temperatures so long as $k_{1c} >> W_1$. Using the data from the glass, we obtain $k_{2e} = 7.5 \times 10^2\ \mathrm{s}^{-1}$, in reasonable agreement with the least-squares results.

Level Assignments. Both $|1\rangle$ and $|2\rangle$ can confidently be attributed to CT states,[4] but several possibilities remain for specific assignments. For example, from the viewpoint of one-electron orbital energies different excited states arise depending on which of the (split) metal 3d orbitals is the origin of the promoted electron; i.e., some states can be envisaged as having both CT and d–d excitation. In fact, depending on the d-orbital occupation the geometry may vary,[37] and this, among other things, may affect the respective transition moments. Alternatively, different ligand π^* orbitals can serve as the terminus for the transferred electron.[38] Still another possibility is that the levels can differ in spin multiplicity.[26]

Given the fact that intersystem crossing is usually rapid in metal complexes,[29] state $|2\rangle$, the lowest energy excited state, is expected to be a triplet state. In accord with this assignment, the estimated k_{2e} value falls into the "normal" range for triplet states (1–$10^4\ \mathrm{s}^{-1}$).[39] Although we have no a priori way of assigning a multiplicity to state $|1\rangle$, the k_{1e} value we obtain seems too large for a triplet state. (Note that the order of magnitude obtained for k_{1e} does not depend on our assumed value of $g_1/g_2 = {}^1/_3$.) Even in the case of osmium(II) complexes where the spin–orbit coupling interaction should be much larger, the radiative rate constant from analogous triplet CT states is only ca. $10^5\ \mathrm{s}^{-1}$.[40] On the other hand, the calculated k_{1e} value falls in the range expected for singlet states (10^6–$10^9\ \mathrm{s}^{-1}$),[39] in support of assumption 2 above. In the absence of any theoretical results to the contrary, we presume that states $|1\rangle$ and $|2\rangle$ can be associated with the lowest energy CT configuration of the complex.[41]

A final point worth noting is that the calculated ΔE is in fair agreement with spectroscopically obtained singlet–triplet splittings that have been reported for related ruthenium(II) and iron(II) complexes exhibiting low-lying metal-to-ligand CT excited states.[42] It should be emphasized that such comparisons can only be made in a qualitative sense because the d–π^* orbital overlap patterns are likely to be very different for these systems. As a consequence the exchange integrals, and hence the ΔE values,[43] will differ as well.

Conclusions. The temperature dependence of the solution emission from complexes of the type $\mathrm{Cu(NN)_2}^+$ can be understood in terms of two thermally equilibrated excited states separated by ca. 1800 cm^{-1}. The lower of the two is assigned as a triplet state associated with the lowest energy $\mathrm{d}^9\pi^{*1}$ configuration. The other state has a substantially greater radiative rate constant and is tentatively assigned to the associated singlet charge-transfer state. A similar scheme has been found to adequately describe emission from $\mathrm{Cu(PPh_3)_2(NN)^+}$ systems in the solid state.[26,27] Thus, a multiple-level scheme of this type may be of general importance in determining the photophysical properties of copper(I) complexes involving heteroaromatic ligands.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation through Grant No. CHE 81-05003 and the Public Health Service through Grant No. GM 22764.

Appendix

The steady state is defined by eq 8 and 9, where I_a is the

$$\eta_1 I_a = W_1[1] + k_{1c}[1] - k_{2c}[2] \tag{8}$$

$$\eta_2 I_a = W_2[2] + k_{2c}[2] - k_{1c}[1] \tag{9}$$

absorption rate and $\eta_1 I_a$ and $\eta_2 I_a$ are the respective pump rates of states $|1\rangle$ and $|2\rangle$, the concentrations of which are expressed as [1] and [2]. Combining these equations and defining $\beta = \eta_2/\eta_1$ yield eq 10. When $k_{2c} >> W_2$ and $k_{1c} >> W_1$, the

$$K = \frac{[1]}{[2]} = \frac{W_2 + (\beta + 1)k_{2c}}{\beta W_1 + (\beta + 1)k_{1c}} \tag{10}$$

expression for K reduces to k_{2c}/k_{1c} as stated in the text. Equations 3 and 4 in the text assume $\eta_1 = 1$ and $\eta_2 = 0$.

Registry No. $\mathrm{Cu(dmp)_2}^+$, 21710-12-3; $\mathrm{Cu(bcp)_2}^+$, 47895-81-8; $\mathrm{Cu(tmbp)_2}^+$, 47718-57-0.

---

(37) Buckner, M. T.; Matthews, T. G.; Lytle, F. E.; McMillin, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 5846–5848.

(38) Day, P.; Sanders, N. *J. Chem. Soc. A* **1967**, 1530–1536, 1536–1541.

(39) Reference 25, p 28.

(40) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630–632.

(41) If $|1\rangle$ is associated with the low-energy shoulder that appears in the absorption spectrum at ca. 520 nm, a very approximate value of k_{1e} can be estimated[25] from the product $10^4\epsilon_{\mathrm{max}} \approx 10^7\ \mathrm{s}^{-1}$.

(42) Felix, F.; Ferguson, J.; Gudel, H. U.; Ludi, A *J. Am. Chem. Soc.* **1980**, *102*, 4096–4102, 4102–4106.

(43) Salem. L. "Electrons in Chemical Reactions: First Principles"; Wiley-Interscience: New York, 1982; pp 188–192.

