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# *N,N*-Di-iso-propylcarbamato Complexes of Boron

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*N,N*-di-*iso*-propylcarbamato derivatives of boron(III) have been synthesized from di-*iso*-propylamine and boron trichloride in the presence of carbon dioxide. With a large excess of amine, a single boron product was obtained, $[NH_2{}^iPr_2][B(O_2CN^iPr_2)_4]$, **1**, while with a lower excess a mixture of **1** and of the dinuclear derivative $[B_2(O_2CN^iPr_2)_6]$, **2**, was produced. By heating in vacuo at 60 °C, solid **1** slowly converted to **2**. The transformation was reversible, **2** giving **1** back with di-*iso*-propylamine under carbon dioxide at atmospheric pressure. The molecular structure of both compounds was established by X-ray diffraction methods. Compound **1** is constituted by ion-pairs where the ammonium cation is hydrogen-bonded to the mononuclear anion. Compound **2** is a dinuclear species with two bridging carbamato ligands. In both derivatives, boron shows tetrahedral coordination. As IR- and $^1H$ NMR spectra of the two species are well differentiated, it is possible to monitor the interconversion of **1** and **2** by both spectroscopic methods.

## Introduction

Further advancing our systematic studies on *N,N*-dialkylcarbamates of transition- and nontransition elements,[1] we turned our attention to boron. Although boron has a relatively low abundance in the Earth's crust (0.001%), its chemistry is extensively studied in both experimental and theoretical fields, and several derivatives, nearly all involving boron−oxygen bonds, are widely used in industry.[2] Moreover, in recent years its biological role has been recognized, initially in plants and recently also in mammals and humans.[3]

Lappert in his pioneering work on metal amides reported the compound $B(O_2CNMe_2)_3$ as obtained by carbonation of preformed $B(NMe_2)_3$.[4] In this paper we describe two *N,N*-di-*iso*-propylcarbamates of boron, obtained from di-*iso*-propylamine, boron trichloride, and carbon dioxide, together with their structures and spectroscopic properties. Concerning the alkyl group ($^i$Pr), its choice was aimed at comparing the boron derivatives with the already known aluminum carbamato complexes.[5]

## Results and Discussion

The reaction of $BCl_3$ with $NH^iPr_2$ and $CO_2$ in toluene led to precipitation of $[NH_2{}^iPr_2]Cl$ and to formation of soluble boron carbamato complexes. By using an amine/boron molar ratio of about 15, a single boron product formed, $[NH_2{}^iPr_2][B(O_2CN^iPr_2)_4]$, **1** (see eq 1), while with a lower excess a mixture of **1** and $[B_2(O_2CN^iPr_2)_6]$, **2** (see eq 2), was obtained, the yield increasing by lowering the amine concentration.

$$BCl_3 + 8NH^iPr_2 + 4CO_2 \rightarrow [NH_2{}^iPr_2][B(O_2CN^iPr_2)_4] + 3[NH_2{}^iPr_2]Cl \quad (1)$$

$$2BCl_3 + 12NH^iPr_2 + 6CO_2 \rightarrow [B_2(O_2CN^iPr_2)_6] + 6[NH_2{}^iPr_2]Cl \quad (2)$$

**1** and **2** interconvert according to equilibrium 3. By treatment of solid **1** in vacuo at about 60 °C, a weight decrease was observed and **2** was formed quantitatively in about 2 days. On the other hand, **2**, suspended in toluene

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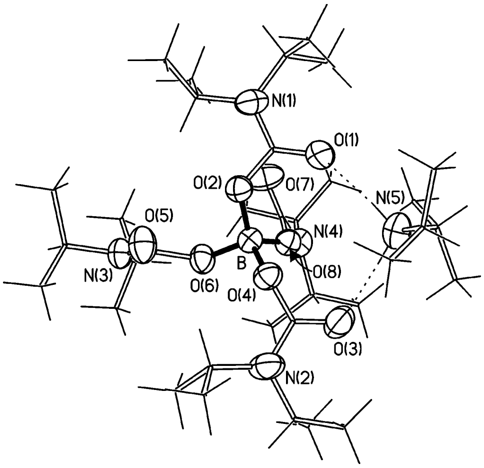

**Figure 1.** View of the molecular structure of $[\mathrm{NH_2}{}^i\mathrm{Pr_2}][\mathrm{B(O_2CN}{}^i\mathrm{Pr_2)_4}]$, **1**. Ellipsoids are at 30% probability.

