Synthesis and Crystal Structure of Hexakis(ammonia–cyanoborane)-sodium Iodide

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The preparation of the crystalline complex $[Na\{NH_3\cdot BH_2(CN)\}_6]I$ from $NMe_3\cdot BH_2I$ and NaCN in liquid NH_3 is described. Structural details have been obtained by single-crystal *X*-ray analysis of the rhombohedral crystals which belong to space group $R\bar{3}$, with $a = b = c = 8.506(4)$ Å, $\alpha = \beta = \gamma = 82.54(4)°$, and $Z = 1$. The structure has been solved by the heavy-atom method from 1 293 unique reflections measured by diffractometer and refined by full-matrix least-squares calculations to R 0.063. The $NH_3\cdot BH_2(CN)$ units are arranged in a regular octahedral manner about both the Na^+ and I^- ions with $Na^+ \cdots N$(cyano) 2.487(4) Å and $Na^+ \cdots N{-}C$ 134.2(4)°; evidence for a linear correlation between such distances and angles in related complexes is presented. The B–N, B–C, and C≡N distances are 1.581(8), 1.579(8), and 1.152(7) Å, respectively.

ALTHOUGH several adducts of cyanoborane have been prepared,[1] there has been only one report of the synthesis of the parent compound, ammonia–cyanoborane.[2] Our attempts to repeat the preparation of this compound by the method of Bratt *et al.*[2] were unsuccessful, resulting instead in the production of a novel octahedral complex which we have identified as $[Na\{NH_3\cdot BH_2(CN)\}_6]I$. We report the synthesis of this complex and its characterization by single-crystal *X*-ray analysis.

EXPERIMENTAL

Infrared spectra were run as Nujol mulls or KBr discs on Perkin-Elmer 137 or 297 spectrometers. The mass spectrum was obtained on an MS-902 spectrometer at the Research Triangle Institute Centre for Mass Spectrometry, Research Triangle Park, North Carolina. Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Sodium cyanide, hexane, ammonia, and anhydrous diethyl ether were obtained commercially and used without further purification. The complex $NMe_3\cdot BH_2I$ was prepared by use of published procedures [3] and sublimed before use.

Preparation of $[Na\{NH_3\cdot BH_2(CN)\}_6]I$.—Sodium cyanide (20.5 g, 0.42 mol) and $NMe_3\cdot BH_2I$ (82 g, 0.41 mol) were placed in a flask (500 cm^3) which was equipped with a magnetic stirring bar and attached to a standard vacuum system. Following evacuation of the flask, NH_3 (*ca.* 250 cm^3) was condensed into it at −78 °C. The mixture was then stirred and allowed to warm slowly to room temperature with excess of NH_3 being allowed to escape through a mercury bubbler. After stirring at room temperature overnight, the remaining NH_3 was removed *in vacuo* leaving a white solid which was stirred with three separate portions (25—50 cm^3) of anhydrous diethyl ether; the decantates were combined and filtered under nitrogen. Hexane was then added slowly with gentle swirling until faint cloudiness became evident, at which point the solution was allowed to stand for 1—3 d. The product was collected by filtration and dried *in vacuo* to give $[Na\{NH_3\cdot BH_2(CN)\}_6]I$ (8.94 g, 27.0%), m.p. 94—95.5 °C. When excess of hexane was added beyond the point of first visible cloudiness, some precipitation of an unidentified powder-like substance of high melting point (>140 °C) was observed. When this occurred, all the solvents were removed *in vacuo* and the residue was subjected to the above procedure. The mass spectrum of the complex contained a peak at m/e 55 (relative intensity 18.1) which is assignable to $[BCH_4N_2]^+$, the $[M - 1]^+$ ion of $NH_3\cdot BH_2(CN)$. The i.r. spectrum consisted of absorptions at 3 280s,br, 3 150s,br, 2 760w, 2 405s, 2 345m (sh), 2 260m, 2 195m, 2 110w, 1 770w,br, 1 635w, 1 575m, 1 385s, 1 175m, 1 130s, 1 070m, 905s, 815m, and 710m cm^{-1} (Found: C, 15.05; H, 6.35; B, 12.7; N, 34.9. Calc. for $C_6H_{30}B_6IN_{12}Na$: C, 14.85; H, 6.20; B, 13.35; N, 34.65%).

