structure,[30] which is similar to that of π-$C_6H_6Sn(AlCl_4)_2$·C_6H_6.[2b]

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Supplementary Material Available: Observed and calculated structure factors together with unobserved structure factors (26 pages). Ordering information is given on any current masthead page.

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(13) A single general reflection of average intensity in the middle of the λ, ϕ, 2θ range used for data collection has been found by us to be as reliable as several standards, particularly if they are well chosen (at least for small-molecule structures). With modernization of the instrument and subsequent faster driving speeds this philosophy has been replaced by that of multiple standard peaks (measurements). In addition, for these structures reported herein, three independent general reflections were measured once a day and their decomposition paralleled that of the single standard.
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Synthesis and Structure of the $B_{11}H_9Se_3^{2-}$ Ion

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Reaction of $NaB_{11}H_{14}(dioxane)_{2.5}$ with ammonium polyselenide formed the $B_{11}H_9Se_3^{2-}$ ion in low yield. The structure of this unexpected product has been determined by X-ray diffraction techniques. The dianion is a disubstituted derivative of $B_{11}H_{11}^{2-}$. The Se_3 chain is bonded to two adjacent boron atoms of the closo cage and is exo to the polyhedral boron structure. Boron-11 NMR suggests that the molecular ion is fluxional at room temperature.

Recently we have found that sodium polyselenide is a useful reagent for insertion of one or two selenium atoms into cage borane structures. For example, reaction of decaborane(14) with $Na_2(Se_x)$ formed $B_{10}H_{11}Se^{-1}$ and treatment of $Na(B_9H_{14})$ with this reagent gave $B_9H_9Se_2$.[2] We thought that reaction of the $B_{11}H_{14}^-$ ion with polyselenide ion would lead to the known molecule $B_{11}H_{11}Se$.[3] However, the product of this reaction was a red dianion. The synthesis and X-ray structure elucidation of this novel molecular ion are presented in this report.

Experimental Section

The boron-11 NMR spectrum was obtained at 70.6 MHz with a Varian HR-220 spectrometer and was externally referenced to BF_3·$O(C_2H_5)_2$ (with positive values downfield). The infrared spectrum was obtained as a KBr disk employing a Perkin-Elmer 283 spectrometer. The ultraviolet–visible spectrum was measured with a Cary 14 instrument. The elemental analysis was performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

The $NaB_{11}H_{14}(dioxane)_{2.5}$ was prepared by the literature procedure.[4]

$[(C_2H_5)_4N]_2B_{11}H_9Se_3$. The ammonium polyselenide solution was prepared as previously described employing sodium (0.64 g, 0.028 mol) and selenium (4.2 g, 0.053 g-atom).[1] A solution of $NaB_{11}H_{14}(dioxane)_{2.5}$ (5.0 g, 0.013 mol) in 5 mL of water was added to the polyselenide solution, and the reaction mixture was stirred for 48 h at room temperature. After this time, a saturated solution of tetraethylammonium chloride was added to the mixture until precipitation was complete. The resulting solid was isolated by filtration in air and was washed with two 10-mL portions of water. The crude solid was dissolved in a minimum of acetonitrile. A few milliliters of water was added to the solution, and then the solvent was slowly removed by rotary evaporation to give 0.54 g (6% yield based on $NaB_{11}H_{14}(dioxane)_{2.5}$) of $[(C_2H_5)_4N]_2B_{11}H_9Se_3$ as orange plates.

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Anal. Calcd for $C_{16}H_{49}B_{11}N_2Se_3$: C, 30.73; H, 7.90. Found: C, 30.47; H, 7.76. Electronic spectrum (acetonitrile solution, molar extinction coefficient in parentheses): 245 (7460), 277 sh (4970), 350 sh (1810) nm. Infrared spectrum (KBr mull): 2995 (w), 2500 (vs), 1480 (m), 1460 (s), 1395 (m), 1365 (w), 1310 (w), 1185 (m), 1160 (m), 1080 (w), 1045 (m), 1000 (m), 945 (w), 925 (w), 910 (w), 860 (w), 820 (w), 790 (m), 685 (w) cm^{-1}.

