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K-39 Quadrupolar and Chemical Shift Tensors for Organic Potassium Complexes and Diatomic Molecules

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Solid-state potassium-39 NMR spectra of two potassium complexes of crown-ether-based organic ligands (**1**·KI and **2**) have been acquired at 11.75 and 21.1 T and interpreted to provide information on the ^{39}K quadrupolar and chemical shift tensors. The analyses reveal a large potassium chemical shift tensor span of 75 ± 20 ppm for **1**·KI. This appears to be the first such measurement for potassium in an organic complex, thereby suggesting the utility of potassium chemical shift tensors for characterizing organic and biomolecular K^+ binding environments. Compound **2** exhibits a cation−π interaction between K^+ and a phenyl group, and therefore, the ^{39}K NMR tensors obtained for this compound must be partly representative of this interaction. Analyses of potassium-39 spin-rotation data for gaseous $^{39}K^{19}F$ and $^{39}K^{35}Cl$ available from molecular beam experiments performed by Cederberg and co-workers reveal the largest potassium CS tensor spans known to date, 84.39 and 141 ppm, respectively. Collectively, the results obtained highlight the potential of ultrahigh-field potassium-39 solid-state NMR spectroscopy and, in particular, the wide range of the anisotropy of the potassium CS tensor when organic and diatomic systems are considered.

Introduction

Potassium-39 solid-state nuclear magnetic resonance (SSNMR) spectroscopy holds great potential for the characterization of inorganic, organic, and biomolecular potassium complexes. The quadrupolar nature of the nucleus ($I = 3/2$; $Q = 5.85$ fm^2), low magnetogyric ratio (1.2500608×10^7 rad T^{-1} s^{-1}), and concomitant low resonance frequency signify that ^{39}K remains a challenging nucleus to study by SSNMR spectroscopy, despite its high natural abundance of 93.3%.[1,2] Work in the 1980s and 1990s by Oldfield,[3] Bastow,[4] and Dye,[5] among others, demonstrated the feasibility of using ^{39}K SSNMR to study solid inorganic and organic potassium-containing compounds. However, only in 2007 was the first truly comprehensive study of potassium electric field gradient (EFG) and chemical shift (CS) tensors in inorganic salts reported by Moudrakovski and Ripmeester.[6] Wu et al. have recently demonstrated the potential of ^{39}K SSNMR in the characterization of biomolecular systems;[7] however, to our knowledge, no information on potassium CS tensors in organic or biomolecular binding environments is available. Given the current increased interest in high-field ^{39}K SSNMR, an objective of the present work is therefore to establish the importance of ^{39}K CS anisotropy in the interpretation of ^{39}K SSNMR spectra of organic potassium complexes.

The organic potassium complexes studied in the present work are presented in Figure 1. In the KI complex of compound **1**, the potassium ion is coordinated by three oxygen atoms and two nitrogen atoms within the 4,10-diaza-15-crown-5 ring; additionally, there is a weak ion pairing with the nearby iodide counterion ($r_{K\cdots I} = 3.52$ Å; cf. the equilibrium bond length of the diatomic KI in the gas phase,[8] 3.04781 Å). In compound **2**, [K([18]crown-6)(NPh$_2$)], the potassium ion is coordinated by six oxygen atoms within the crown ether ring, and additionally, potassium−phenyl interactions are present, as shown by the X-ray crystal structure.[9] These K^+−phenyl interactions serve as a model for alkali metal cation−phenylalanine side-chain interactions in proteins and similar interactions with purine and pyrimidine moieties in nucleic acids. The analysis of compound **2** is therefore important since cation−π interactions are of fundamental interest from the perspective of understanding weak noncovalent bonding modes.[10−12] Previous studies have demonstrated the utility of ^{23}Na and ^{39}K SSNMR in characterizing cation−π interactions.[13,14]

It is not particularly well-appreciated that CS tensor spans are also available for diatomic molecules indirectly from high-resolution molecular beam spectroscopy.[15,16] To place the data obtained for organic potassium complexes in context, we additionally present an analysis of the nuclear spin-rotation data

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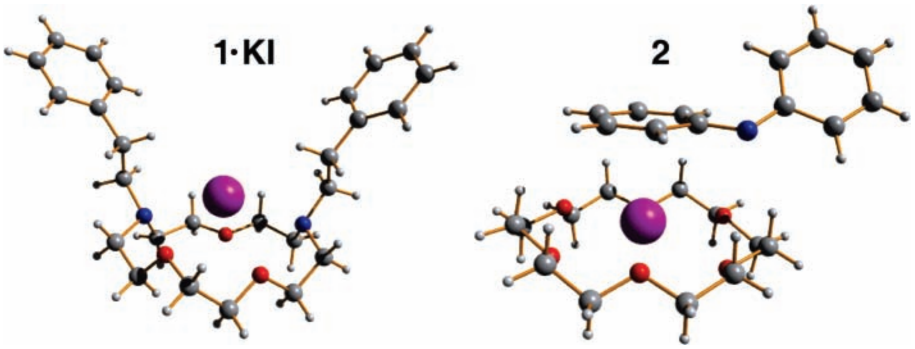

