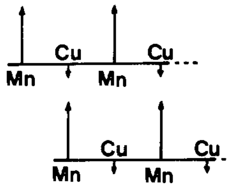
nearest-neighbor ion, giving again an antiferromagnetic interaction.[3] This is true not only for the Mn$^{II}$Mn$^{II}$ interaction in **1** but also for any hypothetical Mn$^{II}$Cu$^{II}$ interaction. At first sight, one might believe that it is not possible to achieve a ferromagnetic ordering since all the interchain interactions are certainly antiferromagnetic. In fact, there is an evident solution to this problem: replacing the Cu$^{II}$Cu$^{II}$ and Mn$^{II}$Mn$^{II}$ interchain interactions by Mn$^{II}$Cu$^{II}$ interactions. This is realized, for instance, if every other chain is displaced by half of a repeat unit along the *b* axis. The low-temperature spin structure for two adjacent chains may then be schematized as



with a parallel alignment of all the $^5/_2$ spins. Even if the displacement of every other chain is less than half of a repeat unit, the Mn$^{II}$Cu$^{II}$ interchain interaction may be dominant and a three-dimensional ferromagnetic ordering may occur. We will report soon on the first compound of this kind.[32]

**Registry No.** **1**, 101935-07-3; **2**, 105661-45-8; Na$_2$[Cu(pba)], 61344-73-8.

**Supplementary Material Available:** Tables V and VI, giving anisotropic thermal parameters and bond distances and angles involving hydrogen atoms (2 pages); a listing of structure factors (7 pages). Ordering information is given on any current masthead page.

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# Chemical Behavior and Structure of Triply Bridged Pyrazaboles of the Type RB($\mu$-pz)$_2$($\mu$-OBRO)BR[1]

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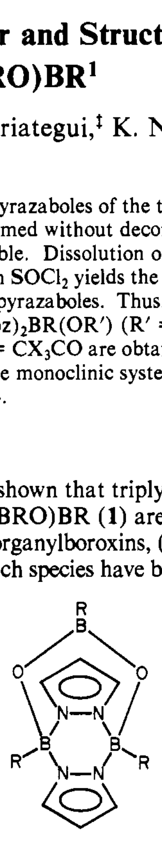
Triply bridged pyrazaboles of the type RB($\mu$-pz)$_2$($\mu$-OBRO)BR (**1**, R = $C_2H_5$, $C_6H_5$; Hpz = pyrazole) are thermally quite stable and can be sublimed without decomposition even under atmospheric pressure. At room temperature they are resistant to water but are not soluble. Dissolution of **1** in protonic solvents occurs with complete breakdown of the molecule. Halogenation of **1** (R = $C_2H_5$) with $SOCl_2$ yields the pyrazabole RClB($\mu$-pz)$_2$BRCl. The latter compound is a valuable material for the preparation of various other pyrazaboles. Thus, reaction with alkali-metal alkoxide or with alcohol in the presence of triethylamine gives access to R(R′O)B($\mu$-pz)$_2$BR(OR′) (R′ = $CH_3$, $C_2H_5$), the first examples of *B*-alkoxypyrazaboles; with $(CX_3CO)_2O$ (X = H, F), the species with R′ = $CX_3CO$ are obtained. The crystal and molecular structures of **1** with R = $C_2H_5$ were determined. The molecule crystallizes in the monoclinic system in space group $P2_1/c$ with $a$ = 7.587 (2) Å, $b$ = 12.415 (2) Å, $c$ = 16.387 (3) Å, $\beta$ = 90.50 (2)°, and $Z$ = 4.

## Introduction

Recently, it has been shown that triply bridged pyrazaboles of the type RB($\mu$-pz)$_2$($\mu$-OBRO)BR (**1**) are formed with surprising ease on interaction of triorganylboroxins, (-BRO-)$_3$, with pyrazole, Hpz.[2,3] Subsequently, such species have been observed as products in various other reactions, suggesting that the framework of **1** is chemically quite stable. The present study reports a more detailed investigation of the chemical properties of species of type **1** and of products derived thereof. In addition, the crystal and molecular structures of **1** with R = $C_2H_5$ have been determined by X-ray diffraction.



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## Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded of solutions in $CDCl_3$ on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield shifts from the reference shift (internal $Me_4Si$ for $^1H$ and $^{13}C$ NMR, external $Et_2O{\cdot}BF_3$ for $^{11}B$ NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants $J$ are given in Hz. Mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer.

Crystals of **1** with R = $C_2H_5$ were obtained from methylene chloride/hexane. A prismatic specimen was mounted on the tip of a thin glass fiber for X-ray examination and data collection. All data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K$\alpha$ radiation. Unit cell parameters were obtained by least-squares refinement of the angular setting from 25 reflections, well distributed in reciprocal space and lying in a $2\theta$ range of 15–30°. Four standard reflections were monitored and showed no significant decay. The data were corrected for Lorentz and polarization effects. All crystallographic computations were carried out by using the SDP package. The structure was solved by a combination of direct methods (MULTAN 11/82) and difference Fourier techniques. Refinement was by full-matrix least squares. Analytical atomic scattering factors were used throughout the structure refinement with both the real and imaginary components of the anomalous dispersion included for all atoms. All of the non-hydrogen atoms were located on the $E$ map. In the final refinements the thermal parameters of these atoms with the exception of H24 and H25 were located on Fourier difference maps and their positional and isotropic

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0020-1669/87/1326-0143$01.50/0