Contribution from the Department of Chemistry,
Brock University, St. Catharines, Ontario, Canada L2S 3A1

Nitrogen-15 and Boron-11 Nuclear Magnetic Resonance Studies of Trimethylamine Adducts of the Mixed Trihalides of Boron

JACK M. MILLER

Received September 16, 1982

^{15}N and ^{11}B NMR spectra have been measured for the trimethylamine adducts of the mixed trihalides of boron. $J(^{11}\mathrm{B}{-}^{15}\mathrm{N})$, though covering a narrow range, correlates well with $\delta(^1\mathrm{H})$, $\delta(^{13}\mathrm{C})$, $J(^1\mathrm{H}{-}^{11}\mathrm{B})$, and $J(^{11}\mathrm{B}{-}^{19}\mathrm{F})$ and less so with $\Delta\delta(^{11}\mathrm{B})$ (the complexation shift) parameters, which have been related to the B–N electron density or bond strength. $\delta(^{15}\mathrm{N})$ and $\delta(^{11}\mathrm{B})$ do not show such a correlation but rather correlate with each other, showing primary dependence on halogen-induced effects, those species containing fluorine falling on a separate curve from the other halogens. Pairwise additivity is observed for $\delta(^{11}\mathrm{B})$, $\delta(^{15}\mathrm{N})$, and $J(^{11}\mathrm{B}{-}^{15}\mathrm{N})$, with pairwise parameters showing correlations with the sum of electronegativities or van der Waals radii.

Introduction

The use of nuclear magnetic resonance to study the trimethylamine–boron trihalide adduct system began with our ^{1}H study[1] nearly 20 years ago, shortly thereafter further extended by the work of Heitsch[2] and ourselves.[3] With our preparation of trimethylamine adducts of the mixed trihalides

---

(1) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1964).

0020-1669/83/1322-2384$01.50/0 © 1983 American Chemical Society

of boron,[4,5] the number of adducts in the homologous series was extended from 4 to 20, with the preliminary correlations between $\delta(^1H)$ and $J(^1H-^{11}B)$ and the strength of the B–N bond being confirmed as the work was extended from ^1H spectra to ^{19}F, ^{11}B, and finally ^{13}C data.[4-9] We showed that the pairwise additivity approach of Vladimiroff and Malinowski[10] was applicable to $\delta(^{11}B)$, $\delta(^{19}F)$, and $J(^{11}B-^{19}F)$ parameters[6] as well as to $\delta(^1H)$ and $\delta(^{13}C)$.[8] The excellent correlations of all these NMR parameters for up to 20 compounds suggest that, for this adduct system, NMR correlations to B–N bond strength are valid, though one must still use them with caution as indicated in our recent review.[11] For example, $\delta(^{11}B)$ is not a measure of B–N bond strength, but if one uses the complexation shift, $\Delta\delta$, then this parameter shows the same trends as the other chemical shifts.

Nitrogen-15 NMR would appear to be ideal for the study of donor–acceptor interactions of nitrogen ligands, but experimental difficulties, even with enriched samples (where cost may still restrict the quantity of actual sample available), have limited such studies. One of the few studies of this type is that of Martin et al.[12] These authors found that, with Bruker WP-60 and WH-90 spectrometers, saturated solutions of ureas were required in 15-mm tubes to be able to work at natural abundance. Up to 50 000 scans were used for nitrogens without directly bonded hydrogens, $Cr(acac)_3$ relaxation reagent being required. In an early work,[13] Clippard and Taylor report briefly on B–N couplings (obtained from ^{11}B data) of three simple boron trihalide adducts, but their work was never followed up, presumably because of the experimental difficulties with CW NMR technology. In our work, the $Me_3N{\cdot}BX_nY_{3-n}$ adduct (98% ^{15}N enriched) were available only as dilute solutions in methylene chloride sealed in 5-mm, heavy-walled NMR tubes (3 mm i.d.) and, when our first ^{15}N experiments were attempted in 1973 on a Varian XL-100, no signals could be observed. Even in 1981, with a Bruker WH-400 spectrometer, excessive consumption of machine time precluded completion of this study. It was only this year, with the installation of a new pulse programmer permitting use of the INEPT pulse sequence for polarization transfer from ^1H to ^{15}N, that the current study could be completed. We now report on the ^{15}N chemical shifts of the trimethylamine adducts of the mixed trihalides of boron, the $^{11}B-^{15}N$ coupling constants (obtained for both the ^{15}N and the ^{11}B experiments), and the corresponding ^{11}B chemical shifts.

Experimental Section

Adduct Preparation. Nitrogen-15-enriched trimethylamine (98%, Merck Sharp and Dohme) was used to prepare BF_3, BCl_3, BBr_3, and BI_3 adducts, and the mixed adducts were then formed in situ in the NMR tube by the addition of a heavier boron halide to a methylene chloride solution of the appropriate $Me_3N{\cdot}BX_3$ adduct of the lighter halide.[5] The NMR tubes were sealed and stored at low temperature until the NMR data could be collected.

