α-D-threofuranose, 80877-72-1; β-D-threofuranose, 80877-73-2; D-threose hydrate, 107890-70-0; α,γ-D-arabinopyranose, 608-45-7; β-D-arabinopyranose, 6748-95-4; α-D-lyxopyranose, 608-46-8; β-D-lyxopyranose, 608-47-9; α-D-ribofuranose, 32445-75-3; β-D-ribofuranose, 36468-53-8; α-D-ribopyranose, 7296-59-5; β-D-ribopyranose, 7296-60-8; α-D-xylopyranose, 6763-34-4; β-D-xylopyranose, 2460-44-8; α-D-allopyranose, 7282-79-3; β-D-allopyranose, 7283-09-2; α-D-altrofuranose, 41846-93-9; β-D-altrofuranose, 40461-79-8; α-D-altropyranose, 7282-80-6; β-D-altropyranose, 7283-10-5; α-D-galactopyranose, 3646-73-9; β-D-galactopyranose, 7296-64-2; α-D-glucopyranose, 492-62-6; β-D-glucopyranose, 492-61-5; α-D-glucopyranose, 7282-78-2; β-D-glucopyranose, 7283-08-1; α-D-mannopyranose, 7296-15-3; β-D-mannopyranose, 7322-31-8; α-D-talofuranose, 51076-04-1; β-D-talofuranose, 41847-63-6; α-D-talopyranose, 7282-81-7; β-D-talopyranose, 7283-11-6.

Cesium-133 Solid-State Nuclear Magnetic Resonance Spectroscopy of Alkalides and Electrides

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Abstract: ^{133}Cs MAS-NMR spectra were measured for alkalides and electrides that contain complexed cesium cations and, in one case, the cesium anion. The chemical shifts of the cesium cations in alkalides of Cs$^+$(15C5)$_2$ and Cs$^+$(18C6)$_2$ are +27 ± 3 and -60 ± 2 ppm, respectively, except for Cs$^+$(18C6)$_2$·Cs$^-$, which shows temperature-dependent chemical shifts through two phase changes. The shifts range from -40 to -50 ppm for Cs$^+$(18C6)$_2$ and from -205 to -240 ppm for Cs$^-$. Depending on the method of preparation, the NMR spectrum of compounds prepared from cesium and cryptand[2.2.2], C222, show either one or two peaks, which correspond to the inclusive and exclusive complexed cations. Since all samples are essentially diamagnetic, the anions could be Cs$^-$ ions broadened beyond detection limits, trapped electrons that are spin-paired, or mixtures of ceside and electride. The paramagnetic electride Cs$^+$(18C6)$_2$·e$^-$ shows a temperature-dependent Knight shift due to unpaired electron density at the cesium nucleus. The fractional atomic character of Cs$^+$ is only 3.3×10^{-4}, in agreement with the view that electrons are trapped at anionic sites well away from Cs$^+$. A compound of mixed anionic stoichiometry, Cs$^+$(18C6)$_2$·Na^-_xe$^-_{1-x}$, was prepared from solutions with the nominal values x = 0.2 and 0.8 and gives four temperature-dependent paramagnetic peaks in addition to a peak caused by precipitation of the pure iodide. The four peaks indicate that sodium anions can substitute for electrons in up to three of the eight nearest anionic sites about a complexed cation. This shows that each electron in Cs$^+$(18C6)$_2$·e$^-$ interacts with all eight of its cationic neighbors and is not preferentially localized on one of them.

Complexed cations, formed from simple alkali metal cations and crown ethers or cryptands, are sufficiently stable to reduction that salts with alkali metal anions (M$^+$C·N$^-$, known as alkalides) or with electrons at the anionic sites (M$^+$C·e$^-$, known as electrides) can be formed. The first alkalide, Na$^+$C222·Na$^-$ (C222 = cryptand[2.2.2]), was synthesized in 1974[1] and has been characterized by single-crystal X-ray diffraction,[2] optical spectroscopy,[3,4] powder conductivity,[5] and more recently by photoelectron emission and fluorescence spectroscopy.[6] The nature of the sodium anion was best characterized by NMR, first in solutions of Na$^+$C222·Na$^-$ in ethylamine,[7,8] THF and methylamine,[8] and later in the solid state with polycrystalline Na$^+$C222·Na$^-$.[9] Other NMR studies of Na$^-$ in solution[10-13] showed that the chemical shift of this anion in each case was the same as the chemical shift calculated for Na$^-$ in the gaseous state.[14-16] Thus, the sodium anion was shown to be a genuine spherical anion with a filled 3s orbital that is not strongly affected by its environment.[17] Similar conclusions resulted from NMR studies of K$^-$, Cs$^-$, and Rb$^-$ in solution.[8,13,18,19]

To date more than 40 alkalide and electride compounds have been synthesized, and magic angle sample spinning NMR (MAS-NMR) has become a primary technique for their characterization. The oxidation state of an ion or element in a compound is easily identified by the chemical shift of the resonance. The cationic and anionic species in an alkalide, which always contains two alkali metal nuclei, can often be properly identified by NMR. Signals have been detected in the solid state for Na$^+$·C and Na$^-$,[9,20] K$^-$,[18] Rb$^-$,[21] and Cs$^+$·C and Cs$^-$.[22,23] In these expressions, C represents a cryptand such as C222 or a crown ether, such as 18-crown-6 (18C6) or 15-crown-5 (15C5).[24] No signal was detected for either K$^+$C[18] or Rb$^+$·C[21] because of extreme quadrupolar line broadening that could not be reduced by MAS.

