Multiple spin probe NMR studies of ionic structure in 1-methyl-3-ethylimidazolium chloride–AlCl$_3$ molten salts

W. Robert Carper*, J. Lloyd Pflug and John S. Wilkes
Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado Springs, CO 80840-6528 (USA)

(Received September 3, 1991; revised November 27, 1991)

Abstract

The microdynamics of a room temperature molten salt system consisting of 1-methyl-3-ethylimidazolium chloride (MEICl), AlCl$_3$ and NaCl is investigated by ^{13}C, ^{23}Na and ^{27}Al NMR relaxation methods and viscosity measurements. This study supports the existence of a complex containing MEI$^+$, AlCl$_4^-$ and Na$^+$. The dual spin probe (DSP) method is extended to ^{23}Na, which has a liquid state quadrupole coupling constant of 1.0 MHz in this complex.

Introduction

Room temperature molten salts consisting of mixtures of 1-methyl-3-ethylimidazolium chloride (MEICl) and AlCl$_3$ are potential aprotic solvents for studying a wide range of inorganic and organic solutes [1–7]. These solvents are of definite interest as battery electrolytes and other types of electrochemical agents [8–10].

The composition of these MEICl–AlCl$_3$ ionic liquids has a considerable effect on its Lewis acid–base and general physical properties. Melts with excess AlCl$_3$ are termed acidic and those with excess MEICl are Lewis basic. In acidic melts the predominate anions are AlCl$_4^-$ and Al$_2$Cl$_7^-$, while in basic compositions Cl$^-$ and AlCl$_4^-$ are present. At neutral composition ($N = 0.5$, where N is mole fraction AlCl$_3$) electrochemical [11] and spectroscopic probes [2, 5] indicate that AlCl$_4^-$ is the only detectable anion. We have recently shown that the addition of NaCl as a ternary component buffers the medium to Lewis neutrality, where AlCl$_4^-$ is the only anion [12].

It is important to understand the microdynamics of these molten salt systems if they are to be developed as electrochemical and solvent systems in the future. The use of ^{13}C NMR relaxation studies provides useful information about the dynamics and structure of various chemical systems and chloroaluminate melts in particular [13]. In a previous work [13], ^{13}C relaxation measurements were used to investigate the motion and interactions of the MEI cation as a function of temperature and magnetic field. The results [13] indicate that AlCl$_4^-$ in a NaCl buffered $N = 0.55$ melt (AlCl$_4^-$ > MEI$^+$) forms a complex by interacting with the C-2, C-4 and C-5 hydrogens on the MEI$^+$ ring shown in Fig. 1. This report [13] was followed by a study [14] in which the dual spin probe (DSP) method [15] was used to verify the existence of MEI (AlCl$_4$)$_n^{-(n-1)}$ complexes in basic ($N = 0.33$) and neutral ($N = 0.50$) binary MEICl–AlCl$_3$ composition, plus a ternary MEICl–NaCl–AlCl$_3$ melt that has the ionic composition Na$_{0.22}$ MEI$_{0.78}$ AlCl$_4$. ^{27}Al and ^{13}C NMR relaxation results confirmed the existence of the chloroaluminate–MEI$^+$ complexes and yielded ^{27}Al liquid state quadrupole coupling constants.

Application of the DSP relaxation method usually involves ^{13}C dipolar relaxation rates which are defined by eqn. (1), the basic equation in which the ^{13}C nucleus is relaxed by ^{1}H [16]:

$$R_1^{\mathrm{dd}} = N_{\mathrm{h}}(\hbar\gamma_{\mathrm{c}}\gamma_{\mathrm{h}})^2 r_{\mathrm{ch}}^{-6}\tau_{\mathrm{eff}} \qquad (1)$$

where R_1^{dd} ($=1/T_1^{\mathrm{dd}}$) is the dipolar relaxation rate, N_{h} is the number of hydrogens attached directly to the carbon atom,. γ_{c} and γ_{h} are gyromagnetic ratios and $r_{\mathrm{ch}} = 1.09 \times 10^{-8}$ cm. τ_{eff} is the effective correlation time and varies exponentially with temperature.

