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Susan A. Bourne[a]; Renate H. Haueisen[a]; Roger Hunter[a]
[a] Department of Chemistry, University of Cape Town, Rondebosch, South Africa

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Preparation and structure of an air stable sodium cyanoborate salt

SUSAN A. BOURNE, RENATE H. HAUEISEN and ROGER HUNTER

Department of Chemistry, University of Cape Town, Rondebosch, 7700, South Africa

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The structure of the disodium 1,6-bis(B-cyano-9-boratabicyclo[3.3.1] non-9-yl)hexane inclusion compound with dimethylformamide guests (1) is reported. Crystal data: (1) is triclinic, $P\bar{1}$ with a=13.661(2), b=13.821(2), c=14.917(4) Å, α=75.98(2), β=73.08(1), γ=86.92(1)°, Z=2, Dc=1.096 g cm^{-3}. The final R value was 0.071 for 4439 reflections and 575 variables. The anion's hexane spacer is held in a *cisoid* conformation to allow coordination of the cyano groups to the sodium cations. The DMF molecules are tightly bound to the host; thermal analysis was used to evaluate the strength of binding and established that only four of the six guests are released before the decomposition of the complex.

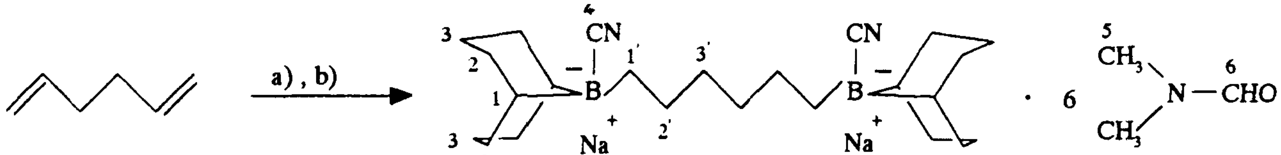
INTRODUCTION

The cyanidation[1] of organoboranes to afford cyanoborates, followed by Lewis acid induced 1,2-migration of a group from boron to the cyano carbon is a well documented process in synthetic organic chemistry. The intermediate cyanoborate is normally not isolated in view of its air-sensitivity, and is usually prepared in THF. We have recently reported[2] that bis(methyltriphenylphosphonium)1,6-bis(B-cyano-9-boratabicyclo[3.3.1]non-9-yl)hexane (2) forms both solid and liquid clathrates with furan, depending on the water content. An X-ray structure of the solid clathrate beween (2) and furan (1:2) revealed hydrogen bonding between a cyano nitrogen and a hydrogen of a phosphonium methyl holding the coordination-assisted lattice together. (2) was synthesized from the intermediate sodium salt (1) which crystallized out of solution as a coordination complex with DMF that had been used as solvent for the cyanidation (Scheme 1).

In this paper, we report on the X-ray structural analysis of (1) as it is the first documented X-ray structure of an air-stable sodium cyanoborate salt. As with the furan clathrate of (2), the cyano nitrogen plays an important structural role.

RESULTS AND DISCUSSION

Details of data collection and structure refinement are given in Table 1. Atomic coordinates are given in Table 2. Anisotropic thermal parameters, bond lengths and angles and tables of observed and calculated structure factors have been deposited. Figure 1 is a perspective view of 1 which shows the atomic labelling used and the coordination of the anion, the sodium cations and the six DMF guests. Each sodium ion is coordinated to four DMF oxygens and one anionic nitrogen atom in a distorted square pyramidal arrangement. Na-O bonds are in the range 2.373(4)–2.478(5) Å. Na-N bonds are between 2.408(7) and 2.453(6) Å. The cation, anion and DMF guests are thus linked by this complicated coordination network. Two of the DMF molecules (labelled E and H)



(1)

a) 9-BBN (2eq) / THF / 0°C to RT

b) NaCN (2eq) / DMF

(2) = bis-$\overset{+}{\mathrm{Me}}\mathrm{PPh}_3$ salt of (1)

Scheme 1

Table 1 Crystal data, details of data collection and refinement.