NMR Spectra. (a) ^1H NMR. At the time of preparation, the samples were monitored by ^1H NMR with a Varian A-60 with ^{11}B decoupling as described previously.[5] At the time the ^{15}N spectra were obtained, ^1H spectra were obtained on the Bruker WH-400 to double check the sample composition. The greater dispersion of the 400-MHz ^1H spectra precluded the necessity of ^{11}B decoupling. No attempt was made to optimize resolution as $J(^1H-^{11}B)$ data have been extensively reported already.[5] A sample spectrum is shown in Figure 1A. Shifts were consistent with those obtained at 60 MHz.[5]

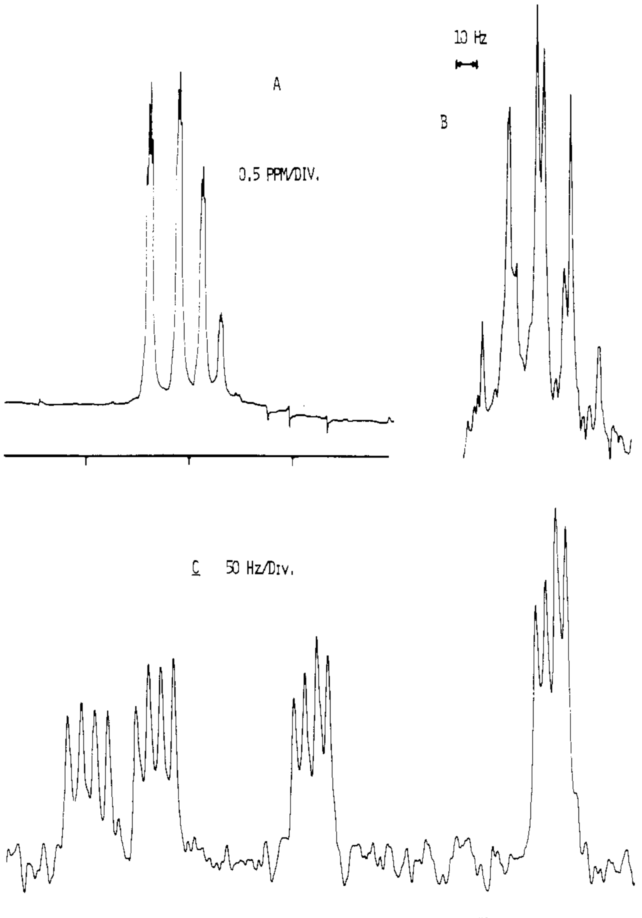

Figure 1. (A) ^1H NMR spectra of the $Me_3N{\cdot}BCl_3$, $Me_3N{\cdot}BCl_2I$, $Me_3N{\cdot}BClI_2$, and $Me_3N{\cdot}BI_3$ systems. (Low digital resolution spectra are adequate to distinguish the species present.) (B) ^{11}B NMR spectrum of $Me_3N{\cdot}BF_3$ showing $J(^{11}B-^{19}F)$ and $J(^{11}B-^{15}N)$. (C) ^{15}N NMR spectra of the $Me_3N{\cdot}BX_nY_{3-n}$ system (X = Cl, Y = I, n = 0–3).

(b) ^{11}B NMR. The ^{11}B spectra (^1H decoupled) were obtained initially on a Varian XL-100 at the time of preparation, i.e. 32.1080 MHz, 256 scans, 8-μs pulses with no delay, 3012-Hz sweep width for a 4K data table after transformation. Immediately following the ^{15}N experiments, the ^{11}B data collections were repeated with a Bruker WP-60. Results were consistent, but a greater digital resolution was used to permit more accurate measurement of $J(^{11}B-^{15}N)$ than were obtained from the XL-100 ^{11}B data and from the WH-400 ^{15}N data (19.250 MHz, 100–500 scans, sweep widths of 3750 and 750 Hz with 0.9 and 0.18 Hz/point digital resolution after transforming the 8K quad detection FIDs into a 4096-point spectrum); 30° (2.2 μs) pulses were used with no additional delay after data acquisition. Line broadenings of 0.5 and 0.1 Hz were used. Spectra were referenced to external $Me_2O{\cdot}BF_3$. Figure 1B shows the BF_3 system.

(c) ^{15}N NMR. A Bruker WH–400 spectrometer equipped with a software-controlled pulse programmer capable of controlling phases and pulsing both observe and decoupling channels was used to obtain the ^{15}N data via the INEPT[14,15] pulse sequence with a delay of 2 s($^1/_4J$(N–H) by using values appropriate to quaternary nitrogen–methyl couplings. Typically, 16–500 scans were adequate for good spectra, compared to 5000 scans with a long waiting period between scans and poorer S/N before INEPT was available. ^1H-decoupled

---

(2) C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965).

(3) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **44**, 899 (1966).

(4) J. S. Hartman and J. M. Miller, *Inorg. Nucl. Chem. Lett.*, **5**, 831 (1969).

(5) B. Benton-Jones, M. E. A. Davidson, J. S. Hartman, J. J. Klassen, and J. M. Miller, *J. Chem. Soc., Dalton Trans.*, 2603 (1972).

(6) J. S. Hartman and J. M. Miller, *Inorg. Chem.*, **13**, 1467 (1974).

(7) B. W. Benton and J. M. Miller, *Can. J. Chem.*, **52**, 2866 (1974).

(8) J. M. Miller and T. R. B. Jones, *Inorg. Chem.*, **15**, 284 (1976).

(9) H. Binder and E. Fluck, *Z. Anorg. Allg. Chem.*, **381**, 116 (1971).

(10) T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, **46**, 1830 (1967).

(11) J. S. Hartman and J. M. Miller, *Adv. Inorg. Chem. Radiochem.*, **21**, 147 (1978).