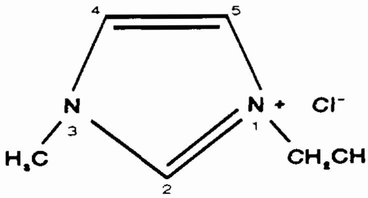

Fig. 1. MEI cation (positions are labeled).

---

*Author to whom correspondence should be addressed. Present address: Department of Chemistry, Wichita State University, Wichita, KS 67208, USA.

0020-1693/92/$5.00

Equation (1) is operative under the 'extreme narrowing condition' ($\omega\tau_{\rm eff} \ll 1$) which is usually applicable for small molecules including the chloroaluminate melts [13]. The determination of $R_1^{\rm dd}$ as a function of temperature provides activation energies (E_a) which are indicative of a molecules ability to move through the medium [17]. The E_a results can indicate the strength of interactions between an ion such as MEI^+ and its nearest neighbors (Cl^-, $AlCl_4^-$ or $Al_2Cl_7^-$) [13, 14].

In a similar manner, a nucleus of spin greater than 1/2 that relaxes primarily through a quadrupolar mechanism can be used as a NMR 'probe' to monitor isotropic molecular tumbling [15]. If there is a distortion from tetrahedral or octahedral symmetry, nuclei such as ^{23}Na and ^{27}Al will be under the influence of an electric field gradient which produces the quadrupole interaction. The quadrupole interaction is affected by the reorientation motion of the ^{23}Na or ^{27}Al containing molecule (complex) and the quadrupolar relaxation rate in the 'extreme narrowing region' is given by [16, 18]:

$$R_1 = \frac{1}{T_1} = \frac{3\pi^2}{10}\,\frac{(2I+3)}{I^2(2I-1)}\left(1+\frac{z^2}{3}\right)\left(\frac{e^2Qq}{h}\right)^2\tau_c \qquad (2)$$

where $I=3/2$ for ^{23}Na and 5/2 for ^{27}Al, eQ is the nuclear electric quadrupole moment, eq is the maximum component of the electric field gradient tensor, and z is the asymmetry parameter of the electric field gradient tensor. The quadrupole coupling constant, QCC, is given by:

$$QCC = \frac{e^2Qq}{h} \qquad (3)$$

There are several problems associated with the determination of QCC, particularly in the case of ^{27}Al and to some extent ^{23}Na, for which there are few reports of compounds in the liquid and solid state [19–21]. If however, a secondary spin probe such as ^{13}C is available within the complex, it is possible to equate $\tau_{\rm eff}$ from eqn. (1) and τ_c from eqn. (2), providing that the motion is isotropic within the 'extreme narrowing region' [16, 22]. This allows the calculation of QCC, assuming that z^2 approaches zero. This latter assumption has been shown to be correct in the case of $AlCl_3$ [23]. In this report the multiple spin probe relaxation times of ^{13}C (dipolar), ^{23}Na and ^{27}Al will be correlated and used to study the molecular dynamics of the 0.55 $AlCl_3$–MEICl–NaCl melt over the temperature range of 0–70 °C.

Experimental

Materials

The 1-methyl-3-ethylimidazolium chloride and chloroaluminate molten salts were prepared as previously described [1]. All materials were stored under anhydrous helium gas atmosphere in a dry box. All molten salt preparations and manipulations were performed in the dry box. Samples were loaded into 5 or 10 mm sample tubes, capped and sealed with a torch.

