J. Phys. Chem. A **2000,** *104,* 7629−7634

A Magnetic Resonance Study of Complex Formation between the Neutral Phenalenyl Radical and Alkali Metal Ions in Dilute Alcohol Solutions

David W. Dwyer,[†,‡] Michael F. Ciraolo,[†] David C. Gilbert,[†,§] and David C. Doetschman*,[||]

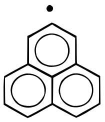
Department of Chemistry, State University of New York at Brockport, Brockport, New York 14420, and
Department of Chemistry, Binghamton University, State University of New York,
Binghamton, New York 13901-6016

Received: March 15, 2000; In Final Form: June 9, 2000

In previous work from our laboratories we have characterized the molecular motion of phenalenyl in the supercage of cation-exchanged X- and Y-zeolites using continuous wave−electron paramagnetic resonance (CW-EPR) and pulsed-EPR techniques. The trends in activation energies with cation size and Lewis acidity and in EPR line widths provided circumstantial evidence for a weak covalent interaction between the neutral phenalenyl π-system and the cations. This work on phenalenyl and alkali metal cations in solution provides ^{7}Li nuclear magnetic resonance (NMR) and CW-EPR spectroscopic evidence for this type of interaction. Moreover, to our knowledge it is the first example of a *neutral* radical−alkali metal ion complex in solution. In rigorously dried alcohol solutions this interaction results in the formation of a complex between neutral phenalenyl and Li^+ or Na^+, which is in equilibrium with solvated phenalenyl and the respective cation. The forward and reverse rates for this equilibrium for Li^+ and phenalenyl in methanol allow for an analysis of ^{7}Li NMR data acquired at 320 K in the fast exchange limit, which yields an equilibrium constant of $29 \pm 4\ M^{-1}$. Analysis of the CW-EPR data for Na^+ and phenalenyl in methanol at 295 K in the slow exchange limit produces an isotropic Na hyperfine frequency for the phenalenyl−Na^+ complex of 4.2 ± 0.1 MHz. This hyperfine frequency reflects a Fermi contact with the Na nucleus of ca. 0.5% of the nonbonding π-electron spin density from phenalenyl.

Introduction

In previous work we have studied the molecular motion of phenalenyl (PNL) **(I)** in the supercage of cation exchanged X- and Y-zeolites using CW- and pulsed-EPR techniques. This study indicated a possible correlation between the CW EPR spectrum of the neutral phenalenyl radical and the nuclear magnetic moments of the exchanged alkali metal cations Li^+, Na^+, K^+, Rb^+, and Cs^+.[1] This correlation is believed to result from the formation of a PNL-cation Lewis acid−base complex. Understanding the nature of such a complex may be important in revealing the unique catalytic properties of these zeolites. Phenalenyl **(I)** undergoes predominantly in-plane reorientation in the NaX zeolite cage to about 200 K.[1,2] Above this temperature, the molecule approaches a free, isotropic rotation, as out-of-plane reorientations catch up with rapid, in-plane reorientation.[1,2] Studies of the relatively small activation energies on exchanged cation are consistent with a model[1] in which there is a bonding interaction between the π-system of the phenalenyl ring system and the empty s-orbital of the cation. The bond remains substantially intact, while the phenalenyl reorients in its plane but is broken when it reorients out-of-plane. The increasing phenalenyl EPR line widths with exchanged cation nuclear magnetic moment[1] give additional evidence for this model of phenalenyl−cage interaction. The line width dependence indicates that the unpaired π-electron resides in an orbital that is being mixed with s-orbital character on the cations of the zeolite cage. The resulting spin density on the cation nucleus results in an, as yet, unresolved nuclear hyperfine structure. The hyperfine interaction has been observed recently, however, for Li^+, Na^+, and Cs^+ in X- and Y-zeolites loaded with phenalenyl with electron spin echo envelope modulation spectroscopy.[3] Recent NMR,[4] UV,[5] and ODMR[6] spectroscopic studies of these zeolites have shown indirect evidence that Lewis acid−base complex formation between neutral, diamagnetic guests with aromatic π-electron systems and exchanged alkali metal cations occurs at various temperatures. The studies also show that the energetics of this complex formation may be important in the catalytic activity of these host zeolites. The literature[7] also suggests that the lack of formation of this type of π-complex may favor a different catalytic mechanism where Bronsted acid sites play an important role in the chemistry that the guest molecule undergoes. Clearly, a study of the energetics of the formation of Lewis acid−base complexes between neutral aromatic free radicals and alkali metal cations would contribute to a better understanding of these important zeolite host environments.


(I)

In this work we have undertaken a systematic study of Lewis acid−base complex formation between phenalenyl radical and

---

* Corresponding author. Fax: 607-777-4478. E-mail: ddoetsch@binghamton.edu.

[†] State University of New York at Brockport.

[‡] Present address: S.A.I.C., P.O.S.T., Suite 803, 1225 Jefferson Davis Hwy., Arlington, VA 22202.

[§] Present address: Department of Chemistry, Binghamton University, State University of New York, Binghamton, NY 13901-6016.

[||] Binghamton University.