In addition to the identification of alkali metal cations and anions in alkalides and electrides by measurement of the chemical

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(24) IUPAC names: 18-crown-6, 1,4,7,10,13,16-hexaoxacyclooctadecane, abbreviation 18C6; 15-crown-5, 1,4,7,10,13-pentaoxacyclopentadecane, abbreviation 15C5; cryptand[2.2.2], 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, abbreviation C222.

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shifts, analysis of the line shape, both in static and MAS narrowed spectra, can provide information about the interaction of the ions with their environments. The quadrupole coupling constants, $\chi = e^2qQ/h$, have been determined for $^{23}Na^+{\cdot}C222$[20] (χ = 1.2 MHz), $^{133}Cs^+{\cdot}(18C6)_2$[25] ($\chi$ = 89.6 kHz), and $^{133}Cs^+(15C5)_2$[25] (χ = 42.7 kHz). In all cases, the asymmetry parameter, η, was zero within experimental error. Upper limits for the quadrupole coupling constants have been established for Na^- ($\chi \leq 0.23$ MHz),[20] K^- ($\chi \leq 0.1$ MHz),[18] and Rb^- ($\chi \leq 1.3$ MHz).[21] The relatively small value of the quadrupolar interaction in the anions testifies to their large, diffuse, spherical nature.

Some properties of ^{133}Cs NMR in alkalides and electrides have been previously reported.[22,23] The isolation of the electride, $Cs^+(18C6)_2{\cdot}e^-$, was verified by ^{133}Cs NMR when the compound with a 1:2 ratio of Cs to 18C6 gave an NMR spectrum that consisted of a single paramagnetically shifted peak. The compound of stoichiometry Cs(18C6), originally thought to be an electride,[26] was shown to be the ceside, $Cs^+(18C6)_2{\cdot}Cs^-$, by virtue of a two-peak spectrum: the $Cs^+(18C6)_2$ resonance was near the value seen for other diamagnetic $Cs^+(18C6)_2$ salts, while the Cs^- peak was upfield from this by about 160 ppm.[22] Two other cesium compounds, the sodide,[9] $Cs^+(18C6)_2{\cdot}Na^-$, and the rubidide,[21] $Cs^+(18C6)_2{\cdot}Rb^-$, have been characterized by ^{133}Cs NMR.

The favorable NMR properties of the ^{133}Cs nucleus make the study of cesium-containing alkalides and electrides useful for several reasons. (a) The small quadrupole moment permits detection of the complexed cation. (b) The chemical shift of Cs^+ is extremely sensitive to electron density at the nucleus and may be used to evaluate the percent atomic character of the complexed cesium cation in electrides. (c) The NMR peak of Cs^- may be used to positively identify cesides, and it is also useful to study the influence of the surroundings on the chemical shift and line width of Cs^-. (d) The presence of mixed alkalide/electride crystals can be easily distinguished from mixtures of the pure crystals by the effect on the NMR peaks. The present study was undertaken to provide a bettern understanding of the nature of cesium-containing alkalides, electrides, and mixtures.

Experimental Section

Alkalides and electrides are synthesized by anaerobically introducing stoichiometric amounts of the metal(s) and complexant into an evacuable vessel and dissolving them in polar amines and/or ethers. Crystals are formed by adding less polar amines or ethers to lower the dielectric constant and then cooling the solution. The compounds are very reactive and must be handled under vacuum or in inert atmosphere at all times. Further, most compounds must be handled at temperatures below −20 °C to avoid thermal decomposition. Details of the purification of materials and of the synthetic methods have been described elsewhere.[27,28]

NMR spectra were obtained at 47.24 MHz (at Dow Chemical Co., 8.4 T, pulse length = 6.0 μs, 10-s repetition time) and at 65.61 MHz (at the University of Illinois at Urbana–Champaign, 11.7 T, pulse length = 4.5 μs, 10-s repetition time) with Andrews-Beam-type MAS probes. The spinning gas was cooled by passing it through a copper coil immersed in an acetone/dry ice bath. Spinning rates were 2 to 4 kHz. The Andrews spinners were made of Delrin or poly(methyl methacrylate)-d_8. The spinners were loosely filled with the polycrystalline sample in an inert (dry N_2) atmosphere glovebag. Spectra were also obtained at 23.62 MHz (4.2 T, pulse length = 4.5 μs, 2.5-s repetition time) by using a variable-temperature Doty probe with rotors made of sapphire and equipped with low-temperature end caps. The rotors were firmly packed with the polycrystalline samples in inert atmosphere bags. Spinning rates were typically 1.5 to 3 kHz. The spinning gas was passed through a liquid-nitrogen heat exchanger and warmed to the desired temperature with a feedback-controlled heater. The temperature of the spinning gas was measured with a copper–Constantan thermocouple inserted in the gas line just before the stator. Further calibration of the temperature is described later. Chemical shifts were measured with respect to a value of 0 ppm for Cs^+(aq) at infinite dilution. Observed line widths are reported as $\Delta\nu_{1/2}$, the full width at half-height.