When the complex was heated to 105 °C for 1 h there was no change in the i.r. spectrum or m.p. An aqueous solution of the complex (in an evacuated flask) was stable towards evolution of H_2 over a period of at least 2 d.

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Acid Hydrolysis of [Na{$NH_3 \cdot BH_2(CN)$}$_6$]I.—When the complex (0.096 g, 0.198 mmol) was mixed with excess of concentrated HCl in an evacuated flask on a vacuum system, hydrogen evolution was very slow. The evolved hydrogen was transferred by a Toepler pump and measured in a gas burette (Found: 0.052 mmol, 2.18% after 1 h; 0.196 mmol, 8.24% after 70 h. Calc. based on 12 hydridic hydrogen atoms per mol of complex: 2.38 mmol).

Basic Hydrolysis of [Na{$NH_3 \cdot BH_2(CN)$}$_6$]I.—When the complex (0.150 g, 0.309 mmol) was allowed to react with excess of 1N NaOH in an evacuated flask, more rapid hydrogen evolution was observed (Found: 3.62 mmol, 97.6% after 45 min; 3.68 mmol, 99.2% after 20 h. Calc. based on 12 hydridic hydrogen atoms per mol of complex: 3.71 mmol).

Crystal Data.—$C_6H_{30}B_6IN_{12}Na$, $M = 485.2$, Rhombohedral, $a = b = c = 8.506(4)$ Å, $\alpha = \beta = \gamma = 82.54(5)^\circ$, $U = 601.0$ Å^3, D_m (flotation) $= 1.34$ g cm^{-3}, $Z = 1$, $D_c = 1.340$ g cm^{-3}, $F(000) = 244$. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) $= 110$ cm^{-1}. Space group $R\bar{3}(C^2_{3i})$ by structure solution and refinement.

Crystallographic Measurements.—Preliminary unit-cell dimensions and space-group information were obtained from oscillation and Weissenberg photographs taken with Cu-K_α radiation and from precession photographs taken with Mo-K_α (λ 0.710 7 Å) radiation. For intensity measurements, a crystal of dimensions *ca.* 0.24 × 0.24 × 0.24 mm, sealed inside a thin-walled glass capillary to prevent deterioration, was orientated on an Enraf–Nonius CAD-3 automated diffractometer (nickel-filtered Cu-K_α radiation; 3° take-off angle). Refined unit-cell parameters were derived from least-squares treatment of the θ, χ, and ϕ angles for 40 accurately centred high-order reflections widely separated in reciprocal space. The effects of absorption were determined from the ϕ dependence of the $3\bar{3}3$ reflection measured at χ 90°. Intensities for all the accessible reflections to θ 67° were recorded by the θ—2θ scanning procedure with scan widths $(1.00 + 0.50\tan\theta)^\circ$. Stationary background measurements were made at each end of the scan range for half the duration of the scan period. Instrument and crystal stability, monitored throughout by remeasuring the intensity of the 202 reflection after each batch of 99 measurements, showed only insignificant random variation. From a total of 2 158 measurements, the 1 885 reflections for which $I > 2.0\sigma(I)$, where $\sigma^2(I)$ = (scan count + total background count), were corrected for absorption, Lorentz, and polarization effects, and equivalent forms then merged into a unique set of 1 293 observed reflections which were used for the structure refinement.