NMR measurements

^{23}Na, ^{27}Al and ^{13}C spectra were recorded on a JEOL FX90Q (23.65, 23.29 and 22.49 MHz) spectrometer as described previously [13]. Temperature measurements were calibrated against methanol or ethylene glycol and are accurate to within 0.5 °C. Pulse widths were typically 15.5 (^{23}Na), 15.7 (^{27}Al) and 18.5 (^{13}C) μs. Longitudinal relaxation times were measured by the inversion–recovery method (180°–τ–90°–T) with $T > 5T_1$. For all melt samples the experiments used at least 12 delay times (τ) and relaxation times were obtained from least-square fits of the magnetization as a function of τ. NOE (η') measurements were made using the gated decoupler method [24] in which the fully decoupled spectrum is compared with one in which decoupling is present only during the acquisition time. The estimated error in the NOE measurements is in the 5–10% range [24].

Viscosity measurements

Viscosities were measured as reported earlier [4].

Results

^{23}Na relaxation mechanisms

The change in ^{23}Na relaxation rates over the temperature range of 0–70 °C is shown in Fig. 2 for the NaCl buffered N=0.55 melt ($AlCl_4^- > MEI^+$). The anion is $AlCl_4^-$ and the cations are MEI^+ and Na^+. The ^{23}Na Arrhenius plot contains three distinct exponential regions (0–30, 30–55, 55–70 °C) whose E_a values (23, 18 and 13.4 kJ) decrease by approximately 4.6 kJ with increasing temperature. A previous study [14] of the ^{27}Al quadrupolar relaxation rates in the same NaCl buffered melt yielded two exponential regions (0–27.5, 27.5–70 °C) with E_a values of 26 and 20 kJ, respectively.

Determination of the ^{23}Na QCC

As is the case for ^{27}Al, there are few reports in the literature for ^{23}Na complexes in the liquid state [20, 21, 25]. A NMR study of ^{23}Na cryptates in methanol–D_2O (95/5) using the dual spin probes ^{23}Na and ^{13}C produced ^{23}Na QCC values from 1.01 to 2.20 MHz [25]. The ^{23}Na QCC values in the cryptate complexes decrease as the number of oxygens increase around the ^{23}Na, forming a more symmetrical electrical field

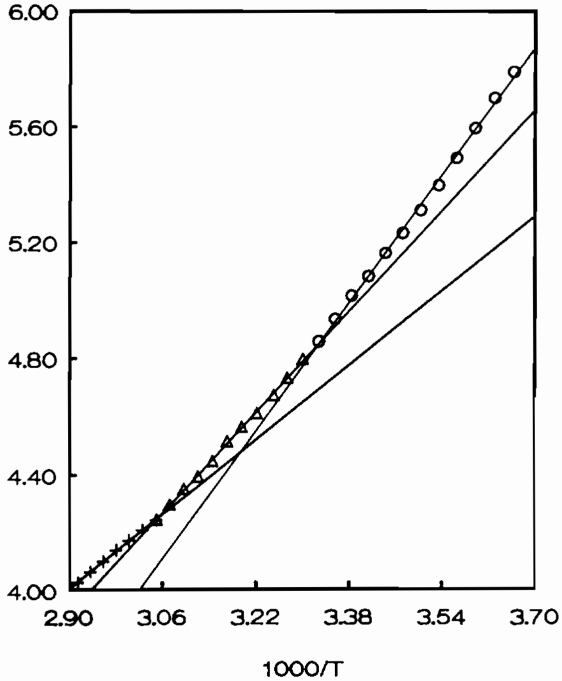

Fig. 2. In relaxation rates (^{23}Na) vs. 1000/T for $Na_{0.22}$ $MEI_{0.78}$ $AlCl_4$ melt.

environment. The dual spin probe (DSP) method requires that the molecular tumbling is isotropic and that τ_{eff} in eqn. (1) is identical to τ_c in eqn. (2). If this is true, then QCC is determined from ^{13}C R_1^{dd} values and from ^{23}Na R_1 values, assuming that $z^2=0$. This last assumption may introduce a small error into the determination of QCC.

