, m, 6 H); ¹³C: δ 1.47, 2.31 (Me₃Si), 41.89, 44.99 (Ar-CH₂-N), 104.95, 110.40, 113.37 (Ar-C2, -C3), 140.11, 140.25 (Ar-C4), 157.31, 162.83 (Ar-C1); ²⁹Si: δ -1.16, 7.66 (Me₃Si). NMR (hexane-THF, C_6D_6): ²⁹Si: δ -3.80 (Me₃Si).

Dimethylaluminium-N-trimethylsilylfurfurylamide (3). 1.86 ml of a 2 M hexane solution of trimethylaluminium (3.72 mmol) were added to a solution of 0.63g (3.72 mmol) N-trimethylsilylfurfurylamine in 20 ml hexane at room temperature. Evolution of gas took place and the reaction mixture became light yellow. Heating to reflux resulted in a clear yellow solution and light orange crystals separated after 3 d at ambient temperature. Yield: 1.43 g (3.17 mmol; 85%), bp 145–148 °C/10⁻² mbar. Anal. $C_{20}H_{40}Al_2N_2O_2Si_2$, $M = 450.69$ g mol⁻¹; Calc. C, 53.30; H, 8.95; N, 6.22. Found: C, 51.77; H, 9.21; N, 6.44%. NMR (C_6D_6): ¹H: δ -0.15, -0.12 (AlMe₂, d, 6 H), 0.07, 0.08 (Me₃Si, d, 9 H), 4.22 (Ar-CH₂-N-, s, 2 H), 5.91–6.96 (Ar-CH, m, 3 H); ¹³C: δ -3.13 (AlMe₂), 2.33 (Me₃Si), 44.63 (Ar-CH₂-N-), 110.56, 110.89 (Ar-C2, -C3), 142.12 (Ar-C4), 152.08 (Ar-C1); ²⁹Si: δ 13.24 (Me₃Si); ²⁷Al: δ 174.3.

X-Ray crystallography

A STOE IPDS diffractometer was used (Mo-K α , $\lambda = 0.71073$ Å, graphite monochromator) for the X-ray structure determination of the single crystals. The structures of compounds **1**, **2** and **3** were solved by direct methods and refined by full matrix least squares methods (data are listed in Table 1). Anisotropic thermal parameters for all non-hydrogen atoms in the final cycles, isotropic refinements for H atoms positioned by geometry. SHELXS 97^{21a} and SHELXL 97^{21b} computer programs were used.

CCDC reference numbers 186253–186255.

See <http://www.rsc.org/suppdata/dt/b2/b205350k/> for crystallographic data in CIF or other electronic format.

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