**Table I.** Summary of Crystallographic Data and Data Collection Procedures for **1** with R = $C_2H_5$[a]

| | |
|---|---|
| formula | $C_{12}H_{21}B_3N_4O_2$ |
| fw | 258.8 |
| cryst size, mm | 0.38 × 0.50 × 0.60 |
| space group | $P2_1/c$ |
| *a*, Å | 7.587 (2) |
| *b*, Å | 12.415 (1) |
| *c*, Å | 16.387 (3) |
| α, deg | 90 |
| β, deg | 90.50 (2) |
| γ, deg | 90 |
| *Z* | 4 |
| *V*, Å$^3$ | 1524.9 |
| $d_{calcd}$, g/cm$^3$ | 1.230 |
| μ, cm$^{-1}$ | 0.8 |
| *F*(000) | 648 |
| 2θ, deg | 4.50 |
| total no. of reflcns | 2711 |
| no. of unique reflcns | 2155 |
| no. of variables used | 267 |
| *R*[b] | 0.037 |
| $R_w$[c] | 0.049 |
| *g*[d] | 1.63 |

[a] In this and all subsequent tables esd's are given in parentheses. [b] $R = [\sum||F_o| - |F_o||/\sum|F_o|]$. [c] $R_w = \{\sum w(|F_o| - |F_o|)^2/\sum w|F_o|^2\}^{1/2}$, $w = [\{\sigma(|F_o|)\}^2 - (\kappa|F_o|^2)]^{-1}$ ($\kappa = 0.04$). [d] $g = [\sum w(|F_o| - |F_o|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ (NO = number of observations; NV = number of variables).

thermal parameters were refined. They were calculated for H24 and H25 with *d*(C-H) = 0.95 Å and *B*(H) = (*B*(C22) + 1.0). These were included in the last two cycles but were not refined. At a late stage in the structure determination the extinction coefficent was refined. A summary of the crystallographic data and data collection procedures is given in Table I.

**$C_2H_5B(\mu\text{-pz})_2(\mu\text{-OBC}_2H_5O)BC_2H_5$.**[2] NMR data: δ ($^{13}$C) (proton decoupled) 134.0, 125.8, 9*, 8.8, 8.6. $^1$H and $^{11}$B NMR data have been reported previously.[2] Mass spectrum (14 eV): *m/z* (5% or higher relative abundance) 258 (14), 257 (100), 256 (71), 255 (21), 202 (6), 201 (100), 200 (50).

**$C_6H_5B(\mu\text{-pz})_2(\mu\text{-OBC}_6H_5O)BC_6H_5$.**[2] Mass spectrum (14 eV): *m/z* (5% or higher relative abundance) 431 (18), 430 (60), 429 (51), 428 (15), 354 (22), 353 (100), 352 (73), 351 (17), 250 (6), 249 (35), 248 (15).

**$(C_2H_5)ClB(\mu\text{-pz})_2BCl(C_2H_5)$.** A mixture of 0.65 mL (8.9 mmol) of $SOCl_2$ and 1.17 g (4.1 mmol) of $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$ (R = $C_2H_5$), which gave a clear solution, was slowly heated in an oil bath. When a bath temperature of 110 °C was reached, a vigorous reaction started, and the bath was removed when about half of the reaction mixture had solidified, i.e. within ca. 5 min. Once the reaction subsided, the mixture was briefly heated (5–10 min, oil bath at 110 °C). After being cooled to room temperature, the pasty reaction product was subjected to a vacuum of 1 Torr for 24 h at room temperature. A solid residue, 1.09 g (93%), of the crude title compound, mp 176–177 °C, remained. It was recrystallized twice from toluene to give 0.7 g of colorless crystals, mp 180–181 °C. Anal. Calcd for $C_{10}H_{16}B_2Cl_2N_4$ ($M_r$ 284.79): C, 42.17; H, 5.66; B, 7.59; Cl, 24.90; N, 19.67. Found: C, 42.00; H, 5.71; B, 7.53; Cl, 23.82; N, 19.55.

NMR data: δ ($^1$H) 8.05 (2 H, d, *J* = 2.5), 6.63 (1 H, t, *J* = 2.5), 1.10 + 0.70 (5 H, unresolved m); δ ($^{11}$B) 4.2 (s, $h_{1/2}$ = 110 Hz).

No molecular ion M was observed in the mass spectrum of the compound, but an ion cluster near *m/z* 255 evidenced the ready loss of an ethyl group from the parent. The general fragmentation pattern closely paralleled that of other pyrazaboles containing boron-bonded hydrocarbon or halogen substituents.

**$(C_2H_5)(CH_3O)B(\mu\text{-pz})_2B(C_2H_5)(OCH_3)$.** A 15-mL aliquot of methanol containing 5 mmol of $KOCH_3$ was added to 1 g (ca. 3.5 mmol) of $(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$, and the mixture was heated with stirring to gentle reflux. A clear solution was obtained within 10 min, and heating was continued for 1 h. After the mixture was cooled to room temperature and the solvent was evaporated under reduced pressure, the colorless residue was washed twice with 10 mL of water each and was dried under vacuum to give ca. 0.8 g of colorless product, mp (after sublimation under vacuum at a bath temperature of 120–130 C) 96–98 °C.

The same compound but in a slightly different isomer ratio (4:1 as based on $^1$H NMR data) and of mp 109–110 °C was obtained by using the dehydrohalogenation procedure employing triethylamine; see alternate procedure described below.

Anal. Calcd for $C_{12}H_{22}B_2N_4O_2$ ($M_r$ 275.96): C, 52.23; H, 8.04; B, 7.83; N, 20.30; O, 11.59. Found: C, 52.29; H, 8.29; B, 7.54; N, 20.12.

