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.

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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)

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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-

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picolinic acid (H_2DPA, pyridine-2,6-dicarboxylic acid),[25] but it has three ionizable protons as compared with two for H_2DPA.[26] The $(DPA)_3$ complexes of the lanthanides, $Ln(DPA)_3^{3-}$, are well characterized in the solid state[27] and in solution,[28-32] and we found the $Dy(DPA)_3^{3-}$ anion to be a good SR for the ^7Li and ^{23}Na aquo cations.[1] Thus, the possible $Dy(CA)_3^{6-}$ anion would seem to be a good candidate as a SR for metal cationic resonances. Also, since three-compartment transport studies such as in some epithelial tissue preparations[40] require both down- and upfield SR, we sought to prepare the $Tm(CA)_3^{6-}$ complex. According to dipolar hyperfine shift theory, analogous Dy(III) and Tm(III) complexes will always produce opposite shifts of the same substrate resonance.[12,41]

Experimental Section

Chelidamic acid (Aldrich) was recrystallized according to the method of Bag et al.[26] The tris complex of Dy^{3+} (or Tm^{3+}) was prepared in situ by adding up to 9 equiv of LiOH slowly (buret), with stirring, to a stoichiometric aqueous dispersion of $DyCl_3$ (or $TmCl_3$) (Alfa) and the insoluble H_3CA. The synthesis is described by the reaction

$$DyCl_3 + 3H_3CA + 9LiOH \rightarrow Li_6Dy(CA)_3 + 3LiCl$$

The pH must be monitored continuously and never allowed to rise above 6 or 7 (even transiently) during the early stages lest Dy^{3+} hydrolysis and precipitation become a problem. After complex formation is complete (clear solution, obtained at pH ca. 8 or by warming at slightly lower pH values), the pH can be raised further (see below) provided the concentration of divalent metal cations is not too high. An in situ synthesis from Dy_2O_3 that avoids the extra countercations, as we reported earlier for the bis(nitrilotriacetate) (NTA^{3-}) complex of Dy^{3+},[1] has also been accomplished. Since this is a doubly heterogeneous synthesis (the oxide is also insoluble), it requires stirring and warming, even before base is added, for hours if not days.

Compositions of solutions for NMR spectroscopy and for pH measurement are given in the text and figure captions. The NMR spectra were obtained on Varian XL-100 (2.35 T), Nicolet NT-300 (7.05 T), and Bruker WH-400 (9.40 T) spectrometers. These were always field-frequency locked on the ^2H resonance of ^2H_2O present in the solvent, which thus served as an internal reference. The isotropic hyperfine shift, Δ, was measured as the difference of the observed resonance position from the resonance position of the cation in the absence of shift reagent. Upfield shifts are reported as positive. Field-frequency locking on the ^2H resonance eliminates contributions to the observed values from bulk magnetic susceptibility. This correction would be imperfect if the ^2H resonance of ^2H_2O itself suffered any hyperfine shift. However, this is expected to be very small since the molar ratio of $SR:H_2O$ never rises above 3×10^{-3} in this work and since these SR have few, if any, inner-sphere coordination positions available for H_2O.[32] For similar reasons, the pH variation of Figure 1 does not itself alter the resonant frequency of the ^2H_2O ^2H peak. Other spectroscopic details are given in the figure captions.