Crystallography

An irregularly shaped crystal of approximate dimensions 0.15 × 0.20 × 0.20 mm was used for the X-ray study. The crystal was mounted on a glass fiber using silicone grease and placed directly on the goniostat which was equipped with a gaseous nitrogen cooling system[6] and the sample maintained at −130 ± 5 °C throughout characterization and data collection. The diffractometer used was locally constructed[7] and consisted of a Picker four-circle goniostat interfaced to a Texas Instruments 980B minicomputer. The source was a molybdenum target monochromatized by means of a graphite crystal (002 plane), and the source–sample and sample–aperture distances were 23.5 and 22.5 cm, respectively. The receiving aperture dimensions were 2.5 mm wide by 4.0 mm in height. An ultrastable goniometer designed to minimize frosting and interference was used to hold the sample.

The sample was characterized using a systematic search procedure in which all reflections located in a limited region of reciprocal space are located and centered. A model of the reciprocal lattice is then constructed and examined for symmetry and systematic extinctions.[6] On the basis of such a procedure, the crystal was found to be monoclinic with extinctions corresponding to $P2_1/a$. Thirteen reflections were centered in both positive and negative regions of 2θ using an automated top/bottom–left/right slit assembly (which was the basis of the goniostat alignment), and the angular data from these reflections was refined to yield the final cell dimensions of a = 13.570 (5) Å, b = 14.835 (6) Å, c = 14.745 (4) Å, and β = 88.80 (1)°. The calculated density based on four molecules per unit cell is 1.40 g/cm^3, and the linear absorption coefficient is 36.9 cm^{-1} (λ(Mo K$\bar{\alpha}$) 0.71069 Å).

All data in the $+h,+k,\pm l$ quadrant were collected for the range $4.0 < 2\theta < 50.0°$, and a limited sphere of complete data were collected to compare symmetry-equivalent data and check for systematic errors. A standard θ–2θ scan technique was used with a speed of 3.0°/min over a range symmetrically disposed 1.0° on either side of the calculated positions of the Kα_1 and Kα_2 peaks, and 10 s background counts were recorded at each extreme of the scan. During the data collection, four reflections were monitored after every 100 measurements and examined for systematic trends. The intensities of the four showed only random fluctuations and no systematic trends, the largest deviation being ±4.5% for one standard and the average for the four being ±2.7%.

The data were corrected for background, Lorentz, and polarization effects using formulas which have been given previously. On the basis of prior experience an "ignorance factor" of 0.07 was used in calculating the standard errors based on counting statistics. The final data set consisted of 3781 unique structure amplitudes of which 3341 had $I > 0.0$, 2830 had $I > \sigma(I)$, and 2289 had $I > 2.33\ \sigma(I)$. For the purpose of least-squares refinement, only those amplitudes with $I > 0.0$ were utilized. Owing to the irregular shape of the crystal, no absorption correction was attempted (μ(Mo Kα) 36.9 cm^{-1}).

Direct methods were used to locate the three selenium atoms, and the positions were confirmed by Patterson techniques. Standard Fourier techniques were then used to locate all remaining nonhydrogen atoms.[9] Anisotropic refinement rapidly converged, and a difference Fourier map was then examined in an attempt to locate the hydrogen atoms. It was possible to locate peaks in positions which were chemically reasonable for hydrogens on all but two of the methyl carbons and three borons, although numerous other peaks of larger intensity were present which were not in proper bonding range for hydrogens. In addition, there were numerous peaks of larger than 1.5 e/Å^3 in the vicinity of the three selenium atoms. Attempts to refine the positional parameters for these hydrogen atoms were unsuccessful in that several of the peaks would shift to chemically unreasonable positions. Attempts to use the hydrogen positions as fixed-atom contributors did not significantly improve the residuals, and difference maps based on these refinements did not locate any further possible hydrogen atoms. For these reasons it was decided that the hydrogens which had been located were of sufficient doubt to preclude their use, and they were omitted from the final refinements.

