complexes is probably due to the conjugated nature of the phenanthroline and bipyridyl which in some way leads to a greater electronic interaction with the anions.

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CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, LIVERMORE, CALIFORNIA

The Crystal and Molecular Structure of Tetramethylammonium Hexahydrohexaborate[1]

BY RILEY SCHAEFFER,[2] QUINTIN JOHNSON, AND GORDON S. SMITH

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Eberhardt, *et al.*, have explicitly pointed out that a $B_6H_6^{2-}$ ion of octahedral symmetry can be well-described by a closed-shell electronic structure.[3] In less explicit fashion, the treatment of MB_6 borides by Longuet-Higgins and Roberts leads to a similar conclusion, since the internal electronic structure is undisturbed if the external B–B bonds linking octahedra in the boride structure are replaced by external B–H bonds.[4] Recent isolation by Boone of salts containing the $B_6H_6^{2-}$ ion makes it possible to confirm this structure.[5] We have now carried out a complete X-ray structure analysis of tetramethylammonium hexahydrohexaborate.

The powder pattern can be indexed on the basis of a face-centered cubic lattice with $a = 11.84 \pm 0.01$ Å., suggesting a gross structure of the m_2x salt based on the antifluorite structure. The calculated density, assuming four molecules per unit cell, is 0.89 g. cm.$^{-3}$ compared with 0.88 ± 0.02 g. cm.$^{-3}$ measured by Boone.

Crystals grown from water solution were examined by precession and Weissenberg methods. Systematic extinctions are consistent with space groups F432, F$\bar{4}$3m, and Fm3m. The intensities of 59 independent reflections were measured with Mo Kα radiation (λ 0.7107 Å.) on a G.E. XRD-5 diffractometer equipped with a single-crystal orienter.

The structure was solved by noticing that the antifluorite structure can accommodate the octahedral $B_6H_6^{2-}$ ion at the origin and the tetrahedral (disregarding hydrogen) $N(CH_3)_4^+$ ion at $\pm^1/_4, {}^1/_4, {}^1/_4$. Reasonable values for the two parameters which relate to the size of the ions can be guessed from expected bond distances. Preliminary structure factor calculations verified this model.

From a difference Fourier based on this structure, the boron-bonded hydrogen atom was readily located, but the methyl hydrogens gave the appearance of free rotation. As an approximation to free rotation, half-hydrogen atoms were introduced in 192-fold general positions of space group Fm3m. Least-squares refinements yielded bond distances as well as temperature factors that were unacceptable. The resolution of the difference Fourier was poor because only a small amount of data were available. If the methyl hydrogen atoms were fixed, but had a large thermal parameter, the appearance would probably be one of free rotation; therefore, two alternate structures in this space group were considered in which hydrogen atoms were fixed. These structures, which have hydrogen atoms located in mirror planes, differ by a 60° rotation of the methyl group. One structure resulted in no improvement over free rotation, but the other structure gave realistic bond distances and temperature factors as well as a substantial improvement in the R factor.

This structure, with anisotropic temperature factors for boron and carbon, was refined by a full-matrix, least-squares program until the parameter shifts were less than one-tenth of the estimated standard deviation.[6] The final R factor was 5.3%. As an approximation to a weighting scheme appropriate for diffractometric data,[7] the following was used: $W = F_o^{1/4}$ for $F_o < A$, $W = A^{5/4}F_o^{-1}$ for $F_o > A$. Scaled to the structure factor data in Table II, A is 6.

Final parameters for all atoms are shown in Table I. The notation is that of "International Tables for X-ray Crystallography," Vol. I.[8] Observed and calculated structure factors are shown in Table II and pertinent bond distances are given in Table III.

Powder photographs, using chromium radiation (λ Kα_1 2.28963 Å.), of the corresponding cesium salt show a pseudo-primitive cubic cell, $a = 4.78$ Å., due to the overwhelming scattering of cesium. Weak lines require the true cell to be a face-centered cubic lattice with $a = 9.561 \pm 0.001$ Å. Isomorphism with the tetramethylammonium salt would appear likely.

TABLE I

FINAL ATOMIC PARAMETERS FOR $[N(CH_3)_4]_2B_6H_6$

24	B	(*e*)	$x = 0.1007 \pm 0.0008$
			$\beta_{11} = 0.0071 \pm 0.0010$
			$\beta_{22} = 0.0088 \pm 0.0006$
32	C	(*f*)	$x = 0.3219 \pm 0.0004$
			$\beta_{11} = 0.0137 \pm 0.0005$
			$\beta_{12} = -0.0065 \pm 0.0009$
8	N	(*c*)	$B = 3.9 \pm 0.3$ Å.^{2}
24	H_1	(*e*)	$x = 0.194 \pm 0.006$
			$B = 3.3 \pm 1.8$ Å.^{2}
96	H_2	(*m*)	$x = 0.368 \pm 0.003$
			$z = 0.269 \pm 0.004$
			$B = 8.7 \pm 1.5$ Å.^{2}