10.1021/jp0009857 CCC: $19.00

alkali metal cations in dry alcohol solutions. Direct evidence for the existence of a π-complex between phenalenyl and an alkali cation is reflected in the CW-EPR data for methanol solutions of Li^+ and Na^+ containing phenalenyl and in the ^7Li NMR data for the Li^+ solutions. The dilute alcohol solutions provide a potentially isotropic environment in which to study this type of interaction. This environment allows for the determination of the isotropic magnetic resonance parameters for these complexes. Knowledge of these parameters will help in the characterization of the complexes in the more anisotropic environment of the zeolite hosts. Moreover, to the best of our knowledge, an EPR study of complex formation between any *neutral* π-type radical and an alkali metal cation in solution cannot be found in the literature, although there are numerous studies of complexes between π-type *anion* radicals and alkali metal cations. This is not surprising when one considers that ion pair formation between π-type radical anions and large cations with smaller atomic hyperfine frequencies[8] such as K^+ result in hyperfine interactions which are often too weak to observe with CW-EPR at X-band.[9] Clearly, under the same conditions the interaction between an alkali cation and a neutral radical would be expected to generate an even weaker hyperfine interaction.

The observation by CW-EPR of complexes between π-type radical anions and alkali metal cations has been known for many years.[9−12] For example, isotropic hyperfine frequencies of 2−6 MHz have been observed in solution with π-type radical anions from room-temperature[10] and low-temperature[12] CW-EPR measurements. Equilibrium equations for the solutions of metal cations and radical anions have been used to model the CW-EPR data acquired at various temperatures for Na^+ complexing with the radical anion from naphthalene[12] and Na^+ and K^+ complexing with the pyracene radical anion.[11] In both of these studies a temperature range was investigated, which included equilibration rates in the fast exchange limit[13] and slower rates, where specific broadened hyperfine transition line widths can be interpreted as an alternating-line-width effect.[14] The rates for exchange of the alkali metal ions between two identical[11] and two different[12] radical anion complexes were determined from the data showing the alternating-line-width effect. Equilibrium constants were determined for Na^+ equilibrating between two different complexes with the naphthalene radical anion above the temperature of the fast exchange limit.[12] The temperature-dependent equilibrium constant data was then used to determine ΔH for this equilibrium.[12] The phenalenyl radical complex with alkali metal cations in alcohol solution studied in this work should be able to be represented by a similar thermodynamic equilibrium model.

There are many examples in the literature of ^1H and ^{13}C NMR studies of π-type complexes between transition metal ions and neutral diamagnetic organic π-electron systems.[15] There are a few examples of ^1H, ^{13}C, and ^7Li NMR studies of π-type complexes between alkali metal ions and neutral diamagnetic organic π-electron systems.[4] In a recent study[16] of a π-complex between 4 Li^+ and a corannulene^{4-} ion, a π-complex "sandwich" dimer was observed where 4 Li^+ were sandwiched between 2 corannulene^{4-} with 2 Li^+ above and below the corannulene anion rings. The rate of exchange between the 4 Li^+ on the inside of the sandwich and 4 Li^+ on the outside was determined with ^7Li NMR data.[16] The exchange involved the coelescence of the two different ^7Li nuclear resonance frequencies and line widths at ca. 240 K with the slow exchange limit starting at 190 K and the fast exchange limit at 290 K.[16] Although the hyperfine interaction would make it very difficult to follow the phenalenyl/Li^+ complex solution in this study with the same type of ^7Li NMR study of the ^7Li resonance frequencies, it should be possible to study the paramagnetic line broadening of the uncomplexed Li^+ in a similar manner.

Experimental Section

Sample Preparation. Phenalenyl radical stock solutions were prepared in dried *n*-hexane (Aldrich, hplc grade) and characterized for formal phenalenyl concentrations with UV spectroscopy as described previously.[17] Formal phenalenyl concentrations ranged from 3.9 to 6.2 mM with an average of 5.0 ± 0.6 mM. Methanol (Aldrich, hplc grade) was distilled from magnesium turnings and transferred under argon to an atmosphere box. Appropriate amounts of freshly cut sodium and lithium metal were massed on an analytical balance, dissolved in dried methanol solvent, and diluted in volumetric glassware under argon in an atmosphere box. Aliquots of each solution were removed and titrated with a 2° standard HCl solution to a bromthymol blue endpoint in order to check each sample for metal alkoxide concentration. In all cases the concentrations determined from titration were the same, within experimental error ($<\pm 5\%$), as those determined from massing the metals before dilutions. Metal alkoxide concentrations of 1.0, 0.8, 0.5, 0.3, 0.1, and 0.01 M were prepared for the Li^+ and Na^+ solutions. A typical radical−metal ion solution was prepared by transferring 1.00 mL of phenalenyl stock solution in a 10.0 mL round-bottom flask sealed under argon to a rotoevaporator. The solution was rotoevaporated to a solid residue, then sealed under argon, and transferred to an atmosphere box. A 1.00 mL volume of metal alkoxide solution was then added and the resulting solution was transferred to a 4.0 mm o.d. Pyrex EPR tube. The EPR tubes were transferred under argon to a vacuum line and taken through three freeze−pump−thaw cycles at $<10^{-3}$ Torr before being flame-sealed in the tube under vacuum. The resulting sealed tubes of 5.0 ± 0.6 mM phenalenyl solutions with $Li^+CH_3O^-$ and $Na^+CH_3O^-$ concentrations in methanol as described above were stored in a freezer until needed. Duplicate samples were prepared for the 1.0, 0.1, and 0.01 M Li^+ and Na^+ methanol samples with 5.0 ± 0.6 mM phenalenyl. These samples were prepared with the same protocol except that after sealing on the vacuum line they were opened under argon and transferred back to the rotoevaporator setup. The methanol solvent was removed and 1.0 mL of dried *n*-hexane was added to the solid residue. The resulting solutions were transferred to EPR tubes under argon, treated on the vacuum line, and stored for later use as described above. CW-EPR spectra were acquired for all of these duplicate samples under the conditions described below, and in each case the spectra were of free PNL with signal intensities that were within experimental error of the original PNL stock solution. $Li^+CH_3O^-$ 1.0, 0.8, 0.5, and 0.3 M stock solutions were transferred in 4.0 mm EPR tubes under argon, treated on the vacuum line as above and stored for later use.

