$Ni[BzP(C_6H_5)_2]_2Br_2$[25] have recently been reported.

Registry No. $[Co(en)_3]Cl_3 \cdot 3H_2O$, 14883-80-8; $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$, 16165-32-5; $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$, 20523-47-1; $[Cr(en)_3][Co(CN)_6] \cdot xH_2O$, 56114-36-4; $[Co(en)_3][Cr(CN)_5NO] \cdot 2H_2O$, 55991-03-2; $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$, 28852-88-2; $[Ni(en)_3][(C_6H_5)_4B]_2$, 41685-81-8; $[Ni(en)_3](C_2H_3O_2)_2 \cdot 2H_2O$, 55991-04-3.

Supplementary Material Available. Tables III and IV, listing the observed Raman wave number shifts and infrared frequencies, respectively, for compounds **6**, **7**, **9**, **10**, and **11** (see Table I), will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50109+-10-75.

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Nucleoside Complexing. Longitudinal Relaxation Studies of Metal Binding Sites in Adenosine and Cytidine

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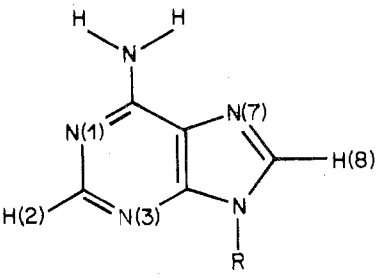
Our interest in finding specific metal-containing reagents for probing nucleic acid structures[2a] has led us to use PMR relaxation techniques[2b] as tools. One such technique, the line broadening induced by the Cu^{2+} ion, has been questioned recently, when Martin showed that this broadening was greatly influenced by scalar coupling.[3] Scalar coupling cannot occur unless a bond is formed.[2b] However, the extent of coupling may not diminish uniformly as the number of bonds between the paramagentic center and the resonating nucleus increases. The scalar coupling term influences longitudinal relaxation times (T_1) to a much smaller extent.[2b,3] For the Cu^{2+} ion, the relaxation is not exchange limited[3] and thus, T_{1P}^{-1} the difference between the T_1^{-1} of a resonance in the presence and the absence of the paramagnetic metal ion, is a measure of the inverse sixth power of the distance between the Cu^{2+} (or other paramagnetic centers) and the nucleus of concern.[2b] The *relative* values of T_{1P}^{-1} for different nuclei in a given ligand can be used to deduce the metal binding site.

Line-broadening studies using the Cu^{2+} ion form a very important body of information in the coordination chemistry of nucleic acids and nucleic acid constituents. Good crystalline samples of the complexes of interest are difficult to obtain, and, consequently, few crystal structures, which might serve to verify the assignments, have been reported.[4] We have recognized for some time that line broadening may be complicated by scalar coupling. As part of our search for selective reagents, we have checked some binding site assignments by using longitudinal relaxation. Our assignments agreed with those of Eichhorn.[4,5] The report by Martin[3] prompts us to report our results.

Results and Discussion

The nucleic acid constituents which are most useful in our studies are the nucleosides, consisting of a ribose sugar and a heterocyclic base capable of permitting selective bonding.[2a] For two nucleosides, adenosine (I) and cytidine (II) (R = ribose



I II

for both), longitudinal relaxation studies have provided information not obtainable by line broadening. Adenosine (I) has two apparently similar binding sites for attachment of metals, one on the six-membered ring and one on the five-membered ring of the purine heterocycle.[5] From line-broadening studies it is fairly certain that the five-membered ring site is N(7).[5] The six-membered ring site could be either N(1) or N(3).[5] The evidence for these sites is the nearly equal broadening of the H(2) and H(8) resonances of adenosine in DMSO when the Cu^{2+} ion is added.[5] Because the broadening may be a result of scalar coupling,[3] it is not possible either to assign the six-membered ring bonding site or to estimate the relative importance of the binding to the six-membered ring and to the five-membered ring sites.