In this study, we will hypothesize that MEI $(AlCl_4)_n$ Na_m complexes provide a basis for the use of the DSP method. If this is valid, the combination of ^{13}C relaxation data from the nucleus of MEI$^+$ can be used to determine the QCC for the associated Na$^+$. This is accomplished by plotting the ^{13}C dipolar relaxation rates at each temperature versus the Na relaxation rates over the temperature range 0–70 °C. If $\tau_{eff}=\tau_c$, then from eqns. (1) and (2),

$$R_1^{dd}/N_h(\hbar\gamma_c\gamma_h)^2 r_{ch}^{-6}=R_1(^{23}\mathrm{Na})/\alpha\chi^2 \qquad (4)$$

where

$$\alpha=\frac{3\pi^2}{10}\frac{(2I+3)}{I^2(2I-1)}\left(1+\frac{z^2}{3}\right)$$

Consequently, a plot of R_1^{dd} versus R_1 (^{23}Na), will have a zero intercept and a slope, S, equal to (5):

$$S=N_h(\hbar\gamma_c\gamma_h)^2 r_{ch}^{-6}/\alpha\chi^2 \qquad (5)$$

Consequently, the QCC $(=\chi)$ equals (6):

$$QCC=\chi=(\hbar\gamma_c\gamma_h)(N_h/\alpha_S)^{1/2} r_{ch}^{-3} \qquad (6)$$

The ^{13}C NMR dipolar relaxation rates, R_1^{dd} were determined from NOE (η') measurements using eqn. (7) [26]:

$$R_1^{dd}=\eta' R_1/1.988 \qquad (7)$$

The results for the $Na_{0.22}$ $MEI_{0.78}$ $AlCl_4$ melt are plotted versus ^{23}Na R_1 values in Fig. 3 for the C4 ($\cong$C5) and C2 monoprotic carbons in the MEI$^+$ nucleus over the temperature range 0–70 °C. The validity of eqn. (4) is verified with near zero intercepts and similar slopes for C4 ($\cong$C5) and C2 carbons. Use of eqn. (6), (assuming that $z^2\cong 0$), yields QCC values of 1.03 (C2) and 0.97 (C4$\cong$C5) MHz.

The average of the two QCC values, 1.0 MHz, was used to calculate ^{23}Na correlation times, τ_c, from eqn. (2) over the temperature range 0–70 °C.

The relationship between ^{23}Na NMR correlation times and temperature in the viscosity dependent region is given by eqn. (8) [27]:

$$\tau_c=\tau_0+(\eta\tau_{red}/T) \qquad (8)$$

where $\tau_{red}=V/k$, and τ_0 is often equated with free rotation times [27], $\tau_{fr}=(2\pi/9)(I_m/kT)^{1/2}$. This latter relationship represents an extrapolation from the hydrodynamic region, through the kinetic region and into the inertial limit of a completely free rotor model [28]. The τ_{red} value obtained from eqn. (8) is equated with a temperature and viscosity independent value of molecular volume (V), and consequently a determination of the Stokes radius for a given complex [13, 27]. In