(12) M. L. Martin, M. L. Filleux-Blanchard, G. J. Martin, and G. A. Webb, *Org. Magn. Reson.*, **13**, 396 (1980).

(13) P. H. Clippard and R. C. Taylor, *Inorg. Chem.*, **8**, 2802 (1969).

(14) G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, **101**, 760 (1979); G. A. Morris, *ibid.*, **102**, 428 (1980).

(15) D. P. Burum and R. R. Ernst, *J. Magn. Reson.*, **39**, 163 (1980).

Table I. Chemical Shifts and Coupling Constants

	$\delta(^{15}N)^a \pm$ 0.03 obsd (calcd)^b	J(B–F), Hz	$J(^{15}N-^{11}B) \pm$ 0.1, Hz obsd (calcd)^b	$\delta(^{11}B)^c \pm$ 0.01 obsd (calcd)^b	$\Delta\delta^d$
$Me_3N{\cdot}BF_3$	−342.01 (−341.9)	15.3	−18.70 (−18.78)	0.64 (0.51)	9.36
$Me_3N{\cdot}BF_2Cl$	−338.0 (−338.2)		−18.61 (−18.30)	5.16 (4.30)	14.64
$Me_3N{\cdot}BF_2Br$	−340.4 (−340.5)	54.2	−18.47 (−18.54)	4.39 (5.60)	14.79
$Me_3N{\cdot}BF_2I$	−344.3^e				
$Me_3N{\cdot}BFCl_2$	−335.9 (−335.7)	60.1	−17.52 (−17.51)	8.24 (7.63)	24.06
$Me_3N{\cdot}BFBr_2$	−339.1 (−339.0)	91.9	−17.44 (−17.37)	3.67 (4.34)	25.30
$Me_3N{\cdot}BCl_3$	−334.00 (−334.2)		−16.50 (−16.43)	10.16 (10.20)	36.34
$Me_3N{\cdot}BFI_2$	−346.5 (−346.5)		−14.30 (−14.30)	−19.0 (−18.11)	
$Me_3N{\cdot}Cl_2Br$	−334.6 (−334.4)		−16.13 (−16.10)	6.71 (7.38)	37.99
$Me_3N{\cdot}BCl_2I$	−336.0 (−335.9)		−15.4 (−15.35)	−3.23 (−2.84)	39.33
$Me_3N{\cdot}BClBr_2$	−335.64 (−335.5)		−15.72 (−15.72)	2.18 (2.89)	40.12
$Me_3N{\cdot}BClBrI$	−336.7 (−337.4)		−14.66 (−14.82)	−9.8 (−9.0)	41.4
$Me_3N{\cdot}BBr_3$	−337.04 (−337.2)		−15.23 (−15.29)	−3.26 (−3.27)	41.96
$Me_3N{\cdot}BClI_2$	−340.7 (−340.5)		−13.93 (−13.91)	−24.75 (−24.21)	42.85
$Me_3N{\cdot}BBr_2I$	−339.77 (−339.6)		−14.30 (−14.82)	−16.97 (−16.85)	43.27
$Me_3N{\cdot}BBrI_2$	−343.38 (−343.2)		−13.20 (−13.18)	−33.88 (−33.83)	44.88
$Me_3N{\cdot}BI_3$	−347.82 (−348.0)		−12.09 (−12.10)	−54.21 (−54.21)	46.31

[a] With respect to nitromethane. [b] Values calculated by using pairwise parameters from Table II. [c] With respect to $Me_2O{\cdot}BF_3$. [d] Complexation shifts are the differences between the ^{11}B shift of the free boron trihalide and the adduct in the same solvent system.[8,11] [e] Very poor signal/noise. Data are questionable.

spectra, referenced to external nitromethane, were obtained with a spectrometer frequency of 40.51 MHz on a 10-kHz sweep width, the 16 K quad data tables being transformed to 8K spectra. A typical spectrum for the Cl/I system is shown in Figure 1C.

Results and Discussion

The nitrogen-15 and boron-11 chemical shifts and the boron–nitrogen coupling constants for the 17 species detected are shown in Table I. However, the data for the two mixed adducts containing both I and F are only tentative as S/N was very bad for these low-abundance species. As noted elsewhere,[11] the hard/soft mix of F and I is significantly discriminated against.

The data are in order of increasing donor–acceptor bond strength for these systems as determined previously from NMR data.[5,8] It is immediately clear that neither the nitrogen nor the boron chemical shifts show a simple correlation with this order though the complexation shifts, $\Delta\delta(^{11}B)$, is reasonably consistent, with complexation shift increasing with increasing bond strength as noted previously.[8,11] $J(^{11}B-^{15}N)$, the boron–nitrogen coupling constants, form a regular trend in reasonable agreement with the observed order of ^1H shifts. Since the absolute magnitude of J decreases as we descend from fluoride to iodide and since $J(^{11}B-^{15}N)$ should be a measure of the "s" electron density in the B–N bond and should increase on going from $Me_3N{\cdot}BF_3$ to $Me_3N{\cdot}BI_3$, we suggest that the sign of this coupling constant is negative. Thus, the −12.9-Hz $J(^{11}B-^{15}N)$ for $Me_3N{\cdot}BI_3$ is larger than the −18.4-Hz $J(^{11}B-^{15}N)$ for $Me_3N{\cdot}BF_3$. When we compare our mutally consistent coupling constant data obtained from both ^{15}N and ^{11}B spectra, the early note of Clippard and Taylor[13] on $J(^{11}B-^{15}N)$ must be questioned, their values being 14–15, 14, and 13 Hz respectively for the BF_3, BCl_3, and BBr_3 adducts, i.e. lower than our values of 18.70, 16.50, and 15.23 Hz, respectively.

