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Communications

Metalations of 1-Aminonaphthalene with $AlMe_3$ and with $ZnEt_2$: Syntheses and Crystal Structures of Cyclobutane-like $[Me_2Al(N(H)naphthyl)]_2$ and Cyclohexane-like $[EtZn(N(H)naphthyl)\cdot THF]_3$

Matthew G. Davidson, David Elilio, Simon L. Less, Avelino Martín, Paul R. Raithby, Ronald Snaith, and Dominic S. Wright*

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

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Summary: Metalation of 1-aminonaphthalene with $AlMe_2$ produces the planar Al_2N_2 ring dimer $[Me_2Al(N(H)\text{-}naphthyl)]_2$ (1), in which there is a trans orientation of the N–H protons. Similar metalation of the same primary amine with $ZnEt_2$ produces the chair-shaped Zn_3N_3 ring trimer $[EtZn(N(H)naphthyl)\cdot THF]_3$ (2), in which the ring N–H protons are all cis. Complex 2 is the first trimeric amido Zn complex to be structurally characterized.

Main-group-metal amides, containing metal–N bonds and usually prepared by the metalation of *secondary* amines (R^1R^2NH; R^1, R^2 = alkyl, aryl), have been structurally characterized for most of the elements.[1] A diversity of solid-state structural types, including rings, clusters, and extended arrays, is known.[2] Complexes produced from metalation of *primary* amines (RNH_2; R = alkyl, aryl) have become widely studied particularly with respect to their thermolysis and the resulting cluster buildup.[3] Recently we reported the structure of the $((naphthylN)Li_2)_{10}\cdot 7Et_2O$ cluster, produced by the dilithiation of 1-aminonaphthalene[4] in Et_2O solvent.[5] The structure is based on a central Li_{14} core of two interlocked Li_8 cuboids sharing one edge. This result illustrates that dimetalation of primary amines is capable of producing large metal clusters. This is all the more likely, given the flat and sterically undemanding nature of the 1-aminonaphthyl and related aromatic amine residues. Indeed, we have found that the 1-aminonaphthyl dianion is a particularly stable ligand for the formation of cluster compounds of other main-group metals.[6] A further synthetic aspect, of particular relevance to this current work, is the possibility of forming mixed-metal aggregates by metalating one of the amine protons with one metal, followed by the metalation of the other (unreacted) proton with a source of a different metal.

We report here the products of metalation of 1-aminonaphthalene with $AlMe_3$[4] and with $ZnEt_2$[4] in ether solvents. The reactions produce respectively the planar

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(1) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1980.

(2) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47.

(3) See, for example structures of Al–N cluster compounds produced by thermolysis of primary amine complexes: (a) McDonald, T. R. R.; McDonald, W. S. *Acta Crystallogr., Sect. B* **1972**, *28*, 1619. (b) Alford, K. J.; Gosling, A. K.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 2197. (c) Hitchcock, P. B.; McLaughlin, G. M.; Smith, J. D.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1973**, 934. (d) Hitchcock, P. B.; Smith, J. D.; Thomas, K. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1433. (e) Amirkhalili, S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1206. (f) Al-Wassil, A.-A. I.; Hitchcock, P. B.; Sarisaban, S.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1985**, 1929.

(4) **Health and Safety Warning**: 1-Aminonaphthalene is a carcinogen, causing cancer of the bladder. $AlMe_3$ and $ZnEt_2$ are pyrophoric materials. They ignite violently in air if used neat. All these materials should be handled under nitrogen or argon using a vacuum line and a glovebox.

(5) Armstrong, D. R.; Barr, D.; Clegg, W.; Drake, S. R.; Singer, R. J.; Snaith, R.; Wright, D. S. *Angew. Chem.* **1991**, *104*, 1702; Angew. *Chem., Int. Ed. Engl.* **1991**, *30*, 1707.