EPR Measurements. CW-EPR spectra were acquired at room temperature with a Micronow 8100A X-band EPR spectrometer upgraded with a Micronow 8320A field controller and data acquisition unit. The acquisition unit was controlled by a Zenith 286 computer with a National instruments GPIB-PCII IEEE-488 board. Typical microwave frequencies were between 9.3 and 9.5 GHz with 1−3 mW of power. The spectrometer was operated with a 25 kHz field modulation at an amplitude of 0.04 to 0.08G. CW-EPR spectra for the 0.1 and 1.0 M Li^+ and Na^+ solutions were also acquired on a Varian 4500 X-band EPR spectrometer with the same model field controller and data acquisition unit as described above. The data

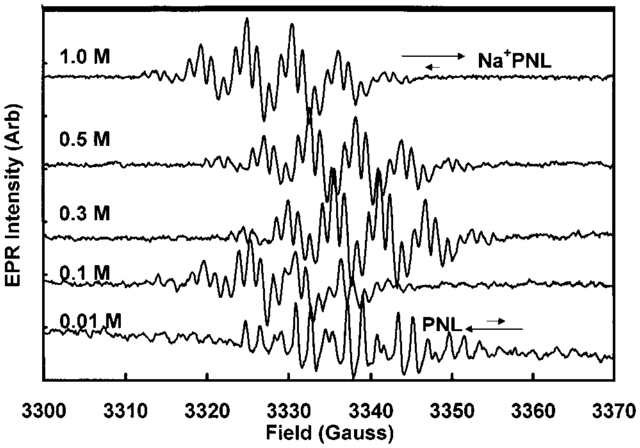


Figure 1. CW-EPR spectra of the PNL-Na^+ samples in methanol acquired at room temperature as a function of $[Na^+]_0$.

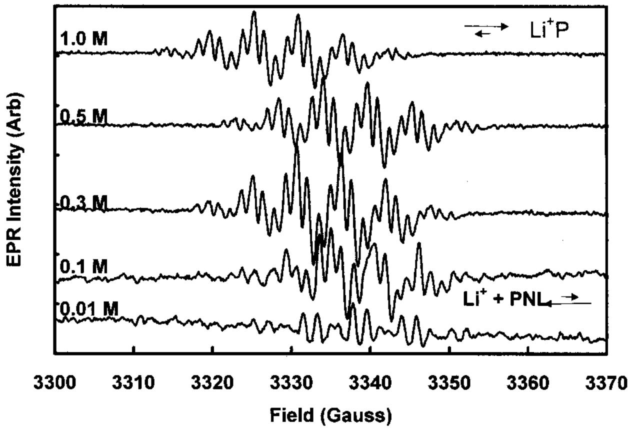


Figure 2. CW-EPR spectra of the PNL$-$$Li^+$ samples in methanol acquired at room temperature as a function of $[Li^+]_0$.