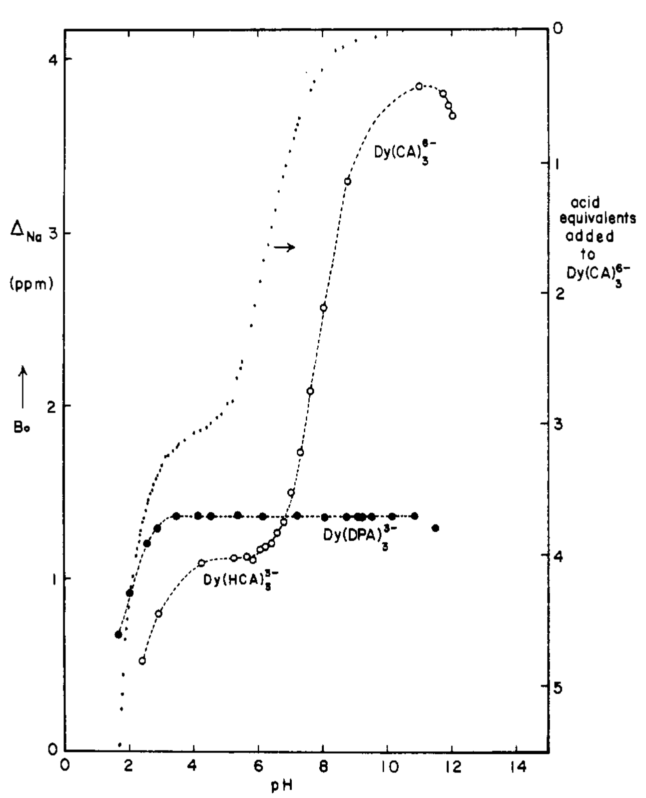

Figure 1. pH dependence of the isotropic hyperfine shift of ^{23}Na (26.5 MHz, 2.35 T), Δ_{Na}, by $Dy(CA)_3^{6-}$ (○) and $Dy(DPA)_3^{3-}$ (●) (left-hand ordinate). The concentrations of the shift reagents, $Li_6Dy(CA)_3{\cdot}3LiCl$ and $Li_3Dy(DPA)_3{\cdot}3LiCl$, were held constant at 20 mM. Sodium was present as the chloride, and the pH was adjusted by the addition of HCl (except at very high pH values, where NaOH was added). The solutions were such that the sodium concentration was held constant at 100 mM below pH 8.8 in the $Dy(CA)_3^{6-}$ titration and below pH 10.2 in the $Dy(DPA)_3^{3-}$ titration. (It rose smoothly to 130 mM at pH 12.1 in the $Dy(CA)_3^{6-}$ titration and to 109 mM at pH 11.5 in the $Dy(DPA)_3^{3-}$ titration.) The chloride concentration varied from 230 mM at pH 2.5 to 160 mM at pH 8.0 and above in the $Dy(CA)_3^{6-}$ titration and from 243 mM at pH 1.7 to 209 mM at pH 10.2 and above in the $Dy(DPA)_3^{3-}$ titration. The solvent was 40% D_2O. The dashed curves are intended merely to guide the eye. Slight precipitation was noted only at the very basic end of the $Dy(DPA)_3^{3-}$ experiment and at the very acidic end of the $Dy(CA)_3^{6-}$ experiment. The temperature was ca. 301 K. A simple pH titration of $Dy(CA)_3^{6-}$ is also shown (dotted points, right-hand ordinate). The complex (i.e., $Li_6Dy(CA)_3{\cdot}3LiCl$) concentration is diluted from 82 to 22 mM during the titration with HCl. The temperature was ca. 296 K.

Results

We sought first to test the efficacy of $Dy(CA)_3^{6-}$ as a shift reagent with ^{23}Na, the most sensitive of the physiological metal cation magnetic nuclei.[33] Figure 1 depicts the upfield hyperfine shift of the $^{23}Na^+$ resonance (left-hand ordinate), induced by the tris(chelidamate) complex of Dy^{3+}, as a function of pH. The stoichiometric complex concentration is 20 mM over the entire pH range. The stoichiometric Na^+ concentration is 100 mM over most of the pH range (<8.8), only rising smoothly to 130 mM in the basic solutions because NaOH was used as base. Thus, the slight decrease in shift at the highest pH values could be due to an increase in the fraction of free sodium. The other conditions are given in the figure caption. An analogous shift vs. pH curve is shown for the tris(dipicolinate) complex. The only difference in conditions for this curve is that the stoichiometric Na^+ concentration rises above 100 mM only

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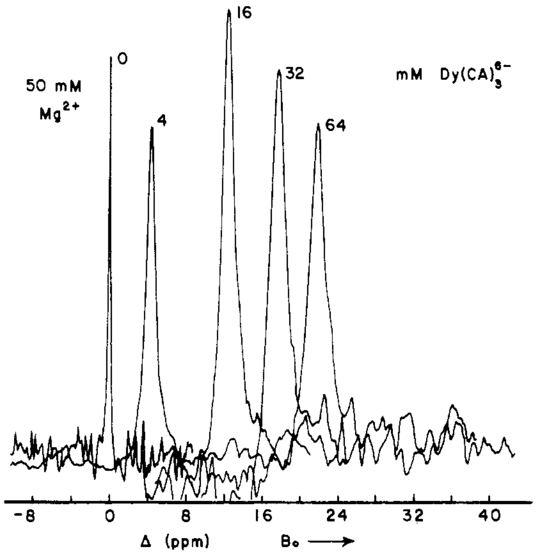