Table I. Atomic Coordinates and Isotropic Thermal Parameters[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Se(1)	3799 (1)	3482 (1)	2952 (1)	24
Se(2)	2450 (1)	2517 (1)	2734 (1)	29
Se(3)	1273 (1)	3533 (1)	3311 (1)	24
B(1)	2688 (11)	5747 (10)	3168 (11)	24
B(2)	3821 (12)	5581 (12)	2603 (11)	28
B(3)	1406 (12)	5657 (11)	3093 (12)	29
B(4)	3165 (11)	4622 (11)	2490 (11)	25
B(5)	1838 (11)	4658 (10)	2736 (11)	22
B(6)	1840 (11)	6385 (11)	2275 (11)	26
B(7)	3164 (12)	6352 (11)	2029 (11)	26
B(8)	3443 (12)	5263 (11)	1489 (11)	25
B(9)	1297 (11)	5358 (11)	1896 (11)	24
B(10)	2328 (10)	4633 (10)	1613 (10)	17
B(11)	2312 (11)	5843 (11)	1287 (11)	24
N(1)	5035 (7)	2476 (7)	297 (6)	18
N(2)	2492 (8)	4275 (8)	6010 (7)	28
C(1)	5004 (9)	1911 (8)	1157 (8)	17
C(2)	4160 (10)	1212 (9)	1162 (10)	30
C(3)	4065 (8)	3034 (9)	251 (10)	23
C(4)	4018 (10)	3679 (9)	−552 (10)	28
C(5)	5122 (9)	1909 (9)	−581 (9)	24
C(6)	6046 (10)	1293 (9)	−603 (10)	32
C(7)	5960 (8)	3102 (9)	329 (9)	22
C(8)	5886 (9)	3803 (9)	1087 (10)	27
C(9)	3092 (10)	3756 (10)	5271 (10)	34
C(10)	3853 (11)	3111 (11)	5666 (11)	42
C(11)	1786 (10)	4886 (9)	5484 (10)	30
C(12)	1105 (10)	4591 (11)	6065 (10)	39
C(13)	3147 (11)	4820 (11)	6624 (11)	41
C(14)	3828 (11)	5502 (12)	6073 (12)	45
C(15)	1922 (12)	3612 (11)	6649 (11)	44
C(16)	1180 (11)	3015 (12)	6159 (12)	49

[a] Numbers in parentheses in this and all succeeding tables represent error in least significant bit(s).

Table II. Important Distances in the Molecule (Å)

Se(1)–Se(2)	2.351 (2)	B(7)–B(8)	1.836 (22)
Se(1)–B(4)	2.023 (16)	B(7)–B(11)	1.776 (22)
Se(2)–Se(3)	2.342 (2)	B(8)–B(10)	1.784 (20)
Se(3)–B(5)	2.016 (15)	B(8)–B(11)	1.789 (21)
B(1)–B(2)	1.751 (22)	B(9)–B(10)	1.807 (20)
B(1)–B(3)	1.749 (21)	B(9)–B(11)	1.779 (21)
B(1)–B(4)	2.043 (22)	B(10)–B(11)	1.858 (21)
B(1)–B(5)	2.091 (21)	N(1)–C(1)	1.520 (14)
B(1)–B(6)	2.004 (22)	N(1)–C(3)	1.557 (14)
B(1)–B(7)	2.000 (22)	N(1)–C(5)	1.547 (16)
B(2)–B(4)	1.689 (23)	N(1)–C(7)	1.563 (15)
B(2)–B(7)	1.689 (23)	N(2)–C(9)	1.552 (16)
B(2)–B(8)	1.794 (22)	N(2)–C(11)	1.540 (16)
B(3)–B(5)	1.674 (22)	N(2)–C(13)	1.516 (17)
B(3)–B(6)	1.714 (22)	N(2)–C(15)	1.556 (17)
B(3)–B(9)	1.828 (24)	C(1)–C(2)	1.545 (18)
B(4)–B(5)	1.830 (20)	C(3)–C(4)	1.525 (18)
B(4)–B(8)	1.789 (21)	C(5)–C(6)	1.552 (17)
B(4)–B(10)	1.738 (20)	C(7)–C(8)	1.529 (18)
B(5)–B(9)	1.787 (21)	C(9)–C(10)	1.532 (19)
B(5)–B(10)	1.773 (21)	C(11)–C(12)	1.538 (18)
B(6)–B(7)	1.826 (22)	C(13)–C(14)	1.583 (22)
B(6)–B(9)	1.786 (23)	C(15)–C(16)	1.533 (22)
B(6)–B(11)	1.771 (23)		