NMR data: δ ($^1$H) 7.86 (d, *J* = 2.3) + 7.84 (d, *J* = 2.4) (2 H total, ratio 1:4), 6.58 (t, *J* = 2.4) + 6.57 (t, *J* = 2.3) (1 H total, ratio 1:4), 2.96 (s) + 2.87 (s) (3 H total, ratio 1:4), 0.65 (m) + 0.45 (m) (5 H); δ ($^{11}$B) 4.9 (s, $h_{1/2}$ = 125 Hz); δ ($^{13}$C) (proton decoupled) 135.0, 134.5, 107.0, 106.7, 50.1, 49.8, 17*, 8.7, 8.5 (most intense signals at 134.5, 106.7, 49.8, and 8.7).

**$(C_2H_5)(C_2H_5O)B(\mu\text{-pz})_2B(C_5H_5)(OC_2H_5)$.** A solution containing 10 mmol of $KOC_2H_5$ in 15 mL of anhydrous $C_2H_5OH$ was prepared by adding the appropriate quantity of potassium metal to anhydrous ethanol, and 1.1 g (3.9 mmol) of $(C_2H_5)ClB(\mu\text{-pz})_2BCl(C_2H_5)$ was added with stirring. The mixture was heated to reflux for 10 min, and after it was cooled to room temperature, all volatile material was removed under vacuum. The solid residue was sublimed under vacuum (bath temperature not to exceed 180 °C) to give 120 mg (10% yield) of a crystalline subliminate, mp 120–122 °C.

**Alternate Procedure.** A quantity, 1.02 g (3.5 mmol), of $(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$ was added with stirring to a solution of 3 mL of triethylamine in 15 mL of ethanol. The mixture was slowly warmed, and a clear solution was obtained at a temperature near 60 °C. The mixture was cooled to room temperature, and volatile material was removed under reduced pressure. The colorless residue was washed five times with 5 mL aliquots of water and dried under vacuum over $P_4O_{10}$ to give 0.91 g (84% yield) of crude product, mp 114–116 °C; mp (after sublimination under high vacuum) 132–134 °C. The analytical data were identical with those of the material described above but the isomer ratio (as based on $^1$H NMR data) was about 5:1 (as compared to a ratio of 3.5:1 obtained by the preceding procedure).

Anal. Calcd for $C_{14}H_{26}B_2N_4O_2$ ($M_r$ 304.01): C, 55.31; H, 8.62; B, 7.11; N 18.43; O, 10.52. Found: C, 55.59; H, 8.86; B, 6.71; N, 18.52.

NMR data: δ ($^1$H) 7.85 (d, *J* = 2.2) + 7.83 (d, *J* = 2.4) (2 H total, ratio 1:5), 6.54 (t, *J* = 2.4) + 6.53 (t, *J* = 2.4) (1 H total, ratio 1:5), 3.09 (q, *J* = 7) + 2.95 (q, *J* = 7) (2 H total, ratio 1:5), 1.10 (t, *J* = 7) + 1.03 (t, *J* = 7) (3 H total, ratio 5:1), 0.96–0.45 (5 H, m); δ ($^{11}$B) 4.7 (s, $h_{1/2}$ = 160 Hz).

**$(C_2H_5)(CF_3COO)B(\mu\text{-pz})_2B(C_2H_5)(OCOCF_3)$.** To a stirred solution of 0.91 g (3.2 mmol) of $(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$ in 12 mL of benzene was added 2.2 mL (15.6 mmol) of trifluoroacetic anhydride. The mixture was slowly warmed to about 50–55 °C when a gas evolution began, which ceased after about 1.5 h. The mixture was then cooled to room temperature, and volatile material was removed under vacuum. A colorless residue, 1.34 g (96%), of crude material of mp 132–135 °C remained, which was recrystallized from cyclohexane to give a pure product, mp 136–137 °C. Anal. Calcd for $C_{14}H_{16}B_2F_6N_4O_2$ ($M_r$ 439.92): C, 38.22; H, 3.67; B, 4.91; F, 25.91; N, 12.73; O, 15.55. Found: C, 38.18; H, 3.84; B, 4.99; F, 25.94; N, 12.38.

NMR data: δ ($^1$H) 8.10 (d, *J* = 2.6) + 8.03 (d, *J* = 2.5) (2 H total, ratio 4:3), 6.56 (1 H, 2 overlapping t), 1.38 (q, *J* = 7) + 1.18 (q, *J* = 7) (2 H total, ratio 4:3), 0.75–0.66 (3 H, m); δ ($^{11}$B) 3.3 (s, $h_{1/2}$ = 175 Hz). Mass spectrum: *m/z* (5% or more relative intensity) 412 (14), 411 (100), 410 (49), 409 (5), 327 (16), 326 (9), 317 (23), 315 (10), 223 (20), 222 (10), 190 (7), 153 (9).

**$(C_2H_5)(CH_3COO)B(\mu\text{-pz})_2B(C_2H_5)(OCOCH_3)$.** To a stirred slurry of 1.01 g (3.5 mmol) of $(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_2)Cl$ and 3 mL of benzene was added 3 mL (29.3 mmol) of acetic anhydride. The mixture was slowly heated to reflux, which was maintained for 6 h. After the mixture was cooled to room temperature, volatile material was removed under vacuum to leave 1.13 g (97%) of crude material, mp (after washing with petroleum ether) 130–132 °C (mp 132–134 °C after recrystallization from cyclohexane). Anal. Calcd for $C_{14}H_{22}B_2N_4O_2$ ($M_r$ 331.98): C, 50.65; H, 6.68; B, 6.51; N, 16.88; O, 19.28. Found: C, 50.46; H, 6.81; B, 6.24; N, 16.80.