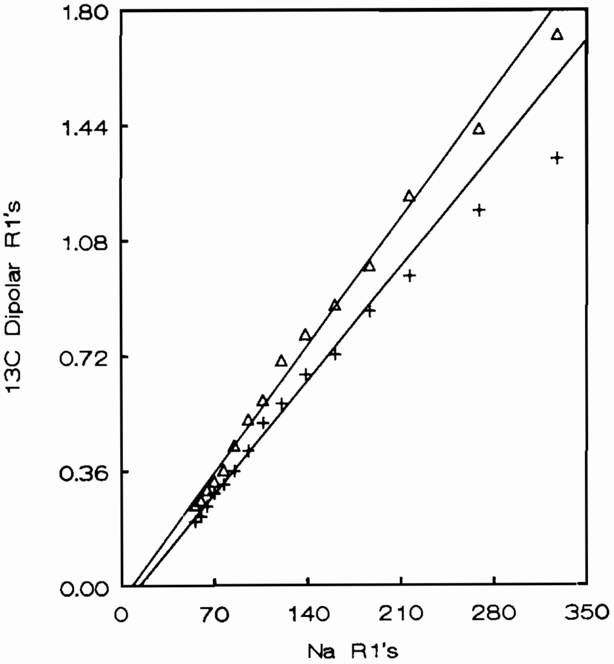

Fig. 3. ^{13}C R_1^{dd} (Δ=C2, + =C4, C5) vs. ^{23}Na R_1 from 0 to 70 °C for $Na_{0.22}$ $MEI_{0.78}$ $AlCl_4$ melt.

the case of anisotropic rotation, the correlation time, τ_c, of a spherical molecule obeying classical mechanics is given by eqn. (9):

$$\tau_c = 4\pi a^3\eta/3kT = V\eta/kT \qquad (9)$$

where V is the molecular volume and the other quantities have their usual meanings. The theoretical basis for eqn. (9) is certainly oversimplified, as the theoretical τ_c values are often ten times larger than the experimental values in cases where there are solute–solvent interactions [13, 27].

Figure 4 is a plot of τ_c versus (η/T) from 0 to 70 °C. The τ_c values for ^{23}Na vary from 14 to 83 ps between 70 and 0 °C, indicating that the 'extreme narrowing condition' ($\omega\tau_c \ll 1$) is met for this system. The free rotation time, τ_0, of 5.9 ps is obtained from the correlation time intercept for ^{23}Na, and may be compared with τ_0 values of 1.82 and 0.85 ps for SnI_4 and $PbCl_4$ obtained by extrapolation of $(I_m/kT)^{1/2}$ values to infinite temperature [13, 27].

The two linear regions, 0–15.0 and 15.0–70 °C have slopes of 427 and 346 ns K cp^{-1} which yield unrealistic stokes radii of 1.10 and 1.03 Å from eqn. (9). These results for the Stokes radii are typical underestimates [13, 28, 29] for these and other systems similar in size, and are far removed from a value of 9.56 Å for MEI^+ determined from diffusion measurements [13, 30].

Quadrupolar spin probe correlation

Previous [14] (^{27}Al–^{13}C) and present (^{23}Na–^{13}C) dual spin probe studies support the existence of a complex containing these nuclei. These results indicate that a plot of ^{27}Al quadrupolar R_1 values versus ^{23}Na quadrupolar R_1 values should be linear with a slope equal to eqn. (10):

$$(0.24)\chi^2(a)\left[1+\frac{z^2(a)}{3}\right]\Big/\chi^2(b)\left[1+\frac{z^2(b)}{3}\right] \qquad (10)$$

where a refers to ^{27}Al and b to ^{23}Na.

Figure 5 contains a plot of ^{27}Al R_1 values versus ^{23}Na R_1 values for the $Na_{0.22}$ $MEI_{0.78}$ $AlCl_4$ melt from 0 to 70 °C. There are two distinct linear regions (0–30, 30–70 °C) with the lower temperature region having a near zero intercept and a slope of 1.12 for the 30–70 °C results. Substituting values of 2.13 (^{27}Al) and 1.00 (^{23}Na) MHz for χ in eqn. (10) yields a theoretical slope of 1.09, a value that is close to the average slope ($\cong$ 1.07) for the entire temperature range.

Conclusions

Results of this and previous studies [6, 13, 14, 30, 31] support the existence of a complex containing MEI^+, $AlCl_4^-$, Cl^- and Na^+ in NaCl buffered MEICl-$AlCl_3$ ionic solutions. The composition of this complex is consistent with MEI^+ attached to at least three $AlCl_4^-$ ions (through H bonds at C2, C4 and C5) which are also coordinated to an unknown number of Na^+ ions. The fact that ^{27}Al and ^{23}Na undergo simultaneous changes in relaxation mechanisms at 30 °C [14] suggests