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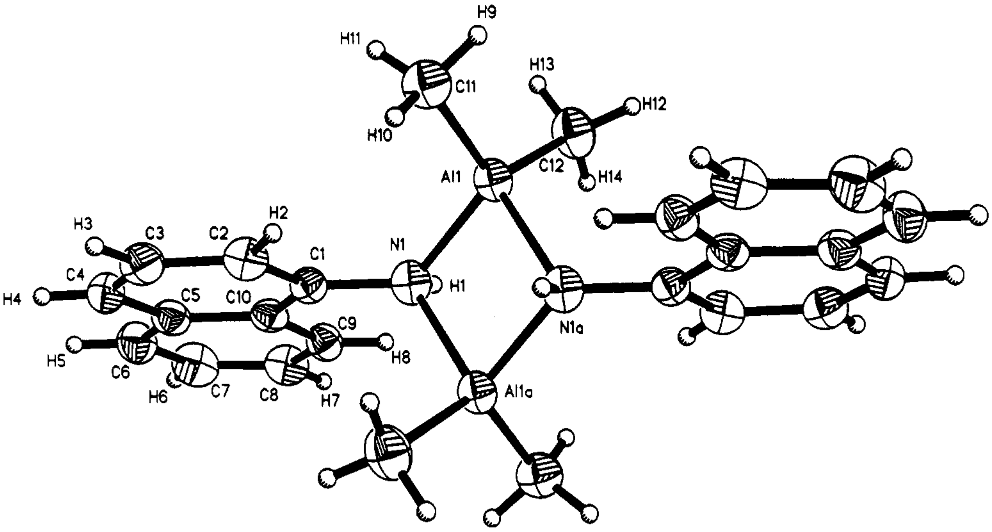

Figure 1. ORTEP drawing of 1 in the asymmetric unit. Thermal ellipsoids at the 50% level are shown. All hydrogen atoms, except those of nitrogen, are omitted for clarity. Selected bond distances and angles: Al(1)–N(1), Al(1A)–N(1A) = 1.966 (2) Å, Al(1)–N(1A), Al(1A)–N(1) = 1.981 (2) Å, N(1)–C(1), N(1A)–C(1A) = 1.431 (3) Å, average Al–C = 1.954 (3) Å; N–Al–N = 87.5 (1)°, Al–N–Al = 92.5 (1)°.

Al_2N_2 ring dimer $[Me_2Al(N(H)naphthyl)]_2$ (1) and the chair-shaped Zn_3N_3 trimer $[EtZn(N(H)naphthyl)\cdot THF]_3$ (2). In both complexes acidic N–H protons are retained. As such, both are potential precursors to mixed-metal compounds and also to further cluster buildup, by loss of MeH and EtH.[3]

Complexes 1 and 2 were prepared by the addition of hexane solutions of $AlMe_3$ and $ZnEt_2$, respectively, to 1 equiv of 1-aminonaphthalene in ether solvents (Et_2O for 1, THF for 2) at 20 °C. Cooling of the resulting solutions gave 1 in 42% yield and 2 in 62% yield.[7]

X-ray crystallographic studies were undertaken on 1 and 2.[8] Complex 1 is a ring dimer, $[Me_2Al(N(H)naphthyl)]_2$ (Figure 1). It contains a centrosymmetric planar Al_2N_2 core in which the unreacted N–H protons adopt a trans conformation. The Al_2N_2 ring has a pattern of alternating length Al–N bonds (Al–N (long) = 1.981 (2) Å; Al–N (short) = 1.966 (2) Å). The Al centers are rendered distorted tetrahedral in their bonding to the amido-N centers and to two Me groups (average Al–C = 1.954 (3) Å).

As a structural type, 1 is unremarkable among amido-Al complexes. Reactions of triorganoaluminums (R_3Al) with a variety of organic acids (amines, alcohols, etc.) have long been known to form complexes akin to 1, in which only one of the organic groups (R) on Al reacts.[9] The recently reported Al_2N_2 dimers $[Et_3SiN(H)AlMe_2]_2$ and $[Ph_3SiN(H)AlMe_2]_2$ have core structures and trans N–H conformations similar to those in 1.[10] However, an unexpected feature is that the naphthyl groups, which are aligned perpendicularly to the Al_2N_2 ring plane, are orientated syn to the N–H protons, leading to a close contact between these protons and the peri C–H atoms of their naphthyl groups (N–H⋯H–C = ca. 1.98 Å).