**Table 1.** Selected Bond Lengths [Å] and Angles [deg] for **1**

| | | | |
|---|---|---|---|
| O(1)−C(1) | 1.210(4) | O(2)−C(1) | 1.331(4) |
| B−O(2) | 1.451(4) | O(3)−C(8) | 1.228(4) |
| O(4)−C(8) | 1.322(4) | B−O(4) | 1.481(4) |
| O(5)−C(15) | 1.217(4) | O(6)−C(15) | 1.329(4) |
| B−O(6) | 1.475(4) | O(7)−C(22) | 1.208(4) |
| O(8)−C(22) | 1.335(4) | B−O(8) | 1.446(4) |
| N(5)···O(1) | 2.716(4) | N(5)···O(3) | 2.758(4) |
| | | | |
| O(2)−B−O(4) | 108.6(2) | O(2)−B−O(6) | 107.5(2) |
| O(2)−B−O(8) | 116.8(2) | O(4)−B−O(6) | 110.9(2) |
| O(4)−B−O(8) | 107.5(2) | O(6)−B−O(8) | 105.6(2) |

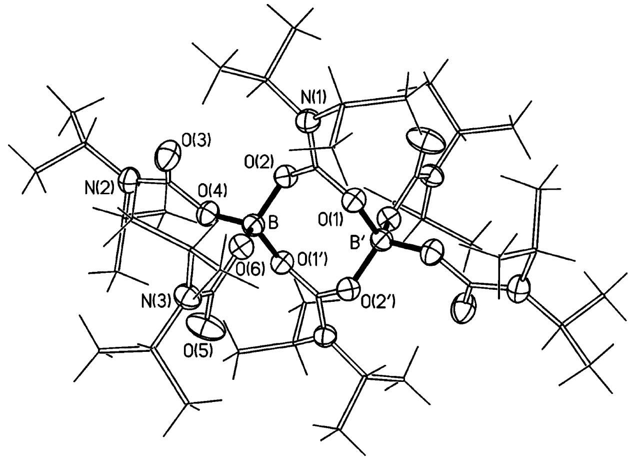

**Figure 2.** View of the molecular structure of $[\mathrm{B_2(O_2CN}{}^i\mathrm{Pr_2)_6}]$, **2**. ′ = −*x*, −*y*, 1 − *z*. Ellipsoids are at 30% probability.

**Table 2.** Selected Bond Lengths [Å] and Angles [deg] for **2**

| | | | |
|---|---|---|---|
| O(1)−C(1) | 1.286(3) | O(2)−C(1) | 1.305(3) |
| B−O(2) | 1.480(3) | O(3)−C(8) | 1.207(3) |
| O(4)−C(8) | 1.342(3) | B−O(4) | 1.451(3) |
| O(5)−C(15) | 1.209(3) | O(6)−C(15) | 1.340(3) |
| B−O(6) | 1.448(3) | B−O(1′) | 1.507(3) |
| | | | |
| O(1′)−B−O(2) | 110.0(2) | O(1′)−B−O(4) | 100.6(2) |
| O(1′)−B−O(6) | 114.1(2) | O(2)−B−O(4) | 110.5(2) |
| O(2)−B−O(6) | 106.1(2) | O(4)−B−O(6) | 115.5(2) |

and treated with an excess of the amine under carbon dioxide, converts to **1**

$$2[\mathrm{NH_2}{}^i\mathrm{Pr_2}][\mathrm{B(O_2CN}{}^i\mathrm{Pr_2)_4}] \rightleftharpoons [\mathrm{B_2(O_2CN}{}^i\mathrm{Pr_2)_6}] + 4\mathrm{NH}{}^i\mathrm{Pr_2} + 2\mathrm{CO_2} \quad (3)$$

Both products are quite soluble in aromatic hydrocarbons, **1** being more soluble than **2** in alkanes. Single crystal X-ray diffraction structures were determined for both compounds.