The addition of the Cu^{2+} ion to cytidine solutions causes the H(5) resonance to broaden almost beyond limits of observation.[5] The H(6) resonance does not broaden appreciably and remains a doublet, coupled with H(5). This result is clearly suggestive of a large scalar component in the broadening. Otherwise, as the H(5) resonance broadened, the coupling to H(6) would have disappeared. This analysis of the broadening effect was recently advanced in the literature,[6] and we had reached the same conclusion. Furthermore, crystal structures of the related cytosine complexes reveal that the H(5) and H(6)

Table I. Approximate M–H Distances (Å) in N(1), N(3), and N(7) Binding Modes of Adenosine[a]

	H-N(6)	H-N(6)	H-C(2)	H-C(8)	H-C(1)'
		N(1) Binding			
M- - -N(1) = 2.00	2.48	4.03	2.91	7.40	6.97
M- - -N(1) = 2.10	2.52	4.10	2.98	7.50	7.07
M- - -N(1) = 2.20	2.57	4.16	3.05	7.59	7.16
		N(3) Binding			
M- - -N(3) = 2.00	6.68	6.78	3.01	5.47	2.43
M- - -N(3) = 2.10	6.78	6.89	3.09	5.54	2.45
M- - -N(3) = 2.20	6.88	6.98	3.16	5.60	2.48
		N(7) Binding			
M- - -N(7) = 2.00	2.56	4.28	6.71	3.20	6.16
M- - -N(7) = 2.10	2.59	4.32	6.80	3.28	6.25
M- - -N(7) = 2.20	2.62	4.35	6.88	3.36	6.35

[a] Idealized hydrogen positions based on the heavy-atom parameters of T. F. Lai and R. E. Marsh, *Acta Crystallogr., Sect. B*, **28**, 1982 (1972): C–H = 1.08 Å, N–H = 1.01 Å. The glycosidic torsion angle was set at 9.9° with 3'-endo puckering of the ribose ring.

Table II. Relaxation Data (T_1P^{-1})[a] for Adenosine (0.2 *M*) in DMSO-d_6 and 4% H_2O (18°)

Metal	H(8)	H(2)	NH_2	H(1)'
Cu(Schiff)[b]	0.9 ± 0.1	1.9 ± 0.1	3.3 ± 0.7	0.42 ± 0.16
Cu(glygly)[c]	1.0 ± 0.2	1.7 ± 0.1	2.1 ± 0.7	0.17 ± 0.14
$CuSO_4$[d]	15.3 ± 0.8	14.9 ± 0.6	20.3 ± 1.0	1.27 ± 0.16
$MnCl_2$[e]	2.2 ± 0.7	1.9 ± 0.2	2.9 ± 0.8	0.4 ± 0.11
$NiSO_4$[f]	1.7 ± 0.6	2.9 ± 0.2	3.5 ± 0.8	0.97 ± 0.22
$Co(CH_3CO_2)_2$[g]	2.3 ± 0.4	2.1 ± 0.3	4.3 ± 0.6	0.47 ± 0.12

[a] Units are 10^{-3} $msec^{-1}$; for each metal species, the absolute values of T_1P^{-1} depend on the metal concentration. The values of T_1P^{-1}, for each metal, are indicative of the relative M–H distance. [b] 5.9×10^{-5} *M*. [c] 3.0×10^{-5} *M*. [d] 2.5×10^{-4} *M*. [e] 1.24×10^{-3} *M*. [f] 6.8×10^{-3} *M*. [g] 1.5×10^{-3} *M*.

hydrogens are almost equidistant from a metal bound to N(3).[7,8] The great disparity between the broadening of the resonances of these hydrogens is indicative of scalar coupling.

Longitudinal relaxation effects on adding the Cu^{2+} ion or copper(II) complexes to DMSO solutions of these nucleosides finally have resolved the problems associated with the line-broadening studies. Furthermore, line broadening is not very effective for studying broad resonances such as NH resonances. Important information can be gained from these resonances because the NH groups will generally be very close to the metal, if the binding sites derived by line broadening[5] are correct.