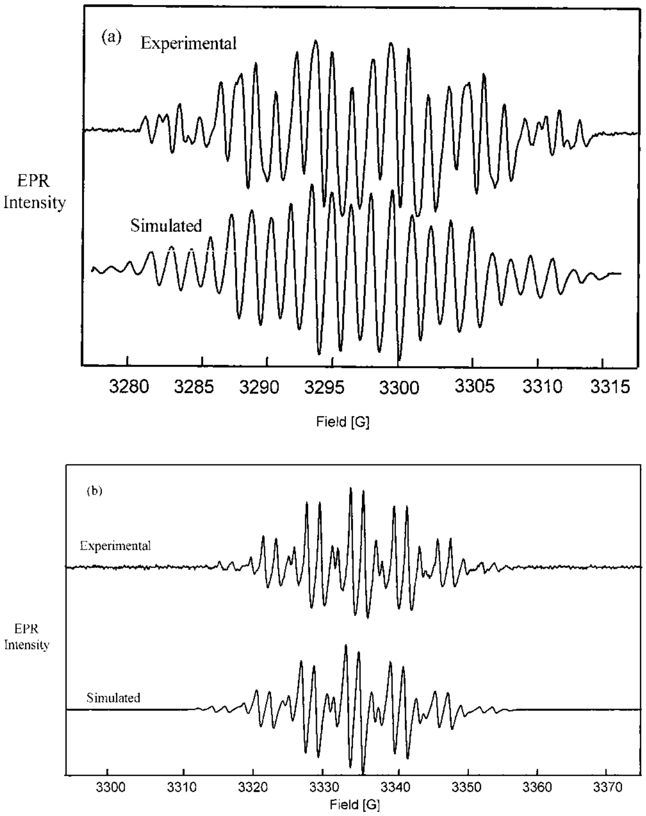


Figure 3. (a) Experimental and simulated CW-EPR spectrum for the PNL$-$$Na^+$ sample with $[Na^+]_0$ = 1.0 mM. (b) Experimental and simulated CW-EPR spectrum for the PNL$-$$Na^+$ sample with $[Na^+]_0$ = 0.01 mM.

acquisition parameters were the same except for the microwave frequency and modulation frequency which were 9.1 to 9.2 GHz and 100 kHz, respectively. Field and frequency measurements were also made for the spectra acquired on the Varian spectrometer. Field measurements were made with a Micronow 5151 ^{1}H NMR gaussmeter and an Albia 550 MHz frequency counter. The frequency counter and a HP540B transfer oscillator were employed for microwave frequency measurements. The EPR sample tubes were placed directly in the rectangular cavities of either the Micronow or Varian spectrometers.

NMR Measurements. ^{7}Li NMR spectra were acquired from 215 to 335 K in ca. 10 K increments with a Bruker AC300 FT-NMR spectrometer equipped with an Aspect 3000 minicomputer and a 10 mm broad band probe fitted with a standard dewar for variable temperature work. The probe was tuned to a ^{7}Li resonance frequency of 116.6 MHz. Typically, a spectrum was acquired as an average of 16 free induction decays with a 20 μs $\pi/2$ pulse and 16K data points with a transformed resolution of 0.06 Hz per point over a 1000 Hz frequency window. The FID data were then transferred over an open aspect data interface to a 90 MHz Pentium computer. Fourier transforming and phasing of the data and subsequent processing were then done with WinNuts 1D NMR software.[18] Variable temperature data was acquired with a Bruker variable temperature unit which was calibrated with a methanol temperature probe[19] from 210 to 338 K to ± 0.8 K. The EPR sample tubes were centered inside a standard 10 mm Pyrex NMR tube with a Teflon tape gasket. The 10 mm NMR tube was then filled with a 0.1 M $LiNO_3$ solution in D_2O (Aldich, 99.9 atom %) which served as a lock solvent and ^{7}Li reference frequency.

Experimental Results

CW-EPR spectra were acquired at room temperature with the Micronow spectrometer for the six PNL$-$$Na^+$ solutions as a function of initial Na^+ concentration (see Figure 1). CW-EPR spectra were acquired at room temperature for the six PNL$-$$Li^+$ solutions as a function of initial Li^+ concentration (see Figure 2). CW-EPR spectra for the 1.0 and 0.01 M $[Na^+]_0$ PNL$-$$Na^+$ solutions were also acquired with the Varian spectrometer along with three field and frequency measurements made at the center line of each spectrum (see Figure 3). The average values for the field and frequency measurements were used to determine the *g* values for the 1.0 M solution. After use, a few of the PNL$-$$Na^+$ and PNL$-$$Li^+$ samples were opened and exposed to the air for 10$-$20 min and then re-sealed with the normal vacuum line protocol. CW-EPR spectra were acquired at room temperature.

^{7}Li NMR spectra for the 1.0, 0.5, and 0.1 M $[Li^+]_0$ PNL$-$$Li^+$ solutions were acquired at 13 temperatures from 215 to 338 K. ^{7}Li NMR spectra for the 0.8 and 0.3 M $[Li^+]_0$ PNL$-$$Li^+$ solutions were acquired at 4 temperatures from 295 to 327 K. The line widths at half-height, $\Delta\nu_{1/2}$, for the Fourier transformed and phased spectra were determined using the WinNuts NMR software.[18] The resulting line widths from all of the NMR spectra are given in Table 1. The 0.01 M $[Li^+]_0$ PNL$-$$Li^+$ solution had a ^{7}Li resonance peak which was too weak to be able to collect usable data. ^{7}Li NMR spectra for the $Li^+CH_3O^-$ 1.0, 0.8, 0.5, and 0.3 M stock solutions were acquired for 4 temperatures from 215 to 338 K and used to determine $\Delta\nu_{1/2}$ values for each sample. The line widths for the stock

TABLE 1: ^{7}Li NMR Line Width Data as a Function of Temperature and $[Li^+]_0$ for Solutions of $PNL-Li^+$ in Methanol[a]

	$\Delta\nu$/MHz				
	$[Li^+]_0$/M				
temperature/K	0.1	0.3	0.5	0.8	1.0
338	2.0		0.9		0.9
327	1.6	1.2	1.1	1.1	0.9
315	1.6	1.3	1.6	1.6	1.2
304	1.3	1.5	1.7	1.7	1.5
295	1.4	2.2	4.3	3.1	1.8
285	1.3		6.3		2.2
275	1.5		6.9		2.3
265	1.5		6.9		2.8
255	1.3		6.7		2.8
245	0.9		6.5		2.5
235	0.7		5.9		2.2
225	0.6		6.0		1.7
215	0.5		6.3		1.4

[a] All of the samples were prepared with $[PNL]_0 = 5.0 \pm 0.6$ mM. All of the $\Delta\nu$ values are recorded in Hz. All of the data have been averaged with $\sigma(\Delta\nu) = +0.1$ Hz. Line widths $\Delta\nu$ are widths at half-height.

solutions were all in the range of 0.3 to 0.5 ± 0.1 Hz for all of the temperatures studied. Chemical shift values referenced to the $LiNO_3$ internal standard were also calculated for each of the samples; however, the changes in chemical shift were too small to be statistically useful in further analysis.