Figure 1. Structures of compounds **1**·KI and **2**, generated from atomic coordinates available from X-ray diffraction data. The iodide counterion is not shown for **1**·KI for clarity. Potassium ions are shown in magenta.

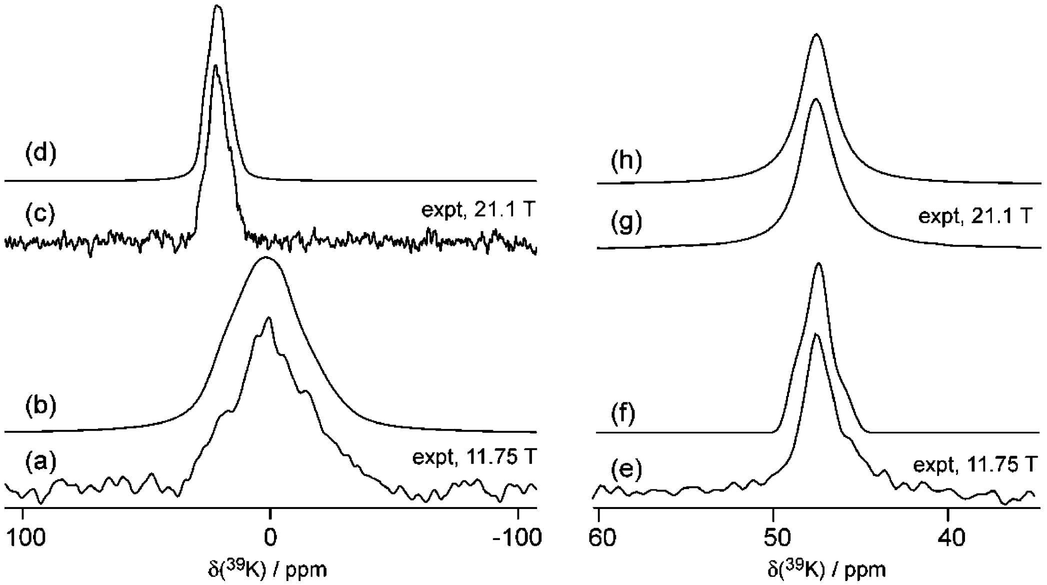

Figure 2. Experimental and simulated ^{39}K MAS NMR spectra of compounds **1**·KI and **2** obtained at 11.75 and 21.1 T. (a) and (c) Experimental spectra of **1**·KI. (b) and (d) Corresponding best-fit simulated spectra. (e) and (g) Experimental spectra of **2**. (f) and (h) Corresponding best-fit simulated spectra.

available from molecular beam electric resonance experiments for $^{39}K^{19}F$ and $^{39}K^{35}Cl$.[17,18]

Experimental Section

The preparations of *N,N′*-bis(2-phenylethyl)-4,10-diaza-15-crown-5 (**1**) and its KI complex, as well as the X-ray crystal structure data for **1**·KI, are reported in the Supporting Information. Compound **2** was prepared according to a literature procedure.[9]

Solid-State NMR Spectroscopy: ^{39}K SSNMR spectra were recorded at 11.75 and 21.1 T using 4 mm MAS probes. Chemical shifts are referenced to 1 M KCl(aq) at 0 ppm. Further experimental details are reported in the Supporting Information.

Quantum Chemical Calculations: All calculations of ^{39}K nuclear magnetic shielding tensors were performed using Gaussian 03.[19] Models of **1**·KI and **2** were built based on the atomic coordinates from their X-ray crystal structures (see Figure 1);[9] the iodide counterion was included in the model for **1**·KI. Hydrogen atom positions were optimized at the B3LYP/3-21G and B3LYP/6-31G* levels for compounds **1**·KI and **2**, respectively, prior to nuclear magnetic shielding tensor calculations. Results were analyzed using EFGShield (version 2.2).[20]