Molecular formula	$C_{42}H_{82}O_6B_2N_8Na_2$
Mass (g mol^{-1})	862.77
Space group	$P\bar{1}$
a (Å)	13.661(2)
b (Å)	13.821(2)
c (Å)	14.917(4)
α (°)	75.98(2)
β (°)	73.08(1)
γ (°)	86.92(1)
Volume (Å^3)	2613(16)
Z	2
F(000)	940
μ (Mo Kα) (cm^{-1})	0.55
Dc (g cm^{-3})	1.096
Dm (g cm^{-3})	1.077
Crystal dimensions (mm)	0.50×0.50×0.40
θ range scanned (°)	1–25
Range of *h, k, l*	±16, ±16, 17
Absorption correction (min, max, ave) (%)	92.8, 99.9, 96.7
Number of unique reflections	9582
Reflections with I>2σ I	4439
Number of parameters	575
R	0.071
Rw	0.071
w	unity
S	1.599
Max/min residual electron density (e Å^{-3})	0.37/-0.23
Max LS shift/esd	0.002

are more tightly held, being bound to both sodium ions.

The conformation of the anion shows some interesting features. The four central carbons of the spacer are forced into an energetically unfavourable *cisoid* conformation in order to bring both cyano groups into the *syn* position with respect to the B-spacer-B axis. This conformation allows all the DMF's to be bound to the same face of the anion in channels, parallel to [001] at y=$^1/_2$. These channels are illustrated in Figure 2, in which the sodium and anion atoms are drawn with van der Waals radii. This *cisoid* form of the spacer only occurs when the cation is small, like sodium. When a larger cation, such as a phosphonium ion is used, the spacer adopts a staggered conformation.[2]

Thermal analysis of this compound, shown in Figure 3, was complex. The differential scanning calorimetry (DSC) trace shows two fairly sharp endotherms with onset temperatures of 49 and 76°C, followed by a broad endotherm between 210–270°C. The corresponding thermogravimetric (TG) curve has a well-defined weight loss of 32.8% which coincides with the first two endotherms in the DSC. This is followed by decomposition at approximately 260°C. The weight loss observed indicates that four of the six DMF guests are released from the host lattice on heating (the calculated weight loss for four DMF guests is 33.9%). The strength with which the guest molecules are held, as evidenced by the thermal analysis, may explain the surprising stability of this sodium cyanoborate salt.

Table 2 Fractional atomic coordinates (×10^4) and Thermal Parameters (Å^2 × 10^3) for (1).

