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Synthesis and Structure of a Cyclic Bismuth Amide

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The chemistry of nitrogen-containing compounds of higher group 15 homologues has attracted considerable interest for 160 years starting with the first report of a phosphorus–nitrogen system by Liebig and Rose.[1,2] More recently, P–N polymers[3,4] and compounds containing low-coordinated phosphorus[5,6] led to an enhanced activity in this field. Going to the heavier group 15 elements, the number of structurally characterized nitrogen-containing compounds decreases remarkably. Especially in the case of bismuth, only a few examples of nitrogen-containing systems are known.[7–12] The first structurally characterized homoleptic bismuth amide was reported by Clegg et al. in 1989.[13] Herein we report a first example of an amino-substituted cyclic bismuth amide characterized by a single crystal X-ray structure analysis.

To a solution of lithiated 2,6-diisopropylaniline in a mixture of diethyl ether and *n*-hexane was added dropwise at room temperature a solution of $BiCl_3$ in THF. The reaction mixture immediately turned deep red. The reaction was carried out in a molar ratio of 3:1.[14] Here 1 equiv of the lithiated aniline serves as a lithiating reagent for the supposed intermediate bismuth–chloro compound **1** (Figure 1).

We were not able to isolate the chloro compound, even carrying out the reaction in a 2:1 ratio.

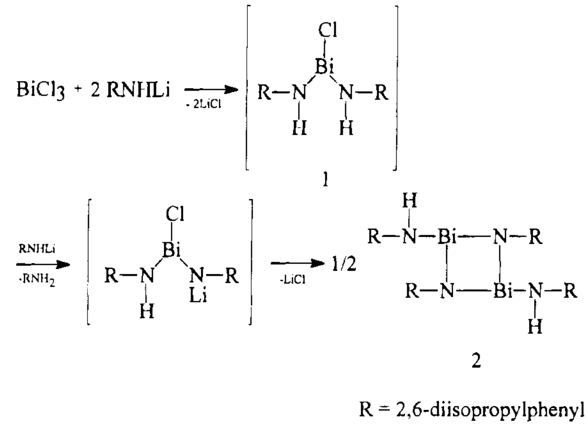

Figure 1.

The salt elimination leading to the cyclic amide **2** we assume to be intermolecular. The product formation seems to be uncorrelated with the reaction conditions. Variation of the molar ratio of the starting materials and the temperature does not affect the constitution of the product; compound **2** was the only detectable molecule. The single-crystal X-ray study reveals an amino-substituted four-membered bismuth–nitrogen ring.[15]

Cyclic and acyclic bismuth–nitrogen bonds in **2** have the same lengths (Bi(1)–N(1a) 2.158(4), Bi(1)–N(1) 2.174(5), Bi-

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(14) 2,6-Diisopropylaniline (15.9 g, 90 mmol) dissolved in diethyl ether (80 mL) was lithiated with *n*-BuLi (5.8 g, 90 mmol) dissolved in *n*-hexane (38 mL). To the lithiated amine was added dropwise at room temperature a solution of $BiCl_3$ (9.46 g, 30 mmol) in THF (60 mL). The reaction mixture immediately turned deep red. After 16 h of stirring, the solvent was removed in vacuo. To the residual oil was added *n*-hexane (40 mL) to isolate the precipitating crude product. Extraction of the solid with hexane (100 mL) in a Soxhlet apparatus and crystallization from the previous filtrate gave 9.8 g (17 mmol, 57%) of **2**: mp 163 °C; MS (EI) *m/z* (%) 768 (3) $[M^+ - 2C_{12}H_{18}N]$, 161 (100) $[C_{12}H_{17}]$; ^{13}C-NMR (100 MHz, C_6D_6, 25 °C, TMS) δ = 24.8 (Me), 25.2 (Me), 28.2 ($CHMe_2$), 29.5 ($CHMe_2$), 120.9 (arom C), 122.4 (arom C), 123.0 (arom C), 125.4 (arom C), 140.7 (arom C), 141.7 (arom C), 144.1 (arom C), 148.6 (arom C); ^1H-NMR (250 MHz, C_6D_6, 25 °C, TMS) δ = 0.98 (d, $^3J(H,H)$ = 7 Hz, 24 H; $CHMe_2$), 1.40 (d, $^3J(H,H)$ = 7 Hz, 24 H; $CHMe_2$), 2.93 (sept, $^3J(H,H)$ = 7 Hz, 4 H; $CHMe_2$), 4.54 (sept, $^3J(H,H)$ = 7 Hz, 4 H; $CHMe_2$), 5.94 (s, 2 H; NH), 6.92 (m, 12 H; arom H); IR (Nujol) ν = 3358 cm^{-1} (N–H).