Table I. Chemical Shifts and Line Widths of ^{133}Cs MAS–NMR Lines in Alkalides and Electrides

compound	σ (ppm)[a]	$\Delta\nu_{1/2}$ (Hz)[b]	spectrometer[c]
$Cs^+(18C6)_2{\cdot}Na^-$	−61	40	B
	−62	160	C
$Cs^+(18C6)_2{\cdot}K^-$	−58	85	B
	−58	188	C
$Cs^+(18C6)_2{\cdot}Rb^-$	−57	115	B
	−57	65	C
$Cs^+(18C6)_2{\cdot}Cs^-$	−41, −49	275, 220	A
	−51	175	B
	−40, −50	168, 300	C
$Cs^+(18C6)_2{\cdot}\mathit{Cs}^-$	−212		A
	−238	350	B
	−210	435	C
$Cs^+(15C5)_2{\cdot}Na^-$	+24	130	A
$Cs^+(15C5)_2{\cdot}K^-$	+24	270	A
$Cs^+(15C5)_2{\cdot}Rb^-$	+29	250	A
$CsC222{\cdot}e^-$	+138, +238	+320, +140	B
	+134, +240	+500, +356	C

[a] Chemical shift relative to a value of 0 ppm for Cs^+(aq) at infinite dilution. [b] $\Delta\nu_{1/2}$ is the full width at half-height. [c] The spectrum was observed at applied fields of (A) 4.2 T, (B) 8.4 T, and (C) 11.7 T.

Results and Discussion

^{133}Cs MAS–NMR of Alkalides. The chemical shifts and line widths of ^{133}Cs nuclei in *alkalide* salts, determined by MAS–NMR, are summarized in Table I.

The chemical shifts of complexed cations in both the 18C6 and 15C5 sandwiched systems are nearly independent of the anion and agree with the values found for halides and thiocyanates.[25] The $Cs^+(18C6)_2$ resonance peak is at −60 ± 2 ppm for all salts except the ceside. The cesium cation is coordinated by 12 crown ether oxygens. The constant chemical shift implies that the structure of the complex does not differ significantly in the sodide, potasside, and rubidide salts. The spectrum of $Cs^+(18C6)_2{\cdot}Cs^-$ is discussed in detail below. The $Cs^+(15C5)_2$ NMR peak occurs at +25 ± 1 ppm for both the sodide and potasside, and at +29 ppm[29] for the rubidide. $Cs^+(15C5)_2{\cdot}Cs^-$ has not been isolated to date. The width of an MAS narrowed line may be due either to second-order anisotropic effects (i.e., second-order quadrupolar broadening) or to incompletely narrowed first-order effects. Insufficient spinning speeds and/or slight deviations of the spinning angle could contribute to residual first-order line widths.[30] Because of the absence of systematic decoupling experiments, the variations in line widths shown in Table I cannot be related to structural effects at this time.

A ceside that has been synthesized and fully characterized is $Cs^+(18C6)_2{\cdot}Cs^-$.[31] The structure of this compound has been determined,[32] and shows that Cs^- is an extremely large anion with a radius of 3.3–3.5 Å. Cs^- is a unique alkali metal anion because low energy d and f orbitals are available. The NMR peaks of both the cation and the anion are paramagnetically shifted from those of the corresponding gaseous ions, and both show temperature-dependent chemical shifts. At low temperatures ($T < 225$ K) the resonance position of the cation is −40 ± 1 ppm and the anion has a chemical shift of −213 ± 2 ppm. Between 230 and 285 K the cationic peak splits into two lines, one at −40 ppm, the other at −50 ppm. The relative intensities of the two lines are approximately 1:1 throughout this temperature range. The anion shifts downfield (from −212 to −205 ppm) with increasing temperature between 230 and 285 K. Above 285 K the anion peak shifts abruptly to −240 ppm, and only the −50-ppm peak appears for the cation. The line width of Cs^-, even with spinning, is 350 Hz at 285 K, twice that of complexed Cs^+ in the same sample.

The chemical shift of Cs^+ in inclusive crown ether and cryptand complexes is due to the Cs–O overlap, and is inversely related to

