

assumes the very rapid establishment of equilibrium between molecules and ion pairs in the coupled equilibria, molecules  $\rightleftharpoons$  ion pairs  $\rightleftharpoons$  free ions, and we therefore conclude that in our systems the formation of the loose ion pair from the tight ion pair is not rate determining. This agrees with the conclusions reached from our kinetic studies<sup>8</sup> on NiLCl<sub>2</sub>.

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### <sup>23</sup>Na Quadrupole Coupling Constants in Different Coordination Shells from <sup>23</sup>Na and <sup>13</sup>C Fourier Transform Nuclear Magnetic Resonance Measurements on Sodium Cryptates

Sir:

Ionic solvation has been investigated by many research groups using most of the available electrochemical and spectroscopic methods, including nuclear magnetic resonance spectroscopy.<sup>1</sup> Among metal cations, much work has been done on the sodium cation by direct observation on the <sup>23</sup>Na nmr chemical shifts and quadrupolar broadening effects.<sup>2-13</sup>

Knowledge of <sup>23</sup>Na quadrupolar coupling constants,  $\chi_{Na} = (e^2qQ/h)$  ( $eQ = ^{23}\text{Na}$  nuclear quadrupole moment), and electric field gradients,  $eq$  in various coordination states, would be of much interest to the understanding of the nature of cation solvation, but such determinations are hampered by the uncertainties in solvation number<sup>14</sup> and the fluctuation of the coordination sphere.

Stable sodium complexes with well-defined coordination shells provide a unique way to study the solvated cation, as shown by recent <sup>23</sup>Na studies<sup>15-17</sup> of Na<sup>+</sup> complexes of natural<sup>15</sup> and synthetic<sup>18</sup> macrocyclic ligands.

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Macrobicyclic ligands<sup>19</sup> forming cryptate-type cation inclusion complexes,<sup>20</sup> in which the coordination shell entirely surrounds the cation, should be well suited for such studies since these complexes are much more stable<sup>21</sup> than the macrocyclic ones and cation exchange is slower (see below).

We present here the results of a study of <sup>23</sup>Na nuclear quadrupolar coupling constants in four "frozen" coordination shells containing as binding sites two nitrogens and four, five, or six oxygens or four oxygens and two sulfurs, *i.e.*, the sodium cryptates of ligands **1**, **2**, **3**, and **4**, respectively. Assuming zero asymmetry parameter, the quadrupolar relaxation time  $T_q$  of the <sup>23</sup>Na nucleus is given by eq 1<sup>22</sup> (nuclear spin of <sup>23</sup>Na =

$$T_q^{-1} = \pi\Delta\nu = (2\pi^2/5)(e^2qQ/h)^2\tau_c \quad (1)$$

<sup>3/2</sup>).  $\chi_{Na}$  may be calculated from the line width  $\Delta\nu$  of the <sup>23</sup>Na resonance if the rotational correlation time,  $\tau_c$ , of the motions of the sodium complex is known. Since  $\tau_c$  values estimated in the usual way from the molecular radius and Debye's relation may be in error (generally too long) by one order of magnitude,<sup>23</sup> we employed an indirect *double nuclear spin probe* method.<sup>24,25</sup>

Using the dipole-dipole relaxation equation (2) one

$$T_1^{-1}(^{13}\text{C}) = n^2\hbar^2 \gamma_H^2\gamma_C^2 r_{CH}^{-6} \tau_c = 4.4046 \times 10^{10} \tau_c \quad (2)$$

$$(n = 2 \text{ for a CH}_2 \text{ group; } r_{CH} = 1.085 \pm 0.005 \text{ \AA})$$

may obtain  $\tau_c$  from the <sup>13</sup>C relaxation times  $T_1$  (<sup>13</sup>C) of the CH<sub>2</sub> carbons of the sodium cryptates. Then, making the reasonable assumption that, in the quite rigid complexes,  $\tau_c$  (from <sup>13</sup>C data) also represents the reorientational motions which modulate the <sup>23</sup>Na quadrupolar interaction, one may introduce  $\tau_c$  in eq 1 and calculate  $\chi_{Na}$  from  $\Delta\nu$ . The <sup>13</sup>C nmr spectra and relaxation times and the <sup>23</sup>Na spectra have been measured by the Fourier transform technique. Spectral data and results calculated with eq 1 and 2 are given in Table I.<sup>26</sup>

The *correlation times* of the four cryptates (Table I) are about a factor of 5 *shorter* than those which are cal-