NMR data: δ($^1$H) 8.01 (d, *J* = 2.4) + 7.95 (d, *J* = 2.4) (2 H total, ratio 12:1), 6.51 (1 H, unsym t, *J* = 2.5), 1.94 (s) + 1.88 (s) (3 H total, ratio 1:12), 1.32 (q, *J* = 7.5) + 1.12 (unresolved q) (2 H total, ratio 12:1), 0.68 (3 H, t, *J* = 7.5); d ($^{11}$B) 2.7 (s, $h_{1/2}$ = 165 Hz). Mass spectrum: *m/z* (5% or more relative intensity) 304 (15), 303 (100), 302 (47), 301 (6), 273 (21), 272 (15), 261 (17), 260 (8), 193 (66), 192 (31), 191 (5), 151 (10), 150 (5).

## Results and Discussion

**Thermal Stability of the Pyrazaboles of Type 1.** *B*-Triorganylboroxins, $(-BRO-)_3$, react readily with pyrazole, Hpz, to form triply bridged pyrazaboles of the type $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$ (**1** with R = $C_2H_5$, $C_5H_5$).[2,3] The original B–O bonds of the boroxin that remain in the pyrazabole **1** are quite resistant to additional attack by Hpz. Even when a mixture of **1** and Hpz was heated to reflux for several hours in the absence of solvent

**Table II**

| | *m/z* | | | | | |
|---|---|---|---|---|---|---|
| | 459 | 458 | 457 | 456 | 455 | 454 |
| fa(calcd) | 0.0159 | 0.1036 | 0.4015 | 0.3382 | 0.1182 | 0.0180 |
| fa(obsd) | 0.0160 | 0.1037 | 0.3708 | 0.3500 | 0.1352 | 0.0184 |

(at bath temperatures near 180–200 °C), only small amounts of the expected pyrazabole R(pz)B($\mu$-pz)$_2$BR(pz) were formed and about 80% of **1** was recovered unchanged.

The thermal stability of the pyrazabole **1** with R = $C_2H_5$ is illustrated by the fact that it can be sublimed (argon cover, 205 °C bath temperature, 9 h) under atmospheric pressure without any decomposition. Carefully dried (at 60 °C and under vacuum for 8 h) **1** with R = $C_6H_5$ is also thermally quite stable. When heated to 220–230 °C (bath temperature) for 9 h either under vacuum (3 Torr) or in an inert (argon) atmosphere, the material sublimed without decomposition. However, a material that was not predried underwent substantial decomposition under the same conditions: Pyrazole and some of the original compound sublimed off and the residue was found to be primarily a mixture of the starting material together with (–BRO–)$_3$, R$_2$B($\mu$-pz)$_2$BR$_2$, $B_2O_3$, and what seemed to be the pyrazabole RB($\mu$-pz)$_2$[$\mu$-(OBR)$_2$O]BR.

Evidence for the formation of the latter ring expansion product rests on the observation of a very minor ion cluster for the molecular ion M of the species as well as a more intense cluster for the M – 77 ion (i.e., loss of a phenyl group), $C_{24}H_{21}B_4N_4O_3$, in the mass spectrum of the thermolysis residue. The fractional abundances (fa) of the ion cluster correspond well with the calculated data as shown in Table II.

Similarly, an extremely small ion cluster corresponding to *m/z* M – 77 for M = RB($\mu$-pz)$_2$[$\mu$-(OBR)$_3$O]BR was observed. However, these ring expansion products could not be separated from the mixture and no pure materials were obtained.

These cited observations indicate that traces of water promote rearrangement processes of **1** at elevated temperatures. The resultant scrambling of phenyl substituents and formation of the symmetrical pyrazabole R$_2$B($\mu$-pz)$_2$BR$_2$1 is not really surprising. The formation of the indicated ring expansion products is an unexpected feature that is likely to originate from the interaction of **1** with (–BRO–)$_3$, which is formed by the initial hydrolysis of **1**. The various processes may be illustrated by eq 1–3.

$$\mathbf{1} + H_2O \rightarrow (\text{–BRO–})_3 + 2\text{Hpz} \qquad (1)$$

$$\mathbf{1} + {}^1/_3(\text{–BRO–})_3 \rightarrow \text{RB}(\mu\text{-pz})_2[\mu\text{-(OBR)}_2\text{O}]\text{BR} \qquad (2)$$

$$\mathbf{1} + {}^1/_3(\text{–BR–O–})_3 \rightarrow \text{R}_2\text{B}(\mu\text{-pz})_2\text{BR}_2 + \text{B}_2\text{O}_3 \qquad (3)$$

Indeed, heating of dry **1** with R = $C_6H_5$ with an excess of (–BRO–)$_3$ for 4 h at 220 °C gave a glassy product. The excess of (–BRO–)$_3$ could be sublined off, and the remainder of the material was further sublimed to give a sublimate, mp 152–156 °C. Mass spectral data again suggested that this latter product consisted primarily of the pyrazaboles R$_2$B($\mu$-pz)$_2$BR$_2$ and R($\mu$-pz)$_2$[$\mu$-(OBR)$_n$O]BR with $n$ = 1 and 2. The sublimination residue consisted mainly of boric oxide. Hence, the overall processes of this latter reaction may be illustrated by eq 2 and 3, above.