Atom	*x/a*	*y/b*	*z/c*	*Uequiv*
Na(1)	3270(2)	5184(2)	7974(2)	58(1)
Na(2)	1303(2)	5391(2)	9775(2)	55(1)
B(1A)	1055(5)	7771(5)	12020(5)	54(3)
C(1A)	1513(5)	7292(5)	12910(4)	60(3)
C(2A)	919(5)	6330(5)	13538(5)	77(3)
C(3A)	-253(5)	6442(6)	13914(5)	84(4)
C(4A)	-726(5)	7028(5)	13158(5)	75(3)
C(5A)	-130(5)	8000(5)	12535(4)	67(3)
C(6A)	-137(6)	8782(6)	13111(6)	91(4)
C(7A)	479(6)	8551(6)	13834(6)	95(5)
C(8A)	1517(6)	8076(6)	13473(5)	87(4)
C(9A)	1079(4)	6955(5)	11384(4)	60(3)
N(9A)	1116(4)	6433(5)	10893(4)	77(3)
C(11)	1706(5)	8721(5)	11243(5)	72(3)
C(12)	2815(5)	8484(5)	10709(5)	80(3)
C(13)	3425(6)	9320(6)	10012(5)	93(4)
C(14)	4512(5)	9064(5)	9485(5)	78(3)
C(15)	4594(5)	8627(5)	8621(4)	65(3)
C(16)	5686(4)	8383(5)	8117(4)	62(3)
B(1B)	5883(5)	8076(5)	7101(5)	48(3)
C(1B)	7088(4)	7842(4)	6616(4)	56(2)
C(2B)	7190(5)	7390(5)	5750(5)	76(3)
C(3B)	6733(5)	7988(6)	4989(5)	81(4)
C(4B)	5714(5)	8474(5)	5359(4)	70(3)
C(5B)	5592(4)	8902(4)	6240(4)	57(3)
C(6B)	6249(5)	9849(5)	6008(5)	74(3)
C(7B)	7406(5)	9691(5)	5705(5)	75(3)
C(8B)	7742(5)	8789(5)	6365(5)	71(3)
C(9B)	5195(5)	7072(5)	7315(4)	54(3)
N(9B)	4701(4)	6383(4)	7470(4)	71(3)
O(1C)	-1804(3)	5950(3)	11045(3)	66(2)
C(1C)	-1366(5)	6760(5)	10766(5)	63(3)
N(1C)	-1728(4)	7591(4)	10281(4)	71(3)
C(11C)	-2669(6)	7565(7)	9990(6)	101(4)
C(12C)	-1146(7)	8541(5)	9992(7)	113(5)
O(1D)	107(3)	4241(3)	10994(3)	74(2)
C(1D)	-142(5)	4277(5)	11852(5)	73(3)
N(1D)	44(4)	3531(5)	12531(4)	75(3)
C(11D)	537(7)	2613(7)	12292(7)	117(5)
C(12D)	-221(8)	3614(8)	13533(6)	129(6)
O(1E)	3137(3)	5102(3)	9660(3)	73(2)
C(1E)	3695(5)	5589(5)	9916(5)	63(3)
N(1E)	3691(4)	5442(4)	10836(4)	65(3)
C(11E)	2999(7)	4718(7)	11607(5)	107(4)
C(12E)	4363(6)	6054(6)	11098(6)	102(5)
O(1F)	5868(4)	6276(4)	12402(4)	91(3)
C(1F)	6343(6)	6962(6)	12509(5)	77(3)
N(1F)	5955(5)	7888(4)	12458(4)	83(3)
C(11F)	6592(8)	8669(5)	12544(6)	108(5)
C(12F)	4973(7)	8161(7)	12260(7)	120(6)
O(1G)	7223(4)	4705(5)	13444(4)	112(3)
C(1G)	7126(6)	4866(6)	14236(6)	91(4)
N(1G)	6483(5)	4391(5)	15035(4)	84(3)
C(11G)	5790(9)	3626(9)	15015(8)	172(7)
C(12G)	6443(7)	4568(7)	15977(6)	118(5)
O(1H)	2134(3)	6545(3)	8319(3)	71(2)
C(1AH)	2009(12)	7429(12)	8354(15)	81(9)
C(1BH)	2367(12)	7259(13)	7593(14)	82(8)
N(1H)	2150(4)	8171(5)	7593(5)	84(4)
C(2AH)	2063(25)	9189(17)	7605(28)	155(21)
C(3AH)	2583(14)	7907(16)	6574(12)	119(11)
C(2BH)	1619(15)	8427(18)	8584(15)	120(11)
C(3BH)	2392(18)	9008(18)	6799(18)	141(12)

