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Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

$[B_9H_{13}]^{2-}$, an *arachno*-$[B_nH_{n+4}]^{2-}$ Dianion: Synthesis, Characterization, and Molecular Structure

Thomas D. Getman, Jeanette A. Krause, Philipp M. Niedenzu, and Sheldon G. Shore*

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The *arachno*-$[B_9H_{13}]^{2-}$ dianion has been synthesized as the $K_2[B_9H_{13}]$ and $Na_2[B_9H_{13}]$ salts through deprotonation of $K[B_9H_{14}]$ by KH in glyme and through deprotonation of $Na[B_9H_{14}]$ by $NaNH_2$ in liquid ammonia. Due to explosions that occurred during the preparation and handling of both $Na_2[B_9H_{13}]$ and $Na[B_9H_{14}]$, studies of $Na_2[B_9H_{13}]$ were terminated. The potassium salt is insoluble in ether solvents but is soluble in liquid ammonia. It is solubilized in acetonitrile when a cryptand is added as a complexing agent. The structure of $[(Krypt2.2.2)K]_2[B_9H_{13}]$ was determined from a single-crystal X-ray study. The basic structure of $[B_9H_{13}]^{2-}$ is similar to that of the room-temperature structure of $[B_9H_{14}]^-$ with one of the hydrogens removed. Endo hydrogens on the perimeter of the open face of the structure are disordered. This disorder implies the existence of isomers in the solid state and is compatible with the fluxional character of these hydrogens in solution.

nido-$[B_nH_{n+2}]^{2-}$ and *arachno*-$[B_nH_{n+4}]^{2-}$ dianions have received much less attention[1-5] than *closo*-$[B_nH_n]^{2-}$ dianions.[6] Only two arachno dianions, $[B_5H_9]^{2-}$ and $[B_{10}H_{14}]^{2-}$, prepared by the two-electron reduction of B_5H_9[1] and $B_{10}H_{14}$[4] have been studied in any detail. Preparation of *arachno*-$[B_9H_{13}]^{2-}$ through the deprotonation of $Cs[B_9H_{14}]$ by butyllithium[2] was reported several years ago. While some chemical properties were described, no structural or spectroscopic details were given for $[B_9H_{13}]^{2-}$. The synthesis, X-ray structure, NMR spectra, and IR spectra of *arachno*-$[B_9H_{13}]^{2-}$, tridecahydrononaborate(2–), are presented here.

Results and Discussion

The reaction of $K[B_9H_{14}]$ with KH in glyme produces $K_2[B_9H_{13}]$ in high yield (reaction 1). $K_2[B_9H_{13}]$ is air sensitive;

$$K[B_9H_{14}] + KH \rightarrow K_2[B_9H_{13}] + H_2 \qquad (1)$$

however, it is stable under an N_2 atmosphere for periods of several months without noticeable decomposition. When it is heated to 60 °C for 48 h, slight decomposition is observed by boron-11 NMR spectroscopy. At 100 °C, significant decomposition occurs with the formation of a variety of *closo* boron hydride dianions: $[B_{10}H_{10}]^{2-}$ (27%), $[B_9H_9]^{2-}$ (16%), $[B_7H_7]^{2-}$ (14%), $[B_{12}H_{12}]^{2-}$ (11%) (percentages refer to the boron content of the sample as determined by boron-11 NMR spectroscopy). Also present are $[BH_4]^-$ (~5%) and four unidentified resonances (–6.0 ppm (d, J unresolved), –21.3 ppm (d, $J = 102$ Hz), –34.1 ppm (t, J unresolved), and –40.3 ppm (d, $J = 123$ Hz)), which account for approximately 27% of the boron in the sample. The potassium salt is insoluble in THF and glyme, but it is soluble in NH_3. It is also soluble in acetonitrile when the potassium cations are complexed by Krypt2.2.2.[7] In THF a slurry of $K_2[B_9H_{13}]$ apparently reduces $Ti(C_5H_5)_2Cl_2$ with the formation of the $[B_9H_{12}]^-$ anion (identified by boron-11 NMR spectroscopy[8]) and reacts with neat $Si(CH_3)_2Cl_2$ to form n-$B_{18}H_{22}$ in low yield.

Attempted deprotonation of $Na[B_9H_{14}]$ by NaH in glyme was very sluggish, even at 40 °C. Therefore, $Na_2[B_9H_{13}]$ was prepared through the deprotonation of $Na[B_9H_{14}]$ by $Na[NH_2]$ in liquid ammonia (reaction 2). Several unaccounted for explosions that

$$Na[B_9H_{14}] + Na[NH_2] \rightarrow Na_2[B_9H_{13}] + NH_3 \qquad (2)$$

occurred during the preparation of $Na_2[B_9H_{13}]$ and the precursor salt $Na[B_9H_{14}]$ caused us to abandon further study of these salts.