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Table II. Summary of Calculated and Representative Observed Chemical Shifts of Alkali Metal Anions

compound	σ(M), calcd	σ(M), obsd		T (K)	ref
		soln	solid		
$^{133}Cs^-$(g)	−346.4				16 (see also 47)
Cs/C222/THF(Cs^-)		−292		202	8
$Cs^+(18C6)_2\cdot$*Cs^-*			−213	220	this work
$Cs^+(18C6)_2\cdot$*Cs^-*			−240	285	this work
$^{87}Rb^-$(g)	−213.6				16
Rb/12C4		−191			13
Rb/C222/EA		−185		233	8
Rb/C222/THF		−197		227	8
$Cs^+(15C5)_2\cdot$*Rb^-*			−189 (2)		21
$Cs^+(18C6)_2\cdot$*Rb^-*			−194	~260	21
$^{39}K^-$(g)	−103.4				16
K/Cs/12C4		−94.2			19
K/15C5/Me_2O		−101			18
$K^+(15C5)_2\cdot K^-$			−105 (1)		18
$Cs^+(18C6)_2\cdot K^-$			−115 (10)		18
$^{23}Na^-$(g)	−63.4				16
Na/C222/THF		−62.8		269	8
Na/12C4		−61.8			13
$Na^+C222\cdot$*Na^-*			−61	~260	9
$Cs^+(18C6)_2\cdot$*Na^-*			−61	~260	9

the mean Cs–O distance.[25] The change in paramagnetic shift of $Cs^+(18C6)_2\cdot Cs^-$ from other $Cs^+(18C6)_2$ salts probably results from a different conformation of the 18C6 molecules in the ceside which shortens the mean Cs–O distance at T = 225 K from 3.35 to 3.30 Å.[32] The temperature dependence of the cationic chemical shift indicates that two different environments exist for the complexed cation; between 230 and 285 K they coexist, perhaps as dimers, and above 285 K only the -50-ppm environment is seen. No structural information exists to describe the cation that gives the -50-ppm resonance, but the complexed cation probably has a mean Cs–O contact distance shorter than that seen in salts of other anions, and longer than that of the low-temperature phase.

The resonance position of Cs^- is notable for its appreciable paramagnetic shift from that calculated for Cs^-(g). Its chemical shift and those of other alkali metal anions have been measured in solution and in the solid state; Table II shows these resonance positions and compares them with the calculated values for M^-(g). The paramagnetic deviations from the gas-phase chemical shifts as well as the spread of observed shifts increase with increasing atomic weight. The paramagnetic Ramsey shift is inversely proportional to the energy difference between the ground and excited states.[33] Since Cs^- and Rb^- have low-lying d and f orbitals available, they show appreciable Ramsey shifts, whereas Na^- and K^- retain more nearly pure s^2 configurations.

The Cs^- shift with temperature and the large residual line width suggest that the amount of excited-state character in the ground state of Cs^- in the crystal is very sensitive to the local structure about the anion. The anion peak shifts gradually downfield by +10 ppm as the temperature is increased from 225 to 285 K, probably because of increased thermal motion of the crown ethers which reduces the effective radius of the anionic cavity. A smaller cavity would favor the more confined electron density of 5d or 4f orbitals over the more diffuse 6s orbital. Above 285 K the chemical shift changes abruptly by −40 ppm, probably because of a phase transition which changes the local environment of the anion.

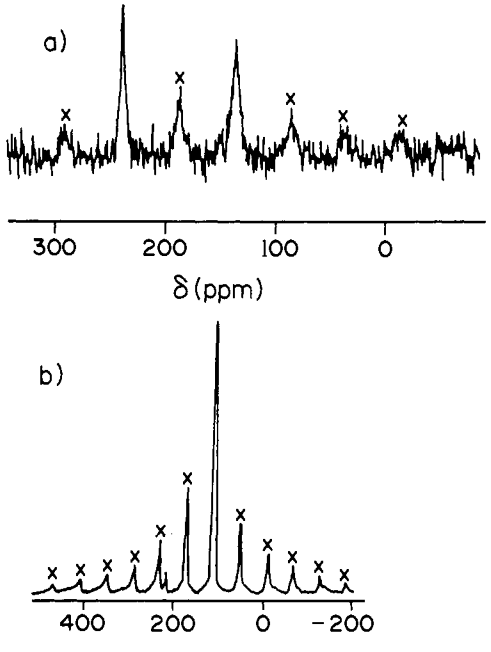

Figure 1. ^{133}Cs MAS–NMR spectra of two samples prepared from cesium metal and cryptand[2.2.2]: (a) sample from Cs-rich solution, rapidly precipitated, measured at 8.4 T; (b) sample from C222-rich solution, slowly precipiated, measured at 11.7 T. Peaks marked × are spinning sidebands.

MAS–NMR of $Cs^+C222\cdot e^-$. In contrast to the rich variety of alkalide and electride salts that contain sandwich complexes of Cs^+ with crown ethers, no heteronuclear compounds have yet been isolated with the Cs^+C222 cation. Indeed, until recently, when the structure of a crystal of the ceside, $Cs^+C222\cdot Cs^-$, was determined by X-ray diffraction,[32] it was thought that only electrides could be formed, regardless of the solution stoichiometry. The absence of the Cs^- NMR peak was taken as evidence that only electrides were present. The ^{133}Cs MAS–NMR spectra, as illustrated in Figure 1, showed two lines, whose relative intensities depended on the method of preparation of the sample. The two-peak spectrum is similar to the complex spectrum seen for mixtures of inclusive and exclusive $Cs^+C222\cdot SCN^-\cdot H_2O$.[25] The more paramagnetically shifted peak corresponds to the inclusive complex.