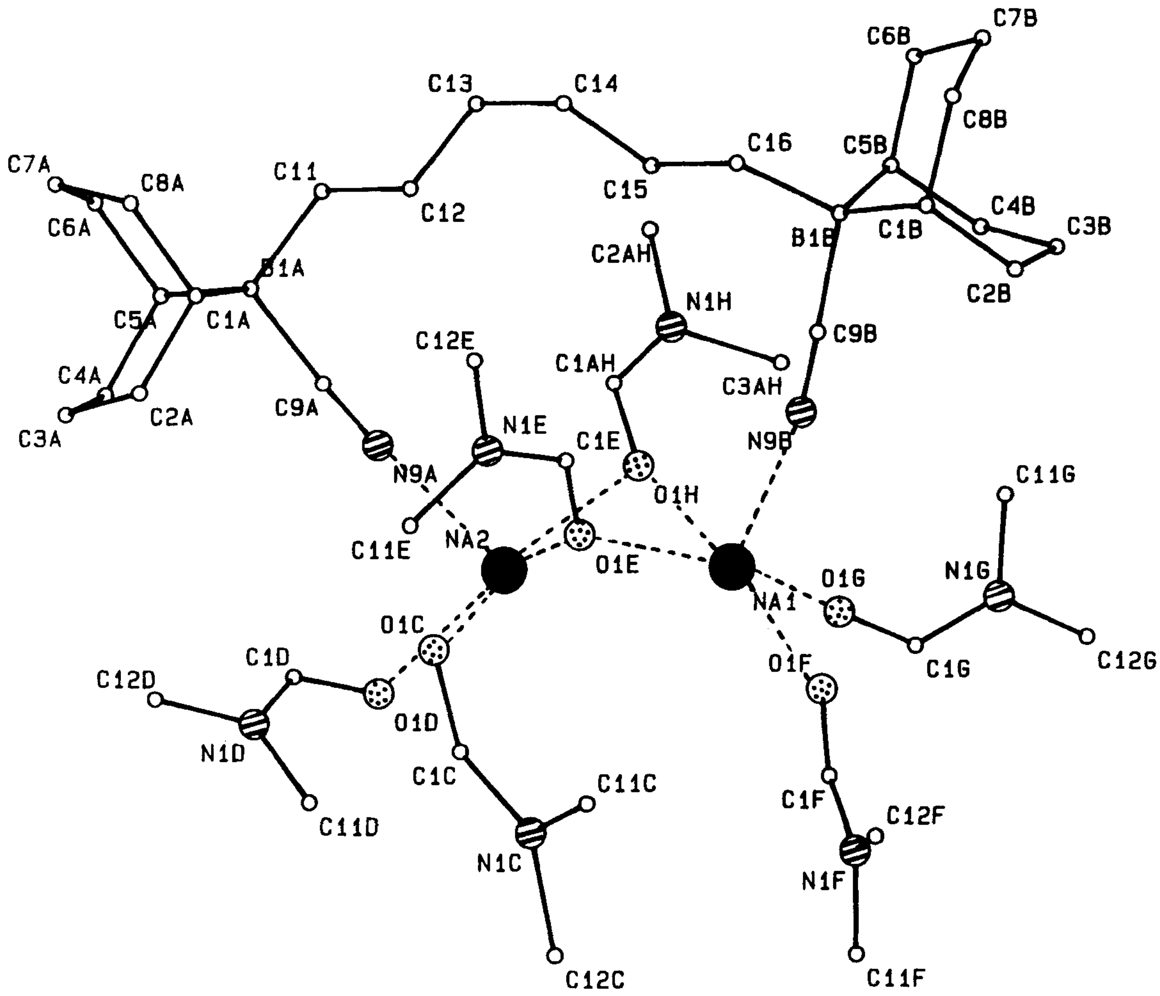


Figure 1 Perspective view of (**1**). Sodium ions are shaded, nitrogens shown as striped and oxygens as dotted circles.

EXPERIMENTAL

Preparation of the Disodium 1,6-bis(B-cyano-9-boratabicyclo[3.3.1]non-9-yl)hexane—DMF clathrate (1)

To a solution of 9-BBN (0.5 M in THF, 40 ml, 20 mmol) cooled to 0°C was added 1,5-hexadiene (1.2 ml, 10 mmol) via syringe. The mixture was stirred overnight at room temperature before removal of the THF by distillation at atmospheric pressure followed by pumping *in vacuo*. To the resulting liquid was added dry, deoxygenated DMF (1 ml per 10 mmol of diene), dry sodium cyanide (1.2 g, 24.5 mmol) and the mixture stirred until the reaction had cooled to room temperature. The clear solution was then pipetted into a dry sample tube leaving residual sodium cyanide behind. Over a period of time the sodium cyanoborate . 6 DMF salt crystallized out and this was filtered and washed with dry ether to afford (**1**) (2.34 g, 29%) as a colourless solid; m.p. 79–81°C, (Found: C, 57.9; H, 9.4; N, 12.3; $C_{42}H_{82}B_2N_8Na_2O_6$ requires C, 58.5; H, 9.6; N, 12.9%)

ν_{max} 2909, 2859, 2833, 2149, 1670, 1094 cm^{-1}

δ_H ($CDCl_3$, 200 MHz) 0.2 (4H, m, H-1'), 0.37 (4H, br.s., H-1), 1.05–1.9 (32H, m, H-2, H-3, H-2', H-3'), 2.82 (3H, s, H-5), 2.93 (3H, s, H-5), 7.96 (1H, s, H-6)

