mental doping of **5** up to $y = 1.1$ does not lead to a further increase in conductivity. Doping stochiometries exceeding $y = 1.1$ could not be achieved; these doped polymers are not stable and loose iodine already at room temperature. π-radical cations are formed by the oxidation of the metal macrocycle stack **5** by iodine, which is proved by a symmetric ESR signal ($g = 2.0030$). The iodine is thereby reduced to I_3^-. The characteristic totally symmetric scattering pattern ($\nu = 103$ cm^{-1}) of I_3^- in $[(TBPGeO)I_y]_n$ is observed in the resonance Raman spectrum (exciting wavelength 482.5 nm) accompanied by an overtone. The peaks due to I_5^- and I_2 are not detected.

The present study of doped and undoped $[TBPGeO]_n$ (**5**) indicates that **5** in comparison with $[PcGeO]_n$ can be equally well used in constructing conducting cofacially assembled macrocyclic bridged polymers.

We have not yet succeeded in preparing the corresponding siloxane $[TBPSiO]_n$, for which a shorter interring distance and consequently a higher conductivity after doping are expected.

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First Observation by ^{39}K NMR of K$^-$ in Solution and in Crystalline Potassides

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The first salt of an alkali-metal anion (alkalide) was synthesized more than a decade ago.[1,2] This was followed by alkali-metal NMR studies of Na$^-$, Rb$^-$, and Cs$^-$ in solution[3-9] and of Na$^-$ and Cs$^-$ in crystalline alkalides.[10-12] All attempts to observe K$^-$ by ^{39}K NMR were, however, unsuccessful.[4,8,13] We now report the first NMR observation of K$^-$ both in solution and in crystalline potassides. This provides *direct* proof of the existence of K$^-$ in solids, as suggested by optical spectra of thin films.[14-16]

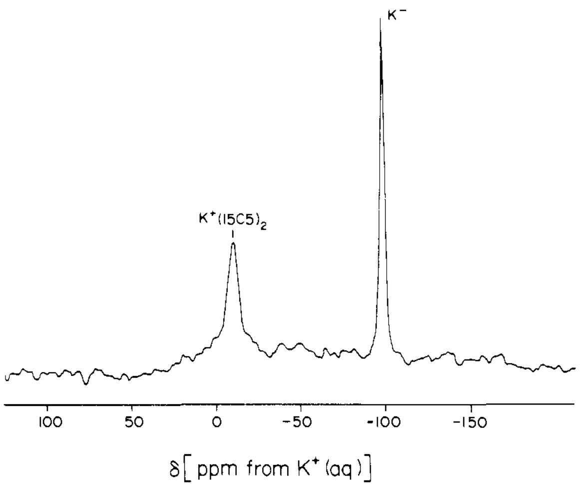

Figure 1. ^{39}K NMR spectrum of K$^+$(15crown5)$_2$·K$^-$ in dimethyl ether (0.06 M) at 220 K, 20 400 acquisitions with 10-Hz exponential broadening.

A Bruker WH 180 multinuclear spectrometer operating at a field strength of 4.227 T was used to record the ^{39}K spectra (frequency = 8.40 MHz). Dimethyl ether (Me$_2$O) was distilled into an evacuated 10-mm NMR tube that contained a weighed amount of crystalline K$^+$(15-crown-5)$_2$·K$^-$. The tube was then flame-sealed under vacuum. Polycrystalline samples for static and magic angle sample spinning (MAS) ^{39}K NMR studies were loaded while cold into axial Doty rotors under a dry nitrogen atmosphere.

The spectrum of a 0.06 M solution of K$^+$(15-crown-5)$_2$·K$^-$ in Me$_2$O is shown in Figure 1. The peaks at −9.9 and −99.3 ppm are assigned to K$^+$(15-crown-5)$_2$ and K$^-$, respectively. The measured chemical shift of the gaseous potassium atom is −101 ± 5 ppm[17] and the anion is expected to be 2 ppm more diamagnetic at −103 ± 5 ppm.[18] The negligible solubility of potassium in Me$_2$O rules out the presence of uncomplexed potassium. The narrower line width of the K$^-$ peak (20 Hz) compared with that of K$^+$(15-crown-5)$_2$ (50 Hz) reflects the more spherical environment of K$^-$.

The prevous failure to observe K$^-$ in solution[4,8,13] may result from the equilibrium

$$K^- \rightleftharpoons K^+ + 2e^-(solv)$$

since K$^-$ is more dissociated than Na$^-$, Rb$^-$, or Cs$^-$.[19,20] Rapid equilibration to give paramagnetic solvated electrons (or intermediate species such as K·) would substantially broaden the K$^-$ NMR peak. The low donicity of Me$_2$O shifts the equilibrium to the left, thus permitting observation of K$^-$.

The static ^{39}K NMR spectrum without ^{1}H decoupling and the decoupled static and MAS spectra of polycrystalline K$^+$(15-crown-5)$_2$·K$^-$ are shown in Figure 2. Only the single peak of K$^-$ at −105 ppm is observed. The full widths at half-height are 300, 175, and 40 Hz, respectively. The residual width of the central transition ($m = {}^1/_2$, $m = -{}^1/_2$) upon spinning and ^{1}H decoupling gives a *maximum* quadrupolar coupling constant, e^2qQ/h, of about 0.1 MHz.[21]

The absence of the cation NMR peak in solid K$^+$(15-crown-5)$_2$·K$^-$ indicates that e^2qQ/h for K$^+$ in the complex must be greater than 0.5 MHz since we could have detected a signal of line width ≤1000 Hz. Since Na$^+$ cryptand[2.2.2] has a quadrupolar coupling constant of 1.2 MHz,[22] a value greater than 0.5 MHz in the present case is not unexpected.