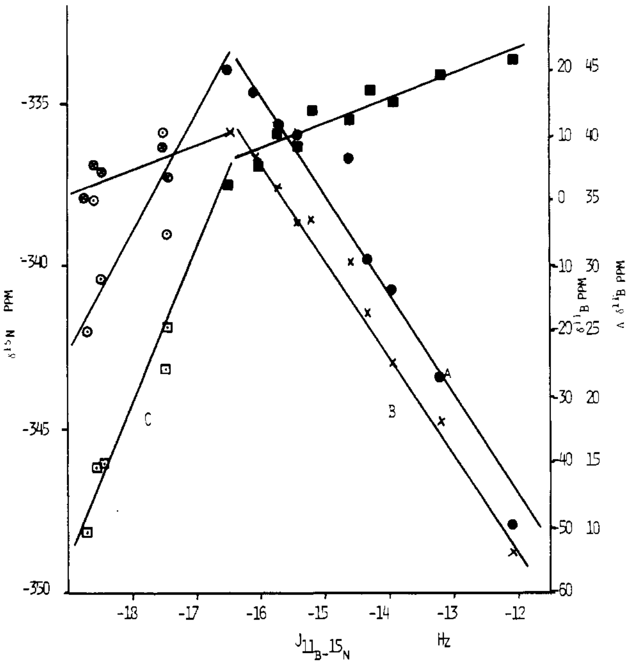

Figure 2. Plots of $\delta(^{15}N)$, $\delta(^{11}B)$, and $\Delta\delta(^{11}B)$ vs. $J(^{11}B-^{15}N)$: ●, $\delta(^{15}N)$; ⊙, $\delta(^{15}N)$ for F-containing species; ×, $\delta(^{11}B)$; ⊗, (^{11}B) for F-containing species; ■, $\Delta\delta(^{11}B)$; ⊡, $\Delta\delta(^{11}B)$ for F-containing species.

(a) Chemical Shift and Coupling Constant Correlations. In Figure 2, we show plots of both the ^{15}N and ^{11}B chemical shifts and the ^{11}B complexation shift vs. $J(^{11}B-^{15}N)$. In both chemical shift cases, the curves fall into two parts. The B—N coupling therefore, rather than either the B or N chemical shifts, most closely follows the order of B—N strength. First, there are the compounds that do not contain fluorine, which give points that fall on reasonably straight lines. For both boron and nitrogen shifts, the fluorine-containing species fall on separate curves, the slopes being flatter and opposite in sign and the curves not being linear. For the ^{11}B complexation shift, again there is a change in slope for the fluorine-containing species but no change in sign. This was not apparent from our previous study[8] based on Fluck's partial ^{11}B data,[9] though it can be seen in retrospect (Figure 2 in ref 8) that the $Me_3N{\cdot}BBr_3$ point has deviated from the straight line through the fluorine-containing species in a correlation of $\Delta\delta(^{11}B)$ with $\delta(^{13}C)$. Thus, neither $\delta(^{11}B)$ nor $\delta(^{15}N)$ is a reliable measure of the donor–acceptor bond strength. Similarly, $\Delta\delta(^{11}B)$ gives a valid order but not the linear correlation to be seen for $\delta(^1H)$, $\delta(^{13}C)$, $\delta(^{19}F)$, $J(^{11}B-^{19}F)$ and $J(^1H-^{11}B)$, or $J(^{11}B-^{15}N)$ to be shown below. Both N and B chemical shifts appear to be dominated by halogen effects rather than simple donor–acceptor inductive effects.

In Figure 3, we show plots of $\delta(^1H)$ and $\delta(^{13}C)$ vs. $J(^{11}B-^{15}N)$, and here we see the good linear correlations of the type reported previously.[8] There is no anomalous region for the fluorine-containing species. The $\delta(^{11}B)$ and $\delta(^{15}N)$ deviations for fluorine-containing systems thus may well reflect significant residual multiple B–F bonding even in the tetrahedral adducts, which act particularly to perturb the chemical shifts of the donor and acceptor atoms. The B–N coupling therefore, rather than either the B or N chemical shifts, most closely follows the order of B–N strength. This explanation would imply a linear effect in ^{19}F measurements, $\delta(^{19}F)$ and $J(^{11}B-^{19}F)$, and

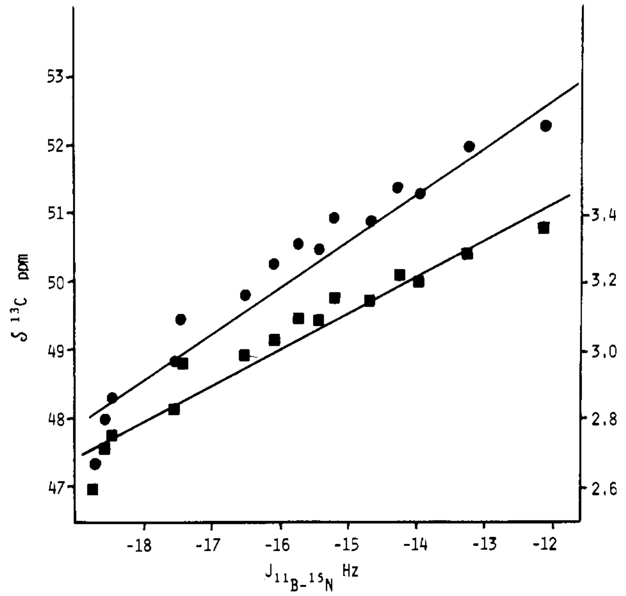

Figure 3. Plots of $\delta(^{13}C)$ and $\delta(^{1}H)$ vs. $J(^{11}B-^{15}N)$: ●, ^{1}H data; ■, ^{13}C data.