The results of a calculation of the M–H distances for a metal placed at the three bonding sites for adenosine are given in Table I. If the favored interpretation[4,5] of the line-broadening studies is correct, from these distances, one would expect to see roughly equal values of T_1P^{-1} for the H(2) and H(8) resonances. Furthermore, the T_1P^{-1} for the amino resonance should be relatively large. (In both the N(7) and N(1) complexes the amino group will be close to the metal center.) These expectations are realized (Table II). The T_1P^{-1} for the resonance of H(1)' (hydrogen on C(1)' of the ribose moiety) is small, and this result excludes significant bonding at N(3). The metal (at N(7)) to H(8) distance is longer than the metal (at N(1)) to H(2) distance. This means that, according to the idealized geometry, the N(7) site is slightly (about 2 times) favored by the Cu^{2+} ion.

In accordance with the cautions of Martin,[3] line broadening was rather deceptive in our studies aimed at seeking a complex which might coordinate at only one of the sites on adenosine. The Schiff base complex (chloro)(*N*-methyl-*N*'-salicylideneethylenediamine)copper(II)[9] causes extensive broadening of the H(2) resonance with little broadening of the H(8) resonance (Figure 1). This result might lead one

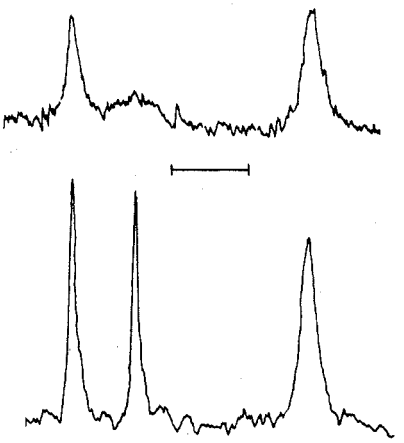


Figure 1. Traces of the ^1H NMR spectrum of adenosine (0.2 *M*, DMSO, 28°, 60 MHz Varian A-60, bar 20 Hz) with no metal present (lower trace) and with Schiff base complex (1.07×10^{-4} *M*) present (upper trace). Signals left to right are assigned[5] to the H(8), H(2), and NH_2 resonances.

Table III. Distances (Å) in Some Copper–Cytosine Complexes[8]

		Schiff base	Glycylglycine
Cu–H distance	Cu- - -H–N(4)	2.86	2.80
	Cu- - -H–N(4)	4.27	4.10
	Cu- - -H(5)–C(5)	5.16	5.08
	Cu- - -H(6)–C(6)	5.66	5.66
Cu–N(3) distance		2.01	1.98

to believe that the complex coordinates only to N(1) to an appreciable extent. However, this conclusion is not supported by the T_1P^{-1} data (Table II). From the data for this complex and various other metal species (Table II), it seems clear that bonding to both N(1) and N(7) will usually be important. Recent results with Pt(II) complexes[10] also suggest that N(1) and N(7) bondings are both important. Line broadening appears to overemphasize the degree of bonding to the N(1) position suggesting that scalar coupling is more effective for the H(2) resonance. This analysis agrees with the results of Martin on AMP.[3]

In principle, it should be possible to extract more specific information from T_1P^{-1} data.[2b] However, for adenosine, slight distortions from ideal geometries will greatly influence the percentages of each isomer calculated from the T_1P^{-1} data. The general trend is obvious. It is likely that, for any given combination of metal-containing species and solvent, there will be small changes in the percentages of N(1) and N(7) isomers in solution. We are presently engaged in an attempt to isolate a set of such isomers in crystalline form.

Cytidine poses interesting problems from the point of view of relaxation phenomena. There is little doubt that cytidine usually coordinates to metals via N(3).[11] However, the heterocyclic portion of the molecule contains no hydrogens which have sharp ^1H NMR resonances and which are close to the N(3) bonding site. Therefore, line broadening is not as useful a criterion for bonding site assignment as it is for adenosine. The line-broadening phenomena for cytidine can be understood as arising from metal binding at N(3). For N(3) bonding, the T_1P^{-1} will be largest for the amino hydrogen resonance. The T_1P^{-1} values for the H(5), H(6), and H(1)' resonances will be similar.