**1** (see Figure 1) is constituted by ion pairs, the cation being hydrogen-bonded to the mononuclear anion, $[\mathrm{B(O_2CN}{}^i\mathrm{Pr_2)_4}]^-$, containing monodentate carbamato groups. Boron shows a distorted tetrahedral geometry with O−B−O angles ranging from 105.6° to 116.8°. The more relevant bonding parameters of boron atom are listed in Table 1. Each cation interacts, through two hydrogen-bonds, with two terminal oxygen atoms of the anion, the hydrogen-bonded O···N distance corresponding to 2.74 Å (av.). Each ion-pair has Van der Waals contacts with the neighboring ones, the absence of an extended net of hydrogen-bonds within this compound accounting for its high solubility in hydrocarbons. Compounds containing moieties comparable with $[\mathrm{B(O_2CN}{}^i\mathrm{Pr_2)_4}]^-$ are, for instance, $\mathrm{K[B(O_2CMe)_4]}$[6] and $\mathrm{Si(O_2CN}{}^i\mathrm{Pr)_4}$.[5] In the former product the bond lengths associated with the $\mathrm{BO_4C_4O_4}$ core are similar to those observed in **1**. In $\mathrm{Si(O_2CN}{}^i\mathrm{Pr)_4}$ the Si−O bond lengths of the terminally bonded carbamato groups are, as expected, longer than the B−O bond lengths (av. 1.62 Å, compared with 1.46 Å in **1**), the other parameters being similar to those observed in $[\mathrm{B(O_2CN}{}^i\mathrm{Pr_2)_4}]^-$.

The two boron centers of **2** contain two bridging bidentate carbamato groups, see Figure 2. Each boron completes its tetrahedral coordination with two oxygen atoms of two terminal monodentate ligands. In the analogous aluminum compound, $[\mathrm{Al_2(O_2CN}{}^i\mathrm{Pr_2)_6}]$,[5] the hexacoordinated aluminum centers contain bidentate terminally bonded ligands. Nevertheless, both compounds have a similar $\mathrm{M_2(}\mu\mathrm{\text{-}O_2CNR_2)_2}$ core, characterized by the eight-membered ring. The M−O bond distances in the boron complex are shorter than in the aluminum one, the average $\mathrm{M{-}O_b}$ ($\mathrm{O_b}$ = oxygen atom of the bridging carbamato groups) distances being 1.49 and 1.82 Å for M=B and Al, respectively, while the $\mathrm{M{-}O_t}$ ($\mathrm{O_t}$ = oxygen atom of the terminal carbamato groups) distances are 1.45 (B) and 1.94 (Al) Å, respectively. These differences are consistent with the corresponding ionic radii,[7] namely 0.11 Å for tetracoordinated boron, and 0.53 Å for hexacoordinated aluminum. Table 2 lists the bond lengths and angles around boron atoms. The ring B−O−C−O−B−O−C−O has been observed so far in only three other boron compounds.[8] Those rings, which are built by two bridging carboxylic acids, are puckered and their shape may be compared with that of cyclohexane. **2** shows a chair shaped cycle like that found in the centrosymmetric $\mathrm{(C_8H_{14})}$-B−O−C(Ph)=O−B$\mathrm{(C_8H_{14})}$−O−C(Ph)=O,[8a,b] but with shorter B−O distances: 1.49 Å rather than 1.55 Å. A larger number of cycles of this type are found with gallium and

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aluminum compounds, a di-*iso*-propyl carbamato derivative of aluminum being more strictly comparable with **2**,[9] showing the same puckering.

