on the final solutions. A typical experiment is described in detail.

An unbuffered solution (initial pH 4.5) $\sim$0.002 *M* in $(H_3N)_5CoNCS^{2+}$ and $\sim$0.065 *M* in peroxodisulfate was allowed to react at room temperature. Absorption spectra of the yellow solution after 18 and 48 hr were nearly identical and, in the 400–600-mμ region, closely matched that calculated for a mixture containing 50% cyanopentaammine and 50% hexaammine. (Below 400 mμ the observed absorption rises continuously above that calculated.) At 72 hr, one-third of the solution was passed through a cation resin column (Dowex 50 X4, 50–100 mesh, acid form, 1.5 × 20 cm). The yellow band which formed near the top was eluted with 3 *M* $HClO_4$ (which had previously been shown to effect a separation of the cyanopentaammine and hexaammine species). The first 25 ml of eluent (colorless) was discarded; the next 64 ml was collected and the absorption spectrum was obtained. The spectrum coincided with that of cyanopentaamminecobalt(III) ion (except for some increased absorption below 400 mμ) at a concentration about 40% of the total cobalt present. This eluent solution was concentrated by warming to about 60°. After 4 days the reddish black(!) solid (C) which had formed was filtered off and recrystallized from perchloric acid to give a yellow product (D) a portion of which was dissolved in water and scanned (300–600 mμ) on a Beckman DBG spectrophotometer. The similarity of this spectrum to that of an authentic sample of cyanopentaamminecobalt(III) perchlorate is shown by the data in Table I.

Further confirmation of the identity of the product is provided by the infrared spectrum of the yellow solid (D): Reported:[5] sharp peak at 2145 cm^{-1}. Found: sharp peak at 2135 cm^{-1}.

H_2O_2–$((C_2H_5)_4dien)PdNCS$ or -SCN.[6]—The product of the oxidation of isothiocyanatotetraethyldiethylenetriaminepalladium(II) ion and its thiocyanate analog with hydrogen peroxide in approximately neutral solution has been identified as the corresponding cyano complex, $((C_2H_5)_4dien)PdCN^+$, on the basis of solution spectra studies. It was also found that the cyano complex formed readily on mixing equimolar quantities of cyanide ion (as the sodium salt) and either of the palladium–thiocyanate linkage isomers described above.

Discussion

The observations reported above leave little doubt that cyano complexes are formed in the oxidation processes studied.

Previous work on the oxidation of free thiocyanate ion has established cyanide ion as a product[7] in several cases. Wilson and Harris, in some careful studies of thiocyanate oxidation by hydrogen peroxide, have shown that HCN is produced nearly quantitatively in acidic solution[8] but that $NH_3 + HCO_3^-$ are formed in neutral solution.[9]

The peroxodisulfate oxidation of captive thiocyanate reported here has the opposite acid dependence, producing $Co(NH_3)_6^{3+}$ in acidic solution and $(H_3N)_5CoCN^{2+}$ in the absence of added acid.

An interesting feature of these reactions is that N-bonded thiocyanate is converted to presumably C-bonded cyanide. For the cobalt cases this is most likely the result of a rapid intramolecular isomerization of the type recently proposed for some similar cyano complexes.[10,11] With the palladium complexes it seems more likely that free cyanide is formed and reenters the coordination sphere in a subsequent substitution step.

Finally it may be suggested that the "oxidative substitution" reaction reported here might be of considerable utility in preparing specific cyano complexes which are presently unknown.

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[6] Previously reported by K. Schug and A. J. Sadowski, Tenth International Conference on Coordination Chemistry, Japan, Sept 1967.

[7] Several examples are given by B. J. Heinrich, M. D. Grimes, and J. E. Puckett, "Treatise on Analytical Chemistry," Vol. 7, I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, Section A, Part II, p 87 ff.

[8] I. R. Wilson and G. M. Harris, *J. Am. Chem. Soc.*, **83**, 286 (1961).

[9] I. R. Wilson and G. M. Harris, *ibid.*, **82**, 4515 (1960).