Structure Analysis.—The measured crystal density when considered in conjunction with the mass-spectral data and elemental analysis suggested the presence of an iodine atom. Since the actual nature of the complex was unknown, the structural problem was treated initially as belonging to space group $P1$ with the iodide ion placed at the origin of the unit cell. Evaluation of three-dimensional Patterson and iodine-phased (R 0.31) Fourier syntheses revealed a large peak at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ which was ascribed to a sodium ion since this was present in the synthetic procedure and could accord with the anticipated high site symmetry. A subsequent difference-Fourier synthesis (R 0.29) yielded positions for three pairs of centrosymmetrically related N–B–C–N units. After refinement of atomic positional and isotropic thermal parameters to R 0.087 by several cycles of full-matrix least-squares calculations, inspection of the co-ordinates molecules revealed that they conformed to the six-fold general positions of space group $R\bar{3}$, and all the subsequent calculations were performed by use of the appropriate equivalent positions.

Hydrogen-atom positions were then located in a difference-Fourier synthesis and, with their contributions included in the next structure-factor calculation, R decreased to 0.070. Several further rounds of least-squares calculations, during which hydrogen-atom positional and isotropic thermal parameters, boron, carbon, and nitrogen positional and anisotropic thermal parameters, and sodium and iodine isotropic thermal parameters were varied, brought the refinement to convergence at R 0.063. Final values for the atomic positional parameters are in Table 1.

TABLE 1

Fractional atomic co-ordinates (× 10^4; H, × 10^3) with estimated standard deviations in parentheses

Atom	x	y	z
Na	5 000(—)	5 000(—)	5 000(—)
I	0(—)	0(—)	0(—)
N(1)	1 978(5)	−1 050(5)	6 095(5)
B(2)	1 994(8)	640(7)	5 074(8)
C(3)	3 441(6)	1 475(6)	5 434(6)
N(4)	4 443(6)	2 177(5)	5 664(6)
H(1A)	107(11)	−176(10)	581(11)
H(1B)	180(9)	−111(9)	719(9)
H(1C)	293(8)	−163(8)	591(8)
H(2A)	93(6)	147(6)	539(6)
H(2B)	215(11)	45(11)	373(12)

A list of observed and calculated structure amplitudes and thermal parameters is in Supplementary Publication No. SUP 22126 (11 pp.).*

For all the structure-factor calculations, scattering factors for ionic sodium and iodine (corrected for the real part of anomalous dispersion [4]), and for neutral boron, carbon, and nitrogen, were taken from ref. 5, and for hydrogen from ref. 6. In the least-squares calculations, $\Sigma w\Delta^2$ was minimized, with weights w being assigned according to the scheme $w^{\frac{1}{2}} = 1$ for $|F_o| \leqslant 32.0$ and $w^{\frac{1}{2}} = 32.0/|F_o|$ for $|F_o| > 32.0$; no systematic dependence was revealed when $\Sigma w\Delta^2$ was analysed in ranges of $|F_o|$. Calculations were made on an I.B.M. 370/165 computer at the Triangle Universities Computation Centre, North Carolina, using locally written programs.

RESULTS AND DISCUSSION

The X-ray analysis establishes that the crystalline reaction product is the 6 : 1 ammonia–cyanoborane complex with sodium iodide, [Na{$NH_3 \cdot BH_2(CN)$}$_6$]I. The atom-numbering scheme and packing arrangement in the crystal are shown in Figure 1. Interatomic distances and angles are in Table 2.

The iodide ions are located at the corners of the rhombohedral unit cell (Wyckoff position 1*a*,[7] $\bar{3}$ site

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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symmetry) and the sodium ions are at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ (Wyckoff position 1*b*, $\bar{3}$ site symmetry). Interposed between these ions are the $NH_3{\cdot}BH_2(CN)$ units which occupy the six-fold *general* positions of space group $R\bar{3}$ and are consequently distributed in a regular octahedral arrangement around both the sodium and iodide ions.