Results and Discussion

Presented in Figure 2 are the magic angle spinning (MAS) central transition (CT) NMR spectra of solid **1**·KI and **2** obtained in magnetic fields of 11.75 and 21.1 T. The second-order quadrupolar broadening of the CT is small; however, a distinct second-order line shape may be observed for **1**·KI, particularly at 11.75 T. For **2**, the line width changes only marginally at higher magnetic field, indicating that quadrupolar effects are very small. Spectral simulations (Figure 2) provide the ^{39}K isotropic chemical shift (δ_{iso}), quadrupolar coupling constant (C_Q), and quadrupolar asymmetry parameter (η_Q) for **1**·KI and **2** (Table 1). The value of C_Q for **1**·KI, 673 ± 60 kHz, is small for a quadrupolar nucleus in a binding environment with no inherent crystallographic symmetry. For **2**, there is a small second-order quadrupolar effect at 11.75 T. We can only realistically conclude that C_Q is less than 200 kHz; the fits presented in Figure 2 used values of 170 kHz for C_Q and 0.70 for η_Q. Several iterative fits were carried out using different starting parameters to ensure that the final parameters and reported errors are correct.

Koller et al. have shown that a more symmetrical distribution of atoms in the coordination sphere of sodium ions results in lower values of C_Q than those for sodium cations with planar

TABLE 1: Selected Experimental K-39 and Na-23 Quadrupolar and Chemical Shift Tensor Parameters

compound	nucleus	$\lvert C_Q \rvert$/MHz	η_Q[g]	δ_{iso}[a]/ ppm	Ω / ppm[d]	κ[d]	α,β,γ (°)[d]	reference
1·KI	^{39}K	0.673 ± 0.060	0.61 ± 0.10	28.3 ± 1.0	75 ± 20	0.37 ± 0.15	35 ± 15, 62 ± 5, 65 ± 15[e]	this work
2	^{39}K	<0.2	0.70 ± 0.20	48.3 ± 0.5	<10	n/a	n/a	this work
sodium lariat ether[b] (2 sites)	^{23}Na	2.92 ± 0.05	0.41 ± 0.04	−8.4 ± 1.5	7 ± 4	0.4 ± 0.4	86 ± 20, 84 ± 20, 90 ± 20	ref 14
		3.15 ± 0.08	0.18 ± 0.04	−7.4 ± 1.5	4 ± 3	0.7 ± 0.3	0 ± 20, 78 ± 30, 33 ± 40	
NaBPh$_4$	^{23}Na	1.24 ± 0.05	0.0 ± 0.1	−45.6 ± 0.5	14 ± 2	1	n/a	ref 13
KBPh$_4$	^{39}K	1.32 ± 0.05	0.0 ± 0.1	−92 ± 1	*c*	n/a	n/a	ref 13
^{39}K^{19}F	^{39}K	−7.981013 (0.000008)	0.0[f]	−	84.39 ± 0.25 ($v = 0$)	0.0[f]	−	this work and ref 17
^{39}K^{35}Cl	^{39}K	−5.69147 ± 0.00004	0.0[f]	−	141 ± 6 ($v = 0$)	0.0[f]	−	this work and ref 18

[a] K-39 chemical shifts ($\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})$ /3) are referenced to 1 M KCl(aq).
[b] *N*-(2-(3-(5-methoxy)-indolyl)ethyl)aza-15-crown-5, sodium tetraphenylborate salt.
[c] Too small to be reliably measured.[13]
[d] The span (Ω) of the CS tensor is defined as $\delta_{11} - \delta_{33}$, where $\delta_{33} \leq \delta_{22} \leq \delta_{11}$; the skew ($\kappa$) is equal to $3(\delta_{22} - \delta_{iso})/\Omega$. See reference 20 for the Euler angle conventions used.
[e] The equivalent angles used in Simpson simulations are 65, 62, and 125° for the CS interaction and 0 0, and 0° for the quadrupolar interaction.
[f] By symmetry.
[g] $\eta_Q = (V_{11} - V_{22})/V_{33}$ where $|V_{33}| \geq |V_{22}| \geq |V_{11}|$.