[10] J. Halpern and S. Nakamura, *ibid.*, **87**, 3002 (1965).

[11] J. Espenson and J. P. Birk, *ibid.*, **87**, 3280 (1965).

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Piperazinobisdiborane and Its Polymeric Consequences[1]

BY ANTON B. BURG AND BRUNO IACHIA

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The chemistry of the aminodiborane type $R_2NB_2H_5$[2] was extended some time ago to include cyclic aminodiboranes of the type $C_nH_{2n}NB_2H_5$.[3] However, attempts to make a double $=NB_2H_5$ from piperazine failed on account of occlusion effects which could not be overcome by using conventional organic solvents. We now confirm that the pyrolysis of $C_4H_8(NH)_2{\cdot}BH_3$ (containing some occluded piperazine) leads to polymers which resist strong acids, fail to sublime under high vacuum, and remain solid at 300°. Neither such pyrolysis products nor the original BH_3 adduct could be dissolved in acetone, acetonitrile, triethylamine, methyl chloride, or dichloromethane; and dimethyl sulfoxide or dimethylformamide dissolved them only slightly.

It appeared that the adduct $C_4H_8(NH)_2{\cdot}BH_3$ had formed a weakly dipole-bonded polymer in which the second ring-nitrogen atom was protected from attack by more diborane; then heating this adduct in the presence of occluded piperazine would lead to $=N(BH)N=$ patterns serving to connect the $C_4H_8N_2$ rings and so form a strong polymer. Also, the remaining $=NBH_2$ situations would not be chain-terminal because they would dimerize in the manner of $(CH_3)_2NBH_2$.[2]

For a different approach to such polymers, it seemed well to make the new compound $C_4H_8(NB_2H_5)_2$, from which a tertiary base could remove $2BH_3$ to form the $C_4H_8(NBH_2)_2$ unit, just as $(CH_3)_2NBH_2$ is formed from $(CH_3)_2NB_2H_5$.[2] However, this synthesis would re-

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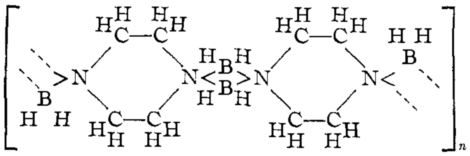
[1] It is a pleasure to acknowledge the generous support of this research by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government. We are grateful also to our colleague Dr. K. L. Servis for making possible the use of the Varian HA-100 nmr instrument and to Dr. R. E. Williams of Space-General Corp. for the loan of a 32.1-Mc radiofrequency unit and probe.

[2] A. B. Burg and C. L. Randolph, Jr., *J. Am. Chem. Soc.*, **73**, 953 (1951), *et ante.*

[3] A. B. Burg and C. D. Good, *J. Inorg. Nucl. Chem.*, **2**, 237 (1956).

quire a solvent wherein the second nitrogen-base atom would be available for bonding BH_3. The plan for such a solvent came from recent studies of BH_3 transfer among aminoboron hydrides.[4] It was argued that piperazine could remove BH_3 from $(CH_3)_2NB_2H_5$, forming $(CH_3)_2NBH_2$ and $HNC_4H_8NH \cdot BH_3$. Loss of H_2 would leave $HNC_4H_8NBH_2$, solubilized because $(CH_3)_2NBH_2$ would combine with it in the manner of the R_2NBH_2 dimerization. Then the addition of diborane at an appropriate temperature would produce $C_4H_8(NB_2H_5)_2$. In fact, this method succeeded.

Also, a 2:1 mixture of $(CH_3)_2NB_2H_5$ and $C_4H_8(NH)_2$ at 200° formed the pure polymer



Under high vacuum at 240–250°, this white solid vaporized, apparently by dissociation of the N_2B_2 rings, and recombination was slow enough for the vapor to pass through the high-vacuum line (including stopcocks) at 25° or to permit some vapor-phase infrared spectroscopy. The absence of B–H–B bridge frequencies showed that the polymer had not undergone any disproportionation analogous to the reversible conversion of $(CH_3)_2NBH_2$ to $[(CH_3)_2N]_2BH$ and $(CH_3)_2NB_2H_5$.[2] Even after several resublimations, the pure polymer seemed not to have suffered any such change.