Table I. Crystallographic Data for $[(Krypt2.2.2)K]_2[B_9H_{13}]$

formula	$C_{36}H_{85}B_9K_2N_4O_{12}$
fw	941.74
space group	$P2_1/c$ (No. 14)
molecules/unit cell	4
temp, °C	–35
a, Å	25.696 (3)
b, Å	10.280 (4)
c, Å	21.205 (6)
β, deg	110.6 (2)
vol of unit cell, Å^3	5242.5
cryst dimens, mm	0.45 × 0.50 × 0.55
ρ(calcd), g cm^{-3}	1.193
μ, cm^{-1}	2.3
scan mode	ω–2θ
isotropic extinction param	4.5044×10^{-8}
radiation (λ, Å)	Mo Kα (0.710 730)
data collection limits, deg	4–50
no. of unique reflections	9198
no. of reflections used in structure refinement ($>3\sigma(I)$)	5050 (617 variables)
$R_F = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.046
$R_{wF} = \sum w^{1/2}\lvert\Delta F\rvert/\sum w^{1/2}\lvert F_o\rvert$	0.061
weighting scheme	$w = [\sigma(I)^2 + (KI)^2]^{-1/2}$, $K = 0.03$

The structure of $[(Krypt2.2.2)K]_2[B_9H_{13}]$ was determined (Tables I and II) from a single-crystal X-ray diffraction study. Selected bond distances and bond angles are given in Tables III and IV. The basic structure of $[B_9H_{13}]^{2-}$ (Figure 1) is similar to that of $[B_9H_{14}]^-$.[9,10] Its boron framework can be derived from the decaborane(14)[11] framework by removing either one of the equivalent B(6) and B(9) boron atoms. There are four endo hydrogens in the structure. They are disordered over five positions on five boron atoms, indicated by dotted circles in Figure 1, and are assigned occupancies of 0.8. These hydrogens as well as the nine exo hydrogens were located on difference maps and refined. Disorder of the endo hydrogens in the crystal implies the existence of isomers in the solid state and is compatible with the fact that these hydrogens are fluxional in solution. Five isomers (two enantiomeric pairs and a geometric isomer) can be derived from the X-ray structure by selective removal of endo hydrogens.

Structural parameters of $[B_9H_{13}]^{2-}$ are consistent with those observed in boron hydride species.[11] Two of the endo hydrogens