Analysis and Discussion

The CW-EPR spectra for the $PNL-Na^+$ solutions as a function of $[Na^+]_0$ in Figure 1 range from the well-known[17] isotropic PNL spectrum for $[Na^+]_0 = 0.01$ M to a spectrum with a more complicated hyperfine pattern for $[Na^+]_0 = 0.5$ M. The more complicated spectrum remains essentially unchanged from 0.5 to 1.0 M $[Na^+]_0$. Below $[Na^+]_0 = 0.5$ M the spectra appear to be a superposition of two spectra from 0.3 M down to 0.01 M where the free PNL spectrum dominates. These qualitative observations can be explained by a simple thermodynamic equilibrium between an alkali metal ion M^+ (Na^+ in this case) and the neutral PNL radical,

$$PNL + M^+ \Leftrightarrow PNL-M^+ \qquad (1)$$

For $[PNL]_0 = 5.0$mM this equilibrium is forced almost completely to product by 0.5 M or higher $[Na^+]_0$, which would result in the observation of the EPR spectrum of the $PNL-Na^+$ complex. The observation of a possible superposition of two spectra for $[Na^+]_0$ between 0.5 and 0.01 M could also be explained by this equilibrium model if the equilibration rate were in the slow exchange limit.[14] In this limit one would expect the observed EPR spectrum to be some linear combination of the PNL spectrum and the spectrum of the $PNL-Na^+$ complex. For $[Na^+]_0 = 0.01$ M this equilibrium is forced almost completely to the reactant side, which would result in the observation of the EPR spectrum of PNL.

Simulation of the PNL and $PNL-Na^+$ complex CW-EPR spectra were done with a procedure described previously[1,17] with two modifications. An isotropic ^{23}Na hyperfine term was added to the previous Hamiltonian for PNL[17] and a Lorentzian rather than Gaussian line width function was employed. The simulated spectra were least-squares fit to the experimental spectra for the $PNL-Na^+$ solutions with $[Na^+]_0 = 1.0$ M and $[Na^+]_0 = 0.01$ M using a previously described procedure.[1] The isotropic *g* values determined above for both samples were kept constant while the isotropic ^{1}H hyperfine frequencies for the meta, a_m, and para, a_p, protons in PNL, the isotropic ^{23}Na hyperfine frequency, a_{Na}, and the Lorentzian line width, ΔH, were allowed to least-squares fit to the spectra. The parameters of best fit were $a_m = -17.8 \pm 0.1$ MHz, $a_p = 6.2 \pm 0.1$ MHz, $a_{Na} = 4.2 \pm 0.1$ MHz, and $\Delta H = 1.3 \pm 0.1$ G for the $[Na^+]_0 = 1.0$ M sample and $a_m = -17.8 \pm 0.1$ MHz, $a_p = 6.2 \pm 0.1$ MHz, $a_{Na} = 0.0 \pm 0.1$ MHz, and $\Delta H = 1.0 \pm 0.1$ G for the $[Na^+]_0 = 0.01$ M sample. The value of $a_{Na} = 0.0 \pm 0.1$ MHz for the 0.01 M sample, which differs statistically from the value at 1.0 M, is probably an artifact of the insensitivity of the fit to the small concentration of the complex present in the 0.01 M $[Na^+]_0$ sample. The calculated spectra of best fit are shown in Figure 3. These results support the equilibrium in eq 1 in the limits of high and low Na^+ concentration. The isotropic values for a_p and a_m are within error estimates of the normal experimental values for PNL in solution.[17] The approximately 4*G* (H_m), 6*G* (Na), and -18*G* (H_p) coupling constants and the nearly integral fractional relationships between them give the spectrum its appearance as a pseudo-sextet of multiplets. Thus the presence of the Na hyperfine coupling, in addition to the relatively unchanged proton couplings, gives the spectrum an easily distinguishable appearance. The ΔH values are significantly larger than expected for just PNL in solution.[17] This may involve some unresolved anisotropic coupling with the Na^+ and/or hyperfine interactions with the solvent. ΔH may also have a contribution from exchange due to Na^+ exchange between symmetry equivalent locations with respect to the PNL molecular framework. See the discussion at the end of this paragraph. The possible contribution of an exchange of the Na^+ between different PNL sites to the observed ΔH was considered in terms of an overall line width and an alternating line width.[12] Unfortunately, the room-temperature conditions and concentrations ranges available did not permit an observable variation in the experimental EPR line widths. It is clear that the solvent plays an important role in the formation of these complexes. Several of the $PNL-Na^+$ solutions were exposed briefly to atmospheric moisture. The resulting CW-EPR spectra of those samples showed no sign of the $PNL-Na^+$ spectrum. All these samples showed a free PNL EPR spectrum regardless of the Na^+ concentration. Apparently the introduction of small amounts of water to the dry methanol solvent disrupts the formation of the complex. The isotropic ^{23}Na hyperfine frequency of 4.2 MHz reflects a relatively small interaction with the Na nucleus. Given an atomic ^{23}Na hyperfine frequency of 885.81 MHz,[8] the hyperfine frequency for this $PNL-Na^+$ complex involves a Fermi contact interaction with the Na nucleus where only 0.5% of the nonbonding π-electron spin density from PNL is shared with the metal ion. This represents a relatively weak covalent interaction. The spectrum for the $[Na^+]_0 = 1.0$ M $PNP-Na^+$ solution was well-fit by a calculated spectrum with an isotropic hyperfine interaction for the Na^+. Therefore, within the limits of the propagated error in this fit, the interaction or the time average of the interaction of the Na^+ with PNL in this Lewis acid/base complex must be symmetric with respect to the 3-fold symmetry axis of the rapidly reorienting PNL ring system. This Na^+–phenalenyl interaction would appear to resemble more nearly the sigma $2s-\pi$ orbital type of interaction found in the Li^0 complex with benzene than the π $2p-\pi$ orbital type of interaction found in the Li^0 complex with acetylene and ethylene in the work of Manceron et al.[20]