Synthesis of Piperazinobisdiborane.—A vacuum-sealed glass tube containing 4 ml of liquid $(CH_3)_2NB_2H_5$, 1.4 mmol of sodium-dried piperazine, and 3.4 mmol of diborane was heated for 24 hr at 100°. The H_2 was pumped off through a −196° trap and measured, and the readily volatile components were removed through a trap *in vacuo* at −20°. The desired $C_4H_8(NB_2H_5)_2$ was sublimed into the high-vacuum system by warm-air heating; yield, 160.5 mg or 1.17 mmol (85%). A white solid by-product was heated *in vacuo* to remove a small sublimate identifiable as the polymer $(H_2BNC_4H_8NBH_2)_n$. The final residue melted at 140–145° but underwent thermosetting, becoming more refractory on heating. The resulting glassy resin seemed to be permanently air stable.

Characterization.—The purity of the slightly volatile main product was indicated by its very sharp melting point (84.5°) and a set of vapor tensions (Table I) conforming well to the linear equation $\log P = 10.912 - (3335/T)$. The measurements were not extended into the liquid region, for abnormal increases of pressure indicated dissociation.

The molecular weight was determined in solution in hexane at 30°, by means of an immersed differential tensimeter, as 149 (calcd, 137.4). The high result is attributed mostly to a slight loss of BH_3 groups, leading to BN_2B bridging. Such dissociation was observed also during high-vacuum sublimation at or near room temperature; then a second sublimation left a residue having the infrared spectrum of $(H_2BNC_4H_8NBH_2)_n$. It seemed that the dissociation was aided by polymer bonding but could be minimized by the presence of diborane.

TABLE I

VOLATILITY OF SOLID $C_4H_8(NB_2H_5)_2$

Temp, °C	45.0	50.0	55.0	60.0	65.0	69.0	73.0
P_{obsd}, mm	2.62	3.95	5.63	8.02	11.33	14.51	19.00
P_{calcd}, mm	2.70	3.92	5.63	8.00	11.25	14.66	19.01

For analysis, pure $C_4H_8(NB_2H_5)_2$ with concentrated aqueous HCl (16 hr at 120°) yielded 9.96H_2/mol (calcd, 10.0). Another sample, similarly attacked by methanol and HCl (using just enough of each for the purpose, to avoid forming CH_3Cl), yielded 97.4% of the expected $B(OCH_3)_3$, which was distilled off, dissolved in water, and titrated as boric acid. The residue of $C_4H_8(NH)_2 \cdot 2HCl$ was titrated potentiometrically by standard base, showing 98.0% of the expected amount. The same hydrochloride from a parallel run was crystallized from methanol and melted at 315–320°, like a mixture with authentic $C_4H_8(NH)_2 \cdot 2HCl$.

The infrared spectrum of $C_4H_8(NB_2H_5)_2$ vapor was recorded at 51° by the Beckman IR7 instrument, using an 8-cm sealed-glass cell with KBr windows, air-heated in an asbestos box. The analogy to $(CH_3)_2NB_2H_5$[5] guided most of the assignments in the following list of frequencies (cm^{-1}) of peaks, shoulders (sh), and broad humps (b), with relative intensities in parentheses: C–H stretching, 3031 (1.6), 3001 (1.2), 2941 (3.0), and 2883 (0.9); B–H terminal stretching, 2545 (10), 2540 sh (9.5), 2475 (9), 2471 sh (7), 2379 b (0.7), and 2345 (1.0); B–H–B bridge stretching, 1909 b (0.4), 1876 b (0.5), and 1638 (4.3); CH_2 deformation, 1459 (2.6), 1374 b (2.0), 1328 b (1.6), and possibly 1285 (2.2); BH_2 bending, 1195 (1.8), 1154 (1.3), and 1118 (3.4); B–N stretching, triplet at 1044 (5.2); CH_2 rocking, 1002 (1.5); C–N stretching, 958 (4.4) and 690 (0.4); BH_2 rocking, 879 b (0.5) and 794 (0.4); B–B stretching and BH_2 torsion, 768 (2.5), 740 (2.4), and 622 b (0.5); CH_2 torsion and N–CH_2 bending, 429 b (0.5), 420 (0.4), and 399 (0.4). The relative intensities were calculated by the definition $k = (100/8P) \log (I_0/I)$ for pressure P in centimeters.