Figure 2. Natural-abundance ^{25}Mg NMR spectra (24.5 MHz, 9.40 T) of mixtures of $MgCl_2$ (50 mM) and varying amounts of $Li_6Dy(CA)_3{\cdot}3LiCl$ in 50% D_2O. The stoichiometric concentrations of $Li_6Dy(CA)_3{\cdot}3LiCl$ are, as indicated, 0, 4, 16, 32, and 64 mM. The temperature was ca. 297 K. For each spectrum, the number of free-induction decays accumulated was 1000 and the total acquisition time was 205 s. The vertical scales differ.

above pH 10.2 and then only to 109 mM in the most basic solution. The CA complex induces a much larger (by almost a factor of 3) shift than the DPA complex at high pH even though they are very similar below pH 7.

The right-hand ordinate of Figure 1 measures a separate pH titration in terms of the number of acid (HCl) equivalents added to a tris(chelidamate)dysprosate(III) complex solution. It is clear that a three-proton pK_a of ca. 6.5 exists for the CA complex under these conditions. Another pK_a of ca. 1.7 involves more protons. These values are in good agreement with literature results, which indicate that metal ion coordination lowers the highest pK_a of chelidamic acid from ca. 11 to ca. 6.5.[26] The higher pK_a is ca. 8 in the shift vs. pH curve for the CA complex because the ionic strength is lower (averaging ca. 0.5 M) for the NMR curve than for the pH titration (averaging ca. 1 M). The pK_a is known to be dependent on ionic strength,[26] and we have recently found the slope, $\Delta pK_a/\Delta I$, to be ca. −3 for the Tb^{3+} complex.[34]

Figure 2 shows natural-abundance ^{25}Mg NMR spectra (24.5 MHz) of 50 mM $MgCl_2$ in the presence of varying amounts of $Li_6Dy(CA)_3{\cdot}3LiCl$. Experimental details are given in the figure caption. An upfield isotropic hyperfine shift, Δ, is clearly observed. The line appears to retain a Lorentzian shape as it is shifted (indicating that the spectrum remains in the "fast motional narrowing" condition[35]). Some broadening induced by the shift reagent is observed, but it is small compared to the shift.

The hyperfine shifts of the resonances of Figure 2 along with those of other $^{25}Mg^{2+}$ resonances, $^{39}K^+$ resonances (14.0 MHz), and $^{23}Na^+$ resonances (26.5 MHz) are plotted as a function of shift reagent to cation molar (stoichiometric) ratio, ρ, in Figure 3. The experimental details are given in the figure caption. The continuous nature of the curves indicates that the equilibrium interactions of the cations with the shift reagents responsible for the shifts are labile on the respective chemical shift NMR time scales. The Mg^{2+} curve shows that very large shifts (in ppm) can be obtained. Dilution of Mg^{2+} from 50 to 20 mM (not shown) has no significant effect on the curve. This is not true for the K^+ and Na^+ data, where concentration raises the curves (not shown), as we found earlier for the interaction of Na^+ with $Dy(NTA)_2^{3-}$.[1] Thus, the Mg^{2+} binding to the SR may be significantly stronger and closer to saturation than the K^+ and Na^+ binding. This would be consistent with electrostatic considerations.[1]