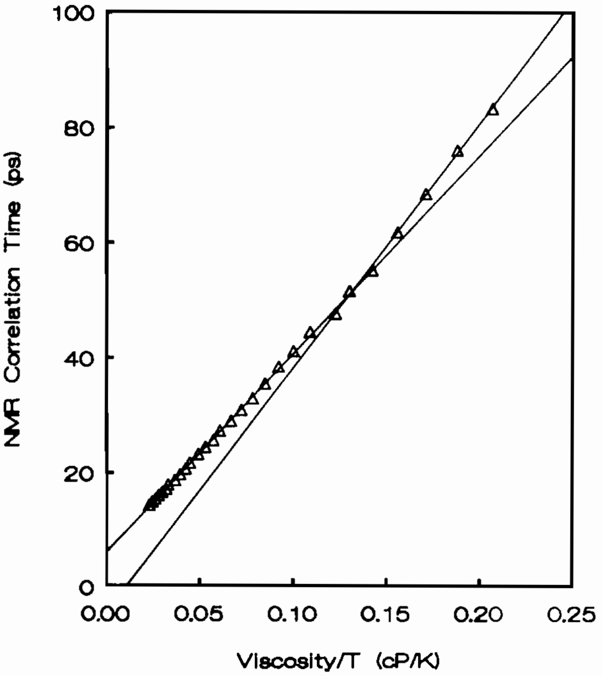

Fig. 4. τ_c (^{23}Na NMR) vs. η/T for $Na_{0.22}$ $MEI_{0.78}$ $AlCl_4$ melt.

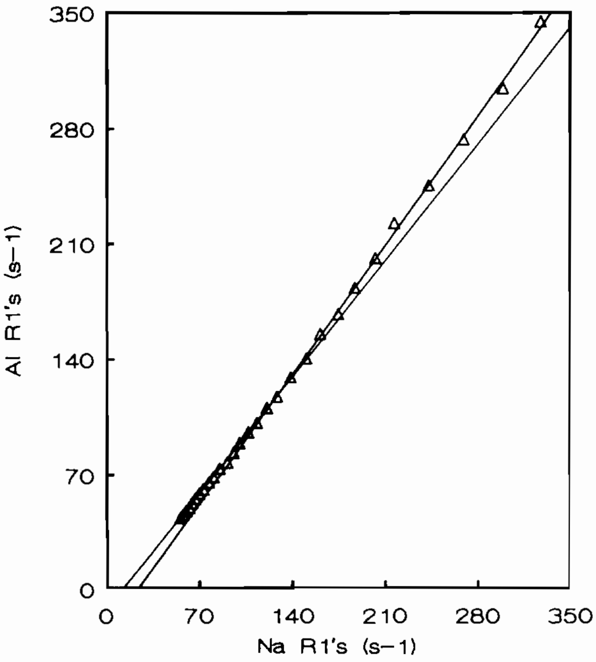

Fig. 5. ^{27}Al R_1 vs. ^{23}Na R_1 from 0 to 70 °C for $Na_{0.22}$ $MEI_{0.78}$ $AlCl_4$ melt.

that Na^+–$AlCl_4^-$ interactions change in a manner similar to the packing of ions in various types of crystal lattice. At the same time, the change in *QCC* of ^{23}Na relative to ^{27}Al (Fig. 5) indicates a change in symmetry at approximately 15 °C for one or both species and suggests the existence of isomeric complexes.

Acknowledgements

The authors thank Mrs Linda E. Pukajlo for her patience in preparing this manuscript. W.R.C. thanks the National Research Council for a Senior Associateship.