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*, Å^{2a}	atom	*x*	*y*	*z*	*B*, Å^{2a}
				A. $[B_9H_{13}]^-$					
B(1)	0.7562 (2)	0.1985 (4)	0.3158 (2)	3.49 (9)	H(400)	0.741 (1)	−0.027 (3)	0.268 (2)	5.1 (9)^{b}
B(2)	0.7918 (2)	0.3239 (4)	0.2899 (2)	3.51 (9)	H(500)	0.850 (1)	0.115 (3)	0.306 (1)	4.0 (8)^{b}
B(3)	0.7197 (2)	0.3392 (4)	0.2748 (2)	3.43 (9)	H(504)	0.779 (1)	0.124 (3)	0.216 (1)	1.3 (7)^{b,c}
B(4)	0.7442 (2)	0.0742 (4)	0.2583 (2)	4.1 (1)	H(600)	0.851 (1)	0.345 (3)	0.227 (2)	5.1 (9)^{b}
B(5)	0.8067 (2)	0.1613 (4)	0.2779 (2)	3.94 (9)	H(601)	0.784 (1)	0.249 (4)	0.165 (2)	4 (1)^{b,c}
B(6)	0.8055 (2)	0.3027 (5)	0.2165 (2)	4.4 (1)	H(700)	0.752 (1)	0.514 (3)	0.220 (1)	4.6 (8)^{b}
B(7)	0.7489 (2)	0.4104 (4)	0.2195 (2)	3.8 (1)	H(701)	0.737 (1)	0.326 (3)	0.172 (2)	3.1 (8)^{b,c}
B(8)	0.6784 (2)	0.3313 (5)	0.1894 (2)	4.2 (1)	H(800)	0.641 (1)	0.394 (4)	0.178 (2)	6.0 (9)^{b}
B(9)	0.6902 (2)	0.1841 (4)	0.2529 (2)	4.0 (1)	H(801)	0.678 (2)	0.260 (4)	0.149 (2)	5 (1)^{b,c}
H(100)	0.761 (1)	0.185 (3)	0.366 (1)	4.1 (8)^{b}	H(900)	0.651 (1)	0.151 (3)	0.263 (2)	5.3 (9)^{b}
H(200)	0.826 (1)	0.383 (3)	0.331 (1)	4.7 (8)^{b}	H(904)	0.701 (1)	0.137 (3)	0.201 (1)	1.2 (6)^{b,c}
H(300)	0.702 (1)	0.402 (3)	0.307 (1)	4.9 (8)^{b}					
				B. $[(Krypt2.2.2)K]^+$ Cation 1					
K(1)	0.09565 (3)	0.16734 (6)	0.93889 (3)	2.67 (1)	C(6)	0.1723 (2)	0.4300 (4)	1.0550 (2)	5.2 (1)
N(1)	0.0559 (1)	−0.0024 (3)	0.8161 (1)	3.76 (7)	C(7)	0.0830 (2)	0.4059 (4)	1.0667 (2)	6.0 (1)
N(2)	0.1312 (1)	0.3364 (3)	1.0609 (1)	4.05 (7)	C(8)	0.0332 (2)	0.3237 (5)	1.0516 (2)	6.6 (1)
O(1)	0.10451 (9)	0.2562 (2)	0.81656 (9)	3.45 (5)	C(9)	−0.0360 (2)	0.2187 (5)	0.9655 (3)	10.2 (1)
O(2)	−0.0150 (1)	0.0793 (3)	0.8910 (1)	5.95 (7)	C(10)	−0.0529 (2)	0.1682 (7)	0.9046 (3)	12.0 (2)
O(3)	0.1468 (1)	−0.0717 (2)	0.9400 (1)	4.08 (6)	C(11)	−0.0368 (2)	0.0385 (4)	0.8237 (2)	5.8 (1)
O(4)	0.15717 (9)	0.3921 (2)	0.9389 (1)	3.73 (5)	C(12)	0.0011 (2)	−0.0559 (4)	0.8101 (2)	5.2 (1)
O(5)	0.0139 (1)	0.2885 (3)	0.9835 (1)	6.05 (7)	C(13)	0.0959 (2)	−0.1075 (4)	0.8230 (2)	4.72 (9)
O(6)	0.16865 (9)	0.0693 (2)	1.0600 (1)	3.80 (6)	C(14)	0.1175 (2)	−0.1678 (4)	0.8920 (2)	4.73 (9)
C(1)	0.0513 (2)	0.0762 (4)	0.7569 (2)	4.8 (1)	C(15)	0.1759 (1)	−0.1256 (4)	1.0040 (2)	4.20 (9)
C(2)	0.1004 (2)	0.1626 (4)	0.7662 (2)	4.73 (9)	C(16)	0.2065 (2)	−0.0225 (4)	1.0509 (2)	4.7 (1)
C(3)	0.1501 (1)	0.3433 (4)	0.8266 (2)	3.96 (8)	C(17)	0.1963 (2)	0.1575 (4)	1.1125 (2)	5.0 (1)
C(4)	0.1482 (2)	0.4479 (3)	0.8742 (2)	4.08 (9)	C(18)	0.1562 (2)	0.2536 (4)	1.1203 (2)	5.2 (1)
C(5)	0.1568 (2)	0.4895 (4)	0.9860 (2)	5.0 (1)					
				Cation 2					
K(2)	0.39763 (3)	0.14146 (7)	1.07009 (3)	3.08 (2)	C(24)	0.3948 (2)	0.4080 (4)	0.9500 (2)	7.2 (1)
N(3)	0.4470 (1)	−0.0398 (3)	1.1838 (1)	3.56 (7)	C(25)	0.3074 (2)	0.4012 (4)	0.9675 (2)	5.0 (1)
N(4)	0.3510 (1)	0.3230 (3)	0.9555 (1)	4.85 (8)	C(26)	0.3241 (2)	0.4540 (4)	1.0371 (2)	5.2 (1)
O(7)	0.3574 (1)	−0.1128 (2)	1.0598 (1)	4.99 (7)	C(27)	0.3454 (2)	0.3997 (4)	1.1502 (2)	4.9 (1)
O(8)	0.51063 (9)	0.0705 (3)	1.1061 (1)	4.98 (7)	C(28)	0.3517 (1)	0.2898 (4)	1.1981 (2)	4.68 (9)
O(9)	0.39726 (9)	0.2106 (2)	1.1994 (1)	3.66 (5)	C(29)	0.4076 (2)	0.1098 (4)	1.2476 (2)	4.81 (9)
O(10)	0.3290 (1)	0.0427 (3)	0.9449 (1)	5.61 (8)	C(30)	0.4562 (2)	0.0312 (4)	1.2475 (2)	4.5 (1)
O(11)	0.4709 (1)	0.2893 (3)	1.0225 (1)	6.13 (7)	C(31)	0.4086 (2)	−0.1473 (4)	1.1776 (2)	4.50 (9)
O(12)	0.3313 (1)	0.3499 (2)	1.0840 (1)	4.24 (6)	C(32)	0.3853 (2)	−0.2063 (4)	1.1083 (2)	5.3 (1)
C(19)	0.5001 (2)	−0.0882 (4)	1.1816 (2)	5.1 (1)	C(33)	0.3351 (2)	−0.1650 (4)	0.9942 (2)	5.0 (1)
C(20)	0.5371 (2)	0.0137 (5)	1.1698 (2)	5.4 (1)	C(34)	0.2998 (2)	−0.0707 (4)	0.9457 (2)	5.8 (1)
C(21)	0.5453 (2)	0.1702 (5)	1.0958 (3)	8.3 (1)	C(35)	0.2936 (2)	0.1354 (5)	0.8990 (2)	8.1 (2)
C(22)	0.5214 (2)	0.2244 (5)	1.0305 (2)	8.2 (1)	C(36)	0.3279 (2)	0.2488 (5)	0.8932 (2)	7.9 (1)
C(23)	0.4466 (2)	0.3372 (5)	0.9561 (2)	8.4 (1)					