The rate of rotation of the amino group of cytidine is slow relative to that of most such groups.[12] In nonaqueous solvents it is possible to observe separate resonances for the two different environments. The Cu to hydrogen distances observed in two cytosine complexes are given in Table III. Both NH's are closer to the metal than are H(5) and H(6). In DMSO, the H(5) resonance overlaps with the H(1)' resonance. However,

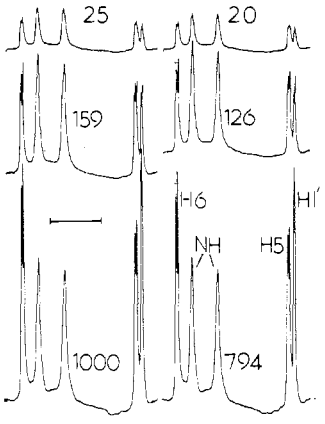


Figure 2. ^{1}H NMR spectrum of a cytidine (0.2 *M*) solution (DMSO-d_6, 4% H_2O, 0.7 *M* in LiCl, 4.23 × 10^{-5} *M* in $MnCl_2$, 18°) at various times (indicated on figure in msec) after the spoil pulse. Signals are assigned in the trace at lower right. The bar is 200 Hz (220-MHz spectrometer).

Table IV. T_1P^{-1} [a] Data for Cytidine (0.2 *M*) in DMSO-d_6, 0.7 *M* LiCl, and 4% H_2O (18°)

Metal	NH[b]	H(6)	H(5)	H(1)'
Cu-(Schiff)[c]	0.274 ± 0.06	0.042 ± 0.01	0.022 ± 0.01	0.027 ± 0.01
$MnCl_2$[d]	0.599 ± 0.08	0.173 ± 0.01	0.279 ± 0.01	0.123 ± 0.01

[a] Units are 10^{-2} $msec^{-1}$; for each metal, relative not absolute values are important. [b] Both resonances are the same within experimental error. [c] 5.86 × 10^{-5} *M*. [d] 4.23 × 10^{-5} *M*.

addition of chloride ion shifts the H(5) resonance downfield[13,14] and also allows better resolution of the NH resonances.[14]

The relaxation measurements (Figure 2) led to the T_1P^{-1} data in Table IV. As expected from the model of N(3) bonding, the T_1P^{-1} values for the H(5) and H(6) resonances are similar to each other and much smaller than the values for the NH resonances. The T_1P^{-1} values for the NH resonances are identical in both the absence and the presence of paramagnetic metals. This result is interpreted by us to mean that the rate of rotation of the amino group is sufficiently rapid to average T_1 for the two environments but not rapid enough to collapse the two signals. The rotation rates found for other cytosine derivatives[12] and the T_1 values found in this study are of the correct magnitude to make this explanation feasible. The main point here is that N(3) bonding is entirely consistent with the relaxation data. Furthermore, the explanation for the line-broadening effects on the H(5) and H(6) resonances is also consistent with the longitudinal relaxation effects on these resonances. The copper Schiff base has the same characteristic line-broadening effects as the Cu^{2+} ion.

In conclusion, our study has shown that the binding site assignments based on line-broadening studies[4,5] are clearly correct for the most ambiguous case—that of the two-bonding-site nucleoside, adenosine. We also confirmed N(3) bonding in cytidine. Other studies in our laboratory agree with the bonding of the Cu^{2+} ion to the N(7) of guanosine. We see no reasons to doubt any of the bonding assignments made by using the line-broadening technique.[4,5] Certainly it is quite simple to check all past broadening studies using T_1P^{-1}. We doubt such a study is worth the time. Rather it seems likely that all the assignments made earlier, including those for the binding of the Cu^{2+} ion to polynucleotides, will prove to be correct. There is a vast amount of data pointing to the established binding sites. These data were collected by various techniques[15] and with many different metal centers.[4] The bonding sites found by line broadening agree with all of this empirical background and also with theoretical considerations. However, the demonstrated importance of scalar coupling in line-broadening studies using the Cu^{2+} ion[3] makes bonding assignments by this technique hazardous.[16] Moreover, T_1P^{-1} data can provide more information than line-broadening studies.