**Solvolysis Reactions of 1.** Despite the fact that unreacted pyrazole was removed from the product of the synthesis of the triply bridged pyrazabole **1** with R = $C_2H_5$ by washing with water at room temperature, the compound dissolved in hot water but with immediate decomposition. Both Hpz and RB(OH)$_2$ could be extracted (with $CCl_4$) from the concentrated aqueous solution and were identified by mass spectrometry. The compound was also found to be soluble in methanol (even without heating), but solvolysis occurred immediately. The initial products of the solvolysis were identified (by mass spectrometry) as RB(OCH$_3$)$_2$, (–BRO–)$_3$, and Hpz. When the solution was allowed to stand at room temperature, further arrangements occurred and the species B(OCH$_3$)$_3$, R$_2$BOCH$_3$, R$_2$BOH, and R$_2$B($\mu$-pz)$_2$BR$_2$ were identified as products. These findings were substantiated by performing the solvolysis with $CD_3OD$.

**Table III**

| R = $C_2H_5$ | $\delta(^{11}B)$ (approximate relative intensity) | | | |
|---|---|---|---|---|
| RB($\mu$-pz)$_2$($\mu$-OBRO)BR | 31.5 (1) | | 1.8 (2) | |
| +pyridine | 32.3 (1) | 22.8 (2.5) | 1.5 (2) | |
| +triethylamine | 31.7 (4) | 22.6 (1) | 1.6 (8) | –0.1 (2) |
| +diethylamine | 30.1 (2) | 22.6 (3) | 1.5 (5) | |
| +ammonia | 30.8 (1) | 21.6 (2) | 1.5 (3.5) | |

It is worth noting that the ready exchange even of boron-bonded hydrocarbon groups was also observed on methanolysis of (–B-$C_2H_5$O–)$_3$. A strong exothermic reaction was observed when the two reagents were mixed at room temperature. After the mixture stood for 3 h, mass spectral data of the reaction product indicated the formation not only of RB(OCH$_3$)$_2$ and RB(OCH$_3$)(OH) but also of B(OCH$_3$)$_3$ and the diethylboron species R$_2$BOH and R$_2$BOCH$_3$. Again, these data could be confirmed by using $CD_3OD$ as reagent.

The pyrazabole **1** with R = $C_6H_5$ was also dissolved in hot (dry) methanol, and the solution was briefly refluxed. After solvent evaporation at room temperature, the residue consisted primarily of the previously characterized[3] adduct (–BRO–)$_3$·Hpz. In addition, free Hpz and the methoxyboranes RB(OCH$_3$)$_2$ and RB(OH)(OCH$_3$) were identified by mass spectrometry; no pyrazabole species could be detected.

**Interaction of 1 with Amines.** As noted above, there seem to be some minor but noteworthy differences in the reactivity of the triply bridged pyrazaboles of type **1** with R = $C_2H_5$ or $C_6H_5$, respectively. This same observation held true in the case of the interaction of compounds of type **1** with amines. For example, in the case of R = $C_6H_5$, treatment with anhydrous amines did not greatly affect **1**: The $^{11}$B NMR spectra of solutions (in $CDCl_3$) of the cited pyrazabole with excess of amines showed only a slight broadening of the signal for the three-coordinate boron at 28.7 ppm (pyridine, pyrazole, diethylamine) and a very minor shift of the signal in some cases (to 27.2 ppm for ammonia and to 27.3 for triethylamine). This observation suggests only very weak coordination, if any. A quite different picture emerged for the interaction of **1** with R = $C_2H_5$ with the same amines. This was least pronounced for the interaction of the pyrazabole with pyrazole, where only a very small (but clearly noticeable) shoulder at approximately 5.5 ppm appeared as a shoulder on the 1.8 ppm signal of the four-coordinate boron of the pyrazabole. In the other cases, e.g. interaction with pyridine, a new signal near 22 ppm appeared, which accounted for even more than one-third of the total boron. This observation would suggest that even some of the pyrazabole boron was changed into another moiety. The experimental NMR observations are summarized in Table III. The signal at 30.8 ppm for the ammonia interaction was extremely broad and may consist of two overlapping signals.

It is apparent that these observations require a more detailed scrutiny. In any case, even at this stage of study they document differences in chemical behavior of **1** depending on R. Such differences were also found in other chemical reactions of species of type **1**. For example, the species with R = $C_2H_5$ readily reacted with $SOCl_2$; for R = $C_6H_5$, no reaction was observed under analogous conditions (see below).

**Crystal and Molecular Structures of 1 with R = $C_2H_5$.** The crystal and molecular structures of **1** with R = $C_2H_5$ were determined by X-ray diffraction. The structure was found to be in complete consonance with that deduced previously[2] from NMR data. It is shown in Figure 1; final positional parameters, their estimated standard deviations, and isotropic thermal parameters are given in Tables IV and V. Selected bond distances and angles are given in Tables VI and VII, respectively. The molecule has approximate $C_s$ symmetry, with the mirror being the least-squares plane defined by C32–C31–B3–O23–B2–C21–C22–O12–B1–C11–C12. Dihedral angles between this plane and the least-squares planes B3–N3–C341–C342–C343–N4–B1 and B1–N1–C121–C122–C123–N2–B3 are 111.2 and 116.2°, respectively. The central $B_2N_4$ ring is in a boat conforamtion, and bond distances and bond angles fall within the normally observed ranges.