A useful comparison is between **2** and the dinuclear $\mu$-oxo acetate $B_2O(O_2CMe_2)_4$,[10] as obtained by reacting $B(OH)_3$ with acetic anhydride. The two tetracoordinated boron centers contain one oxide bridge, two terminal monodentate- and two bridging bidentate carboxylato groups. The B-$\mu$-oxo bond distance is 1.38 Å, while the average $B-O_b$ and $B-O_t$ distances to the acetato ligands are 1.55 and 1.34 Å, respectively, similar to those observed in **2** for the carbamato ligands. It is interesting to note that the structure of the homoleptic boron acetate $[B(O_2CMe)_3]_n$ (or other carboxylates) has not yet been reported, and even its isolation has not been established with certainty.[11]

Compounds **1** and **2** show characteristic IR absorptions in the 1700−1500 $cm^{-1}$ region attributable to the stretching vibrations of the $NCO_2$ group. In the solid state, compound **1** shows four intense bands at 1682, 1661, 1620, and 1606 $cm^{-1}$, to be compared with the solid-state spectrum of $Si(O_2CN^iPr_2)_4$ which, in the same region, shows strong bands at 1698 and 1682 $cm^{-1}$. Although $Si(O_2CN^iPr_2)_4$ and $[B(O_2CN^iPr_2)_4]^-$ have similar connectivity and geometry, in the boron compound the symmetry of the complex is lowered by the presence of the cation, whose strong interactions with the anion produce a decrease of the CO stretching vibrational energy. The IR spectrum of **1** in heptane solution shows two absorptions at 1680 and 1616 $cm^{-1}$, (to be compared with 1705 $cm^{-1}$ observed for $Si(O_2CN^iPr_2)_4$ in $C_2Cl_4$), attributable to $[B(O_2CN^iPr_2)_4]^-$. Moreover, a band at 1590 $cm^{-1}$ can be considered to be diagnostic of the presence of **2** (vide infra). In fact, this band is weak in freshly prepared solutions and becomes progressively more intense because of the effect of the equilibrium 3.

The solid-state IR spectrum of compound **2** shows two strong bands at 1683 and 1588 $cm^{-1}$. The IR spectrum of the dinuclear aluminum complex, $Al_2(O_2CN^iPr_2)_6$, is not directly comparable, as the aluminum centers are hexacoordinate. The spectrum of **2** in heptane is similar to the solid-state spectrum, with strong absorptions at 1690 and 1590 $cm^{-1}$. When a solution of **2** was treated with $NH^iPr_2$ and $CO_2$ ($P = 1$ atm), the conversion to **1** can be monitored by the progressive intensity decrease of the band at 1590 $cm^{-1}$. Starting from a 0.2 M solution of **2**, the conversion is complete when an amine/**2** molar ratio of about 20 is used.

The NMR spectra confirm the IR data in solution. Room temperature spectra of **2** in $C_6D_6$ are comparable with the solid-state structure. The $^{13}C$ spectrum shows resonances at 158.7 and 153.5 ppm, due to the $NCO_2$ group of bridging and terminal ligands, respectively. Regarding alkyl groups, in both CH and $CH_3$ regions, three signals are observed, at 48.3, 46.0, and 45.2 ppm and at 21.7, 21.0, and 20.3 ppm. We suggest that the four isopropyl groups of the bridging ligands are equivalent and produce the signals at 48.3 (*C*H) and 20.3 ppm (*C*$H_3$). On the other hand, in the terminal monodentate ligands the equivalence of the alkyl groups depends on the energy barrier to rotation around the $O_2C-NR_2$ bond. A hindered rotation can explain the presence of two resonances for both the *C*H and the *C*$H_3$ carbon nuclei of these fragments. A comparison with other complexes containing monodentate *N,N*-dialkylcarbamato ligands shows that a precedent of this type was encountered with *cis-cis-trans*-$Ru(O_2CN^iPr_2)_2(CO)_2(PPh_3)_2$,[12] where the two equivalent $O_2CN^iPr_2$ groups produce signals at 44.2 and 46.7 ppm (*C*H) and at 21.3 and 21.9 ppm (*C*$H_3$).

The $^1H$ NMR spectrum of **2** shows multiplets at 4.3 and 4.0 ppm, attributable to the C*H* protons of the bridging and terminal ligands, and doublets at 1.36 and 1.32 ppm, assigned to the methyl protons of the terminal and bridging ligands. The $^1H$ NMR spectrum may be simpler than expected because of overlap of one of the signals of the non equivalent alkyl groups of the terminal ligands with the signals of the bridging groups. It is interesting to note that, unlike the analogous aluminum derivative $Al_2(O_2CN^iPr_2)_6$, there is no rapid exchange, on the NMR time scale, between bridging and terminal groups at room temperature.