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$. [b] Refined isotropically. [c] Assigned occupancy of 0.8.

Table III. Selected Bond Distances (Å) and Esd's for $[B_9H_{13}]^{2-}$

	A. B–B Bond Distances		
B(1)–B(2)	1.776 (4)	B(3)–B(7)	1.757 (4)
B(1)–B(3)	1.776 (4)	B(3)–B(8)	1.749 (4)
B(1)–B(4)	1.718 (4)	B(3)–B(9)	1.757 (4)
B(1)–B(5)	1.793 (4)	B(4)–B(5)	1.755 (5)
B(1)–B(9)	1.756 (4)	B(4)–B(9)	1.763 (5)
B(2)–B(3)	1.772 (4)	B(5)–B(6)	1.944 (4)
B(2)–B(5)	1.754 (4)	B(6)–B(7)	1.847 (5)
B(2)–B(6)	1.726 (4)	B(7)–B(8)	1.880 (5)
B(2)–B(7)	1.754 (4)	B(8)–B(9)	1.977 (4)
	B. B–H Bond Distances		
B(1)–H(100)	1.05 (2)	B(6)–H(600)	1.19 (3)
B(2)–H(200)	1.16 (3)	B(6)–H(601)	1.17 (3)
B(3)–H(300)	1.15 (2)	B(7)–H(700)	1.07 (2)
B(4)–H(400)	1.07 (3)	B(7)–H(701)	1.29 (3)
B(4)–H(504)	1.57 (2)	B(8)–H(800)	1.11 (3)
B(4)–H(904)	1.48 (2)	B(8)–H(801)	1.13 (3)
B(5)–H(500)	1.11 (2)	B(9)–H(900)	1.15 (2)
B(5)–H(504)	1.32 (2)	B(9)–H(904)	1.31 (2)

are semibridging, H(504) and H(904). They have boron–hydrogen distances of B(5)–H(504) = 1.32(2), B(4)–H(504) = 1.57 (2), B(9)–H(904) = 1.31 (2), and B(4)–H(904) = 1.48 (2) Å. The other three endo hydrogens have bond distances of B(6)–H(601) = 1.17 (3), B(7)–H(701) = 1.29 (3), and B(8)–H(801) = 1.13 (3) Å. The shortest boron–boron distance is B(1)–B(4) = 1.718 (4) Å, while the longest boron–boron distances are B(5)–B(6) =

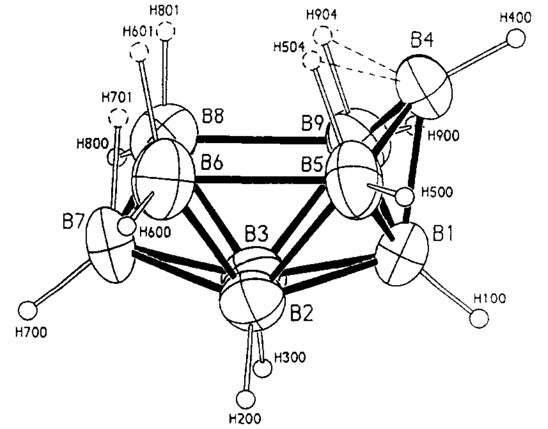

Figure 1. Structure of the $[B_9H_{13}]^{2-}$ dianion (ORTEP plot with 50% probability ellipsoids). Disordered H atoms are indicated by dotted circles. Semibonds are indicated by dotted lines.