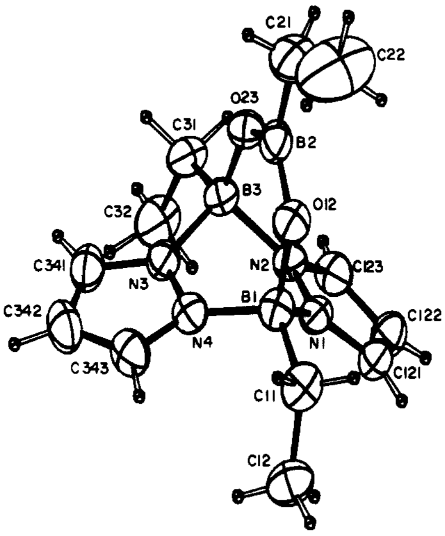

**Figure 1.** ORTEP plot of RB($\mu$-pz)$_2$($\mu$-OBRO)BR with R = $C_2H_5$.

**Table IV.** Positional Parameters and Isotropic Equivalent Parameters of Non-Hydrogen Atoms of **1** with R = $C_2H_5$

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| B1 | 0.4237 (2) | −0.0354 (2) | 0.2468 (1) | 3.15 (4) |
| B2 | 0.7094 (3) | 0.0460 (2) | 0.1970 (1) | 3.44 (4) |
| B3 | 0.6943 (2) | 0.0572 (2) | 0.3506 (1) | 3.03 (4) |
| N1 | 0.3746 (2) | 0.0653 (1) | 0.30191 (8) | 2.86 (3) |
| N2 | 0.5029 (2) | 0.1089 (1) | 0.35035 (8) | 2.84 (2) |
| N3 | 0.6542 (2) | −0.0676 (1) | 0.35846 (8) | 3.00 (3) |
| N4 | 0.5243 (2) | −0.1110 (1) | 0.30984 (8) | 3.07 (3) |
| O12 | 0.5497 (1 | −0.0009 (1) | 0.18584 (7) | 3.56 (2) |
| O23 | 0.7739 (1) | 0.07604 (9) | 0.27163 (6) | 3.31 (2) |
| C11 | 0.2554 (2) | −0.0909 (2) | 0.2072 (1) | 4.04 (4) |
| C12 | 0.1095 (2) | −0.1330 (2) | 0.2624 (1) | 4.72 (4) |
| C21 | 0.8264 (3) | 0.0691 (2) | 0.1198 (1) | 5.24 (5) |
| C22 | 0.7498 (4) | 0.0537 (4) | 0.0392 (2) | 11.8 (1) |
| C31 | 0.8113 (2) | 0.1005 (2) | 0.4243 (1) | 3.69 (4) |
| C32 | 0.7435 (3) | 0.0843 (2) | 0.5112 (1) | 4.74 (4) |
| C121 | 0.2296 (2) | 0.1249 (1) | 0.3092 (1) | 3.42 (3) |
| C122 | 0.2628 (2 | 0.2048 (1) | 0.3623 (1) | 3.83 (4) |
| C123 | 0.4353 (2) | 0.1954 (1) | 0.3868 (1) | 3.38 (3) |
| C341 | 0.7291 (2) | −0.1484 (2) | 0.3994 (1) | 3.78 (4) |
| C342 | 0.6512 (3) | −0.2440 (2) | 0.3776 (1) | 4.42 (4) |
| C343 | 0.5243 (3) | −0.2172 (1) | 0.3211 (1) | 3.89 (4) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

**Table V.** Positional Parameters and Isotropic Thermal Parameters of Hydrogen Atoms of **1** with R = $C_2H_5$

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| H11 | 0.294 (2) | −0.148 (2) | 0.174 (1) | 6.0 (5)* |
| H12 | 0.206 (2) | −0.041 (1) | 0.169 (1) | 4.5 (4)* |
| H13 | 0.015 (3) | −0.159 (2) | 0.233 (1) | 8.9 (7)* |
| H14 | 0.152 (3) | −0.182 (2) | 0.305 (1) | 7.2 (6)* |
| H15 | 0.062 (3) | −0.077 (2) | 0.298 (1) | 7.7 (6)* |
| H21 | 0.882 (3) | 0.136 (2) | 0.121 (2) | 9.5 (7)* |
| H22 | 0.921 (4) | 0.024 (2) | 0.123 (2) | 9.5 (7)* |
| H23 | 0.820 (3) | 0.072 (2) | −0.008 (2) | 10.1 (8)* |
| H24 | 0.642 | 0.094 | 0.035 | 12.8 |
| H25 | 0.719 | −0.022 | 0.033 | 12.8 |
| H31 | 0.927 (2) | 0.067 (1) | 0.419 (1) | 4.1 (4)* |
| H32 | 0.831 (2) | 0.181 (1) | 0.414 (1) | 4.5 (4)* |
| H33 | 0.746 (4) | 0.005 (2) | 0.527 (2) | 11.8 (9)* |
| H34 | 0.625 (3) | 0.106 (2) | 0.518 (1) | 7.0 (6)* |
| H35 | 0.826 (3) | 0.114 (2) | 0.553 (1) | 7.7 (6)* |
| H121 | 0.124 (2) | 0.108 (1) | 0.281 (1) | 3.9 (4)* |
| H122 | 0.182 (2) | 0.261 (2) | 0.380 (1) | 5.0 (4)* |
| H123 | 0.507 (2) | 0.235 (1) | 0.4238 (9) | 3.5 (3)* |
| H341 | 0.822 (2) | −0.134 (1) | 0.428 (1) | 4.3 (4)* |
| H342 | 0.680 (2) | −0.313 (2) | 0.396 (1) | 5.4 (5)* |
| H343 | 0.435 (2) | −0.263 (2) | 0.291 (1) | 4.8 (4)* |

[a] An asterisk indicates that the atoms were refined isotropically.