A sample that was prepared from cesium-rich mixtures of Cs and C222 had both peaks, with nearly the same intensities (Figure 1a), while cryptand-rich starting mixtures gave primarily the more diamagnetic peak (Figure 1b). The two peaks are attributed to the presence of both inclusive and exclusive complexes of the cation. The variation in relative intensities from one preparation to another suggests that polycrystalline samples contain mixtures of crystallites.

The recent identification of ceside crystals with inclusively trapped cesium cations, in preparations that were made in the same manner as the NMR samples,[32] indicates the need for caution in interpreting the behavior of polycrystalline samples. None of the samples showed the NMR signal of Cs^-. Similarly, samples known to contain Rb^- showed no ^{87}Rb signal.[21] We believe that the M^- NMR peaks in these compounds are broadened below the detection limit by strong interactions between adjacent alkali metal anions. In both the ceside and the rubidide neighboring anions are in contact.[32]

It is possible that mixtures of the inclusive ceside and the exclusive electride tend to precipitate from solution. Electron–electron interactions in electrides can be significant, so the diamagnetism of these samples does not preclude the presence of an electride. For example, LiC211 displays temperature-dependent

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spin pairing[34] below 50 K, while $K^+C222{\cdot}e^-$ has a weak "Curie tail" superimposed on a nearly temperature-independent paramagnetic electronic susceptibility.[35]

^{133}Cs MAS-NMR of $Cs^+(18C6)_2{\cdot}e^-$. The first reports of the synthesis and characterization of $Cs^+(18C6)_2{\cdot}e^-$ [22] emphasized the electronic nature of the compound. $Cs^+(18C6)_2{\cdot}e^-$ is a Curie–Weiss paramagnet which shows no magnetic ordering or spin pairing over the temperature range 1.5 to 250 K.[31] The dc conductivity indicates that the electride is a semiconductor with an intrinsic band gap of 0.9 eV; however, the conductivity at X-band microwave frequencies gives an apparent band gap of only ~0.1 eV.[31] The ^{133}Cs MAS-NMR was reported to consist of only one peak at +81 ppm. This paramagnetic shift from that of other $Cs^+(18C6)_2$ compounds could result from either a tighter coordination of the Cs^+ by the crown ethers, or from contact with the paramagnetic electron. NMR can be used to probe the interactions of the trapped electron with the complexed cation in the solid. Structural information now exists for $Cs^+(18C6)_2{\cdot}e^-$.[36] The electride features a cavity at each anionic site in the lattice, presumably occupied by a trapped electron. The electride is nearly isostructural with $Cs^+(18C6)_2{\cdot}Na^-$;[37] the mean Cs–O distance is 3.35 Å in each compound.

The origin of the paramagnetic chemical shift in $Cs^+(18C6)_2{\cdot}e^-$ is the Knight (or contact) shift. The Knight shift results from the strong local magnetic field generated at the nucleus of interest by paramagnetic electron density. The lowest energy unoccupied orbital in Cs^+ in the 6s orbital, which has a nonzero electron density at the nucleus, so that the cation should be very sensitive to any overlap with the paramagnetic trapped electron. The Knight shift is given by[38]

$$K(T) = (8\pi/3N_0)\langle|\psi(0)|^2\rangle\chi(T) \qquad (1)$$

where $\langle|\psi(0)|^2\rangle$ is the average electron density at the nucleus, $\chi(T)$ is the molar magnetic susceptibility, and N_0 is Avogadro's number. For a simple paramagnetic compound, $K(T)$ is proportional to $1/T$, since $\chi(T)$ varies inversely with temperature. Preliminary attempts to measure the chemical shift as a function of temperature revealed a strong variation of the chemical shift with temperature that was approximately proportional to $1/T$. Instrumental temperature control and measurement were poor, however, resulting in inconsistent values from one determination to another.

Measurement of the temperature of the spinning gas prior to its entry into the stator suffers from poor contact of the thermocouple with the gas so that poorly controlled parameters (i.e., flow rate, heat leaks) affect the temperature reading. A different method, devised by English,[39] was therefore used. This method takes advantage of the known temperature dependence of the dipolar splitting of the hydroxyl and methyl protons in methanol.[40] Over the range 220–330 K the splitting, $\Delta\nu$, of the two peaks at 180 MHz may be used to calculate the temperature, T, by

$$T = 435.5 - 0.398\Delta\nu - (3.25 \times 10^{-4})\Delta\nu^2 \qquad (2)$$

The method used to calculate the temperature of an electride sample was to alternately measure the proton splitting in methanol and the chemical shift of the electride at constant gas flow rates, and gas heater power. A value of the chemical shift of the electride was assumed to be at a known temperature if two alternate measurements of the proton splitting and the chemical shift remained constant. Four points measured in this way are shown in Figure 2. The chemical shift (in ppm) fits the equation