Positional parameters and isotropic thermal parameters are listed in Table I, and anisotropic thermal parameters and a listing of the observed and calculated structure amplitudes are available as supplementary material. The final residuals were $R_F = 0.095$ and $R_{wF} = 0.075$.

Results and Discussion

The structure of this unusual dianion product was determined by a single-crystal X-ray study which is illustrated in Figure 1. The cage has an octadecahedral structure similar to that found previously for the isoelectronic molecule

Table III. Important Angles in the Molecule (deg)

Se(2)–Se(1)–B(4)	97.2 (5)	B(1)–B(7)–B(2)	55.9 (9)
Se(1)–Se(2)–Se(3)	94.9 (1)	B(1)–B(7)–B(6)	63.0 (8)
Se(2)–Se(3)–B(5)	97.4 (5)	B(1)–B(7)–B(8)	91.7 (10)
B(2)–B(1)–B(3)	145.5 (13)	B(1)–B(7)–B(11)	97.0 (10)
B(2)–B(1)–B(4)	52.2 (8)	B(2)–B(7)–B(6)	116.5 (12)
B(2)–B(1)–B(5)	103.4 (11)	B(2)–B(7)–B(8)	61.0 (9)
B(2)–B(1)–B(6)	105.3 (11)	B(2)–B(7)–B(11)	112.2 (12)
B(2)–B(1)–B(7)	53.0 (8)	B(6)–B(7)–B(8)	107.6 (11)
B(3)–B(1)–B(4)	102.2 (10)	B(6)–B(7)–B(11)	58.9 (9)
B(3)–B(1)–B(5)	50.7 (8)	B(8)–B(7)–B(11)	59.4 (9)
B(3)–B(1)–B(6)	53.8 (8)	B(2)–B(8)–B(4)	56.2 (9)
B(3)–B(1)–B(7)	106.6 (11)	B(2)–B(8)–B(7)	55.4 (9)
B(4)–B(1)–B(5)	52.5 (7)	B(2)–B(8)–B(10)	107.6 (11)
B(4)–B(1)–B(6)	104.2 (10)	B(2)–B(8)–B(11)	106.8 (12)
B(4)–B(1)–B(7)	82.1 (9)	B(4)–B(8)–B(7)	94.2 (11)
B(5)–B(1)–B(6)	80.6 (9)	B(4)–B(8)–B(10)	58.2 (8)
B(5)–B(1)–B(7)	105.2 (10)	B(4)–B(8)–B(11)	103.0 (11)
B(6)–B(1)–B(7)	54.3 (7)	B(7)–B(8)–B(10)	104.5 (11)
B(1)–B(2)–B(4)	72.8 (10)	B(7)–B(8)–B(11)	58.7 (9)
B(1)–B(2)–B(7)	71.1 (10)	B(10)–B(8)–B(11)	62.7 (8)
B(1)–B(2)–B(8)	101.9 (11)	B(3)–B(9)–B(5)	55.1 (8)
B(4)–B(2)–B(7)	103.6 (12)	B(3)–B(9)–B(6)	56.6 (9)
B(4)–B(2)–B(8)	61.7 (9)	B(3)–B(9)–B(10)	106.8 (10)
B(7)–B(2)–B(8)	63.5 (9)	B(3)–B(9)–B(11)	108.1 (11)
B(1)–B(3)–B(5)	75.3 (10)	B(5)–B(9)–B(6)	95.8 (10)
B(1)–B(3)–B(6)	70.7 (10)	B(5)–B(9)–B(10)	59.1 (8)
B(1)–B(3)–B(9)	100.4 (11)	B(5)–B(9)–B(11)	105.0 (10)
B(5)–B(3)–B(6)	102.9 (12)	B(6)–B(9)–B(10)	104.9 (11)
B(5)–B(3)–B(9)	61.2 (10)	B(6)–B(9)–B(11)	59.6 (9)
B(6)–B(3)–B(9)	60.5 (10)	B(10)–B(9)–B(11)	62.4 (8)