Experimental Section

Measurements of the relaxation times were made on a Varian HR-200 spectrometer equipped with a Fourier transform accessory. The pulse sequence employed was that described by McDonald and Leigh[17] and was a 90°–τ–90°–spoil pulse. Signal intensities were measured and plotted. Data points which appeared erroneous were identified using the plots. These were eliminated and the remaining data were treated with a least-squares program.

Solutions of nucleosides (0.2 *M*) were made in DMSO-d_6. Distilled deionized water or a stock solution of the paramagnetic metal species in water was added. Measurements were made on these partially (4%) aqueous solutions so as to avoid uncertainties as to the amount of moisture in the hygroscopic DMSO. Deuterium oxide was tried first, but the relaxation times of the NH_2 resonances were dependent on the replacement of adjacent hydrogens by deuterium. We wished to avoid this complication. Extensive studies of the effect of water concentrations (>4%) gave no revealing insights into the problems discussed here and no appreciable variation in relaxation times.

The complexes with the Schiff base[9] and with glycylglycine[18] were prepared by literature procedures and had the expected properties. There were no appreciable changes in pH on addition of the metal solutions to the nucleoside solutions. Rather high concentrations of acid or base (greater than 0.01 *M*) were needed to influence the relaxation results. Base additions to the adenosine solutions appear to change the percentages of isomers in favor of the N(7) complex for both the Cu^{2+} ion and the copper complexes. This effect was not studied in detail but may result from changes in the metal species rather than in the nucleosides since obvious color changes were observed.

Acknowledgment. The 220-MHz spectra were obtained at the National Institutes of Health regional facility at the Johnson Foundation. We thank Dr. George McDonald for help in obtaining the spectra. This research was supported by the National Institutes of Health through Grants GM 17172 and GM 20544 from the Institute of General Medical Sciences and through a Biomedical Sciences Institutional Grant.

Registry No. Adenosine, 58-61-7; cytosine, 71-30-7; *N*-methyl-*N*'-salicylideneethylenediamine, 55975-54-7; glycylglycine, 556-50-3; Cu, 7440-50-8; Mn, 7439-96-5; Ni, 7440-02-0; Co, 7440-48-4; cytidine, 65-46-3.

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Degradative Substitution of 1,7-Dimethyl-1,7-dicarba-*closo*-dodecaborane to Form 3-Alkoxynonahydro-7,9-dimethyl-7,9-dicarba-*nido*-undecaborate(1−) Ions. Isomeric Anions

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The treatment of a wide variety of carbon-substituted 1,-2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$ carboranes with alcoholic base has been shown to degrade them to the corresponding carbon-substituted 7,8- or 7,9-$C_2B_9H_{12}^-$ ions.[1] We have found that such treatment of 1,7-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$ can result in degradative substitution to give alkoxy derivatives of 7,-9-$(CH_3)_2$-7,9-$C_2B_9H_{10}^-$, e.g., 7,9-$(CH_3)_2$-7,9-$C_2B_9H_9OR$ (R = CH_3, C_2H_5, and *i*-C_3H_7), as briefly mentioned in a previous publication.[2] We report here a more complete characterization of these compounds which indicates that alkoxy substitution is in the 3 position rather than the previously suggested 2 position.[2]

Experimental Section

General Procedures. Infrared spectra were determined on a Perkin-Elmer 457 as KBr disks. The ^{11}B NMR spectra were recorded on Varian instruments operating at 32.1 and 70.6 MHz (Indiana University) and a Bruker 86.6-MHz instrument (University of Wisconsin); proton NMR spectra were recorded on Varian T-60, HA-100, and 220-MHz (Indiana) spectrometers.

