with barely detectable traces of $CdCrO_4$-II and the other unidentified phase. There is evidence that such an amorphous phase is also present in quench products obtained from lower temperature runs (250–450°) where $CdCrO_4$-II is the major crystalline phase. All the X-ray patterns of $CdCrO_4$-II were of lower intensity than would be expected for the amount of powder used. Moreover, a prominent broad high-intensity region at low 2θ values was always present, again suggesting the presence of an amorphous phase. Further evidence for an amorphous phase is given by infrared data.

Infrared spectra were taken for (a) a sample rich in $CdCrO_4$-II and (b) a nearly amorphous $CdCrO_4$ specimen. The spectra are very similar to each other and also resemble the spectrum of α-$CdCrO_4$.[7] The frequencies (in cm^{-1}) are compared below. The data suggest that the $CdCrO_4$-II-rich samples probably contain much amorphous material and that the CrO_4 groups in the amorphous phase are similar to those in α-$CdCrO_4$.

$CdCrO_4$-II-containing sample	Amorphous	α-$CdCrO_4$
915 + 898	912	915
855	855	865
802	790	805

In summary, it is instructive to compare the crystallographic data for the three polymorphs of $CdCrO_4$. This is done in Table II. Especially noteworthy is the large increase in density in going from α- or β-$CdCrO_4$ to $CdCrO_4$-II. Such a density increase is to be expected in view of the coordination change in Cd, *i.e.*, going from a coordination of six in α- and β-$CdCrO_4$ to an eightfold coordination in scheelite-type $CdCrO_4$-II.

The complete elucidation of the phase equilibria of $CdCrO_4$ at high pressures may require high-pressure X-ray techniques. The fact that a nearly amorphous phase is obtained as quench product from the higher temperature region indicates perhaps that there exists still another high-pressure phase, which is, however, nonquenchable.

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A Cation Derived from BH_2^+ and Acetonitrile

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In a number of recent publications it has been demonstrated that displacement of iodide ions from an iodoborane adduct is a facile route for the synthesis of boronium compounds containing the BH_2^+ unit.[1–5] Although displacement by nitrogen bases can apparently be inhibited by steric factors[4] and can be directed to alternate accessible basic sites, such as the oxygen atom in dimethylformamide,[5] the practical limits imposed on the stability of the boron cation by the weakness of the base have not been established. Even such a weak base as 2-fluoropyridine ($pK_a = -0.44$) forms a stable cation.[4] It is therefore of interest to report the synthesis of a reasonably stable cation of BH_2^+ in which trimethylamine and the very weak base acetonitrile is coordinated to boron.

Results and Discussion

The synthesis of the cation $(CH_3)_3NBH_2NCCH_3^+$ was accomplished in a straightforward manner by iodide displacement from trimethylamine–iodoborane in benzene solution. The identity of the iodide salt was established by conversion to the hexafluorophosphate derivative and by its ir and nmr spectra. The infrared spectrum shows a strong doublet between 2400 and 2500 cm^{-1} assigned to the B–H stretches and a very intense absorption at 1150 cm^{-1} which corresponds to the BH_2 deformation.[1] There also is a relatively broad and intense absorption at 2375 cm^{-1} which is indicative of a coordinated $RC\equiv N$ group.[6] The proton nmr spectrum shows two singlets of appropriate relative intensity, shifted downfield relative to the free ligands.[4] Boron-attached hydrogens could not be detected. The ^{11}B spectrum also showed large line broadening, so that the expected triplet appeared as a very broad band with a width consistent with the magnitude of the coupling constants observed in related compounds.

The iodide salt was decomposed into trimethylamine–iodoborane and acetonitrile at 130°, a substantially lower temperature than the 200° which was apparently necessary for the similar decomposition of bis(trimethylamine)boronium chloride or bromide[7] in which the stronger base trimethylamine was displaced from boron.

Facile displacement of acetonitrile was also evidenced by the behavior of the iodide salt in pyridine solution. The band characteristic of free acetonitrile appeared in the proton spectrum within minutes after dissolution, while trimethylamine remained coordinated to boron. The latter base was only relatively slowly displaced by pyridine at room temperature.

The cation hydrolyzed relatively rapidly in water, so that derivatives could be prepared only in cold solution and with rapid work-up. The pH of hydrolyzing solutions initially was strongly acidic but on

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standing the solutions approached neutrality while gas was evolved. This observation could be explained if initially displacement of acetonitrile occurred producing an acidic water-coordinated cation or if water were added across the $C{\equiv}N$ bond to give $(CH_3)NBH_2NH{=}COHCH_3^+$, also an acid. Attempts to isolate such species however were unsuccessful.

The successful isolation of an addition compound of acetonitrile and $BH_2N(CH_3)_3^+$ is noteworthy from two aspects. First, nitrile adducts of BH_3 are unstable with respect to dissociation and are subject to internal hydride transfer at room temperature, sometimes explosively, to give borazines or polymeric species.[8,9] There was no evidence in this work that reduction of the $C{\equiv}N$ link occurred at room temperature. This is in agreement with the lowered reactivity of boron–hydrogen bonds in trimethylamine–iodoborane or in bis(amine)boron cations[4] relative to the reactivity in BH_3 adducts. Second, in view of the low base strength of acetonitrile it is remarkable that the ion can be obtained at all by halide displacement and that it has reasonable thermal stability.