**Table VI.** Bond Distances (Å) for **1** with R = $C_2H_5$

| | | | |
|---|---|---|---|
| B1–N1 | 1.588 (1) | C342–C343 | 1.370 (2) |
| B1–N4 | 1.587 (1) | C11–H11 | 0.94 (1) |
| B3–N2 | 1.587 (1) | C11–H12 | 0.96 (1) |
| B3–N3 | 1.587 (1) | C21–H21 | 0.94 (2) |
| B1–O12 | 1.452 (1) | C21–H22 | 0.91 (2) |
| B2–O12 | 1.355 (1) | C31–H31 | 0.97 (1) |
| B2–O23 | 1.366 (1) | C31–H32 | 1.03 (1) |
| B3–O23 | 1.451 (1) | C12–H13 | 0.92 (2) |
| N1–N2 | 1.363 (1) | C12–H14 | 0.93 (2) |
| N3–N4 | 1.363 (1) | C12–H15 | 0.98 (2) |
| B1–C11 | 1.585 (2) | C22–H23 | 0.98 (2) |
| B2–C21 | 1.578 (2) | C22–H24 | 0.96 |
| B3–C31 | 1.587 (2) | C22–H25 | 0.97 |
| N1–C121 | 1.332 (1) | C32–H33 | 1.01 (2) |
| N2–C123 | 1.335 (1) | C32–H34 | 0.95 (2) |
| N3–C342 | 1.337 (1) | C32–H35 | 0.99 (2) |
| N4–C343 | 1.330 (1) | C121–H121 | 0.94 (1) |
| C11–C12 | 1.527 (2) | C122–H122 | 0.94 (1) |
| C21–C22 | 1.451 (2) | C123–H123 | 0.95 (1) |
| C31–C32 | 1.531 (2) | C341–H341 | 0.95 (1) |
| C121–C122 | 1.376 (2) | C342–H342 | 0.94 (1) |
| C122–C123 | 1.375 (2) | C343–H343 | 1.01 (1) |
| C341–C342 | 1.372 (2) | | |

**Table VII.** Selected Bond Angles (deg) for **1** with R = $C_2H_5$

| | | | |
|---|---|---|---|
| O12–B1–C11 | 112.21 (9) | O23–B3–N3 | 108.39 (8) |
| O12–B1–N1 | 108.55 (8) | N2–B3–N3 | 102.19 (7) |
| O12–B1–N4 | 107.85 (8) | N2–B3–C31 | 111.71 (8) |
| N1–B1–N4 | 102.09 (7) | N3–B3–C31 | 112.30 (9) |
| N1–B1–C11 | 112.47 (9) | B3–N4–C343 | 132.55 (9) |
| N4–B1–C11 | 112.97 (9) | B3–N4–N3 | 118.76 (8) |
| B1–N1–C121 | 113.32 (8) | N3–N4–C343 | 108.15 (9) |
| B1–N1–N2 | 118.32 (8) | B3–N3–C341 | 133.38 (9) |
| N2–N1–C121 | 108.28 (8) | B3–N3–N4 | 118.76 (8) |
| B3–N2–C123 | 132.86 (8) | N4–N3–C341 | 107.52 (9) |
| B3–N2–N1 | 119.29 (7) | B1–O12–B2 | 128.82 (8) |
| N1–N2–C123 | 107.75 (8) | B2–O23–B3 | 127.28 (8) |
| O12–B2–O23 | 123.42 (9) | N3–C341–C342 | 109.5 (1) |
| O12–B2–C21 | 118.6 (1) | C341–C342–C343 | 105.3 (1) |
| O23–B2–C21 | 117.9 (1) | C342–C343–N4 | 109.5 (1) |
| N1–C121–C122 | 109.2 (1) | | |
| C121–C122–C123 | 105.36 (9) | H121–C121–N1 | 122.0 (7) |
| C122–C123–N2 | 109.4 (1) | H121–C121–C122 | 128.8 (7) |
| B1–C11–C12 | 119.5 (1) | H122–C122–C121 | 127.1 (7) |
| B2–C21–C22 | 118.8 (1) | H122–C122–C123 | 127.5 (7) |
| B3–C31–C32 | 118.3 (1) | H123–C123–C122 | 131.5 (6) |
| O23–B2–C21 | 112.93 (8) | | |
| O23–B3–N2 | 108.71 (8) | | |

It is noteworthy, however, that the B3–O23 and B1–O12 distances are significantly longer than the B2–O23 distances. These differences reflect the fact that B1 and B3 are four-coordinate whereas B2 is three-coordinate. Unfortunately, structural data on $(-BC_2H_5O-)_3$ are not available in the literature. However, the structure of $(-BC_6H_5O-)_3$ has recently been studied by X-ray diffraction.[6] The average B–O bond distance of this latter boroxin was found to be 1.386 (2) Å, i.e. almost intermediate between those observed for **1** with R = $C_2H_5$. The average O–B–O bond angles in the cited boroxin were found to be 118.0 (4)°, and the B–O–B angles were observed with 121.7 (2)°, both values being considerably smaller than those observed for **1** with R = $C_2H_5$ in this present study.

**Preparation and Reactions of RClB($\mu$-pz)$_2$BRCl (R = $C_2H_5$).** The reaction of **1** (R = $C_2H_5$) with $SOCl_2$ readily led to the formation of RClB($\mu$-pz)$_2$BRCl. The $^1H$ NMR spectrum of the latter showed that only one isomer was formed, presumably the one with a cis arrangement of the halogen atoms. On the other hand, **1** (R = $C_6H_5$) did not undergo an analogous reaction under the same conditions. The 4,8-dichloro-4,8-diethylpyrazabole is the first example of a pyrazabole where each of the boron atoms is bonded to one halogen and one hydrocarbon substituent. It is

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(6) Brock, C. P.; Minton, R.; Niedenzu, K., to be submitted for publication.

quite moisture sensitive and hydrolyzes with the preferential generation of **1** (R = $C_2H_5$).