Se(1)–B(4)–B(1)	130.6 (10)	B(4)–B(10)–B(5)	62.8 (9)
Se(1)–B(4)–B(2)	116.2 (10)	B(4)–B(10)–B(8)	61.0 (8)
Se(1)–B(4)–B(5)	112.4 (9)	B(4)–B(10)–B(9)	110.4 (11)
Se(1)–B(4)–B(8)	129.7 (10)	B(4)–B(10)–B(11)	102.2 (10)
Se(1)–B(4)–B(10)	123.2 (10)	B(5)–B(10)–B(8)	112.6 (11)
B(1)–B(4)–B(2)	55.0 (8)	B(5)–B(10)–B(9)	59.9 (8)
B(1)–B(4)–B(5)	65.1 (8)	B(5)–B(10)–B(11)	102.4 (11)
B(1)–B(4)–B(8)	91.6 (10)	B(8)–B(10)–B(9)	111.2 (11)
B(1)–B(4)–B(10)	98.7 (10)	B(8)–B(10)–B(11)	58.8 (8)
B(2)–B(4)–B(5)	118.4 (12)	B(9)–B(10)–B(11)	58.1 (8)
B(2)–B(4)–B(8)	62.1 (9)	B(6)–B(11)–B(7)	62.0 (9)
B(2)–B(4)–B(10)	114.9 (12)	B(6)–B(11)–B(8)	112.2 (11)
B(5)–B(4)–B(8)	109.8 (11)	B(6)–B(11)–B(9)	60.4 (9)
B(5)–B(4)–B(10)	59.5 (8)	B(6)–B(11)–B(10)	103.4 (11)
B(8)–B(4)–B(10)	60.8 (9)	B(7)–B(11)–B(8)	62.0 (9)
Se(3)–B(5)–B(1)	136.0 (10)	B(7)–B(11)–B(9)	111.6 (12)
Se(3)–B(5)–B(3)	118.3 (10)	B(7)–B(11)–B(10)	103.9 (10)
Se(3)–B(5)–B(4)	115.1 (9)	B(8)–B(11)–B(9)	112.3 (11)
Se(3)–B(5)–B(9)	127.9 (10)	B(8)–B(11)–B(10)	58.5 (8)
Se(3)–B(5)–B(10)	120.5 (10)	B(9)–B(11)–B(10)	59.5 (8)
B(1)–B(5)–B(3)	54.0 (8)	C(1)–N(1)–C(3)	108.7 (9)
B(1)–B(5)–B(4)	62.4 (8)	C(1)–N(1)–C(5)	113.5 (10)
B(1)–B(5)–B(9)	89.9 (9)	C(1)–N(1)–C(7)	108.1 (9)
B(1)–B(5)–B(10)	95.9 (9)	C(3)–N(1)–C(5)	107.6 (9)
B(3)–B(5)–B(4)	115.1 (11)	C(3)–N(1)–C(7)	111.5 (9)
B(3)–B(5)–B(9)	63.7 (10)	C(5)–N(1)–C(7)	107.5 (9)
B(3)–B(5)–B(10)	115.7 (12)	C(9)–N(2)–C(11)	105.1 (10)
B(4)–B(5)–B(9)	107.2 (11)	C(9)–N(2)–C(13)	112.2 (10)
B(4)–B(5)–B(10)	57.7 (8)	C(9)–N(2)–C(15)	111.0 (11)
B(9)–B(5)–B(10)	61.0 (8)	C(11)–N(2)–C(13)	111.4 (11)
B(1)–B(6)–B(3)	55.5 (8)	C(11)–N(2)–C(15)	111.8 (11)
B(1)–B(6)–B(7)	62.8 (8)	C(13)–N(2)–C(15)	105.5 (11)
B(1)–B(6)–B(9)	92.8 (10)	N(1)–C(1)–C(2)	112.4 (10)
B(1)–B(6)–B(11)	97.1 (10)	N(1)–C(3)–C(4)	114.6 (10)
B(3)–B(6)–B(7)	116.4 (12)	N(1)–C(5)–C(6)	112.7 (10)
B(3)–B(6)–B(9)	62.9 (9)	N(1)–C(7)–C(8)	112.7 (10)
B(3)–B(6)–B(11)	113.9 (12)	N(2)–C(9)–C(10)	113.0 (12)
B(7)–B(6)–B(9)	109.0 (11)	N(2)–C(11)–C(12)	115.8 (12)
B(7)–B(6)–B(11)	59.2 (8)	N(2)–C(13)–C(14)	112.2 (12)
B(9)–B(6)–B(11)	60.0 (9)	N(2)–C(15)–C(16)	113.8 (12)