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Table IV. Selected Bond Angles (deg) and Esd's for $[B_9H_{13}]^{2-}$

	A. B–B–B Angles		
B(2)–B(1)–B(3)	59.9 (2)	B(8)–B(3)–B(9)	68.7 (2)
B(2)–B(1)–B(4)	107.6 (2)	B(1)–B(4)–B(5)	62.2 (2)
B(2)–B(1)–B(5)	58.9 (2)	B(1)–B(4)–B(9)	60.6 (2)
B(2)–B(1)–B(9)	106.9 (2)	B(5)–B(4)–B(9)	108.8 (2)
B(3)–B(1)–B(4)	109.0 (2)	B(1)–B(5)–B(2)	60.1 (2)
B(3)–B(1)–B(5)	107.1 (2)	B(1)–B(5)–B(4)	57.9 (2)
B(3)–B(1)–B(9)	59.6 (2)	B(1)–B(5)–B(6)	107.3 (2)
B(4)–B(1)–B(5)	59.9 (2)	B(2)–B(5)–B(4)	107.0 (2)
B(4)–B(1)–B(9)	61.0 (2)	B(2)–B(5)–B(6)	55.4 (2)
B(5)–B(1)–B(9)	107.4 (2)	B(4)–B(5)–B(6)	115.1 (2)
B(1)–B(2)–B(3)	60.1 (2)	B(2)–B(6)–B(5)	56.7 (2)
B(1)–B(2)–B(5)	61.1 (2)	B(2)–B(6)–B(7)	58.7 (2)
B(1)–B(2)–B(6)	118.6 (2)	B(5)–B(6)–B(7)	104.6 (2)
B(1)–B(2)–B(7)	113.2 (2)	B(2)–B(7)–B(3)	60.6 (2)
B(3)–B(2)–B(5)	109.1 (2)	B(2)–B(7)–B(6)	57.2 (2)
B(3)–B(2)–B(6)	112.3 (2)	B(2)–B(7)–B(8)	108.2 (2)
B(3)–B(2)–B(7)	59.8 (2)	B(3)–B(7)–B(6)	107.4 (2)
B(5)–B(2)–B(6)	67.9 (2)	B(3)–B(7)–B(8)	57.4 (2)
B(5)–B(2)–B(7)	117.6 (2)	B(6)–B(7)–B(8)	113.9 (2)
B(6)–B(2)–B(7)	64.1 (2)	B(3)–B(8)–B(7)	57.8 (2)
B(1)–B(3)–B(2)	60.1 (2)	B(3)–B(8)–B(9)	55.8 (2)
B(1)–B(3)–B(7)	113.0 (2)	B(7)–B(8)–B(9)	101.6 (2)
B(1)–B(3)–B(8)	119.5 (2)	B(1)–B(9)–B(3)	60.8 (2)
B(1)–B(3)–B(9)	59.6 (2)	B(1)–B(9)–B(4)	58.5 (2)
B(2)–B(3)–B(7)	59.6 (2)	B(1)–B(9)–B(8)	109.2 (2)
B(2)–B(3)–B(8)	113.4 (2)	B(3)–B(9)–B(4)	108.0 (2)
B(2)–B(3)–B(9)	107.1 (2)	B(3)–B(9)–B(8)	55.5 (2)
B(7)–B(3)–B(8)	64.8 (2)	B(4)–B(9)–B(8)	117.6 (2)
B(7)–B(3)–B(9)	116.6 (2)		
	B. H–B–H Angles		
H(504)–B(4)–H(400)	121 (2)	H(701)–B(6)–H(700)	133 (2)
H(904)–B(4)–H(400)	120 (2)	H(801)–B(8)–H(800)	116 (2)
H(504)–B(5)–H(500)	118 (1)	H(904)–B(9)–H(900)	119 (2)
H(601)–B(6)–H(600)	117 (2)		

1.944 (4) and B(8)–B(9) = 1.977 (4) Å.