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(7) Data for 1: A solution of Me_3Al (5.0 mmol; 2.0 mol L^{-1} in hexane) was added to a solution of 1-aminonaphthalene (0.716 g, 5.0 mmol) in 8 mL of dry Et_2O at 20 °C. Stirring for ca. 30 min produced a purple-red solution, refrigeration of which at −5 °C for 2 days afforded colorless cubic crystals of 1: yield 0.42 g (42%); melting point 164–165 °C. Anal. Found: C, 71.9; H, 6.8; N, 7.2. Calcd: C, 72.4; H, 7.0; N, 7.0. IR (solid, Nujol): 3302 (w, N–H str), 3060 (m, C–H str, naphthyl), 1600 (m, C–N str), 1574 cm^{-1} (m, C$\overline{\cdot\cdot}$C str.). ^1H NMR (+25 °C, 250 MHz, C_4D_8O): δ 7.96 (m, 1 H, aryl C–H of naphthyl group), 7.65 (m, 1 H, aryl C–H of naphthyl group), 7.29 (m, 2 H, aryl C–H of naphthyl group), 7.13 (m, 1 H, aryl C–H of naphthyl group), 6.94 (m, 1 H, aryl C–H of naphthyl group), 6.74 (m, 1 H, aryl C–H of naphthyl group), 3.60 (s, 1 H, NH), −0.67 (s, 4 H, Me), −0.93 (s, 2 H, Me). Data for 2: 0.358 g (2.5 mmol) of 1-aminonaphthalene was dissolved in 5 mL of dry THF; 2.5 mL of Et_2Zn (2.5 mmol; 1.0 mol L^{-1} in hexane) then was slowly added at +20 °C. Slow evolution of gas followed and a solution color change from red to light yellow occurred after ca. 30 min of stirring at +20 °C. Cooling the solution to −15 °C for 5 days gave colorless crystals of 2: yield 0.48 g (62%); melting point: gives up THF solvate at ca. 90 °C. Anal. Found: C, 62.2; H, 6.7; N, 4.7. Calcd: C, 62.5; H, 6.5; N, 4.6. IR (solid, Nujol): 3400, 3480 (w, N–H str), ca. 3040 (w, C–H str), 1570 (m, aryl C$\overline{\cdot\cdot}$C), 1275 cm^{-1} (s, C–O, THF); other major bands at 765 (s) and 720 cm^{-1} (s) are characteristic. Compound 2 has poor solubility in THF once crystallized and has no solubility in nonpolar aprotic solvents. As a check on the stoichiometry of 2, a ^1H NMR spectrum was run in CD_3OD, which hydrolyzes the sample. ^1H NMR (+25 °C, 250 MHz, CD_3OD): δ 7.96 (m, 1 H, aryl C–H of naphthyl group), 6.72 (m, 1 H, aryl C–H of naphthyl group), 6.38 (m, 2 H, aryl C–H of naphthyl group), 6.23 (m, 2 H, aryl C–H of naphthyl group), 5.79 (m, 1 H, aryl C–H of naphthyl group), 4.88 (s, 1 H, N–H of naphthylNH group, i.e., present as naphthylNHD), 3.69 (m, 4 H, THF), 1.81 (m, 4 H, THF).