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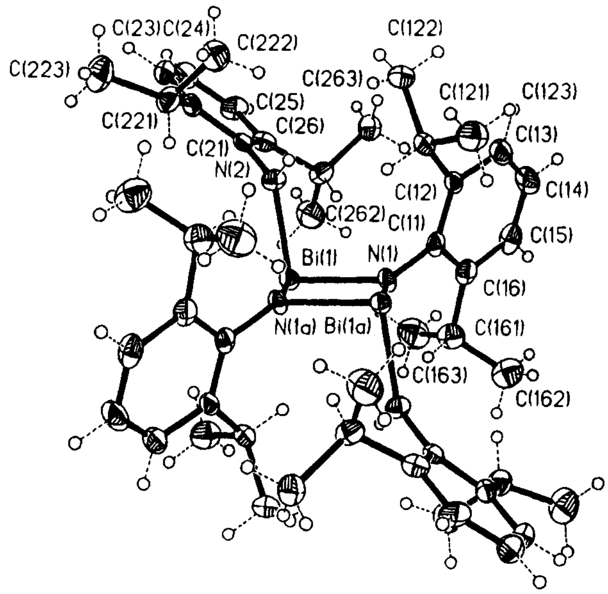

Figure 2. Molecular structure of compound **2**. Selected bond lengths (Å) and angles (deg): Bi(1)−N(1a) 2.158(4), B(1)−N(2) 2.164(4), Bi(1)−Bi(1a) 3.355(3); N(1a)−Bi(1)−N(2) 93.0(2), N(1a)−Bi(1)−N(1) 78.5(2).

(1)−N(2) 2.164(4), Bi(1a)−N(1) 2.158(4) Å). The covalent radii of nitrogen and bismuth give a calculated single-bond length of 2.24 Å.[16] In a recently reported homoleptic bismuth amide the bismuth−nitrogen single bonds range from 2.12(2) to 2.28(2) Å.[13]

Table 1. Selected Bond Lengths (Å) and Angles (deg)

Bi(1)−N(1a)	2.158(4)	Bi(1)−N(2)	2.164(4)
Bi(1)−N(1)	2.174(5)	Bi(1)−Bi(1a)	3.355(3)
N(1)−Bi(1a)	2.158(4)		
N(1a)−Bi(1)−N(2)	93.0(2)	N(1a)−Bi(1)−N(1)	78.5(2)
N(2)−Bi(1)−N(1)	97.4(2)	N(1a)−Bi(1)−Bi(1a)	39.41(11)
N(2)−Bi(1)−Bi(1a)	96.67(12)	N(1a)−Bi(1)−Bi(1a)	39.06(11)
Bi(1a)−N(1)−Bi(1)	101.5(2)	C(11)−N(1)−Bi(1a)	125.4(3)
C(11)−N(1)−Bi(1a)	125.7(3)		

Although the intramolecular Bi−Bi distance (3.355 Å) in **2** is only 10% larger than the Bi−Bi single bond in tetraorganobismuthines,[17,18] a significant metal−metal contact can be excluded.

The bond angles at bismuth in **2** vary from 78.5(2) to 97.4(2)°; the sum of angles at the metal atoms is 269°, exhibiting a trigonal pyramidal coordination geometry. For this reason, the character of the atom orbitals at bismuth contributing to the metal−nitrogen bonds should be almost exclusively p, while the electron lone pair is located in the s orbital.

On the basis of the results of Ando et al.,[7] we believe compound **2** to be an interesting starting material for further reactions. Especially the selective bond cleavage, i.e. by cumulene insertion into the cyclic metal−nitrogen bonds, should lead to new species of metallacycles.

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Supplementary Material Available: Listings of crystal and refinement data, thermal parameters, atom coordinates, and distances and angles (5 pages). Ordering information is given on any current masthead page.

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(15) Crystal data for compound **2**: $C_{48}H_{70}Bi_2N_4$, $M = 1121.04$, space group $P1$, $a = 10.392(8)$ Å, $b = 10.991(10)$ Å, $c = 11.791(9)$ Å, $\alpha = 62.51(41)°$, $\beta = 72.24(3)°$, $\gamma = 83.09(4)°$, $V = 1137(2)$ Å^3, $T = 153(2)$ K, number of reflections = 3516, R1 = 0.0222, wR2 = 0.0539, μ(Mo Kα) = 0.071 073 Å, ϱ(calcd) = 1.637 Mg m^{-3}; Refinement with SHELXL-92 against F^2.

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