Two structures of $[B_9H_{14}]^-$ are known. The structure determined from room-temperature[9a,b] X-ray data contains two fully bridging hydrogens, H(504) and H(904), and three endo hydrogens, H(601), H(701), and H(801). Hydrogen H(701) is closer to B(8) than B(6) with respective distances of 1.70 and 1.99 Å.[9c] A more recent structure determined from low-temperature (–174 °C) X-ray data[10] is in agreement with the room-temperature structure except that hydrogen H(701) is fully bridging B(7) and B(6). In the structure of $[B_9H_{13}]^{2-}$, H(701) is equidistant from B(6) and B(8) with respective distances of 1.69 (3) and 1.69 (3) Å.

Structures resembling the isomers of $[B_9H_{13}]^{2-}$ can be derived by selective removal of endo and bridging hydrogens from the room-temperature $[B_9H_{14}]^-$ structure.[9a,b] The possibility occurred to us that, during the process of crystallizing $[(\text{Krypt2.2.2})K]_2[B_9H_{13}]$, the $[B_9H_{13}]^{2-}$ ion might have extracted a proton from its environment to form $[B_9H_{14}]^-$. Since the unit cell contains $[(\text{Krypt2.2.2})K]^+$ cations and B_9 anions in a 2:1 ratio, another anionic species must be present if $[B_9H_{14}]^-$ did form. The final difference map gives no indication of any other species in the unit cell.

Endo hydrogens, including the semibridging hydrogens, are fluxional on the boron-11 and proton NMR time scales over the temperature range –40 to –70 °C in ND_3. The boron-11 NMR spectrum of $K_2[B_9H_{13}]$ at –40 °C consists of three doublets of relative areas 1:1:1 (–4.55 ppm (d, J = 122 Hz), –24.9 ppm (d, J = 125 Hz), and –29.0 ppm (d, J = 104 Hz)). The doublet character of each signal arises from spin coupling between each boron atom and the relatively nonfluxional exo hydrogen atom to which it is bound. Due to the fluxional hydrogens, the ^{11}B NMR spectrum reflects the pseudo-C_{3v} symmetry of the B_9 framework. There are three sets of boron atoms, each set containing three averaged boron environments: (1) B(4), B(6), B(8); (2) B(5), B(7), B(9); (3) B(1), B(2), B(3). The proton NMR spectrum, ^{11}B spin decoupled at –60 °C in ND_3, consists of four resonances of relative areas 3:3:3:4 (1.94, 0.48, 0.35, and –2.32 ppm), with the last signal representing the averaged endo hydrogen resonances. These NMR spectra are consistent with those obtained[9a] from $[B_9H_{14}]^-$.

Experimental Section

Materials were handled by using standard vacuum-line and inert atmosphere techniques.[12] $K[B_9H_{14}]$ and $Na[B_9H_{14}]$ were prepared from $B_{10}H_{14}$[13] and also from B_5H_9.[14] In the latter case the $[B_9H_{14}]^-$ salts were purified by the method of Benjamin, Stafiej, and Takacs.[13] [*Caution*! During the preparation of $Na[B_9H_{14}]$ and $Na_2[B_9H_{13}]$ several explosions of unknown origin occurred, even when peroxide-free ether was used. If the sodium salts are to be prepared, procedures should be performed behind a safety shield.] Decaborane(14) was obtained from laboratory reserves and sublimed prior to use. Ammonia, sodium dried, was stored at –78 °C. Sodium amide was prepared by a method described by Jolly.[15] Potassium hydride, obtained as a mineral oil dispersion (Aldrich Chemical Co.), was washed with dry pentane to remove the oil and was then stored in a controlled-atmosphere glovebox until use. Glyme (1,2-dimethoxyethane) and diethyl ether were distilled from sodium benzophenone ketyl before use. Acetonitrile was stirred over phosphorus pentoxide for several days and distilled into a storage bulb. Krypt2.2.2[7] (Aldrich Chemical Co.) was stored in the dark until use.

Boron-11 NMR spectra ($\delta(BF_3\cdot OEt_2)$ = 0.00 ppm) were obtained at 96.3 MHz on a Bruker MSL-300 NMR spectrometer. Proton NMR spectra (δ(TMS) = 0.00 ppm) were obtained at 300.1 MHz on a Bruker WM-300 NMR spectrometer. Fourier-transform infrared (FT-IR) spectra were obtained on a Mattson Cygnus 25 spectrometer.

X-ray Crystallography. X-ray diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. Crystallographic parameters are given in Table I. Computations were carried out on a PDP 11/44 computer by using the Structure Determination Package (SDP).[16] All data were corrected for Lorentz and polarization effects, and the structure was solved by a combination of the direct-method MULTAN 11/82 and difference-Fourier techniques with analytical atomic scattering factors used throughout. Full-matrix least-squares refinements were employed. All non-hydrogen atoms were located and refined anisotropically. All hydrogen atoms of $[B_9H_{13}]^-$ were located and refined isotropically. Hydrogen atoms of the cryptand ligands were placed at fixed calculated positions (C–H = 0.95 Å) and given fixed thermal parameters (B(H) = B(C) + 1) for the last three cycles of refinement.