The CW-EPR spectra of the $[Na^+]_0$ concentrations 0.3 M (not shown in Figure 3) and 0.1 M were fit with simple linear combinations of the high- and low-limit $[Na^+]_0$ experimental spectra in Figure 1. The resulting best-fit combinations resulted in ratios of [PNL−Na$^+$]/[PNL] of 20 ± 5 and 60 ± 5 for the 0.1 and 0.3 M samples, respectively. Given the equilibrium expression for eq 1 and the fact that for both these samples $[\mathrm{Na}^+]_0 \gg [\mathrm{PNL}]_0$, equilibrium constant *K* can be determined from the ratios of the calculated spectra as

$$K = [\mathrm{PNL{-}Na}^+]/([\mathrm{PNL}][\mathrm{Na}^+]_0) \qquad (2)$$

Equation 2 can be used to calculate an equilibrium constant from the above data of $K = 190 \pm 20\ \mathrm{M}^{-1}$ at room temperature. The quality of the fits of these calculated spectra to the experimental spectra (see Figure 3) suggests that the assumption of an equilibration rate in the slow exchange limit for eq 1 is valid for the PNL−Na$^+$ solutions at room temperature.

The CW-EPR spectra for the PNL−Li$^+$ solutions as a function of $[\mathrm{Li}^+]_0$ in Figure 2 appear to be similar to the PNL−Na$^+$. They range from the well-known[17] isotropic PNL spectrum for $[\mathrm{Li}^+]_0 = 0.01$ M to a spectrum with a more complicated hyperfine pattern for $[\mathrm{Li}^+]_0 = 0.5$ M. The more complicated spectrum remains essentially unchanged from 0.5 to 1.0 M $[\mathrm{Li}^+]_0$. Below $[\mathrm{Li}^+]_0 = 0.5$ M the spectra appear to be a superposition of two spectra from 0.3 M(not shown in Figure 2) down to 0.01 M where the free PNL spectrum dominates. These qualitative observations can be explained with a simple thermodynamic equilibrium in eq 1 where M$^+$ is Li$^+$. Unfortunately, the more complicated problem of simulating the PNL−Li$^+$ EPR spectrum with the extra hyperfine term from the ca. 8% abundant ^{6}Li has prevented our fitting the high $[\mathrm{Li}^+]_0$ spectrum.

The CW-EPR spectra of the $[\mathrm{Li}^+]_0$ concentrations 0.3 and 0.1 M were fit with simple linear combinations of the 1.0 and 0.01 M $[\mathrm{Li}^+]_0$ experimental spectra in Figure 2. The resulting best-fit combinations resulted in ratios of [PNL−Li$^+$]/[PNL] of 3.0 ± 0.5 and 9.0 ± 0.5 for the 0.1 and 0.3 M samples, respectively. Given that $[\mathrm{Li}^+]_0 \gg [\mathrm{PNL}]_0$ for these samples, eq 2 can be used to calculate an equilibrium constant from the above data of $K = 30 \pm 5\ \mathrm{M}^{-1}$ at room temperature. The quality of the fits of these calculated spectra to the experimental spectra suggests that the assumption of an equilibration rate in the slow exchange limit for eq 1 is valid for the PNL−Li$^+$ solutions at room temperature. Several of the PNL−Li$^+$ solutions were exposed briefly to atmospheric moisture. The resulting CW-EPR spectra of those samples showed no sign of the PNL−Li$^+$ spectrum. All these samples showed a free PNL EPR spectrum regardless of the Li$^+$ concentration. Apparently the introduction of small amounts of water to the dry methanol solvent disrupts the formation of the complex.