References

1 J. S. Wilkes, J. A. Levisky, R. A. Wilson and C.L. Hussey, *Inorg. Chem., 21* (1982) 1263.
2 J. S. Wilkes, J. S. Frye and G. F. Reynolds, *Inorg. Chem., 22* (1983) 3870.
3 A. A. Fannin, L. A. King, J. A. Levisky and J. S. Wilkes, *J. Phys. Chem., 88* (1984) 2609.
4 A. A. Fannin, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes and J. L. Williams, *J. Phys. Chem., 88* (1984) 2614.
5 K. M. Dieter, C. J. Dymek, N. E. Heimer, J. W. Rovang and J. S. Wilkes, *J. Am. Chem. Soc., 110* (1988) 2722.
6 C. J. Dymek and J. J. P. Stewart, *Inorg. Chem., 28* (1989) 1472.
7 J. A. Boon, J. A. Levisky, J. L. Pflug and J. S. Wilkes, *J. Org. Chem., 51* (1986) 480.
8 C. J. Dymek, J. L. Williams, D. J. Groeger and J. J. Auborn, *J. Electrochem. Soc., 131* (1989) 2887.
9 C. J. Dymek and L. A. King, *J. Electrochem. Soc., 132* (1985) 1375.
10 C. L. Hussey, T. B. Scheffler, J. S. Wilkes, and A. A. Fannin, *J. Electrochem. Soc., 133* (1986) 1389.
11 M. Lipsztajn and R. A. Osteryoung, *J. Electrochem. Soc., 130* (1983) 1968.
12 T. J. Melton, J. Joyce, J. T. Maloy, J. A. Boon, and J. S. Wilkes, *J. Electrochem. Soc., 137* (1990) 3865.
13 W. R. Carper, J. L. Pflug, A. M. Elias and J. S. Wilkes, *J. Phys. Chem.,* in press.
14 W. R. Carper, J. L. Pflug and J. S. Wilkes, *J. Am. Chem. Soc.,* submitted for publication.
15 J. J. Dechter and U. Henriksson, *J. Magn. Reson., 48* (1982) 503.
16 A. Abragam, *Principles of Nuclear Magnetism,* Oxford University Press, Oxford, 1961, Ch. 8.
17 G. C. Levy, R. L. Lichter and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance,* Wiley, New York, 1980, p. 211.
18 B. Lindman and S. Forsen, in P. Diehl and E. Fluck (eds.), *NMR Basic Principles and Progress,* Vol. 12, Springer, New York, 1976, p. 22.
19 J. W. Akitt, in J. Mason (ed.), *Multinuclear NMR*, Plenum, New York, 1987, p. 259.
20 J. W. Akitt, in J. Mason (ed.), *Multinuclear NMR*, Plenum, New York, 1987, p. 189.
21 P. Laszlo, *Angew. Chem., Int. Ed. Eng., 17* (1978) 254.
22 V. Vestin, J. Kowalewoki and U. Henriksson, *Org. Magn. Reson., 16* (1981) 119.
23 P. A. Casabella and N. C. Miller, *J. Chem. Phys., 40* (1964) 1363.
24 D. Neuhaus and M. Williamson, *The Nuclear Overhauser Effect in Structural and Conformational Analysis,* VCH, New York, 1989, p. 56.
25 J. P. Kintzinger and J. M. Lehn, *J. Am. Chem. Soc., 96* (1974) 3313.
26 K. F. Kuhlmann and D. M. Grant, *J. Am. Chem. Soc., 90* (1968) 7355.
27 R. T. Boere and R. G. Kidd, in G. A. Webb (ed.), *Annual Reports on NMR Spectroscopy,* Vol. 13, Academic Press, New York, 1982, p. 319.
28 R. E. Waylishen and B. A. Danchura, *Can. J. Chem., 55* (1977) 3602.
29 A. K. M. Masood, R. A. Pethrick, A. J. Barlow, M. G. Kim, R. P. Plowiec, D. Barraclough and R. A. Ladd, *Adv. Mol. Relaxation Processes, 9* (1976) 29.
30 R. T. Carlin and R. A. Osteryoung, *J. Electroanal. Chem., 252* (1988) 81.
31 C. J. Dymek, D. A. Grossie, A. V. Fratini and W. W. Adams, *J. Mol. Struct., 213* (1989) 25.