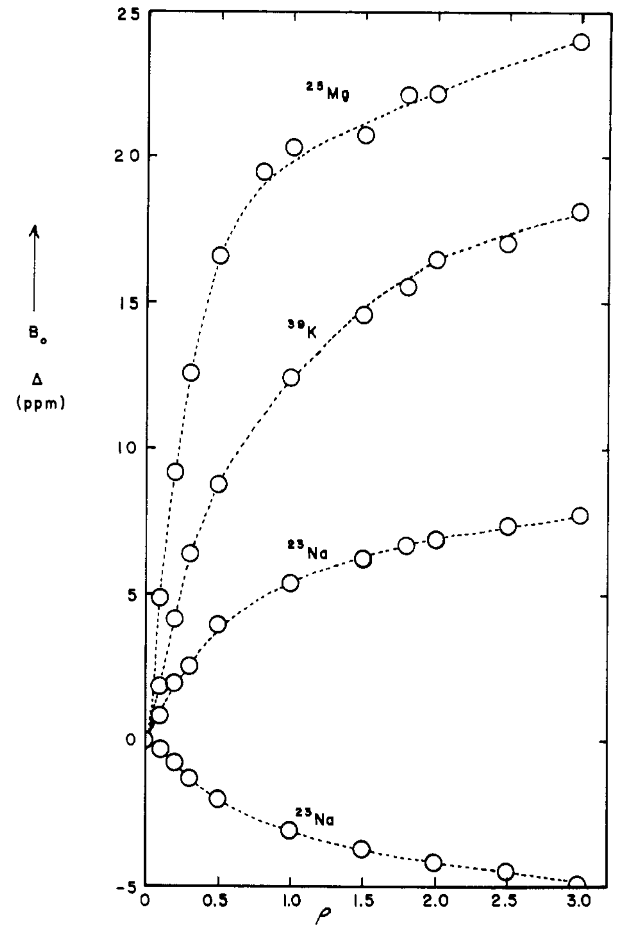
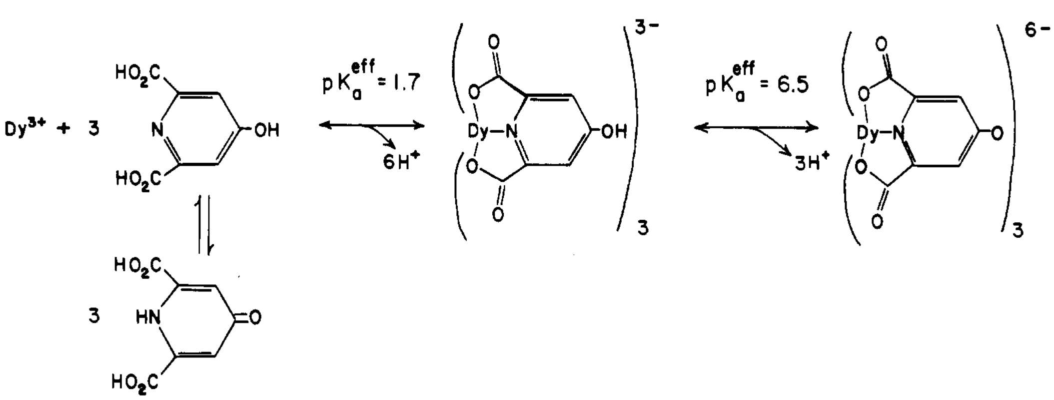


Figure 3. Isotropic hyperfine shift, Δ, of various metal cationic resonances vs. the stoichiometric molar ratio of shift reagent to cation, ρ. In all cases, the metal chloride ($MgCl_2$, KCl, NaCl) concentration is held constant at 50 mM. The magnetic isotope observed is present at natural abundance. In all cases, Tris (tris(hydroxymethyl)aminomethane) buffer was present at a total Tris concentration of 10 mM. The dashed curves are intended merely to guide the eye. For the upper three curves, the shift reagent was $Li_6Dy(CA)_3{\cdot}3LiCl$. In the $MgCl_2$ case (^{25}Mg NMR, 24.5 MHz, 9.40 T), the pH varied smoothly from 8.4 in the solution with no shift reagent to 7.8 in the solution with 150 mM SR. The data include those of Figure 2. The temperature was ca. 297 K. In the KCl case (^{39}K NMR, 14.0 MHz, 7.05 T), the pH varied from 8.7 to 7.7. The temperature was ca. 297 K. In the NaCl case (^{23}Na NMR, 26.5 MHz, 2.35 T), the pH varied from 8.6 to 7.9. The temperature was ca. 301 K. For the lower curve (^{23}Na NMR, 26.5 MHz, 2.35 T), the shift reagent was $Li_6Tm(CA)_3{\cdot}3LiCl$. The pH varied from 8.9 to 7.9. The temperature was ca. 301 K.