The temperature-dependent ^{7}Li NMR data in Table 1 can be analyzed for the rate of equilibration in eq 1 relative to the measurement of line width and resonance frequencies by a plot of $\ln(\Delta\nu_{1/2})$ versus $1/T$.[14] The $\Delta\nu_{1/2}$ data in Table 1 for the PNL−Li$^+$ solution with $[\mathrm{Li}^+]_0 = 1.0$ M has been plotted for this analysis in Figure 4. The temperature range for the region of fast exchange of the Li nuclei involved in eq 1 is clearly evident in Figure 4.[14] Since the $[\mathrm{PNL}]_0$ is constant for all of the different $[\mathrm{Li}^+]_0$ samples, the region of fast exchange should be the same for all of them.[15] The data in Table 1 seem to be in obvious agreement with this assumption for all of the $[\mathrm{Li}^+]_0$ samples except the 0.01 M.

An analysis of the ^{7}Li NMR line width can be described according to the PNL−Li$^+$ equilibrium in eq 1. In the fast exchange limit, the line width $\Delta\nu$ obeys the relationship[14]

$$\Delta\nu = \chi_{\mathrm{PNL-Li}}\,\Delta\nu_{\mathrm{PNL-Li}} + \chi_{\mathrm{Li}}\,\Delta\nu_{\mathrm{Li}} \qquad (3)$$

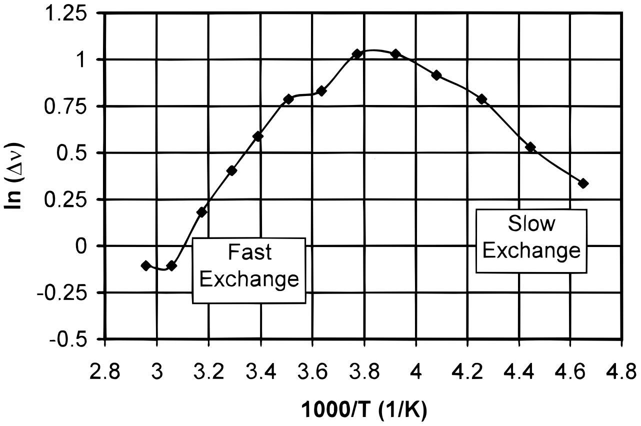


Figure 4. Temperature dependence of the ^{7}Li NMR line width, $\Delta\nu$. Plot of the $\ln(\Delta\nu)$ versus $1/T$ for the temperature-dependent ^{7}Li NMR data in Table 1 at $[\mathrm{Li}^+]_0 = 1.0$ M. The coalescence region (peak) is shown evolving toward the indicated fast and slow exchange limits. Line widths $\Delta\nu$ are widths at half-height.

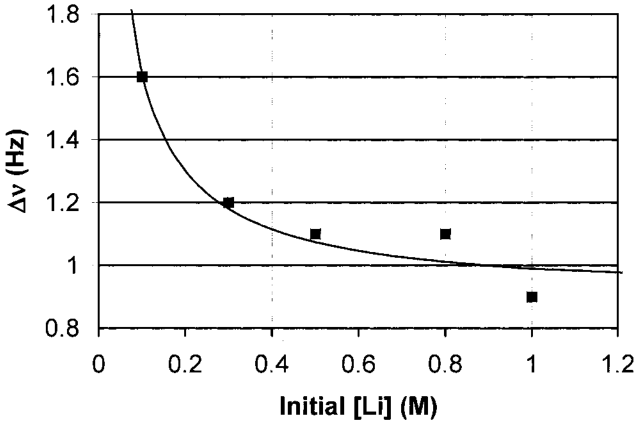


Figure 5. Experimental values of the ^{7}Li NMR line width, $\Delta\nu$, versus $[\mathrm{Li}^+]_0$ for data in Table 1 acquired at $T = 327$ K. The line representing the least-squares best fit of eq 4 with $K = 29 \pm 4\ \mathrm{M}^{-1}$ to the data is also shown. Line widths $\Delta\nu$ are widths at half-height.

where χ represents mole fractions. The line width data $\Delta\nu$ can be used to determine the equilibrium constant *K* in eq 4 (assuming that $[\mathrm{Li}^+]_0 \gg [\mathrm{PNL}]_0$):

$$\Delta\nu = \Delta\nu_{\mathrm{Li}} + \{\Delta\nu_{\mathrm{PNL-Li}}\,[\mathrm{PNL}]_0/(K^{-1} + [\mathrm{Li}]_0)\} \qquad (4)$$

An approach similar to ^{7}Li line-broadening measurements has been employed by Kolodziejski.[21] The PNL−Li$^+$ line width for the complex is treated as an unknown parameter to be determined along with K. The $\Delta\nu_{1/2}$ data in Table 1 for the PNL−Li$^+$ solution at $T = 327$ K, which is in the fast exchange limit determined in Figure 4, was plotted versus $[\mathrm{Li}^+]_0$. The data were then least-squares fit by eq 4 (see Figure 5). The parameters of best fit were $K = 29 \pm 4\ \mathrm{M}^{-1}$, $\Delta\nu_{\mathrm{Li}} = 0.9 \pm 0.1$ Hz, and $\Delta\nu_{\mathrm{PNL-Li}} = 18 \pm 1$ Hz. The $[\mathrm{PNL}]_0$ was assumed to be 5.0 ± 0.6 mM. This equilibrium constant is in good agreement with the *K* values determined from the CW-EPR data of the PNL−Li$^+$ samples. This *K* value is also reasonable when compared with a slightly smaller value for *K* in the PNL−Na$^+$ samples. A smaller *K* value would be expected for a weaker PNL−M$^+$ bond since it would affect the rate for the dissociation of the complex in eq 1.