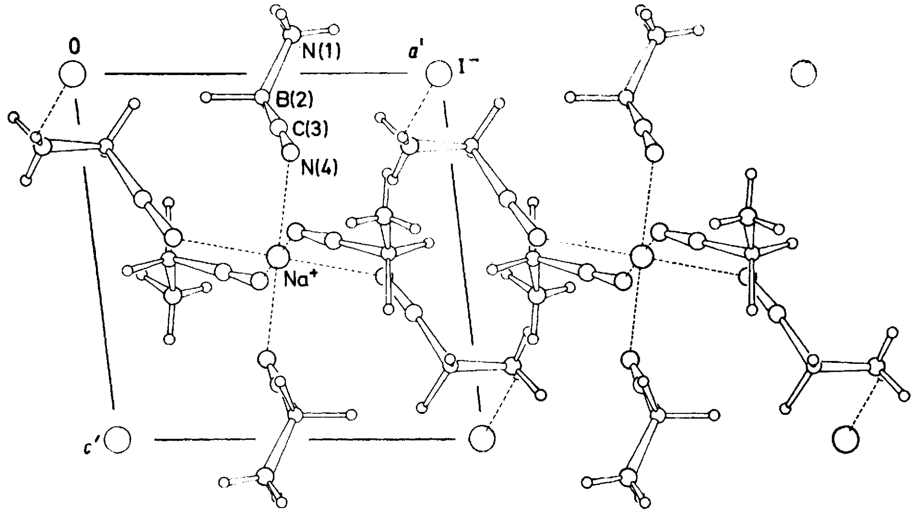

FIGURE 1 Atom-numbering scheme and crystal structure of $[Na\{NH_3{\cdot}BH_2(CN)\}_6]I$ viewed in projection along the *b* axis; small circles denote hydrogen atoms

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances			
N(1)–B(2)	1.581(8)	N(1)–H(1C)	0.89(7)
B(2)–C(3)	1.579(8)	B(2)–H(2A)	1.10(5)
C(3)–N(4)	1.152(7)	B(2)–H(2B)	1.16(10)
N(1)–H(1A)	1.11(9)	N(4) ··· Na	2.487(4)
N(1)–H(1B)	0.92(8)		
(*b*) Angles			
N(1)–B(2)–C(3)	109.7(5)	C(3)–N(4) ··· Na	134.2(4)
B(2)–C(3)–N(4)	175.8(5)		

The $Na^+ \cdots N$(cyano) distance [2.487(4) Å] in the complex is close to the means of 2.492 Å in sodium α,α,α′,α′-tetracyanoquinodimethanide [8] [range 2.418(3)—2.565(4) Å] and 2.512 Å in $Na[C(CN)_3]$ [2.374(3)—2.613(3) Å].[9] Associated with these ranges of distances characterizing distorted octahedral arrangements around Na^+, in each of the latter complexes is a corresponding range (107.4—166.9°) of $Na^+ \cdots N{-}C$ angles. A plot of these angles against the $Na^+ \cdots N$ distances shows that they vary in a systematic manner (see Figure 2) which strongly suggests that the value assumed by the $Na^+ \cdots N{-}C$ angle is not merely a consequence of random crystal-packing forces but may be dependent on the charge density at nitrogen; the shorter is the $Na^+ \cdots N$ distance the closer to 180° is the $Na^+ \cdots N{-}C$ angle, and the longer is the $Na^+ \cdots N$ distance the more bent is the $Na^+ \cdots N{-}C$ angle. (A complete list of the data plotted is available in SUP 22126.) Substitution of the $Na^+ \cdots N$ distance from the present study into the derived least-squares equation through the plotted values [$\theta = al + b$, where θ (°) is the $Na^+ \cdots N{-}C$ angle, $a = -232.1°\ Å^{-1}$, $b = 715.7°$, and l (Å) is the $Na^+ \cdots N$ distance] yields a calculated value for the $Na^+ \cdots N{-}C$ angle of 138.4(1)° which accords well with the experimentally observed value of 134.2(4)°. Since the $Na^+ \cdots N{-}C$ angle found in the title complex lies closer to 120 than to 180°, it appears that canonical form B makes a greater contribution than A. On the other hand, the C(3)–N(4) distance [1.152(7) Å] is in excellent agreement with the normal C≡N value [4,10] [1.158(2) Å] and consequently shows no evidence of any elongation which might be expected to accompany the change in hybridization associated with form B. This observation may be rationalized if the expected elongation from this source is counterbalanced