The MAS-NMR data for several potassides and simple K$^+$ salts are given in Table I. All potassides show only the K$^-$ peak whose

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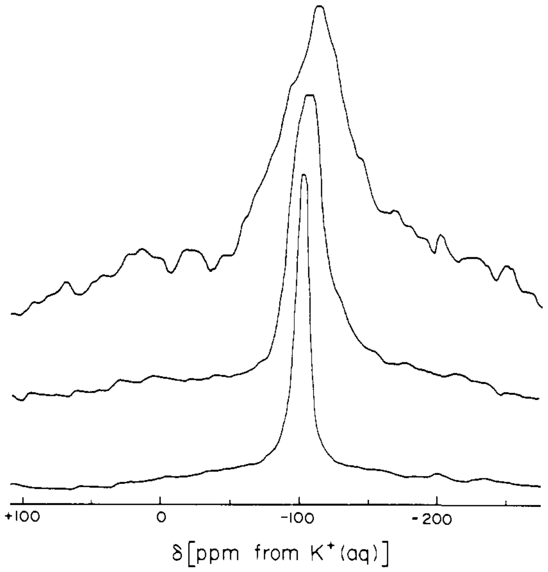

Figure 2. ^{39}K NMR spectra of polycrystalline $K^+(15crown5)_2 \cdot K^-$ at 180 K. (Top) Static spectrum; (middle) static, ^{1}H decoupled spectrum; (bottom) MAS spectrum with ^{1}H decoupling. All spectra were obtained with 3200 acquisitions and have 60-Hz exponential broadening.

Table I. ^{39}K MAS-NMR Chemical Shifts and Line Widths of Polycrystalline Potassides and Simple Potassium Salts

compound	δ, ppm from K⁺(aq)[a]	$\Delta\nu_{1/2}$, Hz
KCl	+46.7 (5)	28
KBr	+54.5 (5)	20
$K^+(15crown5)_2 \cdot K^-$	−105 (1)	70
$Rb^+(15crown5)_2 \cdot K^-$[b]	−105 (2)	120
$Cs^+(15crown5)_2 \cdot K^-$	−105 (5)	220
KRb(18crown6)[b]		no signal
$Cs^+(18crown6)_2 \cdot K^-$	−115 (10)	150

[a] Uncertainty of the last digit given in parentheses. [b] Probably contain both K^- and Rb^- as indicated by rubidium XANES.[23]

chemical shift (-105 ppm, within experimental error) is the same as that calculated for gaseous K^-. The line widths increase with cation size in $M^+(15\text{-crown-}5)_2 \cdot K^-$, suggesting stronger cation–anion interactions.

Possibly the absence of a signal for KRb(18-crown-6) results from strong Rb^+–K^- interactions. The presence of K^- in samples of this composition is suggested from rubidium XANES studies[23] that show the presence of both Rb^+(18-crown-6) and Rb^-.

The ^{39}K NMR studies of K^- both in solution and in potasside crystals show that K^- is a "genuine" anion with two electrons in the 4s orbital that shield the 3p electrons from appreciable interaction with the surroundings. Thus, K^-, as Na^-, shows *no* chemical shift from the gaseous anion. Previous studies show, however, that Rb^- and Cs^- *are* shifted paramagnetically from the corresponding gaseous anion.[4,11,13] This could be caused by less effective shielding of p and/or d electrons by the outer s electrons or by an admixture of p or d character with the ground-state s wave function.

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Note Added in Proof. K^- was recently observed by ^{39}K NMR in solutions of KCs/12-crown-4 in tetrahydrofuran.[24]

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Gas-Phase Electron Transfer: Kinetics of Metallocene Self-Exchange Reactions

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Considerable insight into the kinetics and thermodynamics of chemical processes in solution can be provided by direct study of analogous processes in the gas phase. In this way, factors intrinsic to the molecular species involved can be separated from contributions of the solvent, which can markedly alter (or even reverse) trends observed in the gas phase. The vast majority of such comparisons made thus far involve organic systems,[1,2] but we recently have begun to investigate reactions at metal centers for which direct solution/gas-phase comparisons should be possible. In this report, the kinetics of self-exchange electron-transfer reactions for four metallocenes are considered, and evidence for the observation of intrinsic kinetic barriers is presented.

The contribution of the solvent to activation barriers for electron transfer is known to be significant[3-10] and is often the dominant term for reactions of charged complexes. The total free energy of activation is given theoretically by $\Delta G^*_{tot} = \Delta G^*_{in} + \Delta G^*_{out} + w_r$, where w_r is the work required to bring the reactants together forming the precursor complex, ΔG^*_{in} is the inner barrier presented by the necessary internal reorganization of the reactants, and ΔG^*_{out} is the outer barrier due to reorganization of the solvent.[3,4,8,9] For self-exchange reactions of the metallocenes (1) where one

$$M(C_5H_5)_2 + {}^*M(C_5H_5)_2^+ \overset{k_{et}}{\rightleftharpoons} M(C_5H_5)_2^+ + {}^*M(C_5H_5)_2 \quad (1)$$

reactant is uncharged, the term w_r is negligible. We have initiated studies of gas-phase electron-transfer reactions involving metal centers to provide data necessary to evaluate ΔG^*_{in} directly and, in principle, allow more detailed evaluation of results for solution studies.

The self-exchange reactions of metallocenes are well suited for these initial studies, as they can be examined in solution by a variety of techniques such as NMR,[11,12] EPR,[13] isotopic tracers,[14] electrochemistry,[15,16] and pseudo-self-exchange.[17,18] By far the best characterized is ferrocene/ferrocenium,[19,20] for which a

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