$$\sigma(T) = \sigma(\infty) + K(T) = -61 + (4.06 \times 10^4)/T \qquad (3)$$

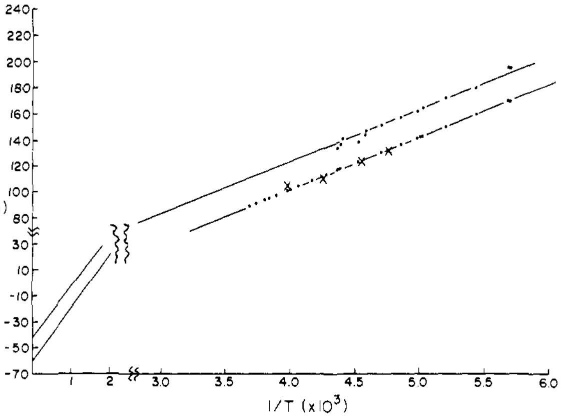

Figure 2. Chemical shift of $Cs^+(18C6)_2{\cdot}e^-$ vs. $1/T$. Temperatures were determined by calibration of the four points designated by the symbol ×. The other points on the lower line were constrained to lie on the least-squares straight line through the calibrated points.

Table III. Fractional Atomic Character of Some $Cs^+\cdots e^-$ Solutions and Solids

compound	electron density	F	ref
$Cs^0(g)$	2.645×10^{25}	1.00	41
Cs (metal)	1.56×10^{25}	0.59	
$Cs{:}NH_3$			
15 MPM	2.12×10^{24}	0.08	43
5 MPM	7.94×10^{23}	0.03	43
Cs:HMPA[a]			
solvated atom	1.93×10^{25}	0.73	41
expanded orbital	6.08×10^{22}	2.3×10^{-3}	41
Cs:MA[a] 273 K	7.42×10^{24}	0.05	41
Cs:EA[a] 273 K	5.03×10^{24}	0.19	41
Cs:iPA[a] 273 K	7.14×10^{24}	0.27	41
$Cs^+(18C6)_2{\cdot}e^-$	8.75×10^{21}	3.3×10^{-4}	this work

[a] Abbreviations used: HMPA, hexamethylphosphoric triamide; MA, methylamine; EA, ethylamine; iPA, isopropylamine.

The value of the chemical shift at infinite temperature [$\sigma(\infty) = -61 \pm 10$ ppm] is within experimental error of the chemical shift of $Cs^+(18C6)_2$ seen in alkalides. This result agrees with the structural data, since the complexed cations in $Cs^+(18C6)_2{\cdot}e^-$ and $Cs^+(18C6)_2{\cdot}Na^-$ have nearly identical structures.

The fractional atomic character of the trapped electron may be calculated from the magnetic susceptibility and the slope of the Knight shift vs. $1/T$. The electronic part of the magnetic susceptibility of $Cs^+(18C6)_2{\cdot}e^-$ at 250 K is $\chi_m^e = 1.37 \times 10^{-3}$ emu/mol. The fractional atomic character is defined as

$$F = \langle|\psi_0|^2\rangle / \langle|\psi_0|^2\rangle_{\mathrm{atom}} \qquad (4)$$

where $\langle|\psi_0|^2\rangle_{\mathrm{atom}}$, the electron density at the nucleus for an isolated gas atom, has been estimated to be 2.645×10^{25} e cm^{-3}.[41] The data given above yield $F = 3.3 \times 10^{-4}$ for $Cs^+(18C6)_2{\cdot}e^-$. Table III compares this value with that of other paramagnetic cesium-containing systems. Lelieur and Rigny measured both the magnetic susceptibilities[42] and the Knight shifts[43] of ammonia solutions and found that solutions containing 2 to 20 mol % cesium (MPM) had fractional atomic characters that ranged from 0.04 to 0.60. The overall electron density in the electride is 1.1×10^{21} e/cm^3 at 216 K, which is approximately the same as that of a 1.5 MPM solution of cesium in ammonia. Yet the contact density at the metal nucleus in the electride is much smaller than that in cesium solutions in ammonia, amines, and other solvents. Metal ions and solvated electrons in ammonia form loosely bound ion aggregates in the intermediate range of metal concentrations between 10^{-2} and 10^{-3} MPM, the majority of which are spin-paired and undetectable by magnetic resonance methods.[44] The para-

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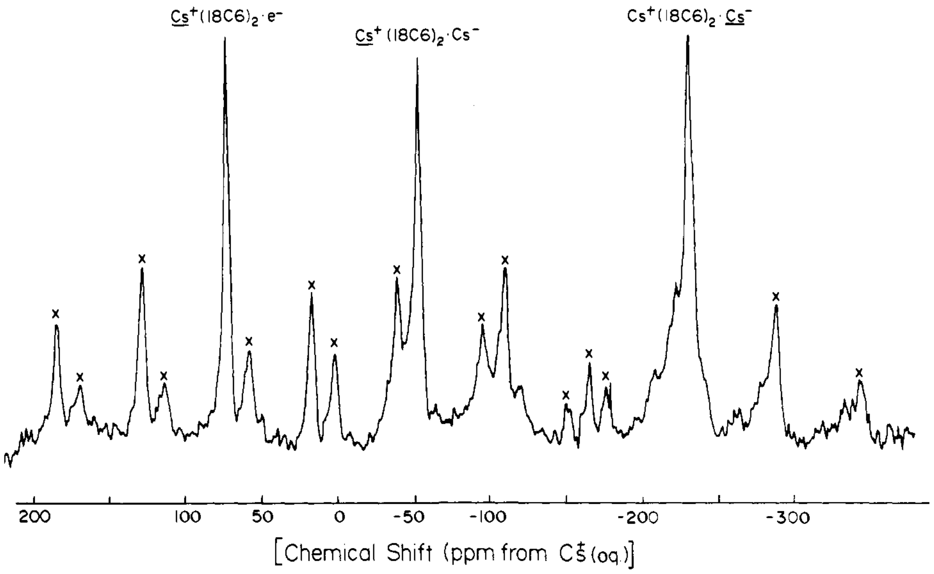