(8) X-ray structure determination for 1: data were collected at 150 K on a Stoe four-circle diffractometer. The compound crystallizes in space group $P2_1/n$, with $a = 6.866$ (1) Å, $b = 9.118$ (1) Å, $c = 17.804$ (2) Å, $\beta = 95.800$ (1)°, $V = 1108.9$ (6) $Å^3$, $Z = 2$, $D_c = 1.193$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 0.143$ mm^{-1} and $F(000) = 424$. A total of 1446 independent reflections were recorded in the range $7° \leq 2\theta \leq 45°$, of which 1268 were considered as observed ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by blocked full-matrix least squares. Naphthyl and N-attached hydrogens were directly located and refined isotropically, and methyl hydrogens were allowed to ride on the relevant carbon atoms and refined with a common isotropic displacement parameter, while anisotropic temperature factors were used for all other atoms. The final agreement factors were $R = 0.051$, $R_w = 0.065$, and GOF = 1.68. Crystal data for 2: data were collected at 200 K on a Stoe four-circle diffractometer. The compound crystallizes in space group Cc, with $a = 22.384$ (5) Å, $b = 12.769$ (4) Å, $c = 16.754$ (4) Å, $\beta = 110.83$ (2)°, $V = 4463$ (2) $Å^3$, $Z = 4$, $D_c = 1.378$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 1.643$ mm^{-1}, and $F(000) = 1944$. A total of 5508 independent reflections were recorded in the range $7° \leq 2\theta \leq 45°$, of which 5228 were considered ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by blocked full-matrix least squares. Hydrogen atoms were placed in idealized positions and allowed to ride on the relevant atoms in the final stages of refinement, while anisotropic temperature factors were used for all other atoms. The final agreement factors were $R = 0.064$, $R_w = 0.084$, and GOF = 1.47.

(9) For an early example see: (a) Brown, H. C.; Davidson, N. R. *J. Am. Chem. Soc.* **1942**, *64*, 316. For more recent examples involving $AlMe_3$ see: (b) Byers, J. J.; Pennington, W. T.; Robinson, G. H.; Hrncir, D. C. *Polydedron* **1990**, *9*, 2205. (c) Waggoner, K. M.; Olmstead, M. M.; Power, P. P. *Polyhedron* **1990**, *9*, 257. (d) Lee, B.; Bennington, W. T.; Robinson, G. H. *Inorg. Chim. Acta* **1991**, *190*, 173. (e) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385. (f) Byers, J. C.; Lee, B.; Pennington, W. T.; Robinson, G. H. *Polyhedron* **1992**, *8*, 967.

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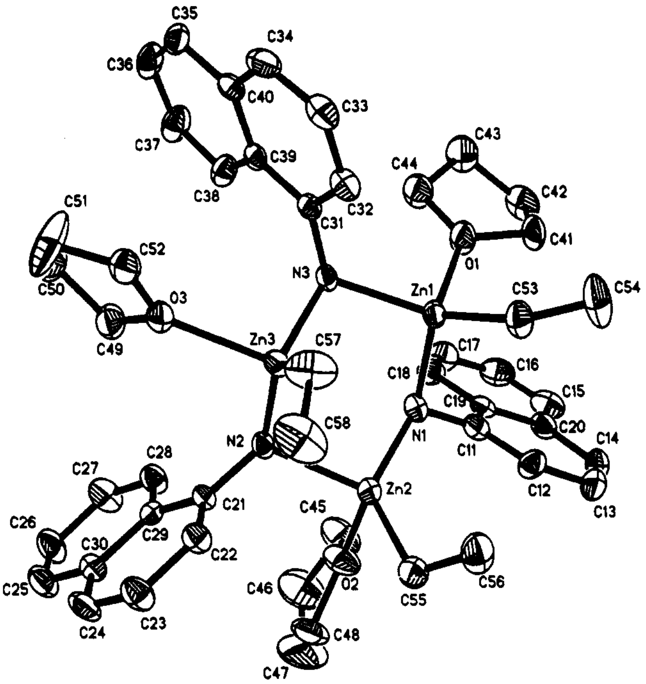

Figure 2. ORTEP drawing of 2 in the asymmetric unit. Thermal ellipsoids at the 50% level are shown. All hydrogen atoms are omitted for clarity. Selected bond distances and angles: Zn(1)–N(1) = 2.125 (8) Å, Zn(2)–N(1) = 2.038 (7) Å, Zn(2)–N(2) = 2.066 (8) Å, Zn(3)–N(2) = 2.035 (7) Å, Zn(3)–N(3) = 2.113 (6) Å, Zn(1)–N(3) = 2.041 (8) Å, average Zn–O = 2.195 (8) Å, average Zn–C = 1.992 (13) Å; average N–Zn–N = 99.7 (3)°, average Zn–N–Zn = 103.7 (3)°.