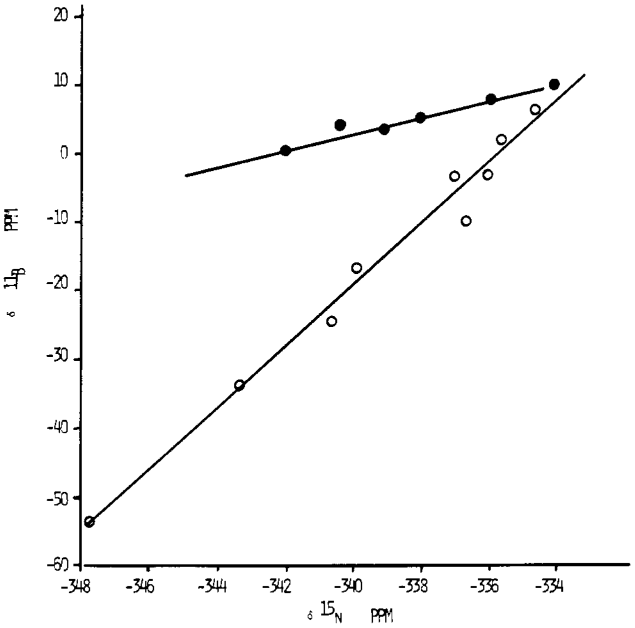

Figure 4. Plot of $\delta(^{11}B)$ vs. $\delta(^{15}N)$: ●, F-containing species; ○, other species.

those for other peripheral nuclei, ^{13}C and ^{1}H, but not for central B or N.

When, however, we plot the two sets of the anomalous NMR parameters $\delta(^{11}B)$ and $\delta(^{15}N)$ against one another, we get two good straight-line fits (Figure 4), one for Cl/Br/I species and the other for the F/X species. Then the small changes in $\delta(^{15}N)$ linearly reflect much larger changes in $\delta(^{11}B)$. In both cases the BI_3 adduct has the highest upfield shift, with the BCl_3 adduct appearing at lowest field and all fluorine-containing species being anomalously upfield of the BCl_3 adduct in both the boron and nitrogen spectra. Thus, it is clear that both boron and nitrogen, i.e. the acceptor and donor nuclei, are subject to the same influence on their chemical shifts. Thus, the halogen substituents rather than any simple B–N bond electron density effects dominate the shifts. It is interesting that chemical shifts of more peripheral nuclei (^{1}H, ^{13}C, ^{19}F), as well as the coupling constants involving boron, appear to be the parameters that best measure B–N strength.

Table II. Pairwise Additivity Parameters[a]

	$\eta_{J(^{11}B-^{15}N)}$, Hz	$\eta_{\delta(^{15}N)}$[b]	$\eta_{\delta(^{11}B)}$[c]
F-F	-6.26	-114.0	-0.44
Cl-Cl	-5.48	-111.4	1.16
Br-Br	-5.10	-112.4	-4.07
I-I	-4.03	-116.0	-21.41
I-Br	-4.57	-113.6	-11.04
I-Cl	-4.94	-112.3	-5.91
I-F	-5.13	-115.3	-1.69
Br-Cl	-5.31	-111.5	-0.62
Br-F	-6.14	-113.3	0.92
Cl-F	-6.02	-112.1	0.64
Me_3N-F			0.61
Me_3N-Cl			2.24
Me_3N-Br			2.98
Me_3N-I			3.34

[a] Calculated by a least-squares routine. [b] Relative to nitromethane. [c] Relative to $Me_2O{\cdot}BF_3$.

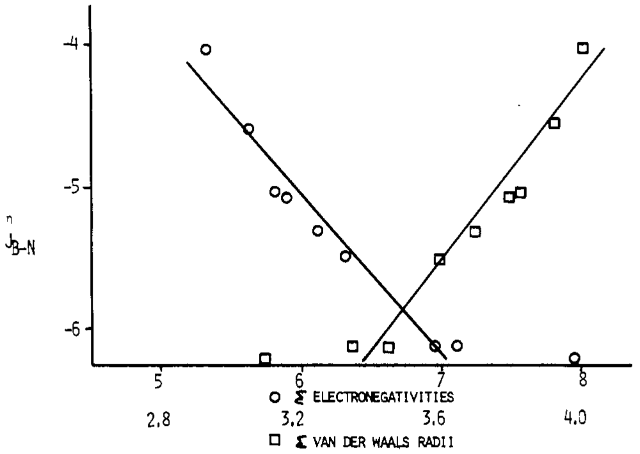

Figure 5. Plot of $\eta_{J(^{11}B-^{15}N)}$ vs. (○) the pairwise sum of the halogen electronegativities and (□) the pairwise sum of the van der Waals radii. The least-squares fit omits the points for the BF_3 adducts, which are anomalous.