$K_2[B_9H_{13}]$. A 100-mL reaction vessel containing a magnetic stir bar was charged, in a glovebox, with $K[B_9H_{14}]$ (297.9 mg, 1.98 mmol) and KH (79.9 mg, 1.99 mmol, 95% activity). The vessel was attached to a vacuum line, and glyme (10 mL) was condensed onto the reactants at –195 °C. The vessel was warmed first to room temperature and then placed in an oil bath maintained at 45 °C. The slurry was allowed to stir for 4 days during which time copious amounts of a white precipitate, $K_2[B_9H_{13}]$, formed. On the basis of H_2 evolved, the reaction was 91% complete. Crude, glyme-insoluble $K_2[B_9H_{13}]$ was isolated in ca. 90% yield (335.4 mg, 1.78 mmol). An analytically pure sample was obtained by extracting the product with NH_3. Anal. Calcd for $K_2[B_9H_{13}]$: K, 41.5; B, 51.6; H, 6.95. Found: K, 42.1; B, 52.14; H, 6.88. IR spectrum (Nujol), ν_{BH}: 2502 (s), 2495 (s), 2476 (s), 2457 (s), 2437 (s), 2429 (s), 2425 (s), 2361 (s), 2354 (s), 2347 (s) cm^{-1}.

$[(\text{Krypt2.2.2})K]_2[B_9H_{13}]$ was formed by dissolving Krypt2.2.2 (93.0 mg, 0.25 mmol) and $K_2[B_9H_{13}]$ (22.3 mg, 0.12 mmol) in acetonitrile. Crystals of $[(\text{Krypt2.2.2})K]_2[B_9H_{13}]$ were obtained by vapor diffusion of diethyl ether into an acetonitrile solution.

$Na_2[B_9H_{13}]$. A 100-mL reaction vessel containing a glass-coated magnetic stir bar was charged, in the glovebox, with $Na[B_9H_{14}]$ (359.0 mg, 2.7 mmol) and $NaNH_2$ (109.0 mg, 2.8 mmol). The vessel was attached to the vacuum line, ammonia (10 mL) was condensed onto the reactants at –78 °C, and the contents of the reactor were stirred for 2 h at –78 °C. The reaction mixture was then warmed by removing the –78 °C bath and stirred while the pressure was monitored by a manometer attached to the vacuum system. As the pressure approached 760 Torr, the vessel was cooled to –78 °C. This procedure was employed for an additional $^1/_2$ h. Volatiles were removed at room temperature under dynamic vacuum, and a white-gray solid remained, which was extracted with THF to yield 335 mg of a white solid. Approximately 66% of this

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solid was $Na_2[B_9H_{13}]$, while the remaining material consisted of $Na[B_9H_{14}]$,[9] $Na[BH_4]$,[17] and $Na[B_6H_9]$[18] as determined by their characteristic boron-11 NMR spectra. Prolonging the reaction time increased the amount of the impurities present.

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Registry No. $K[B_9H_{14}]$, 39296-28-1; $Na[B_9H_{14}]$, 70865-40-6; $Na_2[B_9H_{13}]$, 119391-53-6; $Na[NH_2]$, 7782-92-5; KH, 7693-26-7; $K_2[B_9H_{13}]$, 119391-51-4; $Ti(C_5H_5)_2Cl_2$, 1271-19-8; $[B_9H_{12}]^-$, 12430-26-1; $Si(CH_3)_2Cl_2$, 75-78-5; n-$B_{18}H_{22}$, 21107-56-2; NaH, 7646-69-7; $[(Krypt2.2.2)K]_2[B_9H_{13}]$, 119391-52-5.