$B_9H_9C_2(CH_3)_2$[10] and also for the 11-atom cage of the metallocarborane anion $(C_5H_5)Co(C_2B_8H_{10})Co(C_2B_8H_{10})^-$.[11]

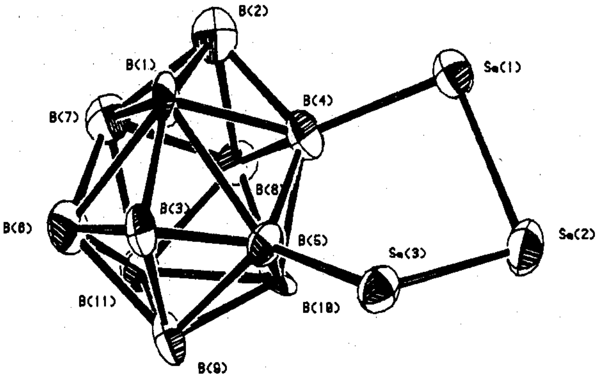

Figure 1. ORTEP drawing of the $B_{11}H_9Se_3^{2-}$ ion.

Table IV. Comparison of Geometries for $B_{11}Se_3H_9^{2-}$ and $B_9C_2H_9(CH_3)_2$

atom in $B_{11}Se_3H_9^{2-}$	dev,[a] Å	atom in $B_{11}Se_3H_9^{2-}$	dev,[a] Å
B(1)	0.045	B(9)	0.012
B(4)	0.037	B(10)	0.030
B(5)	0.024	B(11)	0.004
B(6)	0.041	B(2)[b]	0.181
B(7)	0.033	B(3)[b]	0.218
B(8)	0.016		

[a] From corresponding position in $B_9C_2H_9(CH_3)_2$. [b] Atoms not included in the least-squares fit.