(b) Pairwise Additivity. All three sets of NMR data reported in Table I show pairwise additivity. The pairwise additivity parameters $\eta_{X,Y}$ are reported in Table II for $J(^{11}B-^{15}N)$, $\delta(^{15}N)$, and $\delta(^{11}B)$, with δ and J values calculated by using the pairwise parameters shown in Table I in parentheses.

Neither $\eta_{J(^{11}B-^{15}N)}$ nor $\eta_{\delta(^{15}N)}$ involve donor halogen terms, since both involve observation of a parameter associated with the donor. Only in the case of $\eta_{\delta(^{11}B)}$ are there donor halogen terms. The chemical shifts or coupling constants are related to the pairwise parameters as follows for the $Me_3N{\cdot}BF_2Cl$ adduct:

$$\delta(^{11}B) = \eta_{F,F} + 2\eta_{F,Cl} + \eta_{D,Cl} + 2\eta_{D,F}$$

$$\delta(^{15}N) = \eta'_{F,F} + 2\eta'_{F,Cl}$$

$$J(^{11}B-^{15}N) = \eta''_{F,F} + 2\eta''_{F,Cl}$$

where η,η', and η'' are the $\delta(^{11}B)$, $\delta(^{15}N)$, and $J(^{11}B-^{15}N)$ pairwise parameters, respectively.

As shown previously,[6] boron shift parameters are less reliable than others for adduct systems and display different behavior for the parameters involving fluorine. It would appear that $\eta_{\delta(^{15}N)}$ parameters display similar problems, though there are no donor halide parameters to consider.

Finally, as was observed for $J(^{11}B-^{19}F)$ pairwise parameters, $\eta_{J(^{11}B-^{15}N)}$ parameters, when plotted against either the sum of the electronegativities or the sum of the van der Waals radii of the two interacting nuclei (Figure 5), show an approximately linear relationship. The only significant deviations are observed for $Me_3N{\cdot}BF_3$. Further work is under way to investigate the significance of the apparent steric effects.

In conclusion, therefore, we can add the measurement of boron–nitrogen couplings to the list of effective measures of the relative bond strength of adducts of the boron trihalides, but the nitrogen-15 chemical shift data do not reflect a measure of a simple electron density picture of the B–N bond. Thus, especially in view of the experimental difficulties of the ^{15}N NMR experiment, it would appear to be of greater use and interest to measure $J(^{11}B{-}^{15}N)$ from the ^{11}B NMR spectra, which are much simpler to obtain.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support of this work and the Southwestern Ontario NMR Centre at the University of Guelph for WH-4000 time. We also thank T. R. B. Jones for assistance with the WP-60 spectra and R. Geanangel for helpful discussions and for the XL-100 ^{11}B data.

Registry No. $Me_3N{\cdot}BF_3$, 420-20-2; $Me_3N{\cdot}BF_2Cl$, 25889-87-6; $Me_3N{\cdot}BF_2Br$, 25889-93-4; $Me_3N{\cdot}BF_2I$, 25889-95-6; $Me_3N{\cdot}BFCl_2$, 25889-88-7; $Me_3N{\cdot}BFBr_2$, 25889-94-5; $Me_3N{\cdot}BCl_3$, 1516-55-8; $Me_3N{\cdot}BFI_2$, 25889-96-7; $Me_3N{\cdot}BCl_2Br$, 25889-90-1; $Me_3N{\cdot}BCl_2I$, 25889-97-8; $Me_3N{\cdot}BClBr_2$, 25889-91-2; $Me_3N{\cdot}BClBrI$, 39708-29-7; $Me_3N{\cdot}BBr_3$, 1516-54-7; $Me_3N{\cdot}BClI_2$, 25889-98-9; $Me_3N{\cdot}BBr_2I$, 39708-24-2; $Me_3N{\cdot}BBrI_2$, 39708-25-3; $Me_3N{\cdot}BI_3$, 5041-59-8; ^{15}N, 14390-96-6; ^{11}B, 14798-13-1.

Contribution from the Departments of Chemistry, State University of New York at Stony Brook,
Stony Brook, New York 11794, and University of Guelph, Guelph, Ontario N1G 2W1, Canada

Aqueous Shift Reagents for High-Resolution Cationic Nuclear Magnetic Resonance. 2. ^{25}Mg, ^{39}K, and ^{23}Na Resonances Shifted by Chelidamate Complexes of Dysprosium(III) and Thulium(III)

MARTIN M. PIKE,[†] DAVID M. YARMUSH,[†] JAMES A. BALSCHI,[†] ROBERT E. LENKINSKI,[‡]
and CHARLES S. SPRINGER, JR.*[†]

Received October 26, 1982

The tris complexes of anions of chelidamic acid (H_3CA, 4-hydroxypyridine-2,6-dicarboxylic acid) with dysprosium(III) and thulium(III) have been tested as aqueous shift reagents for the NMR peaks of metal cations. The $Dy(CA)_3^{6-}$ complex was observed to produce significant upfield isotropic hyperfine shifts of the $^{25}Mg^{2+}$, $^{39}K^{+}$, and $^{23}Na^{+}$ resonances (as well as that of $^{87}Rb^{+}$ and the ^{14}N resonance of NH_4^{+}). The $Tm(CA)_3^{6-}$ complex produces a downfield shift of the $^{23}Na^{+}$ peak. The shifts are produced by an interaction between cation and shift reagent anion, which is labile on the chemical shift NMR time scale. The shifts are strongly pH dependent due to protonation of the coordinated ligands.