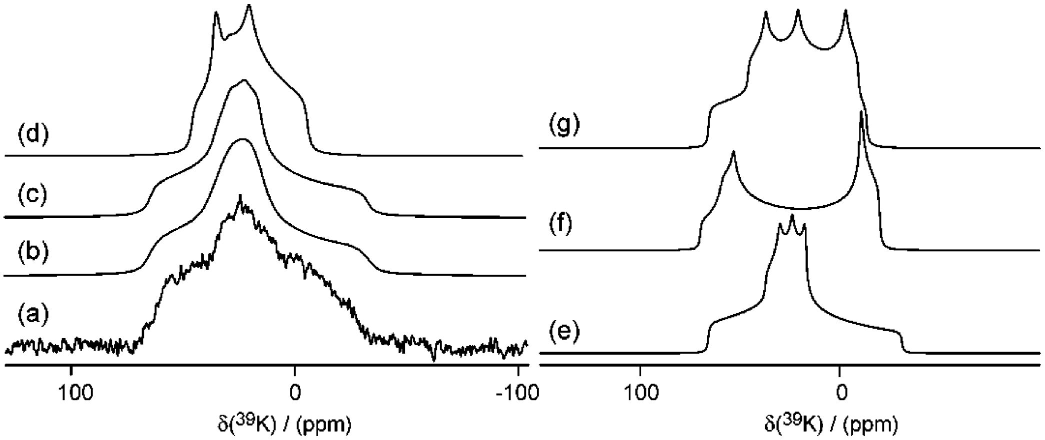

Figure 3. Experimental and simulated ^{39}K NMR spectra of a stationary powdered sample of solid **1**·KI. (a) Experimental, 21.1 T. (b) Four-spin simulation which includes the ^{39}K−^{1}H dipolar coupling interactions for the three nearest protons. (c) Simulated under an isolated spin approximation. (d) Simulated spectrum with the span of the CS tensor set to zero. (b), (c), and (d) incorporate 100 Hz of exponential apodization. (e) Same as (c) but with less broadening to demonstrate the fine structure in the line shape; $\beta = 62°$. (f) Same as (e) but with the angle β set to 0°. (g) Same as (e) but with the angle β set to 90°.

coordination geometries.[21] A qualitative explanation of the reduction in C_Q in **2** compared to that in **1**·KI therefore is that the coordination sphere around potassium is more symmetrical in **2**, resulting in a reduction of the EFG; in the case of **1**·KI, the crown ether coordination geometry is qualitatively more similar to a planar coordination geometry (these results are also consistent with previous calculations on related systems).[14] It is also important to point out that crown ethers such as 18-crown-6 are known to undergo a "merry-go-round"-type motion in the solid state.[22] Such motion could potentially result in some averaging of the ^{39}K EFG tensor in **2**.[23]

We pursued the possibility of characterizing the potassium CS tensors in **1**·KI and **2**. The CS tensor reflects the local effect of molecular orbitals of appropriate symmetry centered on the potassium nucleus. For **1**·KI, we determined a CS tensor span ($\Omega = \delta_{11} - \delta_{33}$) of 75 ± 20 ppm. Shown in Figure 3 is the ^{39}K SSNMR spectrum of a stationary sample of **1**·KI. We first attempted to simulate the spectrum by assuming negligible CS anisotropy, that is, $\Omega = 0$ (Figure 3d). The poor fit to the experimental spectrum immediately indicated the presence of significant potassium CS anisotropy. A series of simulations presented in Figure 3 demonstrates the quality of fit which is obtained with the parameters given in Table 1. Since ^{1}H decoupling was not available for this experiment at 21.1 T, we performed simulations for which the dipolar coupling between ^{39}K and the nearest one, two, or three protons was taken into account (see Supporting Information). The ^{39}K−^{1}H dipolar coupling constants, 243, 201, and 145 Hz, are relatively small due to the small magnetogyric ratio of ^{39}K. Therefore, it is not surprising that including the dipolar interactions merely has a slight broadening effect on the simulated spectrum. These simulations confirm that the dominant effect on the spectrum of stationary **1**·KI is potassium CS anisotropy. Also demonstrated in Figure 3 is the pronounced sensitivity of the simulated spectrum to the angle β between the eigenvectors corresponding to δ_{33} and V_{33}; these additional simulations are intended to further illustrate the validity of our reported parameters. While we have been careful in our interpretation of the spectral data, it is important to recognize that it cannot be guaranteed that the reported parameters provide a unique fit to the spectra. This caveat is not specific to our study but rather a general issue in the simulation of spectra of quadrupolar nuclei which do not lie on symmetry elements.

The CS tensor parameters reported here for organic potassium complexes may be compared with the limited available data for other potassium-containing molecules. The largest span reported in Moudrakovski and Ripmeester's recent study is 61 ppm for K_2MoO_4.[6] To our knowledge, the value of 75 ± 20 ppm for **1**·KI appears to be the first such measurement for a potassium cation complexed within an organic host and the largest CS tensor span measured to date for potassium in any solid compound. This measurement is enabled by the high magnetic field used to record the spectra due to the amplified effect of the CS tensor (in Hz) as B_0 is increased. For example, Widdifield and Schurko have demonstrated the difficulties associated with observing the effect of a span of up to 100 ppm on the ^{39}K NMR spectra of solid potassium metallocenes at 9.4 T.[24]