Supplementary Material Available: Listings of bond distances, bond angles, positional parameters of H atoms, and anisotropic thermal parameters and ORTEP drawings of $[(Krypt2.2.2)K]^+$ (16 pages); a table of calculated and observed structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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Contribution from the Division of Chemical and Physical Sciences, Deakin University, Geelong 3217, Victoria, Australia, and Department of Inorganic Chemistry, University of Melbourne, Parkville 3052, Victoria, Australia

NMR and Electrochemical Investigation of the Redox and Exchange Reactions of Tellurium(II) and Tellurium(IV) Dithiocarbamate Complexes

Alan M. Bond,*[,1] Dainis Dakternieks,*[,1,2] Robert Di Giacomo,[2] and Anthony F. Hollenkamp[1]

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Tellurium-125 NMR and electrochemical data at mercury and platinum electrodes show that tellurium(IV) dithiocarbamate (dtc) complexes $Te(dtc)_4$ are unstable in solution with respect to an internal redox reaction, producing the tellurium(II) complex $Te(dtc)_2$ and thiuram disulfide (tds). The rate at which the equilibrium $Te(dtc)_4 \rightleftharpoons Te(dtc)_2 + tds$ is established and the equilibrium position appear to be solvent dependent. NMR data reveal that intermolecular dithiocarbamate exchange occurs more rapidly in the tellurium(II) complexes than it does in the tellurium(IV) analogues. At mercury electrodes, in addition to the intermolecular ligand-exchange processes identified by ^{125}Te NMR, the exchange reactions $Te(Et_2dtc)_2 + Hg \rightleftharpoons Hg(Et_2dtc)_2 + Te$ and $Te(Et_2dtc)_4 + Hg \rightleftharpoons Hg(Et_2dtc)_2 + Te(Et_2dtc)_2$ are important. Reduction at mercury and platinum electrodes occurs with the same overall equation $Te(Et_2dtc)_n + ne^- \rightleftharpoons Te + nEt_2dtc^-$ (n = 2, 4) but via electrode-dependent pathways. Oxidation at mercury electrodes produces $[Hg_3(Et_2dtc)_4]^{2+}$ and tellurium metal whereas at platinum electrodes different products are obtained.

Introduction

The compounds $Te(Morphdtc)_2$,[3] $Te(Morphdtc)_4$,[4] $Te(Et_2dtc)_2$,[5] and $Te(Et_2dtc)_4$[6] (Et_2dtc = diethyldithiocarbamate and Morphdtc = 4-morpholinecarbodithioate) have been well characterized in the solid state by X-ray crystal structural analysis. However, little is known about the nature and reactivity of these compounds in solution except that solutions of the Te(IV) compound appear to be unstable with time.[6] With a ligand such as dithiocarbamate, dtc^-, which is itself redox active, being readily oxidized to thiuram disulfide, tds, there exists the possibility of an intimate relationship between the two oxidation states of tellurium and the oxidized and reduced forms of the ligand. If equilibria in solution involve either metal- or ligand-based redox reactions, then electrochemical techniques should provide considerable information on the nature of such reactions. However, electrochemical techniques may perturb the system whereas, in contrast, spectroscopic techniques such as nuclear magnetic resonance, NMR, may monitor the species present in the unperturbed situation. NMR and electrochemical techniques therefore should provide complimentary means of investigating the redox-related reactions between tellurium(II) and tellurium(IV) dithiocarbamate complexes in solution.

It has recently been shown by ^{125}Te NMR that organotellurium(IV) complexes containing dithiolate ligands such as diethyldithiocarbamate, ethyl xanthate (S_2COEt) and diethyl dithiophosphate ($S_2P(OEt)_2$), undergo both inter- and intramolecular exchange processes in solution.[7] To date only very few electrochemical studies have been reported for any class of Te(II) and Te(IV) complexes.[8] In the case of dithiocarbamate complexes, no data are available at mercury electrodes but some data exist for the electrochemistry of such complexes at platinum, gold and glassy-carbon electrodes.[9] The presence of a mercury electrode can substantially modify the course of redox processes of labile complexes compared with inert electrode materials such as platinum,[10] and a comparison of data at the different electrode surfaces can provide valuable information on the solution chemistry.

In this paper we report NMR data for $Te(Et_2dtc)_2$, $Te(Et_2dtc)_4$, and $Te(Morphdtc)_2$ in a variety of solvents and an electrochemical investigation at mercury and platinum electrodes of $Te(Et_2dtc)_2$ and $Te(Et_2dtc)_4$ in dichloromethane in order to provide further information on the nature of the redox and exchange processes that may occur between the different oxidation states of tellurium.

Experimental Section

Syntheses. The compounds $Te(Et_2dtc)_n$[11,12] and $Te(Morphdtc)_n$[13,14] (n = 2, 4) were prepared by previously published methods.[8]

Instrumentation. NMR spectra were routinely recorded by using a JEOL FX 100 spectrometer with broad-band decoupling. A JEOL NM 5471 controller was used for temperature control; the temperatures in the probe were measured with a calibrated platinum resistance thermometer. ^{125}Te spectra were recorded at 31.4 MHz, usually on a 20-kHz spectral window, by using external ^7Li lock; the pulse width was 22 μs and the

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