δ_C ($CDCl_3$, 50 MHz) 23.6 (C-1'), 24.4 (C-1), 25.4 (C-3), 26.4 (C-3), 27.0 (C-2'), 30.3 (C-2), 31.7 (C-5), 34.2 (C-3'), 34.6 (C-2), 36.9 (C-5), 152.0 (C-4), 163.7 (C-6)

Thermal analysis

DSC and TG were performed on a Perkin Elmer PC7 Series System. Crystals were air dried and crushed before analysis. Sample weight was *ca.* 5 mg. The temperature was raised from 30 to 350°C at a heating rate of 20°C min^{-1}. The purge gas was dry nitrogen flowing at 40 ml min^{-1}.

X-Ray analysis

A single crystal of (**1**) was mounted in a Lindemann capillary containing mother liquor. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer, using graphite monochromated Mo Kα radiation. A triclinic unit cell was refined using 24 reflections in the region 16

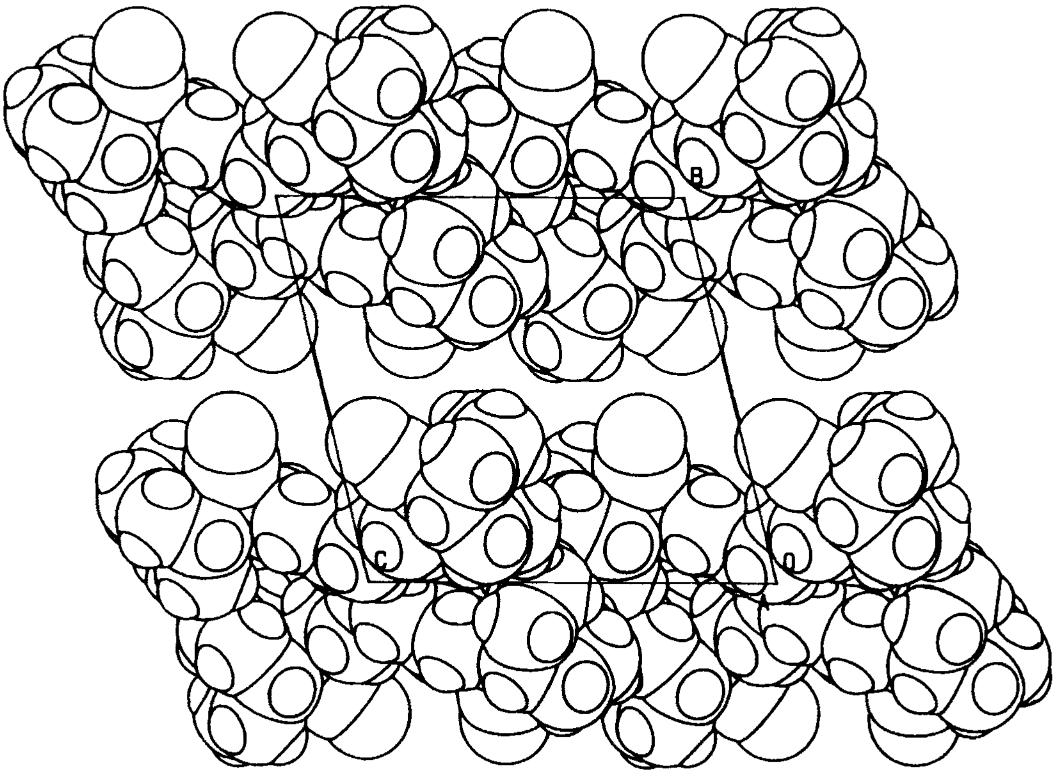


Figure 2 Packing diagram of (**1**) viewed along [100]. The cyanoborate anion and sodium cation are drawn with van der Waals radii. DMF guests are omitted to illustrate the channels they occupy.