Nuclear magnetic shielding (and chemical shift) tensor spans are available for diatomic molecules through an analysis of the spin-rotation constants available from high-resolution microwave or molecular beam spectroscopies.[16] High-precision nuclear spin-rotation data are available for gaseous potassium fluoride[17] and potassium chloride.[18] The nuclear spin-rotation tensor is directly related to the nuclear magnetic shielding tensor, and we extracted the values of $\Omega(^{39}\mathrm{K})$ using the following relationship (where a small "quadrupole term" has been neglected):[25,26]

$$\Omega = \frac{m_{\mathrm{p}} C_{\mathrm{I}}}{2 m g_{\mathrm{I}} B}$$

See ref 27 for additional details. For ^{39}K^{19}F, we determined a potassium CS tensor span of 84.39 ± 0.25 ppm ($v = 0$), while a value of 141 ± 6 ppm ($v = 0$) was determined for ^{39}K^{35}Cl. These results emphasize once again that the span determined for **1**·KI is relatively large, yet reasonable. The span of 141 ppm for ^{39}K^{35}Cl covers essentially the entire range of known isotropic potassium chemical shifts.[6]

The ^{39}K NMR spectrum of a stationary sample of **2** obtained at 21.1 T (not shown) revealed that the span of the ^{39}K CS tensor in this case is less than 10 ppm. This small value is entirely consistent with the ^{23}Na CS tensor spans determined previously for two sodium cations experiencing cation−π interactions.[14] Importantly, the magnitudes of the CS tensor spans for **1**·KI and **2** are very well-reproduced by quantum chemical calculations. For example, a B3LYP/6-31G* calculation on **2** yields a value for Ω of 10 ppm; the same level of theory yields a value of 73 ppm for compound **1**·KI (cf. exptl. values of ≤10 ppm and 75 ± 20 ppm, respectively). Inclusion of the iodide counterion in the model used for **1**·KI was critical in achieving good results. The calculations show that the largest component of the shielding tensor lies approximately along the potassium−iodine internuclear vector. Inspection of the molecular orbitals with large coefficients at potassium reveals that there is no single large MO contributor to the large span; rather, the span must be due to several small contributions from various pairs of occupied and virtual orbitals of appropriate symmetry. Therefore, we tentatively rationalize the difference in spans for **1**·KI and **2** using a symmetry-based argument analogous to that used in the discussion of C_Q (vide infra).

Conclusions

High-field potassium-39 SSNMR spectra have been acquired and interpreted for two organic potassium complexes. Our analysis of the ^{39}K NMR spectra of solid **1**·KI has revealed the first chemical shift anisotropy for K^+ in any organic binding environment, thereby demonstrating the potential utility of the potassium CSA as a probe of potassium ion binding environments in other organic and biomolecular systems. The span of the potassium CS tensor in **1**·KI is, to our knowledge, the largest measured to date by NMR spectroscopy. The large value has been corroborated by quantum chemical calculations. Interestingly, our analyses of nuclear spin-rotation data for gaseous KF and KCl have revealed even larger potassium CS tensor spans, thereby demonstrating the benefits of considering the data available from molecular beam experiments when interpreting NMR data.

While there are too many structural differences between compounds **1**·KI and **2** to enable a simple interpretation of the differences between the NMR data obtained for **1**·KI compared with those obtained for **2**, the results obtained for the latter are interesting in that they are partly representative of a K^+−π interaction. Further studies will be useful to explore whether cation−π interactions can be detected by ^{39}K NMR spectroscopy in a series of more closely structurally similar compounds.

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Supporting Information Available: Full experimental and simulation details, a table of calculated shielding tensors, synthesis of **1**·KI, and X-ray crystal structure data for **1**·KI. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Here, m_p is the mass of a proton, m is the electron mass, C_I is the nuclear spin-rotation constant, g_I is the nuclear g-factor, and B is the rotational constant of the diatomic molecule. Rotational constants were taken from Huber, K. P.; Herzberg, G. Constants of Diatomic Molecules (data prepared by Gallagher, J. W., Johnson, R. D., III). In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology, Gaithersburg MD, 20899, June 2005 (http://webbook.nist.gov). Fundamental constants are from the National Institute of Standards and Technology. http://physics.nist.gov/cuu/index.html. Results for ^{39}K^{19}F are reported for the ground vibrational state; $C_I(v = 0) = 200.5(0.6)$ Hz. Results for ^{39}K^{35}Cl are based on the $v = 0$ rotational constant; the ^{39}K spin-rotation constant ($C_I = 154(7)$ Hz) was reported as being essentially independent of vibrational state.