All preparations were conducted under an atmosphere of nitrogen. The 1,7-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$ was prepared as described in the literature[3] and all other reactants were reagent grade, *i*-C_3H_7OH being dried by percolation through molecular sieves.

General Procedure for Degradative Substitution. The procedure used for a typical preparation of [$(CH_3)_3NH^+$][7,9-$(CH_3)_2$-7,9-$C_2B_9H_9OC_2H_5^-$] is described. The CH_3O and *i*-C_3H_7O derivatives can be prepared by substituting CH_3OH and *i*-C_3H_7OH, respectively, for C_2H_5OH.

A glass-lined autoclave was purged with N_2 and charged with a solution of 1.35 g of KOH in 40 ml of C_2H_5OH before adding 1,7-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$, 2.08 g, 12.1 mmol. The temperature in the autoclave was slowly raised until a surge in pressure was noted at 160° where it was maintained until no further increase in pressure was noted (usually 4–6 hr at 160° and a pressure of 300–400 psi in a 400-cm^3 autoclave). After cooling to 25°, 20 ml of C_2H_5OH was added to the reaction mixture and CO_2 was bubbled into it to precipitate the excess KOH as the carbonate, which was removed by filtration. The filtrate was taken to dryness on a rotary evaporator and the resulting potassium salt was then dissolved in water. If any unreacted carborane was detected at this point, it was removed by filtration and $(CH_3)_3NH^+Cl^-$ was added to the filtrate to give the crude product. Pure [$(CH_3)_3NH^+$][7,9-$(CH_3)_2$-7,9-$C_2B_9H_9OC_2H_5^-$] was obtained by recrystallization from hot water; yield 1.29 g, 4.8 mmol, 40%.

In the case of the CH_3OH preparation a temperature of 140° was generally sufficient for reaction but 160° was required for the *i*-C_3H_7OH preparation.

4-CH_3O-7,9-$(CH_3)_2$-7,9-$C_2B_9H_8$. NaH (85 mg, 3.54 mmol) was added under N_2 to 50 ml of benzene which had been dried over lithium aluminum hydride and distilled in vacuo to a 100-ml, three-neck flask. Then, 507 mg (1.62 mmol) of [$(CH_3)_3NH^+$][3-CH_3O-7,9-C_2-$(CH_3)_2B_9H_9^-$] was added and the mixture was refluxed for 56 hr under N_2. Anhydrous $SnCl_2$ (308 mg, 1.62 mmol) was added and heating was continued for another 40 hr at which time the mixture had turned deep black. The mixture was cooled to 25° and filtered through a glass frit which was then washed with 30 ml of dry benzene. The combined filtrates were evaporated to an oil which was sublimed in vacuo at 40–45° to a −78° cold finger yielding the pure product (62 mg, 20%). Mass spectrum: cutoff at *m/e* 192 corresponding to $^{11}B_9{}^{12}C_5{}^1H_{17}{}^{16}O$.

Table I. ^{11}B and ^1H NMR Data[a]

[Me_3NH^+][3-*i*-C_3H_7O-7,9-$(CH_3)_2$-7,9-$C_2B_9H_9^-$][e]
^{11}B: 0.50 s, 1.34 d (J_{BH} = 140), 2.76 d (J_{BH} = 150), 5.98 d (J_{BH} = 145), 18.63 d (J_{BH} = 145), 22.34 d of d (J_{BH} = 130, J_{BH_μ} = 40), 26.04 d of d (J_{BH} = 135, J_{BH_μ} = 40), 33.51 d (J_{BH} = 137), 38.11 d (J_{BH} = 140)
^1H: 1.07 d (J_{HH} = 6, $(CNCH_3)_2$), 1.40[b] s and 1.44[b] s ($(C-CH_3)_2$), 3.13 s ($N(CH_3)_3$); 3.86 m, br (O-C-H?), NH not observed