The $^{23}Na^+$ curves show similar shapes as those presented earlier[1] for the binding of Na^+ to $Dy(NTA)_2^{3-}$. Since the shift of $^{23}Na^+$ is so pH dependent (Figure 1), the smooth but slight lowering of the pH with increasing ρ in the NMR titration experiments (caption of Figure 3) will tend to depress the magnitude of Δ at high ρ values (possibly by as much as 1 ppm at ρ = 3). As expected from the theory for dipolar shifts,[12,41] the thulium(III) complex induces an isotropic hyperfine shift in the opposite direction (downfield, for the tris(chelidamate)) from that induced by the analogous dysprosium(III) complex. In fact, the ratios of analogous shifts are close to the theoretical ratio of −1.9 (Dy(III):Tm(III)) predicted for pure dipolar shifts.[41] Deviations may arise because the conditions for analogous solutions are not absolutely identical. The broadening of the sodium resonance by $Dy(CA)_3^{6-}$ or $Tm(CA)_3^{6-}$

Scheme I



is not significantly greater than that induced by $Dy(NTA)_2^{3-}$.[1] The $^{39}K^+$ resonances become moderately broadened (width at half-height ca. 60 Hz, at $\rho = 3$) compared to the resonance in the absence of shift reagent (ca. 7 Hz). We have also observed significant shifts of the ^{14}N resonance of NH_4^+ (ca. 15 ppm upfield at 100 mM NH_4^+, 100 mM $Li_6Dy(CA)_3\cdot 3LiCl$, and pH 7.7) and of the $^{87}Rb^+$ resonance (ca. 8 ppm upfield at 100 mM Rb^+ and 10 mM $Li_6Dy(CA)_3\cdot 3LiCl$; 296 Hz, broad) induced by $Dy(CA)_3^{6-}$.

Discussion

From our results, there is little doubt that the equilibria shown in Scheme I obtain for the tris(chelidamate) complex. The $Dy(CA)_3^{6-}$ shift reagent induces a shift approximately 3.5 times as great as that induced by $Dy(HCA)_3^{3-}$ under the condition of Figure 1. Thus, the increased charge on the SR anion does increase the efficacy of the SR. This is probably mainly because the fraction of cation bound to the SR is increased. In order to determine any real changes in the thermodynamic binding constant, one must take into account electrostatic effects on activity coefficients[36] and competitive binding of countercations (including protons) present. Involved analyses of this type are presently under way in our laboratories via computer fittings of the NMR binding isotherms. Preliminary results indicate that we can fit the $Na^+/Dy(CA)_3^{6-}$ curve quite well with two 1:1 formation constants, $K_{Na} = 1579$ M^{-1} and $K_{Li} = 61.5$ M^{-1}, and a limiting shift, $\Delta°_{Na}$, of +11.9 ppm.[42] When this is compared to a similarly good fitting of the $Na^+/Dy(NTA)_2^{3-}$ data of ref 1 ($K_{Na} = 39.5$ M^{-1}, $K_{HTEA} = 14$ M^{-1} ($HTEA^+$ is triethanolammonium), and $\Delta°_{Na} = +20.9$ ppm), we find support for the electrostatic argument stated above. The $Dy(CA)_3^{6-}$ SR does not produce a larger $\Delta°_{Na}$ than $Dy(NTA)_2^{2-}$; instead, it has a larger K_{Na}. A fitting of the $Na^+/Dy(CA)_3^{6-}$ curve admitting the reasonable possibility of simultaneous formation of adducts with two or three Na^+ ions bound would most likely enhance this argument. That is, it would almost certainly yield an even lower value of $\Delta°_{Na}$. Other highly charged shift reagents, $Dy(EDTA)_2^{5-}$ ($EDTA^{4-}$ is ethylenediaminetetraacetate)[24] and $Dy(PPP)_2^{7-}$ (PPP^{5-} is tripolyphosphate),[23] which produce large observed shifts of the $^{23}Na^+$ resonance, have been recently reported.

However, results in our laboratories[37] and others[12] indicate that high negative charge is not the only factor required to produce an efficient shift reagent. We have found that the anions $Dy(TTHA)^{3-}$ and $Tm(TTHA)^{3-}$ ($TTHA^{6-}$ is triethylenetetraminehexaacetate[13]) induce shifts of the $^{23}Na^+$ resonance comparable to those induced by the $Dy(CA)_3^{6-}$ and $Tm(CA)_3^{6-}$ complexes.[37] Bryden et al. have reported that the neutral Dy(NOTA) complex ($NOTA^{3-}$ is 1,4,7-triazacyclononane-*N,N',N''*-triacetate) induces larger shifts of the $^{23}Na^+$ resonance than any of the anionic complexes tested by them, although the (unclear) concentration ratios in their various experiments are not strictly comparable.[12] Anionic SR are preferred for physiological experiments because the vast majority of polyelectrolytes in nature are anionic. Therefore anionic SR will have little tendency to bind to macromolecules or to cross biological membranes.