The ^{11}B nmr spectrum of $C_4H_8(NB_2H_5)_2$ (saturated in hexane) is shown in Figure 1. It is not distinguishably different from $(CH_3)_2NB_2H_5$ at a similar concentration in hexane, except that this shows a chemical shift (measured from methyl borate by the substitution method) 0.9 ppm lower. For "neat" $(CH_3)_2NB_2H_5$ at 35°, however, we confirm earlier reports of lower resolution.[6,7]

The Sublimable Polymer.—The cleanest formation of the N_2B_2-ring-bonded polymer occurred during 2 hr in a sealed tube at 200° and is summarized by the following equation with millimolar stoichiometry.

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(4) A. B. Burg and J. S. Sandhu, *Inorg. Chem.*, **4**, 1467 (1965).

(5) D. E. Mann, *J. Chem. Phys.*, **22**, 70 (1954).

(6) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

(7) D. F. Gaines and R. Schaeffer, *ibid.*, **86**, 1505 (1964).

$$\begin{array}{ccccccc} nC_4H_8(NH)_2 & + & 2n(CH_3)_2NB_2H_5 & \longrightarrow & 2nH_2 & + & 2n(CH_3)_2NBH_2\ + \\ 0.818 & & 1.620 & & 1.651 & & 1.600 \\ & & -0.017 & & & & \\ & & \overline{1.603} & & & & (H_2BNC_4H_8NBH_2)_n \\ & & & & & & 0.818\ (89.7\ \text{mg}) \end{array}$$

The infrared spectrum of this polymer, in the form of a white film deposited from the gas phase upon the gas-cell windows, was recorded (in cm^{-1}) by the Beckman IR7 instrument. The hydrocarbon and C–N modes could be correlated with the 70° vapor-phase spectrum of pure piperazine; however, its complex patterns in the ranges 700–850 and 2700–2840 cm^{-1} were absent, presumably because their intensity was suppressed by the high polarity of the $N–BH_2$ groups. The B–H stretching modes were found at 2433 s, 2408 s, and 2350 m cm^{-1} (not CO_2!), correlating with 2446 vs, 2370 s, and 2230 m cm^{-1} for $(CH_3)_2NBH_2$ vapor. The B–N stretching mode showed at 1218 mw and 1184 s cm^{-1}; *cf.* 1209 s and 1192 s cm^{-1} for $(CH_3)_2NBH_2$ vapor. A characteristic BH_2 motion at 950 vs cm^{-1} compares with a 965–960 vs cm^{-1} doublet for $(CH_3)_2NBH_2$. A strong peak at 878 cm^{-1} is not understood. All of these frequencies are quite distinct from the piperazine spectrum.

Rapid scanning of a quickly heated sample by the Perkin-Elmer 337 instrument showed new peaks at 2550 vs and 2480 s cm^{-1}, evidently representing the monomer vapor. All other peaks correlated closely with those for the film.

The aqueous-HCl hydrolysis of $(H_2BNC_4H_8NBH_2)_n$ gave 100% of the expected hydrogen, but the methanol–HCl solvolysis gave only 70% of the expected piperazine hydrochloride and boric acid. A milky suspension indicated retention of a polymeric condition. Apparently the replacement of B–H by $B–OCH_3$ bonds made it sterically more difficult for the acid to break down the B–N bonds in the new polymeric mass.