The $^1H$- and $^{13}C$ NMR spectra of **1** ($C_6D_6$) are complicated by the presence in solution of **1**, **2**, and $NH^iPr_2$ (see eq 3). However, the $^1H$ NMR spectra of freshly prepared solutions, which contain a minor quantity of **2** only, allow the signals of **1** to be assigned. A broad resonance at 10.4 ppm is attributable to N−H protons. Of the three septets at 4.8, 3.5, and 2.8 ppm (relative intensity 2:2:1), due to the isopropyl CH, the last one is assigned to the cation, while the others are due to the anion. The non equivalence of the eight isopropyl groups of the anion can be related, as discussed above, to the hindered rotation around the $O_2C-NR_2$ bond. An alternate explanation could be derived from the solid-state structural data. In the crystal, two of the four carbamato ligands in each anion are hydrogen bonded to one cation (see Figure 1). If this interaction is maintained in solution, the two pairs of ligands will be nonequivalent. The latter hypothesis appears to be disproved by the $^{13}C$ NMR spectrum, which shows only one resonance (vide infra) attributable to the $O_2$*C*N groups.

Equilibria of the type of eq 3 have already been encountered in carbamato complexes, the first examples being derivatives of Ti(III) and V(III).[13] More recently, systems involving zinc *N,N*-dimethylcarbamato species have been reported.[14] These conversions must be rather common and can explain why an enhanced solubility of the carbamato complexes is often observed in the presence of amine and $CO_2$: this behavior is

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probably related to the fragmentation of the polynuclear neutral complexes to anions of lower nuclearity.

It is interesting to note that, although the complexes containing the $O_2CN^iPr_2$ group are normally hydrolyzed quite readily,[15] the two boron derivatives are rather resistant to this type of attack, this behavior suggesting a slow attack at the tetrahedral boron.

## Conclusions

The new boron derivatives reported in this paper enlarge the family of the *N,N*-dialkylcarbamato complexes of main group elements. In both compounds the tetrahedral boron coordination observed in the solid state is probably maintained in solution. The conversion of the dinuclear $B_2(O_2CN^iPr_2)_6$ to the mononuclear $[B(O_2CN^iPr_2)_4]^-$ is a simple and clear example of fragmentation of this class of derivatives in the presence of amine and $CO_2$. Anionic carbamato complexes of low nuclearity have already been encountered with titanium(III)[13] and zinc(II),[14] while a complex of higher nuclearity has been characterized for magnesium.[16] In all cases, equilibria of the type described below (eq 4, $m > p$) have been evidenced.

$$(1/m)[M(O_2CNR_2)_n]_m + 2xNHR_2 + xCO_2 \rightleftharpoons (1/p)[NH_2R_2]_x[M_p(O_2CNR_2)_{n+x}] \tag{4}$$

The moderate reactivity of the new boron products to moisture suggests their possible use as precursors to $\mu$-oxo derivatives of higher nuclearity, as already established for many *N,N*-dialkylcarbamato complexes.

Finally, the new results suggest that the compound $B(O_2CNMe_2)_3$ obtained by Lappert and co-workers by carbonation of $B(NMe_2)_3$[4] has presumably a dinuclear structure similar to that of the di-*iso*-propyl derivative reported in this paper.

It is interesting to note that, although $BCl_3$ reacts with several secondary amines producing $B(NR_2)_3$, the hindrance due to the branching on the α-carbon atom of the alkylamino group prevents the formation of derivatives like $B(N^iPr_2)_3$, the product of the double substitution only, $BCl(N^iPr_2)_2$, being recovered.[4b] In our derivatives, the encumbrance of the *iso*-propyl groups is moved away from the small boron center by insertion of the $CO_2$ spacer.

## Experimental Section

**General Procedures.** All preparations were carried out in standard Schlenk tubes. Solvents were freshly distilled over conventional drying agents under $N_2$, and all manipulations were carried out under $N_2$ atmosphere, unless otherwise specified.