A close examination of the distances and angles given in Tables II and III indicates that the selenium atoms bridging B(4) and B(5) do not significantly perturb the cage symmetry. A comparison of the bond distances and angles found in the present cage to those of the carborane analogue indicates that the only significant differences are those involving the two carbon atoms. In order to examine the similarity, a least-squares analysis was performed in which the nine boron atoms of the $B_9H_9C_2(CH_3)_2$ molecule were fitted to the corresponding nine atoms of the present ion. The results, shown in Table IV, dramatically show the similarity. The maximum deviation is 0.045 Å for the B(1) atom, and the average deviation between equivalent boron positions is 0.027 Å. The carbon atoms of the carborane cage are displaced by an average of 0.200 Å from the corresponding boron atoms of the $B_{11}H_9Se_3$ cage as would be expected.

Recently the X-ray study of 2,3-$(CH_3)_2$-4,5-$(OH)_2$-10-Br-2,3-$C_2B_9H_6$ (see the numbering in Figure 1) was completed.[12] This molecule has a very marked distortion from the regular octadecahedral structure discussed above. The B(1)–C(2)–B(4)–B(5)–C(3) ring of atoms is partly opened up so that the B(1)–B(4) and B(1)–B(5) distances are a large 2.35 Å. This distortion may be due in part to steric interactions of adjacent exopolyhedral substituents. However it may also be due in part to electronic interactions of the oxygen lone-pair electrons with the cage orbitals. It is interesting to note that the Se_3 substituent of $B_{11}H_9Se_3^{2-}$ does not have the capability to distort the polyhedral framework.

The ^{11}B NMR spectrum of $[(C_2H_5)_4N]_2B_{11}H_9Se_3$ in acetonitrile solvent contained two resonances at −6.9 (singlet, area 2) and −14.2 ppm (doublet, J_{BH} = 134 Hz, area 9). This molecule is probably fluxional at room temperature as appears to be the case for the parent $B_{11}H_{11}^{2-}$ ion.[5] It is possible that the polyhedral rearrangement of this molecule can be slowed down sufficiently at lower temperatures so that the static-structure NMR spectrum can be obtained. A variable-temperature ^1H NMR study is planned. This new molecular ion is only the second type of substituted $B_{11}H_{11}^{2-}$ ion known,[13] and further chemistry on the Se_3 ring of this molecule is underway.

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Registry No. $[(C_2H_5)_4N]_2B_{11}H_9Se_3$, 69069-46-1; $NaB_{11}H_{14}$, 52261-23-1.

Supplementary Material Available: A table of anisotropic thermal parameters and a listing of the observed and calculated structure amplitudes (19 pages). Ordering information is given on any current masthead page.

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Palladium Tetraazaannulenes: Synthesis and Structure of Palladium 5,7,12,14-Tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulene

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The first palladium dibenzotetraaza[14]annulenes have been prepared from the reaction of the free base ligand with bis(benzonitrile)palladous chloride. Analytical data are consistent with the proposed structures. Palladium 5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulene was characterized by single-crystal X-ray diffraction. The structure is monoclinic, space group $P2_1/n$, with $a = 6.497$ (2) Å, $b = 18.652$ (6) Å, $c = 7.429$ (3) Å, $\beta = 104.44$ (3)°, $Z = 2$, and mol wt 448.85. Data were collected using Mo Kα radiation (λ 0.710 69 Å) to a maximum 2θ of 50°. All the atoms, including hydrogen, were located on Patterson and Fourier maps and used in the refinement. The final discrepancy indexes were $R_F = 3.6\%$ and $R_{wF} = 4.6\%$ for 1013 independent reflections with $|F_o| \geq 3\sigma(F_o)$. The molecule has pseudoplanar geometry, a significant departure from other structures reported for this ligand.