Conclusion

This work on phenalenyl and alkali metal cations in solution has employed ^{7}Li nuclear magnetic resonance (NMR) and CW-

EPR spectroscopy evidence to characterize Lewis acid/base complex formation between the neutral phenalenyl radical and alkali metal cations in solution. To the best of our knowledge, an EPR study of complex formation between any neutral π-type radical and an alkali metal cation in solution cannot be found in the literature. In rigorously dried alcohol solutions this interaction results in the formation of a complex between phenalenyl and Li^+ or Na^+, which is in equilibrium with solvated phenalenyl and the respective cation. The forward and reverse rates for this equilibrium for Li^+ and phenalenyl in methanol allow for an analysis of ^{7}Li NMR data acquired at 327 K, which yields an equilibrium constant of 29 ± 4 M^{-1}. Analysis of the CW-EPR data for Li^+ and phenalenyl in methanol at 295 K yields an equilibrium constant of $K = 30 \pm 5$ M^{-1}. Analysis of the CW-EPR data for Na^+ and phenalenyl in methanol at 295 K yields an equilibrium constant of $K = 20 \pm 5$ M^{-1}. Rigorous analysis of the CW-EPR data in the slow exchange limit produces an isotropic Na hyperfine frequency for the phenalenyl$-Na^+$ complex of 4.2 ± 0.1 MHz. This hyperfine frequency reflects a Fermi contact with the Na nucleus of 0.5% of the nonbonding π-electron spin density from phenalenyl. The maintenance of the phenalenyl proton hyperfine structure and the transfer of a relatively small amount of spin density to the metal suggests that the complex is a σ- type complex.[20] However, the a_1'' singly occupied molecular orbital of D_{3h} phenalenyl by symmetry would allow no net interaction with the s orbital of the alkali metal ion situated on the C_3 axis. Thus a time average of equivalent off-axis interactions appears to be implied.

Acknowledgment. The authors thank the National Science Foundation for its support under grants CHE9512274 and CHE9705563.

References and Notes

(1) Doetschman, D. C.; Dwyer, D. W.; Fox, J. D.; Frederick, C. K.; Scull, S.; Thomas, G. D.; Utterback, S. G.; Wei, J. *Chem. Phys.* **1994**, *185*, 343.

(2) Doetschman, D. C.; Thomas, G. D. *Chem. Phys. Lett.* **1995**, *232*, 242.

(3) Doetschman, D. C.; Gilbert, D. C.; Dwyer, D. W. *Chem. Phys.* **2000**, *256*, 37.

(4) Hepp, M. A.; Ramamurthy, V.; Corbin, D. R.; Dybowski, C. *J. Phys. Chem.* **1992**, *96*, 2629.

(5) Ramamurthy, V.; Eaton, D. F.; Casper, J. V. *Acc. Chem. Res.* **1992**, *25*, 299.

(6) Ramamurthy, V.; Casper, J. V.; Corbin, D. R.; Schlyer, B. D.; Maki, A. H. *J. Phys. Chem.* **1990**, *94*, 3391.

(7) Xu, T.; Munson, E. J.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *16*, *1*962.

(8) Weltner, W., Jr. *Magnetic Atoms and Molecules*; Van Nostrand Reinhold: New York, 1983.

(9) Carrington, A.; Santos Veiga, J. dos. *Mol. Phys.* **1962**, *5*, 21.

(10) Santos Veiga, J. dos.; Neiva-Correia, A. F. *Mol. Phys.* **1965**, *9*, 395.

(11) DeBoer, E.; Macker, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 1513.

(12) Hirota, N.; *J. Phys. Chem.* **1967**, *71*, 127.

(13) Zumdahl, S. S.; Drago, R. S. *J. Am. Chem. Soc.* **1967**, *89*, 4319.

(14) Fraenkel, G. K. *J. Phys. Chem.* **1967**, *71*, 139.

(15) For specific examples, see Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders Co.: Philadelphia, 1977.

(16) Ayalon, A.; Sygula, A.; Cheng, P.-C.; Rabinovitz, M.; Rabideau, P. W.; Scott, L. T. *Science* **1994**, *265*, 1025.

(17) Das, U.; Doetschman, D. C.; Dwyer, D. W.; Mustafi, D. *Chem. Phys.* **1990**, *143*, 253.

(18) WinNUTS 32 NMR Data Processing Software Manual, Acorn NMR, Inc., Freemont, CA,1996.

(19) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

(20) Manceron, L.; Schrimpf, A.; Bornemann, T.; Rosendahl, R.; Faller, F.; Stoeckmann, H.-J. *Chem. Phys.* **1993**, *169*, 219.

(21) Kolodziejski, W. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 99.