Thus, the magnitude of the binding equlibrium must also be influenced to some degree by the chemical nature of the cationic binding site on the shift reagent. This presumably involves the free and/or coordinated carboxylate oxygens in these complexes.[12] We previously reported that although, under certain conditions, $Dy(NTA)_2^{3-}$ induces a slightly larger shift in the $^{23}Na^+$ resonance than $Dy(DPA)_3^{3-}$, the opposite is true for the $^{7}Li^+$ resonance.

The strong pH dependence of the hyperfine shift induced by $Dy(CA)_3^{6-}$ could prove useful as another NMR method for pH measurement. However, pH dependence can be a problem in many membrane transport experiments with cell suspensions or cultures or with tissue. Unfortunately, many of the best shift reagents suffer such dependence.[37]

Assuming that the hyperfine shift is totally dipolar (pseudocontact) in nature, there are at least three factors that determine the magnitude and sign of the limiting shift, $\Delta°$. These are the particular lanthanide ion chosen, the asymmetry of the magnetic susceptibility tensor of the lanthanide ion (determined by the molecular structure of the shift reagent anion), and the geometrical coordinates of the cation binding site (its distance from the lanthanide ion and the angular relationships to the principal axes of the magnetic susceptibility tensor.[12,41] We have obtained interesting results that demonstrate that various combinations of these factors are important. Although $Dy(NTA)_2^{3-}$ shifts the $^{7}Li^+$, $^{23}Na^+$, $^{39}K^+$, and $^{43}Ca^{2+}$ resonances upfield, it shifts the $^{113}Cd^{2+}$ resonance downfield. Although K^+ seems to bind to $Dy(NTA)_2^{3-}$, the $^{39}K^+$ resonance is noticeably broadened and the peak is only slightly shifted (<1 ppm upfield at 35 mM K^+ and 105 mM $(HTEA)_3Dy(NTA)_2$; 50 Hz, broad). This is a good SR for $^{23}Na^+$, producing only minimal broadening.[1] Most of our dysprosium(III) complexes produce upfield shifts, and since the dipolar mechanism dominates, the analogous thulium(III) complexes induce downfield shifts. However, the $Dy(TTHA)^{3-}$ complex produces a downfield shift.[37] On the other hand, the $Dy(DOTA)^-$ ($DOTA^{4-}$ is 1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetate) complex, which could be structurally similar to the $Dy(TTHA)^{3-}$ complex, has been reported to induce an upfield shift of the $^{23}Na^+$ resonance.[12] Of course, there is no certainty that $Dy(DOTA)^-$ structurally resembles $Dy(TTHA)^{3-}$. Downfield SR ($Tm(CA)_3^{6-}$, in this paper) will prove particularly useful in studies of compartmented samples (e.g. tissue) in vertical superconducting magnets. For a cylindrical sample coaxial with the static magnetic field, the bulk susceptibility shift, due to a paramagnetic substance, is

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(42) Hillman, D. Z., unpublished results.

downfield.[19,38] Thus, the isotropic hyperfine shift induced by a downfield SR will add to the susceptibility shift in such a case.

The observation of the shift of the $^{25}Mg^{2+}$ resonance is important for possible studies of the physiological divalent cations. The binding of these cations to the shift reagent anion or to the shift reagent ligand could be strong. At higher pH values, precipitation can be observed in $Dy(CA)_3^{6-}$ solutions containing Mg^{2+}. Considerably more precipitation is observed when $Dy(CA)_3^{6-}$ and Ca^{2+} are mixed (likewise with $Dy(DPA)_3^{3-}$). We have observed a shift of the $^{43}Ca^{2+}$ resonance of greater than 40 ppm upfield (ca. 60-Hz line width) induced by $Dy(NTA)_2^{3-}$ (50 mM $CaCl_2$, 75 mM $Li_3Dy(NTA)_2$). However, since this isotope is so rare,[33] many NMR studies of Ca^{2+} biochemistry may be made with $^{113}Cd^{2+}$ as a surrogate.[39] We have observed a downfield shift of over 20 ppm in the $^{113}Cd^{2+}$ resonance induced by $Dy(NTA)_2^{3-}$ (300 mM $CdSO_4$, 100 mM $Na_3Dy(NTA)_2$),[43] although at higher concentrations of Cd^{2+} (as the sulfate) some precipitation is noted. Perhaps SR with smaller charges will be more useful for studies of the divalent cations.