Introduction

Palladium coordination complexes prefer a square-planar arrangement and are known to be among the most stable.[1,2] Ligands such as porphyrins, phthalocyanines, and tetraazaannulenes prefer to coordinate with a metal ion in a square-planar fashion. The fact that palladium porphyrins are very resistive to chemical demetalation illustrates the stability of palladium square-planar complexes.[3] Previous structural characterizations show that divalent metal ions coordinate with the 5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulene ligand in a square-pyrimidal arrangement.[4]

Dibenzotetraaza[14]annulene has been complexed with a variety of metals;[5-13] some of these complexes exhibit unusual geometries.[14-16] Metal tetraazaannulenes have been known to possess chemical and thermal stability as well as high catalytic activity, particularly as electrocatalysts.[17-19] A cobalt tetraaza[14]annulene has been used as the photoactive substituent in a potential solar energy storage system.[20]

To our knowledge, no one has reported a palladium complex of tetraaza[14]annulene. Although these macrocyclic ligands generally influence the physical and chemical properties of the metal,[21] an X-ray diffraction analysis of this first palladium tetramethyltetraazaannulene shows that palladium metal insertion has the effect of flattening a hitherto saddle-shaped ligand into a pseudoplanar configuration.[4,22,23]

Experimental Section

Bis(benzonitrile)palladous chloride[24] and 1,8-dihydro-5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulene (H_2TMTAA)[8] were mixed in refluxing benzene. The title compound, PdTMTAA, was obtained from the resulting precipitate. PdTMTAA crystallized as orange platelets in hexane. PdTMTAA decomposes at 150 °C to a yellow-brown compound, which melts at 260 °C. Anal.[25] Calcd. for Pd($C_{22}H_{22}N_4$): C, 58.87; H, 4.94; N, 12.48; Pd, 23.90. Found: C, 59.18; H, 5.12; N, 12.20; Pd, 23.51. The visible spectrum of PdTMTAA in dichloromethane has two peaks at 415 nm (log ϵ = 4.5) and at 490 nm (log ϵ = 4.2). The infrared spectrum of PdTMTAA in the solid phase (KBr) shows peaks at 1475, 1395, 1070, 820, and 790 cm^{-1}. The mass spectrum is consistent with the structure of PdTMTAA.[26] The parent ions around m/e 448 appear in an isotopic pattern typical of naturally occurring palladium.

Table I. Data Collection and Refinement Details for Pd($C_{22}H_{22}N_4$) (PdTMTAA)

diffractometer: Enraf-Nonius CAD-4[a]
monochromator: graphite crystal
radiation: Mo Kα (λ 0.710 69 A)
takeoff angle: 2.8°
scan speed: 4–20°/min
scan width: 1°
standards: 3
2θ limits of data: 50°

[a] Data taken by Molecular Structure Corp., College Station, TX 77840.

The palladium complex of 1,8-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulene (H_2TAA)[5] has also been prepared. The above complex, PdTAA, was synthesized in a manner similar to the previously described PdTMTAA synthesis. PdTAA was purified by sublimation. Anal.[25] Calcd. for Pd($C_{18}H_{14}N_4$): C, 55.05; H, 3.59; N, 14.26; Pd, 27.09. Found: C, 54.95; H, 3.59; N, 14.01; Pd, 27.56. The visible spectrum of PdTAA is a typical metal insertion spectrum with peaks at 363, 402, 424, 455, and 487 nm in chloroform. The spectrum is very similar to that of NiTAA[5] indicating that PdTAA is a planar molecule.[27]

Crystal Examination and Data Collection

All crystals of PdTMTAA examined were extremely thin plates, the large faces of which were parallelograms. The one selected for X-ray work measured 0.23 × 0.22 × 0.008 mm and was mounted with the fiber axis approximately parallel to the longest edges.

Data were collected by Molecular Structure Corp., College Station, TX. Details are presented in Table I. The following equations were used in reducing the data (Lp is the Lorentz–polarization factor, S is the scan rate, C is the total integrated peak count, B is the total background count, and R is the ratio of scan time to background counting time): $I = S(C - RB)$, $\sigma(I) = [S^2(C + R^2B) + 0.0025I^2]^{1/2}$,

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