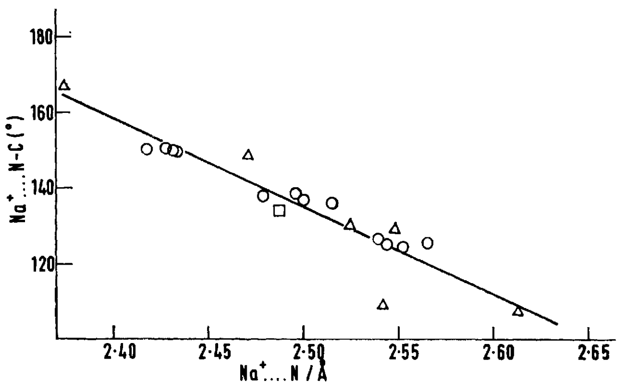

FIGURE 2 Plot of the variation of $Na^+ \cdots N{-}C$ angle with $Na^+ \cdots N$ distance: (○) sodium α,α,α′,α′-tetracyanoquinodimethanide;[8] (△) sodium tricyanomethanide;[9] (□) present work

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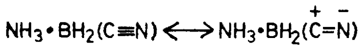
by increased ionic attraction between the carbon and nitrogen atoms in zwitterionic form B, thereby resulting in a constancy of bond length in forms A and B. Similar effects appear to be operative in determining the C–N distances in aliphatic amines [11a] and the N–N lengths in ylides.[11b] Alternatively, in form B the nitrogen atom may be viewed as having a non-equivalent set of sp^2-hybridized orbitals of which one with an above-average amount of s character is directed towards the carbon atom.



$$NH_3\cdot BH_2(C{\equiv}N) \longleftrightarrow NH_3\cdot BH_2(\overset{+}{C}{=}\overset{-}{N})$$

(A) (B)

Bond lengths involving the boron atom are not unusual. The B(2)–C(3) distance [1.579(8) Å] is close to that of 1.56 Å in $[BH_3(CN)]^-$ (ref. 12) and $[BH_2(CN)]_6$,[13] and the B(2)–N(1) bond length [1.581(8) Å] does not differ significantly from those found for other related compounds [14-16] [1.578(7)—1.581(3) Å]. Since it has been demonstrated that B–N distances provide some indication of donor and acceptor strengths,[14,17] the close correspondence between the bond length in the title complex and that of 1.578(8) Å in $NH_3\cdot BH_2(NCS)$ [14] indicates that $BH_2(CN)$ must have an acceptor strength similar to $BH_2(NCS)$. The mean B–H distance (1.13 Å) is also in good accord with accepted values.[4]

The mean N–H distance (0.97 Å) is normal.[4] The shortest separation involving the NH_3 group and the iodide ion is H(1B) $\cdots$ I^- at 2.87 Å with an associated N(1)–H(1B) $\cdots$ I^- angle of 149.1°. This distance is significantly less than the sum of the van der Waals radii [18,19] (3.15 Å) and probably represents a weak hydrogen-bonded interaction.[20]

The procedure used to prepare $[Na\{NH_3\cdot BH_2(CN)\}_6]I$ differed only slightly from that described by Bratt *et al.*[2] for $NH_3\cdot BH_2(CN)$ in that the reaction mixture was allowed to warm to ambient temperature to facilitate removal of NH_3. Although we have found no evidence for uncomplexed $NH_3\cdot BH_2(CN)$ in this system, the compound may be generated from $[Na\{NH_3\cdot BH_2(CN)\}_6]I$ by dissolution in water followed by extraction with diethyl ether. Various alternative preparations of $NH_3\cdot BH_2(CN)$ will be the subject of a subsequent publication.

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