Commercial (Aldrich) boron trichloride and di-*iso*-propylamine were purified by conventional methods. Elemental analyses (C, H, N) were performed by Laboratorio di Microanalisi della Facoltà di Farmacia, Università di Pisa, with a C. Erba mod. 1106 elemental analyzer. IR spectra were measured with a Perkin-Elmer FT-IR mod. Spectrum-one spectrophotometer equipped with ATR accessory. NMR spectra were recorded using a Varian Gemini 200BB instrument, the data being expressed in ppm from TMS for $^1H$ and $^{13}C$, and from $BF_3 \cdot Et_2O$ for $^{11}B$.

**Synthesis of $[NH_2{}^iPr_2][B(O_2CN^iPr_2)_4]$ (1) and Conversion to 2.** Boron trichloride (3.30 g, 28.1 mmol) was condensed into a solution of di-*iso*-propylamine (65 cm$^3$, 0.464 mol) in toluene (200 cm$^3$) at 0 °C. A prompt exothermic reaction occurred with formation of a colorless precipitate. The mixture was stirred and saturated with carbon dioxide. After stirring under carbon dioxide for 3 days, $[NH_2{}^iPr_2]Cl$ was removed by filtration. The chloride-free filtrate was concentrated to a third of its volume, no precipitation of solid material being observed even at 5 °C. After removing all the volatiles in vacuo, the resulting residue was dried for 12 h ($5 \times 10^{-2}$ Torr at 18 °C), and the title compound was recovered (13.62 g, 70% yield). Anal. Calcd for $C_{34}H_{72}BN_5O_8$): C, 59.2; H, 10.5; N, 10.2. Found: C, 58.6; H, 10.7; N, 10.2%. IR (neat solid; 1750−700 cm$^{-1}$): 1682 (s), 1661 (s), 1620 (vs), 1606 (vs), 1502 (w), 1427 (s), 1374 (m), 1363 (m), 1339 (vs), 1323 (vs), 1218 (m), 1189 (m), 1157 (m), 1132 (m), 1098 (w), 1050 (vs), 986 (m), 930 (vs), 887 (s), 864 (m), 814 (m), 768 (m), 755 (m), 715 (w). For IR data in solution (heptane) and for NMR spectra ($C_6D_6$) see the Results and Discussion section. Colorless rod-like crystals for the X-ray diffractometric experiment were obtained by cooling down to 0 °C a solution (heptane) of **1**.

Although no significant weight loss was observed by treating the product in vacuo ($5 \times 10^{-2}$ Torr) at 20 °C, the conversion of **1** into **2** was complete in 32 h at 60 °C: the weight loss from 4.44 g of $[NH_2{}^iPr_2][B(O_2CN^iPr_2)_4]$ (6.44 mmol) was 1.45 g (91% of the calculated amount). The resulting residue gave satisfactory analytical results. Calcd for ($C_{21}H_{42}BN_3O_6$): C, 56.9; H, 9.6; N, 9.5. Found: C, 56.4; H, 10.3; N, 8.9%. IR (neat solid; 1750−700 cm$^{-1}$) 1683 (vs), 1663 (sh), 1588 (s), 1533 (m), 1434 (s), 1400 (w), 1372 (m), 1364 (m), 1335 (s), 1305 (s), 1215 (m), 1202 (m), 1184 (m), 1154 (m), 1135(m), 1103 (m), 1083 (sh), 1071 (sh), 1059 (vs), 1038 (m), 1009 (m), 929 (sh), 916 (vs), 895 (m), 873 (m), 862 (m), 814 (m), 787 (m), 779 (m), 766 (s), 734 (w). IR (heptane solution; 1800−1500 cm$^{-1}$) 1690 (s), 1580 (s). $^1H$ NMR ($C_6D_6$, ppm): 1.2 (d $CH_3$ $^iPr$), 1.3 (d $CH_3$ $^iPr$), 3.9 (m $CH$ $^iPr$), 4.2 (m $CH$ $^iPr$); $^{11}B$-NMR ($C_6D_6$, ppm): −1.3 (s). For the $^{13}C$ NMR ($C_6D_6$, ppm) data, see the Results and Discussion section. X-ray quality colorless small prismatic crystals were obtained by cooling a solution (heptane) of **2** down to 0 °C.