4,8-Dichloro-4,8-diethylpyrazabole afforded access to other novel pyrazaboles. For example, it reacted with potassium methoxide in methanol at room temperature to give the first example of a *B*-alkoxypyrazabole, i.e., $(C_2H_5)(CH_3O)B(\mu\text{-pz})_2(C_2H_5)(OCH_3)$. The corresponding *B*-ethoxy derivative was obtained in similar fashion, and both were also obtained, even in much better yield, by the reaction of the chloro compound with the alcohol in the presence of triethylamine.

Both of the cited alkoxypyrazaboles were obtained as isomer mixtures, as was readily documented by the $^1H$ NMR spectra of the species. The ratio of the isomers was found to be somewhat dependent on the preparative procedure, although in each case the same one was formed in substantially larger quantity. Unfortunately, separation of the isomers has not been possible. Indeed, the existence of cis and trans isomers of pyrazaboles of the type $RR'B(\mu\text{-pz})_2BRR'$ has long been suspected,[7] but only most recently has it been documented by experiment and successful separation of conformers.[8]

4,8-Dichloro-4,8-diethylpyrazabole was also reacted with $(CF_3CO)_2O$ to give the species $R(R'O)B(\mu\text{-pz})_2BR(OR')$ with R = $C_2H_5$ and R′ = $CF_3CO$ with elimination of $CF_3COCl$ and also with acetic anhydride to give the corresponding nonfluorinated species. Again, both species were obtained as mixtures of cis and trans isomers that could not be separated.

The above reactions illustrate that **1** is a valuable precursor for the synthesis of various pyrazaboles containing two different substituents at each boron atom.

**Acknowledgment.** The authors gratefully acknowledge a generous gift of *B*-triethylboroxin from Professor R. Köster, Max-Planck-Institut für Kohlenforschung, Mülheim, West Germany. This work was supported by the Office of Naval Research (K.N.) and the National Science Foundation (S.G.S.).

**Supplementary Material Available:** Listings of anisotropic thermal parameters for non-hydrogen atoms and least-squares planes for **1** with R = $C_2H_5$ (2 pages); a listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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# Models for Methemocyanin Derivatives: Structural and Spectroscopic Comparisons of Related Azido-Coordinated ($N_3^-$) Mono- and Dinuclear Copper(II) Complexes

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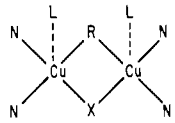
The use of the azide ($N_3^-$) ligand as a probe of the dinuclear copper active site in the dioxygen-transport protein hemocyanin has prompted us to synthesize model complexes that may shed light on the structural and spectroscopic features associated with $N_3^-$ binding to Cu(II) in well-defined chemical systems. We report the synthesis and structural and spectroscopic properties of $N_3^-$ bound to a dinuclear Cu(II) complex and a mononuclear analogue. The dinucleating ligand, L-OH, forms a phenoxo-bridged dicopper(II) complex, **2b**, where each Cu(II) ion is also coordinated in a square-based-pyramidal geometry to the nitrogen atoms of a tridentate py2 unit (py2 = bis(2-(2-pyridyl)ethyl)amine) and to a $\mu$-1,1-$N_3^-$ ligand. A mononucleating analogue, $[Cu^{II}(L'\text{-}O^-)(N_3^-)]$ (**3b**), contains Cu(II) coordinated to the same $N_3O$ donor set provided by L′-OH and a terminally coordinated $N_3^-$ ligand in a coordination environment very similar to that found in **2b**. Compound **2b** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ and $a = 9.583$ (1) Å, $b = 10.123$ (2) Å, $c = 23.758$ (4) Å, $\alpha = 87.19$ (1)°, $\beta = 88.83$ (1)°, and $\gamma = 84.85$ (1)°. Complex **3b** crystallizes in the monoclinic space group $P2_1/c$, with $Z = 4$ and $a = 9.529$ (7) Å, $b = 18.950$ (2) Å, $c = 13.829$ (5) Å, and $\beta = 109.38$ (5)°. Comparisons of the charge-transfer (CT) features observed in UV–vis spectra of these complexes and related chloride and/or nitrate ion containing derivatives of L-OH, L′-OH, and py2 allow assignment of the $PhO^- \rightarrow Cu(II)$ (450–460 nm) and/or $N_3^- \rightarrow Cu(II)$ (370–405 nm) CT bands. Other structural and spectroscopic comparisons are also made.

## Introduction

Extensive spectroscopic and chemical investigations[1–4] have suggested detailed pictures of the active sites of the copper proteins hemocyanin (arthropod and mollusc dioxygen carrier) and the protein tyrosinase (monooxygenase that hydroxylates monophenols). Both of these proteins contain spectroscopically similar dinuclear copper centers that in the reduced state most likely contain three-coordinate Cu(I) with imidazole ligands.[5] Upon oxygenation, a dicopper(II) complex is formed in which two tetragonal copper(II) ions separated by 3.6 Å are thought to be bridged by an endogenous R group and the exogenous $\mu$-1,2-peroxo ligand (X) derived from dioxygen:



In establishment of the nature of the active site, investigations have relied heavily upon spectroscopic studies of the products of binding and interactions of small molecules such as acetate, chloride, azide, etc., in chemically modified hemocyanin or tyrosinase derivatives.[1,2,6] Details such as Cu···Cu distances in the active sites, differences among mollusc and arthropod hemocyanins, and electron delocalization in half-met ($Cu^{II}Cu^{I}$) de-

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