Figure 3. ^{133}Cs MAS–NMR spectrum of a sample precipitated from solution with a Cs:18C6 ratio of 2/3, showing the sample to be coprecipitated $Cs^+(18C6)_2 \cdot e^-$ and $Cs^+(18C6)_2 \cdot Cs^-$. Peaks marked × are spinning sidebands.

magnetic species that do exist are probably "solvent-shared" ion pairs, which consist of a solvated electron and a cation, each with their complete solvation shells.[44] The spin density at the nucleus in metal ammonia solutions between 10^{-2} and 1 MPM is nearly constant[45] with $F \approx 2 \times 10^{-3}$, nearly an order of magnitude higher than in the crystalline electride.

The effect of reducing the dielectric constant of the solvent is to create stronger interionic interactions, mediated by weaker solvent interactions so that paramagnetic ion pairs have more excess electron density at the nucleus, as indicated in Table III for solutions of cesium in methylamine (MA), ethylamine (EA), and isopropylamine (iPA). The contact interaction in frozen solutions of cesium in the highly polar solvent HMPA indicates a different type of excess electron character.[46] Two EPR signals are detected in these solids, one with high contact density at the cesium nucleus ($F \approx 0.73$) attributed to solvated cesium atoms, and the other with a much lower contact density ($F \approx 0.01$).[41] The electron in the low atomic character species was presumed to occupy a large hydrogenic wave function centered on the screened solvated cesium cation, but having very little Cs orbital character.[41]

The trapped electron in $Cs^+(18C6)_2 \cdot e^-$ has exceptionally low cesium s-orbital character relative to other electron–cesium systems. The cesium cation charge is apparently very well screened by its interaction with the crown ether oxygen lone pairs. A monomeric species, in a state similar to that described as the low s-orbital species of Cs/HMPA solutions,[41] might be invoked for the electride. The monomer in this case would have one electron in an extended orbital centered on each complexed cation. A major problem with this description of the crystal as a collection of "expanded atoms" is the observed weak electron–electron interactions. An alternative and better explanation of the low value of F is that the paramagnetic electron density is largely located in and around the anionic cavities, localized by the coulombic attraction to eight nearest-neighbor complexed cesium cations and perhaps by interaction with the adjacent $-CH_2-$ hydrogens. The electron density at each cesium nucleus would then be the sum of the weak interactions with the eight nearest trapped electrons. Studies of electrides doped with sodium anions, described below, favor the latter interpretation of the electronic state in $Cs^+(18C6)_2 \cdot e^-$.

The chemical shift data shown in Figure 2 include a number of points at temperatures that were not calibrated as described above. Rather, the temperature corresponding to each data point was estimated from the peak position so that the plot of $\sigma(T)$ vs. $1/T$ was contrained to be linear. At temperatures below 225 K the spectrum became more complex, in that a second peak, paramagnetically shifted from the original, appeared as a shoulder at ~225 K and increased in relative intesity as the temperature was decreased. The two peaks are separated by about 20 ppm and show a parallel temperature dependence. The increased paramagnetism does not necessarily signal increased electron density at the nucleus, but may instead be a measure of decreased Cs–O distances in the complexed cation. Extrapolation of the paramagnetic peak to infinite temperature gives a chemical shift of −40 ± 10 ppm, the same as that seen in low-temperature $Cs^+(18C6)_2 \cdot Cs^-$ salts. Apparently, at low temperatures, the complexed cation gradually shifts to a conformation that reduces the mean Cs–O distance. The transiton does not appear to be first order, and does not go to completion at the lowest temperature measured.

^{133}Cs MAS-NMR of Mixed Alkalide–Electride Salts. The similar nature of the complexed cation in various electrides and alkalides suggested that crystals of mixed stoichiometry might be prepared. Reduction of the trapped electron density by partial substitution of diamagnetic anions for anionic trapped electrons could significantly alter electron–electron interactions in these materials.