[Me_3NH^+][3-C_2H_5O-7,9-$(CH_3)_2$-7,9-$C_2B_9H_9^-$][e]
^{11}B: 0.74 s, 1.42 d (J_{BH} = 160), 2.69 d (J_{BH} = 160), 6.15 d (J_{BH} = 148), 18.70 d (J_{BH} = 145), 22.24 d of d (J_{BH} = 140, J_{BH_μ} = 40), 25.96 d of d (J_{BH} = 135, J_{BH_μ} = 40), 33.81 d (J_{BH} = 135), 38.10 d (J_{BH} = 140)
^1H: 1.13 t (J_{HH} = 7, CH_3), 1.39[b] s and 1.42[b] s ($C-CH_3)_2$; 3.11 s ($N(CH_3)_3$); 3.63 q (J_{HH} = 7, $O-CH_2$), NH not observed

[Me_3NH^+][3-CH_3O-7,9-$(CH_3)_2$-7,9-$C_2B_9H_9^-$][c,e]
^{11}B: 0.8 s, 2.7 d (J_{BH} = 130), 3.6 d (J_{BH} = 130), 8.0 d (J_{BH} = 140), 17.9 d (J_{BH} = 140), 22.3 d of d (J_{BH} = 135, J_{BH_μ} = 40), 27.3 d of d (J_{BH} = 135, J_{BH_μ} = 40), 34.7 d (J_{BH} = 140), 30.1 d (J_{BH} = 135)
^1H: 1.43 s ($C-CH_3)_2$, 3.12 s ($N(CH_3)_3$), 3.41 s ($O-CH_3$); NH not observed

4-CH_3O-2,3-$(CH_3)_2$-2,3-$C_2B_9H_8$[d,f]
^{11}B: −13.0 s (1), −8.5 d (1) (J_{BH} = 166), 4.0 d (1) (J_{BH} = 150), 9.8 d (2) (J_{BH} = 155), 11.2 d (1) (J_{BH} = 156), 17.8 d (1) (J_{BH} = 147), 22.5 d (1) (J_{BH} = 166)
^1H: 2.03 s ($C-CH_3$), 2.53 s ($C-CH_3$), 3.67 s ($O-CH_3$)

[a] ^{11}B data are given in ppm upfield from a $(C_2H_5)_2O\cdot BF_3$ external standard; ^1H NMR data are given in ppm downfield from TMS internal standard. All chemical shifts are followed by a coupling constant where observed, given in Hz, with a description of the multiplet (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad) and an assignment which corresponds to the observed relative intensity. [b] These resonances were seen at 220 MHz but could not be resolved at 100 MHz. [c] These data were obtained at 32.1 MHz (^{11}B) and 60 MHz (^1H) while the preceding were obtained at 70.6 and 220 MHz, respectively. [d] Proton spectra were obtained at 60 MHz. [e] Solvent acetone-d_6. [f] Solvent chloroform-d_1.

Results and Discussion

Weissenberg photographs of a single crystal of the ethoxy congener showed that the trimethylammonium salt was triclinic with cell parameters of a = 9.80 Å, b = 10.42 Å, c = 11.42 Å, and α = 81° 10', β = 89° 19', γ = 47° 42'. The density calculated for two molecules of ($C_9B_9NOH_{30}$) per cell is 1.04 g/cm^3 and agrees well with that observed experimentally, 1.02 g/cm^3.

The ^{11}B NMR spectra of the three alkoxy derivatives prepared here are nearly superimposable; that of the ethoxy compound was published previously.[2] All of the NMR data are summarized in Table I; it is evident that they are consistent with asymmetric substitution of the boron cage. This is seen most dramatically in the ^{11}B spectra where all nine boron environments are evident. The singlet due to the substituted boron site (0.5–0.8 ppm) shows no bridge hydrogen coupling but two other B–H resonances do (~22 and ~26 ppm). Since bridge hydrogens have always been found between two boron atoms on the nontrigonal face of *nido*-carboranes (positions 10 and 11 here, Figure 1), lower belt substitution is indicated. The 2 and 3 positions provide the only alternatives consistent with a structure with no elements of symmetry. We previously chose the 2 position, but on the basis of the chemical evidence presented below, the 3 position is the better choice.