To convert **2** back to ionic **1**, 0.38 g of **2** (0.86 mmol) was added to a solution of di-*iso*-propylamine (2.4 cm$^3$, 17.2 mmol) in heptane (50 mL) under carbon dioxide at atmospheric pressure. The mixture was stirred for 4 days (until no further gas uptake was observed), and the resulting solution was cooled down to 0 °C yielding colorless crystals (1.48 g; 79.1% yield). The IR spectrum of the recrystallized product was identical to that of **1**.

**X-ray Crystallographic Studies.** X-ray crystallographic analysis of **1** and **2** was performed using synchrotron radiation data, collected at ELETTRA (XRD-1 beam line), Trieste, Italy, $\lambda = 1.0000$ Å. A marCCD detector (marUSA Inc., U.S.A.) and focusing optics were employed for the measurements. Ninety-five diffraction images of the crystal of **1** were collected at R.T. with a 2° oscillation range. The degree of linear polarization was assumed to be 0.95, and the mosaic spread of the crystal was estimated to be 0.42°. Raw data were indexed, integrated, scaled, and reduced using the HKL package.[17] The specimen used ($0.20 \times 0.36 \times 0.49$ mm$^3$) belongs to the orthorhombic system, space group *Pbca* with the lattice parameters listed in Table 3. The intensity data were merged to

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**Table 3.** Crystal Data and Structure Refinements

| compound | **1** | **2** |
|---|---|---|
| empirical formula | $C_{34}H_{72}BN_5O_8$ | $C_{42}H_{84}B_2N_6O_{12}$ |
| formula weight | 689.78 | 886.77 |
| crystal system | orthorhombic | monoclinic |
| space group | *Pbca* (No. 61) | $P2_1/n$ (No. 14) |
| $a$/Å | 37.893(4) | 11.218(1) |
| $b$/Å | 15.673(2) | 20.602(2) |
| $c$/Å | 15.151(2) | 11.453(1) |
| $\beta$/° |  | 95.28(2) |
| $U$/Å$^3$ | 8998.1(19) | 2635.7(4) |
| $Z$ | 8 | 2 |
| $D$calc/Mg·m$^{-3}$ | 1.018 | 1.117 |
| $\mu$/mm$^{-1}$ | 0.573 | 0.653 |
| no. measured | 20236 | 10100 |
| no. unique [$R_{int}$] | 3767 [0.0348] | 2787 [0.0219] |
| No. parameters | 434 | 281 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0684, 0.1877 | 0.0635, 0.1600 |
| $R_1$, $wR_2$ (all data) | 0.0955, 0.2067 | 0.0878, 0.1884 |
| Goodness of fit on $F^2$ | 1.087 | 1.190 |

give 3767 unique reflections, of which 3480 with $I \geq 2\sigma(I)$. The structure was solved using SHELXS-97[18] and refined by full-matrix least-squares procedures. Hydrogen atoms were located from a difference Fourier map. In the final refinement cycle, anisotropic thermal parameters were used for all non-hydrogen atoms while the hydrogens were refined isotropically using a riding model. The final reliability factors are listed in Table 3.

Sixty-three diffraction images of the crystal of **2** were collected with a 3° oscillation range. Raw data were indexed, integrated, scaled, and reduced using the HKL package estimating for the crystal a mosaic spread of 0.38°. The specimen used ($0.08 \times 0.09 \times 0.14$ mm$^3$) showed monoclinic symmetry, space group $P2_1/n$ with the lattice parameters listed in Table 3. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using $F^2$.[18] Non-hydrogen atoms were refined anisotropically. H-atoms were placed in calculated positions and refined by a riding model. The final reliability factors are listed in Table 3. All calculations were performed on a microcomputer using the SHELXL-97 and WINGX programs.[18,19] The X-ray crystallographic data of compounds **1** and **2** in the form of CIF files have also been deposited with the Cambridge Crystallographic Data Center, Dep. No. CCDC 670612 and CCDC 670613, respectively.

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**Supporting Information Available:** X-ray crystallographic data of compounds **1** and **2** in the form of CIF file data. This material is available free of charge via the Internet at http://pubs.acs.org.

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