The interactions of shift reagents with alkaline-earth-metal cations are also important in considerations of studies of alkali-metal cations in the presence of divalent cations, often the physiological situation. The divalent ions interfere in two different ways: (1) by very effectively competing with the monovalent cation for the SR and (2) by competing with the lanthanide ion for the SR ligand (we have demonstrated behavior of this type with Lu^{3+} [1]). Neutral products of this latter reaction or hydrolysis of positive products to form neutral compounds most likely accounts for the precipitations we have noted in some mixtures. Monoligand SR anions may be more immune to this reaction than bis or tris complexes. In both cases, the SR is effectively inactivated.[1,3]

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Registry No. $Li_6Dy(CA)_3$, 86260-93-7; $Li_6Tm(CA)_3$, 86260-94-8; H_3CA, 138-60-3; $DyCl_3$, 10025-74-8; $TmCl_3$, 13537-18-3; LiOH, 1310-65-2; $^{25}Mg^{2+}$, 66650-06-4; $^{39}K^+$, 16686-67-2; $^{87}Rb^+$, 51377-95-8; $^{23}Na^+$, 17341-25-2; nitrogen, 7727-37-9.

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(43) Chu, S., unpublished results.

Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711

The Metal Atom's View of the Bonding in *o*-Benzoquinone, *o*-Dithiobenzoquinone, and *o*-Benzoquinone Diimine Metallacycles of $(\eta^5\text{-}C_5H_5)Co$. A ^{59}Co NQR Study of the *cis*-a_3b_2 Ligand Geometry

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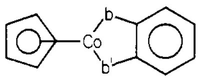
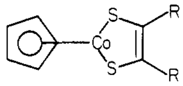
Bidentate *o*-quinone ligands, $bb'C_6H_4$, where b, b′ = O, S, NR (R = H, CH_3, C_6H_5), and 1,2-dithiolenes form complexes with $(\eta^5\text{-}C_5H_5)Co$ containing a five-membered metallacycle ring:

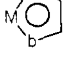




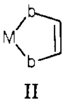
The ^{59}Co nuclear quadrupole resonance spectra show that the ground-state electron distribution of the cobalt atom is directly controlled by the electronegativity of b, b′. Substitution of the metallacycle at the α and β positions only minimally perturbs the electron distribution on the cobalt atom. From the point of view of cobalt, the Co–b interaction is mostly a σ-bond that responds to the push–pull exertion on the electrons by b alone. Co–b π-bonding is not strikingly evident in the NQR spectra. However, the apparent effects of π-bonding on Co were detected in noncyclic $(\eta^5\text{-}C_5H_5)Co(b)b'$ complexes where b, b′ = CO, $P(OR)_3$, PR_3. Comparison of the NQR data for the metallacycles, where the formal oxidation state of cobalt is uncertain, with the noncyclic complexes containing Co(I) suggests that the metallacycles also are best thought of as Co(I) complexes. The reactions of the metallacycle complexes with Lewis acids and bases could be sensitive to the electron distribution on Co. Preliminary results of several such reactions are reported.

Introduction

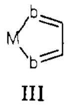
The bonding in unsaturated five-membered metallacycle rings, formulated as I–III, has attracted considerable attention.



I



II



III

The well-known dithiolene complexes, where b = S, have been widely investigated.[1,2] *o*-Benzoquinones,[3] where b = O, *o*-benzoquinone diimines,[4-6] where b = N, and the metallacyclopentadienes,[7] where b = C, are less thoroughly studied but have attracted increasing attention recently. Throughout many of these investigations, the degree of π-electron delo-

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(1) For reviews see: Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303. Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295. McCleverty, J. A. *Ibid.* **1968**, *10*, 49.

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