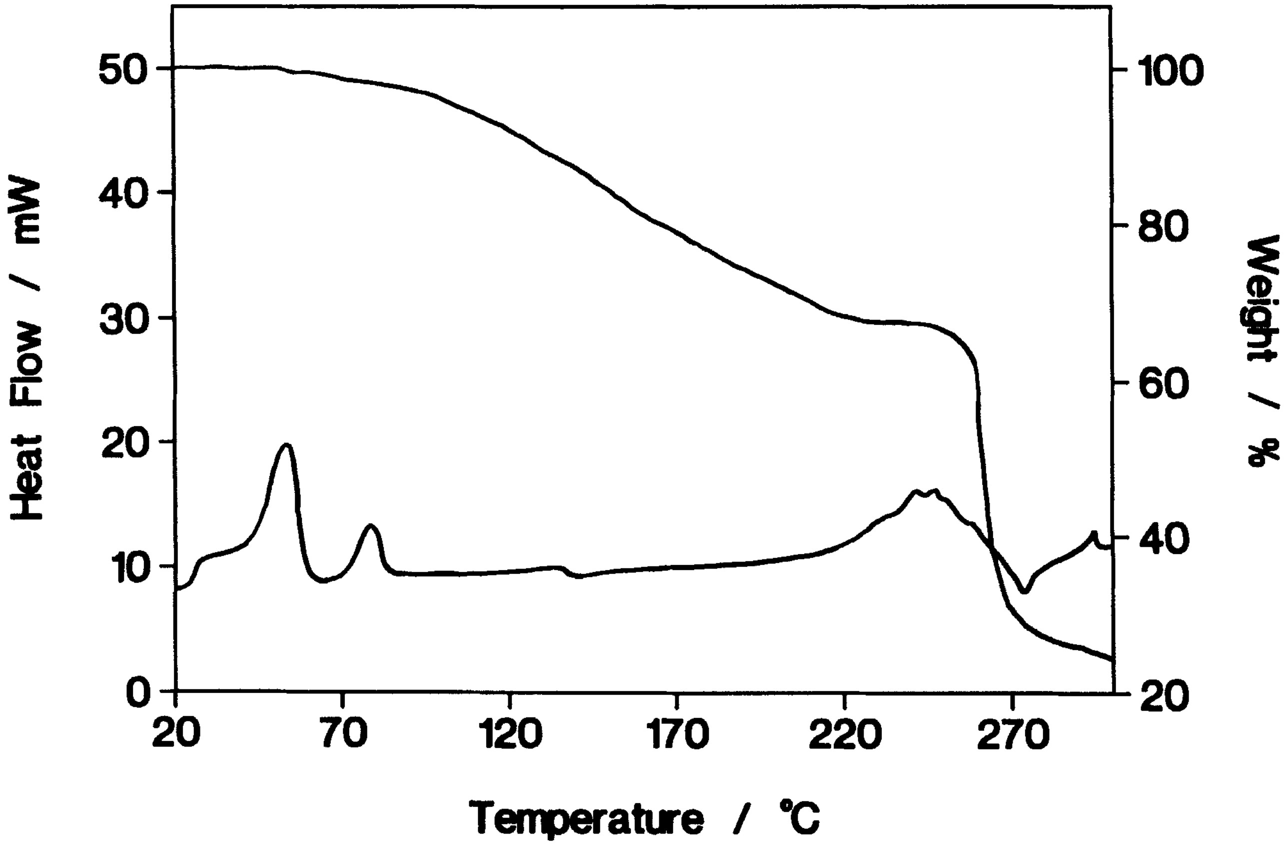


Figure 3 TG and DSC curves for (1).

≤ θ ≤ 17°. Data were collected using the ω-2θ technique and with variable scan width, aperture width and speed. Reference reflections were monitored periodically for intensity and orientation control. An empirical absorption correction, as well as a correction for Lorentz and polarization effects was applied. Further details are given in Table 1.

Structure solution and refinement

The structure was partially solved by direct methods using SHELXS-86[3]. Refinement was carried out using SHELX-76.[4] The final refinement used the blocked-matrix method, with all non-hydrogen atoms treated anisotropically. Hydrogens were placed in geometrically calculated positions on the anion and were linked to common temperature factors. No hydrogens were modelled on the guest DMF molecules. Five of the DMF molecules refined uneventfully, but the sixth (labelled H) proved to be disordered. The nitrogen and oxygen of this molecule were found unambiguously but the methylene carbon was located in two positions. Each was refined with site occupancy of 50%. In addition, four methyl carbons were modelled, each with site occupancy of 50%. Further details of the final refinement are given in Table 1.

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