The trimeric structure of [EtZn(N(H)naphthyl)·THF]$_3$ (Figure 2) can be contrasted with that of dimeric 1. Presumably the formation of the larger ring in 2 is a consequence of the greater ionic size of Zn (ca. 0.74 Å) compared to that of Al (ca. 0.45 Å).[11] Complex 2 has a chair-shaped (cyclohexane-like) Zn_3N_3 core in which, similarly though more dramatically than in 1, there is a pattern of alternating Zn–N distances (average Zn–N (long) = 2.101 (7) Å; average Zn–H (short) = 2.038 (7) Å) (Figure 3). The only other amido–Zn complex so far characterized in the solid state is the unsolvated Zn_2N_2 dimer [MeZnNPh$_2$]$_2$ (average Zn–N = 2.072 (8) Å).[12] A related Zn–N contacted complex is the acetoximate [CH_3Zn·O—N═C(CH_3)$_2$]$_4$ (Zn–N = 2.047 (10)–2.098 (10) Å].[13]

The formation of a trimer for 2, even with THF solvation, testifies to the compact and sterically undemanding nature of the 1-amidonaphthyl ligand. Tetranuclear clusters and cages are by far the most commonly occurring structures for Zn complexes.[14] Only a few Zn_3S_3[15] and Zn_3O_3[16] ring trimers have been characterized. In these, bulky groups which preclude solvation lead to planar rather than chair-shaped Zn_3 cores. Surprisingly, within the Zn_3N_3 core of 2 all the N–H protons adopt an axial and cis conformation

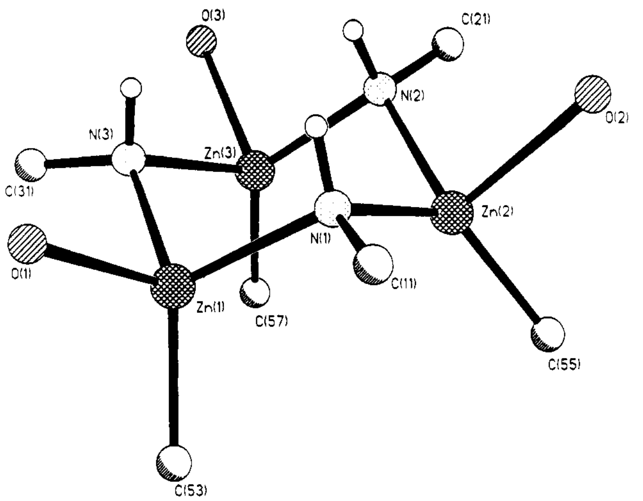

Figure 3. Core Zn_3N_3 ring structure of 2.

(cf. their trans arrangement in 1). This unusual all-cis conformation arises since greater steric repulsion would occur between the *axial* naphthyl groups in the alternative chair form. The equatorial naphthyl groups of 2 have a similarly perpendicular and syn orientation, with respect to their N–H protons, as in 1 (average N–H···H–C = ca. 1.96 Å). In both 1 and 2 this unexpected orientation presumably minimizes repulsion between the N–H proton and the ortho proton of the naphthyl group, as well as minimizing repulsion with the trans (Me, Et) groups.

Finally, both 1 and 2 are further metalated, producing the characteristic yellow fluorescent dianion, on addition of ^{n}BuLi to THF solutions. We are currently investigating the use of the lithiated derivatives of 1 and 2 as precursors to other mixed-metal complexes, i.e., by the addition and subsequent transmetalation of metal salts.

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Supplementary Material Available: Summaries of structure determinations and tables of atomic coordinates, bond lengths, bond angles, and displacement parameters for 1 and 2 (17 pages). Ordering information is given on any current masthead page.

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