Other Polymers.—Various other approaches led to more complex mixed-polymer products, usually more refractory than the pure sublimable $(H_2BNC_4H_8NBH_2)_n$. One experiment began with a demonstration of adduct formation at 25°

$$\begin{array}{ccccc} C_4H_8(NH)_2 & + & (CH_3)_2NB_2H_5 & \longrightarrow & HNC_4H_8NH\cdot(CH_3)_2NB_2H_5 \\ 0.526 & & 1.075 & & 0.524 \\ & & -0.553 & & \\ & & \overline{0.522} & & \end{array}$$

Then the pure adduct during 1 hr at 100° yielded 0.425 mmol of $(CH_3)_2NH$ and 0.626 mmol of H_2, leaving a white solid which neither melted nor volatilized *in vacuo* at 250°. Apparently this was stabilized by N–(BH)–N bonding but also included $(CH_3)_2N–B–H$ material.

Another approach aimed at the process

$$nC_4H_8(NB_2H_5)_2 + 2n(CH_3)_3N \longrightarrow 2n(CH_3)_3NBH_3 + (H_2BNC_4H_8NBH_2)_n$$

running 16 hr at 150° in a sealed tube with toluene as a possible solvent. However, the process was only partially quantitative: although the calculated amount of $(CH_3)_3N$ was absorbed, the recoverable yield of $(CH_3)_3NBH_3$ was only 84% and that of the sublimable polymer was 79%.

Direct dissociation also was tried: a 0.42-mmol sample of $C_4H_8(NB_2H_5)_2$, in a sealed tube immersed in an oil bath, was heated during 20 min from 170 to 210°, yielding $1.40H_2$, $0.06B_2H_6$, and $0.08B_5H_9$ per mole; then the white powdery product was inert to 12 *M* HCl and to various organic solvents. Its infrared spectrum (in a KBr pellet) showed the expected piperazine modes, along with B–H at 2515 cm^{-1} and BH_2 at 945 cm^{-1}. It probably was an intimate combination of $(H_2BNC_4H_8NBH_2)_n$ with boron–hydride units coming from loss of hydrogen from BH_3.

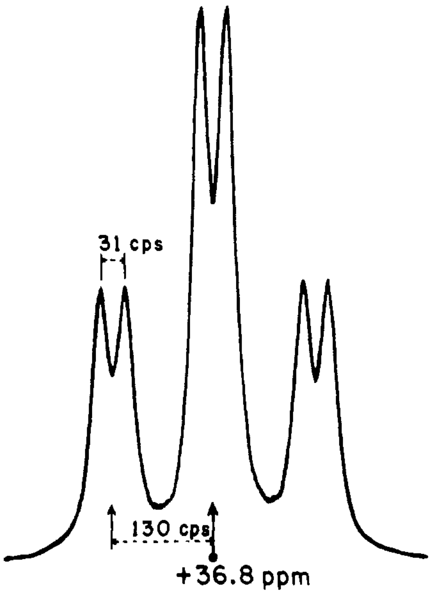

Figure 1.—Boron nmr spectrum of hexane solution of $C_4H_8(NB_2H_5)_2$ at 32.1 Mc. The chemical-shift reference is $B(OCH_3)_3$.

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Transition Metal Molybdates of the Type $AMoO_4$

By A. W. Sleight and B. L. Chamberland

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Considerable confusion has existed regarding structural relationships for molybdates of the type $AMoO_4$ where A is Mg, Mn, Fe, Co, Ni, or Zn. Young and Schwartz[1] have reported that high-pressure modifications of these molybdates are all isotypic with the analogous tungstates ($NiWO_4$ structure[2]). However, none of the structures of the normal (STP) molybdates has been known until recently. Smith and Ibers[3] have now reported the structure of α-$CoMoO_4$, and it

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(1) A. P. Young and C. M. Schwartz, *Science*, **141**, 348 (1963).
(2) R. O. Keeling, *Acta Cryst.*, **10**, 209 (1957).
(3) G. W. Smith and J. A. Ibers, *ibid.*, **19**, 269 (1965).