We have recently reported the development of aqueous shift reagents (SR) for metal cationic NMR[1,2] and have demonstrated their usefulness in bioinorganic chemistry, particularly in the study of transport of alkali-metal ions (Na^+ and Li^+) across model[3] and real[4] biological membranes. Transmembrane transport of the other physiological metal cations, K^+, Mg^{2+}, and Ca^{2+}, is of course also important, and we wish to show that NMR can be used to study these processes as well. Here, we report improved SR and their effectiveness with natural-abundance ^{25}Mg and ^{39}K as well as ^{23}Na NMR. In a separate paper, we report their use in the study of transmembrane transport of Mg^{2+} and K^+.[5]

The usefulness of various paramagnetic lanthanide ions for shifting and/or relaxating nuclear magnetic resonances in aqueous solutions has been known for more than a decade.[6] Most subsequent studies have employed various lanthanide coordination complexes as aqueous hyperfine shift[7-12] or relaxation[7,13-18] reagents and as aqueous susceptibility shift[19] or relaxation[20] reagents. Of the resonances of the physiological alkali-metal or alkaline-earth-metal ions, only that of ^{23}Na has been the subject of specific hyperfine relaxation[21,22] or shifting[1,2,12,23,24] and susceptibility shifting[19] experiments and these have employed paramagnetic lanthanide complexes.

Our results[1,2] and those of others[23,24] indicated that increased charge on the anionic shift reagent was a major determinant of increased effectiveness: our best early SR were trianions,[1,2] Elgavish and Elgavish have employed a pentaanion,[24] and Gupta and Gupta, a heptaanion.[23] Thus, we have considered ways of increasing the charge of the complex. Chelidamic acid (H_3CA, 4-hydroxypyridine-2,6-dicarboxylic acid) has a tridentate coordinating ability almost identical with that of di-

---

(1) Pike, M. M.; Springer, C. S. *J. Magn. Reson.* **1982**, *46*, 348.
(2) Balschi, J. A.; Cirillo, V. P.; le Noble, W. J.; Pike, M. M.; Schreiber, E. C.; Simon, S. R.; Springer, C. S. *Rare Earths Mod. Sci. Technol.* **1982**, *3*, 15.
(3) Pike, M. M.; Simon, S. R.; Balschi, J. A.; Springer, C. S. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 810.
(4) Balschi, J. A.; Cirillo, V. P.; Springer, C. S. *Biophys. J.* **1982**, *38*, 323.
(5) Yarmush, D. M.; Pike, M. M.; Balschi, J. A.; Lenkinski, R. E.; Springer, C. S., manuscript in preparation (for abstract, see: *Biophys. J.* **1982**, *37*, 337a).
(6) Morallee, K. G.; Nieboer, E.; Rossotti, F. J. C.; Williams, R. J. P.; Xavier, A. V. *J. Chem. Soc. D* **1970**, 1132.
(7) Dobson, C. M.; Williams, R. J. P.; Xavier, A. V. *J. Chem. Soc., Dalton Trans* **1974**, 1762.
(8) Elgavish, G. A.; Reuben, J. *J. Am. Chem. Soc.* **1976**, *98*, 4755.
(9) Elgavish, G. A.; Reuben, J. *J. Am. Chem. Soc.* **1977**, *99*, 1762.
(10) Horrocks, W. D.; Hore, E. G. *J. Am. Chem. Soc.* **1978**, *100*, 4386.
(11) Geraldes, C. F. G. C. *J. Magn. Reson.* **1979**, *36*, 89.
(12) Bryden, C. C.; Reilley, C. N.; Desreux, J. F. *Anal. Chem.* **1981**, *53*, 1418.
(13) Lettvin, J.; Sherry, A. D. *J. Magn. Reson.* **1977**, *28*, 459.
(14) Gansow, O. A.; Kavsar, A. R.; Triplett, K. M.; Weaver, J. J.; Yee, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 7807.
(15) Gansow, O. A.; Triplett, K. M.; Peterson, T. T.; Bolto, R. E.; Roberts, J. D. *Org. Magn. Reson.* **1980**, *13*, 77.
(16) Dechter, J. J.; Levy, G. C., *J. Magn. Reson.* **1980**, *30*, 207.
(17) Bearden, W. H.; Cargin, V. M.; Robersen, W. R. *Org. Magn. Reson.* **1981**, *15*, 131.
(18) Wenzel, T. J.; Ashley, M. E.; Sievers, R. E. *Anal. Chem.* **1982**, *54*, 615.
(19) Malloy, C. R.; Smith, T. W.; Delayre, J.; Fossel, E. T., personal communication.
(20) Brindle, K. M.; Brown, F. F.; Campbell, I. D.; Gratwohl, C.; Kuchel, P. W. *Biochem. J.* **1979**, *180*, 37.
(21) Degani, H.; Elgavish, G. A. *FEBS Lett.* **1978**, *90*, 357.
(22) Elgavish, G. A. *Rare Earths Mod. Sci. Technol.* **1982**, *3*, 193.
(23) Gupta, R. K.; Gupta, P. *J. Magn. Reson.* **1982**, *47*, 344.
(24) Elgavish, A.; Elgavish, G. A., personal communication.

[†] State University of New York at Stony Brook.
[‡] University of Guelph.