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(26) The solutions contained stoichiometric amounts of a given ligand and NaCl (0.25 M each) in methanol-D<sub>2</sub>O 95/5. Since the stability constants are very high in this medium (>10<sup>8</sup>),<sup>21</sup> the solution contains only the sodium cryptates. The spectra have been measured at 25.1 MHz for both <sup>13</sup>C (with <sup>2</sup>D lock) and <sup>23</sup>Na (without field-frequency lock and by decreasing slightly the magnetic field). The <sup>13</sup>C relaxation times have been obtained using the inversion-recovery method. The short relaxation times measured (about 1 sec), the size of the molecules and the presence of two protons on each carbon justify the use of eq 2. Indeed the relaxation of these carbon nuclei may be expected to occur almost exclusively *via* the dipole-dipole mechanism (for a discussion see, for example, G. C. Levy, *Accounts Chem. Res.*, **6**, 161 (1973)).

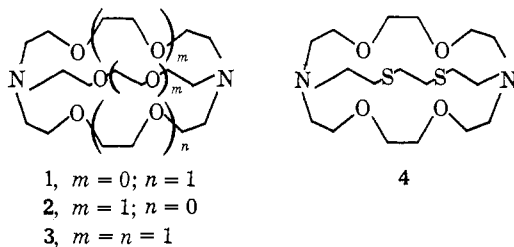
**Table I.**  $^{13}\text{C}$  and  $^{23}\text{Na}$  Nmr Spectral Data, Calculated Correlation Times, and  $^{23}\text{Na}$  Quadrupolar Coupling Constants for Sodium Cryptates of Ligands 1-4<sup>a</sup>

Cryptate	$T_1(^{13}\text{C}),^b$ sec ( $\pm 15\%$ )	$\tau_c(^{13}\text{C}),^b$ psec ( $\pm 15\%$ )	$\delta(^{23}\text{Na}),^c$ ppm ( $\pm 2\%$ )	$\Delta\nu(^{23}\text{Na}),^c$ Hz	$T_q(^{23}\text{Na}),^d$ msec ( $\pm 5\%$ )	$\chi_{\text{Na}},^d$ MHz ( $\pm 10\%$ )
[1,Na <sup>+</sup> ]Cl <sup>-</sup>	1.05	21.5	+11.15	132 $\pm$ 3	2.4	2.20
[2,Na <sup>+</sup> ]Cl <sup>-</sup>	1.25	18.0	-4.25	46 $\pm$ 2	6.9	1.43
[3,Na <sup>+</sup> ]Cl <sup>-</sup>	1.00	22.5	-11.40	29 $\pm$ 1	11.0	1.01
[4,Na <sup>+</sup> ]Cl <sup>-</sup>	1.10	20.5	-6.20	49 $\pm$ 2	6.5	1.38

<sup>a</sup> See ref 26 for experimental details. <sup>b</sup>  $^{13}\text{C}$  relaxation times  $T_1$  and correlation times  $\tau_c$  calculated according to eq 2. The values given are averages over all carbons in the molecules. The spread of  $T_1$  values is about  $\pm 10\%$ . In the case of  $\tau_c$  an error of  $\pm 0.009 \text{ \AA}$  in  $r_{\text{CH}}$  leads to an error of  $\pm 5\%$  in  $\tau_c$ .  $\tau_c$  is given in picoseconds;  $1 \text{ psec} = 10^{-12} \text{ sec}$ . <sup>c</sup>  $\delta$ , shift of  $^{23}\text{Na}$  resonance downfield ( $< 0$ ) from  $0.25 \text{ M NaCl}$  in water (8 Hz line width).  $\Delta\nu$ , full line width at half-height of  $^{23}\text{Na}$  resonance. A  $0.25 \text{ M NaCl}$  solution in methanol-water has  $\delta = -2.70$  ppm and  $\Delta\nu = 19.5 \text{ Hz}$ . <sup>d</sup>  $^{23}\text{Na}$  nuclear quadrupolar relaxation time,  $T_q$ , and coupling constant,  $\chi_{\text{Na}} = (e^2qQ/h)$ , calculated using eq 1 and  $\tau_c(^{13}\text{C})$  values.  $T_q$  is obtained from the full line width  $\Delta\nu$ ; the inhomogeneity contribution to  $\Delta\nu$  is probably less than 1-2 Hz leading to an error (over estimation) in  $\chi_{\text{Na}}$  of about 3% or less.

culated from the Debye relation ( $\tau_c \sim 110 \text{ psec}$  for a molecular radius of about  $5 \text{ \AA}$ ).