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TABLE II
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[N(CH_3)_4]_2B_6H_6$

h	k	l	K|Fo|	Fc	h	k	l	K|Fo|	Fc
0	0	2	92	-95	1	5	9	10	9
0	0	4	32	30	1	7	7	5	3
0	0	6	48	48	2	2	2	53	-54
0	0	8	15	15	2	2	4	8	9
0	0	10	12	12	2	2	6	10	-8
0	2	2	136	140	2	2	8	10	12
0	2	4	6	5	2	2	10	0	0
0	2	6	4	-3	2	4	4	47	-47
0	2	8	11	11	2	4	6	11	9
0	2	10	21	22	2	4	8	17	-17
0	4	4	12	11	2	4	10	13	12
0	4	6	27	-26	2	6	6	33	-35
0	4	8	20	21	2	6	8	16	15
0	4	10	5	-4	3	3	3	51	51
0	6	6	28	29	3	3	5	60	-58
0	6	8	20	-20	3	3	7	8	-9
0	8	8	23	22	3	3	9	12	12
1	1	1	75	73	3	5	5	4	-3
1	1	3	58	58	3	5	7	8	-8
1	1	5	0	1	3	5	9	10	-11
1	1	7	14	15	3	7	7	8	-11
1	1	9	19	19	4	4	4	8	6
1	1	11	7	10	4	4	6	38	-38
1	3	3	48	-46	4	4	8	0	1
1	3	5	16	15	4	6	6	5	-5
1	3	7	0	-2	4	6	8	11	-10
1	3	9	0	4	5	5	5	29	-28
1	5	5	20	-19	5	5	7	17	-16
1	5	7	6	-5	5	7	7	7	-4
					6	6	6	11	-11

TABLE III
BOND DISTANCES IN $[N(CH_3)_4]_2B_6H_6$

B–B	1.69 ± 0.01 Å.
B–H	1.11 ± 0.07 Å.
C–N	1.48 ± 0.01 Å.
C–H	0.99 ± 0.04 Å.

Comments.—Study of the behavior of a small sample of $[N(CH_3)_4]_2B_6H_6$ in a micro-differential calorimeter showed only a weak endothermic change between 405 and 407°K. After cooling to room temperature for 30 min., a second warming period did not reproduce the endothermic change. The observed transition might correspond to conversion of the methyl group to a freely rotating state, but further studies should be carried out.

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CONTRIBUTION FROM THE U. S. NAVAL
ORDNANCE TEST STATION, CHINA LAKE, CALIFORNIA

Azide Salts of *trans*-Diazidotetraamminecobalt(III) Ion

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In the course of studies with *trans*-diazidotetraamminecobalt(III) azide a second crystal form of the compound and a double salt with sodium azide were identified by their powder patterns. Since the appearances in both the solid state and aqueous solution are similar and the inadvertent preparation of the new compounds easy, a report on this possible source of confusion seems desirable.

Experimental

Preparation.—The complex is prepared by Linhard's method.[1] In brief, the double salt precipitates from an aqueous solution saturated with sodium azide, the usual compound (designated form I, the powder pattern has been reported[2]) from solutions one-third or less saturated with sodium azide,[1] and the crystal modification (form II) occasionally results from the rapid precipitation of aqueous solutions of form I with ethanol and ether. The interconvertibility of the three compounds is demonstrated by the following preparations.

(A) *trans*-$[Co(NH_3)_4(N_3)_2]N_3 \cdot NaN_3$ and *trans*-$[Co(NH_3)_4(N_3)_2]$-N_3 (Form I).—Eight grams of freshly prepared $[Co(NH_3)_4$-$(H_2O)_2]Cl_3$ treated according to Linhard[1] yielded 3.2 g. of crude *trans*-$[Co(NH_3)_4(N_3)_2]N_3$. This was dissolved in 70 ml. of water at 23°, filtered, precipitated by saturating with sodium azide, and washed with three 5-ml. portions of ethanol followed by ether; yield 2.4 g., designated **1**. Two grams of **1** precipitated according to Linhard[1] (solution in 48 ml. of water at 40° and precipitation with 24 ml. of saturated aqueous sodium azide at 5°) yields 1.4 g., designated **2**. A 0.5-g. sample of **2** dissolved in 22 ml. of water, filtered, and precipitated by saturating with sodium azide yields 0.5 g., designated **3**. Samples **1** and **3** had the powder pattern of the double salt (Figure 1, pattern C) while **2** was the usual *trans*-$[Co(NH_3)_4(N_3)_2]N_3$ (form I) (Figure 1, pattern A). All three are crystalline, dark blue to the eye, and reddish brown plates under the microscope.

(B) *trans*-$[Co(NH_3)_4(N_3)_2]N_3$ (Form II).—Rapid precipitation of aqueous solutions of form I with ethanol and ether produced brown powders. Unexpectedly, the first preparation showed a distinct powder pattern (Figure 1, pattern B). Later efforts to obtain the new material usually failed (yielding only form I). To the present, four of fifteen efforts have succeeded. While the conditions for the preparation of form II are still not clear, it appears that temperature and the proportions and rate of mixing of the reagents are important. Inadvertent seeding by microscopic nuclei of one form or the other may also contribute to the unpredictability of the reprecipitations. A successful preparation used 0.19 g. of form I dissolved in 22 ml. of water, which was filtered and precipitated with 200 ml. of ethanol followed by four 50-ml. and one 300-ml. portions of ether added with stirring. The temperature was maintained at 28 to 30°; yield 0.14 g.

Once obtained, form II may be reconverted to form I in *ca.* 80% yield by recrystallization according to Linhard[1] or, with more difficulty, by reprecipitation with ethanol and ether. This reluctance to reprecipitate as form I is indicated by the following: four reprecipitations of *ca.* 5-mg. samples yielded only form II, one 5-mg. experiment gave a mixture of I and II, and one of four essentially identical experiments with 25-mg. samples yielded form I. The last used 25 mg. of form II dissolved in 1 ml. of water at 22° and precipitated by the slow (*ca.* 10-min.) addition of 40 ml. of a 1:3 ethanol–ether solution. The yield of form I was greater than 18 mg.

Analysis.—Ionic azide was precipitated as silver azide, washed with ethanol, dried at room temperature, and weighed. Several analyses were checked by solution of the silver azide in nitric acid and precipitation and oven drying of silver chloride. Cobalt was determined gravimetrically as the anthranilate[3] following

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