To place the matter in perspective, dialkylamides of formic and acetic acids, which are rather weak bases, typically have pK_a values of $+0.5$ to -0.5[10] whereas acetonitrile has a pK_a of -10.[10] Similar comparisons can be made from Gutmann's donor numbers[11] (pyridine, 33.1; dimethylformamide, 26.6; acetonitrile, 14.1), which are measures of general coordinating ability. Accordingly, the acetonitrile adduct with BF_3 is completely dissociated in the gas phase at 50°,[12] and literature data indicate that the B–N bond in this compound is at least 24 kcal/mol weaker than the comparable bond in pyridine–boron trifluoride.[12,13] The hypothetical ion $(CH_3)_3NBH_2^+$ thus must be a very strong Lewis acid indeed in order to provide stability toward dissociation for the acetonitrile cation.

It is likely that acetonitrile is close to the lower limit in base strength which is required for practical synthesis of boron cations by iodide displacement with a sterically unhindered base. Qualitative observations indeed indicated that benzonitrile, which is a somewhat weaker base than acetonitrile,[10] did not react with trimethylamine–iodoborane at room temperature. The extremely fast displacement of acetonitrile by pyridine and the marginal hydrolytic stability even in acidic solution also suggest that one is approaching a practical limit of kinetic stability.

Experimental Section

Synthesis.—Sublimed trimethylamine–borane (36.5 g, 0.500 mol), obtained from Callery Chemical Co., dissolved in 200 ml of dry benzene was iodinated with solid iodine (63.5 g, 0.250 mol), which was added in portions over a 40-min period to the cooled and stirred solution.[3] Reagent grade dry acetonitrile (40.0 ml, 0.97 mol) was then added. White crystals slowly precipitated from the solution during 24 hr at room temperature. Product (48 g) was collected after filtration and washing with dry benzene and dry ethyl ether. This corresponded to a 40% yield of $CH_3CNBH_2N(CH_3)_3^+,I^-$. The compound was purified by precipitation from acetonitrile solution (110 g/l.) with twice the volume of benzene: the recovery was 64%. Exposure to the atmosphere was minimized during these operations. *Anal.* Calcd for $CH_3CNBH_2N(CH_3)_3^+,I^-$: C, 25.03; H, 5.89; N, 11.68; B, 4.51; I, 52.90. Found: C, 24.90; H, 5.81; N, 11.85; B, 4.32; I, 53.08.

The iodide salt was converted to the hexafluorophosphate in 60% yield by quick precipitation with excess NH_4PF_6 from an ice-cold aqueous solution. The white salt melted at 110–111°. *Anal.* Calcd for $CH_3CNBH_2N(CH_3)_3^+,PF_6^-$: C, 23.28; H, 5.48; N, 10.86. Found: C, 23.09; H, 5.30; N, 11.03.

Spectral Characteristics.—The infrared spectra of the iodide and hexafluorophosphate derivatives were nearly identical except for the absorptions of PF_6^- at 850 and 560 cm^{-1}. The following bands were observed: 2990 (m), 2490 (vs), 2450 (vs), 2360 (s), 2320 (sh), 2260 (w), 1470–1490 (s), 1445 (w), 1415 (w), 1340–1360 (m), 1210 (w), 1250 (s), 1190 (s), 1150 (vs), 1115 (s), 1035 (m), 1025 (s), 985 (m), 975 (s), 875 (s), 730 (w), 670 (w) cm^{-1}.

The proton nmr at 60 MHz gave two peaks with intensity ratio 3:1. Chemical shifts downfield from internal tetramethylsilane were, for the iodide, 175 ($(CH_3)_3N$) and 127 Hz (CH_3CN) and for the hexafluorophosphate 167 and 158 Hz. The ^{11}B nmr spectrum of the iodide in CH_2Cl_2 at 19.3 MHz gave a broad band at 25.6 ppm upfield from external $B(OCH_3)_3$, with a width of 370 Hz. The absorption appeared to be an unresolved triplet with $J_{BH} \approx 120$ Hz.

Reactions.—A 2.0-mmol sample of the iodide salt was heated in the vacuum line to 130–150°. The gaseous product (1.2 mmol) which was trapped proved to be acetonitrile, identified by its vapor pressure at 0°, 25 mm (lit.[14] 27 mm), and by the agreement of its infrared spectrum with that of an authentic sample. There also sublimed a solid to the cooler portions of the reaction vessel which was identified as trimethylamine–monoiodoborane. Its melting point was 73–74.5° (lit.[15] 73°). On standing in pyridine, the sublimate gave a proton nmr spectrum identical with that of $(CH_3)_3N$, the expected product from transamination.[1,4] A portion of the sublimate was treated with trimethylamine in benzene solution to give the bis(trimethylamine)boronium iodide,[4] which was converted to its PF_6^- salt, mp 203° dec (lit.[16] 200–205°). The residue from the decomposition was not characterized.

Another sample of the iodide salt was dissolved in pyridine. The nmr spectrum immediately after mixing showed one absorption identical with that of CH_3CN in this solvent (3 H) and another farther downfield corresponding to $(CH_3)_3NBH_2C_5H_5N^+$ (9 H).[4]

A further portion of the iodide was warmed in pyridine and then precipitated with CCl_4. The product dissolved in water and precipitated with NH_4PF_6 gave a 30% yield of pure bis(pyridine)-boronium hexafluorophosphate, mp 114–115° (lit.[4] 115°), which was identical in ir and nmr spectra with an authentic sample.

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