The  $^{23}\text{Na}$  chemical shifts show an interesting trend. Whereas oxygen containing organic solvents shift the  $^{23}\text{Na}$  resonance downfield, amines give an upfield shift.<sup>7,10</sup> Indeed the  $^{23}\text{Na}$  resonance is upfield from the reference when the ligand shell contains four oxygens and two nitrogens and shifts downfield as the number of oxygens increases from four to six. Sulfur sites lead to a small downfield shift (Table I).



The  $^{23}\text{Na}$  nuclear quadrupolar coupling constants decrease when the number of oxygens in the ligand shell increases. The electric field symmetry increases as more and more oxygen sites are disposed around the cation. The replacement of two oxygens in 3 by sulfur in ligand 4 causes about the same increase in field gradient as the removal of one oxygen (in 2). The present values of  $\chi_{\text{Na}}$  (Table I) are by a factor of 2-3 higher than those which would be obtained by approximating  $\tau_c$  with the Debye relation. A linear relation has been proposed<sup>4b</sup> between  $\chi_{\text{Na}}$  and the paramagnetic shielding term which dominates<sup>4,7</sup> the  $^{23}\text{Na}$  chemical shifts. Indeed the plot of  $\chi_{\text{Na}}$  against  $\delta(\text{Na})$  (Table I) gives a straight line within experimental accuracy.

Finally, when excess NaCl is added to the cryptate solutions two separate  $^{23}\text{Na}$  signals (free and complexed Na<sup>+</sup>) are observed, showing that cation exchange is slow at  $35^\circ$ . In the case of [3, Na<sup>+</sup>] coalescence occurs at about  $+58^\circ$  giving a free energy of activation  $\Delta G^\ddagger_{58}$  of about  $15.4 \text{ kcal/mol}$  in agreement with previous proton resonance work<sup>27</sup> and with a recent  $^{23}\text{Na}$  nmr study of cation exchange rates in the same compound in ethylenediamine.<sup>28</sup> In [1,Na<sup>+</sup>] and [2,Na<sup>+</sup>] one still observes separate  $^{23}\text{Na}$  resonances at  $+58^\circ$  ( $\Delta G^\ddagger > 16 \text{ kcal/mol}$ ).<sup>29</sup>

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Double probe  $^{13}\text{C}$ ,  $^{23}\text{Na}$  nmr studies may provide detailed information on the electric effects produced by ligand structure, binding sites, ion pairing, and medium<sup>15</sup> as well as on molecular tumbling. Complexes of other metal cations may also be investigated (lithium and cesium for instance).<sup>30</sup>

(30) The use of nitrogen-14 as the quadrupolar nucleus allows similar studies to be performed on nitrogen-containing substances of chemical or biological interest.<sup>24,25</sup>

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## A Linear Relationship between Substituted Pyridine Lone Pair Vertical Ionization Potentials and $\text{pK}_a$

Sir:

A recent communication<sup>1</sup> on the gas-phase proton affinities, PA, of five 4-substituted pyridines pointed out the importance of the question whether solution phase substituent constants apply in the gas phase.

PA's for a series of bases, B:, will be linear functions of vertical lone pair ionization potentials, IP, provided that the rehybridization energies of  $\text{B} \cdot \nu^+$  and homolytic  $\text{B}:\text{H}^+$  bond dissociation energies are constant or are themselves linear functions of IP. If, in addition, the differences in solvation energies between bases, B:, and conjugate acids,  $\text{BH}^+$ , are linear functions of IP, a linear relationship should also exist between  $\text{pK}_a$  and B: lone pair IP. These restrictions preclude the observation of any simple relationship between  $\text{IP}(\text{B}:\cdot)$  and  $\text{pK}_a$  for dissimilar bases, and until now a satisfactory linear  $\text{pK}_a$ - $\text{IP}(\text{B}:\cdot)$  relationship has not been demonstrated for Brønsted bases.

The photoelectron spectra of ten substituted pyridines have been measured and combined with reported spectra for seven chloropyridines,<sup>2</sup> methylpyridines,<sup>3</sup> and fluoropyridines<sup>4</sup> from the literature. Spectra were determined on a Perkin-Elmer Model 16 pe spectrometer and calibrated with argon ( $15.76 \text{ eV}$ ). To ensure valid

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