The preparation of mixed alkalide/electride materials was attempted by using two different alkali metal anions, Cs^- and Na^-, in the presence of $Cs^+(18C6)_2$ complexed cations, for several alkalide mole fractions, x. Figure 3 shows the ^{133}Cs MAS-NMR spectrum for a sample of overall stoichiometry $Cs^+(18C6)_2 \cdot Cs^-_{(0.5)}e^-_{(0.5)}$. The spectrum consists of three lines together with their spinning sidebands. The resonance positions are clearly those of the pure ceside ($\sigma = -50$ and -230 ppm) and the pure electride ($\sigma \approx 77$ ppm at 294 K). Several other samples resulted in similar spectra with only the relative intensities of the lines varying. These results demonstrate that doping electrons into the ceside lattice, or cesides into the electride lattice, is unfavorable. The anionic radius of each of these species has been determined;[32,36] the radius of the anionic cavity of the trapped electron in $Cs^+(18C6)_2 \cdot e^-$ is 2.2 Å whereas Cs^- has a radius of ~3.3 Å in $Cs^+(18C6)_2 \cdot Cs^-$. Lattices which are able to support each anion separately are, in this case, unable to coexist. Mixtures of pure electrides and pure alkalides were useful for establishing the temperature characteristics of the alkalide based on the known temperature dependence of the electride peak.

The ^{133}Cs MAS-NMR spectra of samples with overall stoichiometry $Cs^+(18C6)_2 \cdot Na^-_x e^-_{1-x}$ are shown in Figure 4, parts a and b, for $x = 0.2$ and 0.8, respectively. These spectra consist

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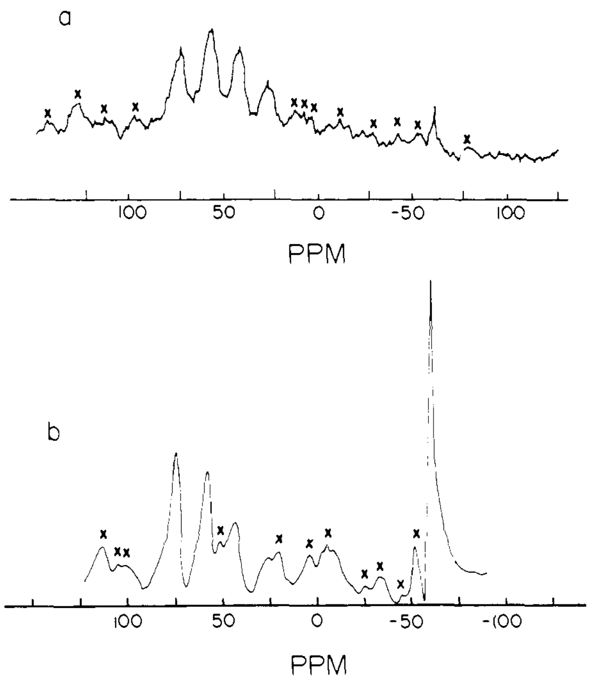

Figure 4. ^{133}Cs MAS NMR spectra of two samples precipitated from solutions of stoichiometry $Cs^+(18C6)_2 \cdot Na^-_x \cdot e^-_{1-x}$, with (a) $x = 0.20$ and (b) $x = 0.80$. Peaks marked × are spinning sidebands.

of five lines at -61, +26, +42, +57, and +73 ppm. The extreme peaks are due to $Cs^+(18C6)_2$ in the pure sodide (-61 ppm) and in the pure electride (+73 ppm). The three intermediate peaks are successively spaced by roughly $^1/_8$th of the distance between the peaks of Cs^+ in the pure electride and the pure sodide. Structural determinations of $Cs^+(18C6)_2 \cdot e^-$[36] and $Cs^+(18C6)_2 \cdot Na^-$[37] indicate that each complexed cation has eight nearest-neighbor anions. The four paramagnetically shifted peaks in the mixed system may thus be attributed to a complexed cation surrounded by eight, seven, six, and five electrons in order of decreasing shift; the remaining anionic sites are occupied by diamagnetic Na^- ions. There does not appear to be any tendency for appreciable doping of the sodide lattice with electrons.

The substitution of Na^- for e^- can occur because the crystal structures of $Cs^+(18C6)_2 \cdot e^-$ and $Cs^+(18C6)_2 \cdot Na^-$ are nearly identical.[36,37] In the monoclinic space group $C2/c$, the parameters of the unit cell of the electride are $a = 13.075$, $b = 15.840$, and $c = 17.359$ Å; $\beta = 92.30°$. The sodide has unit cell parameters $a = 13.581$, $b = 15.684$, $c = 17.429$ Å; $\beta = 93.16°$. The anionic cavity in the sodide is slightly larger in the a–b plane than is the anionic cavity in the electride, resulting in interanionic distances that are 0.1 Å longer in a–b planes, (10.37 Å in the sodide, 10.27 Å in the electride). The cavities in each structure are separated by ~8.7 Å in the c direction. The effect of inserting a sodium anion into the cavity in the electride lattice might be to distort the eight nearest complexed cations away from their equilibrium positions. The cavity sizes suggest that the distortion would have primarily an a–b component so that anionic sites along the c direction from the first impurity center should be better able to include additional sodium anions, possibly leading to chains of Na^- ions along the c direction. The NMR spectra can be accounted for[48] by postulating a regular superlattice in which $^1/_8$th of the electrons are replaced by Na^- ions. There is, however, no crystallographic evidence for such regular substitution.

The temperature dependence of one sample of $Cs^+(18C6)_2 \cdot Na^-_x \cdot e^-_{1-x}$ was measured over the range 190 to 255 K. The spectrum was very noisy so that uncertainties in the chemical shift are as large as ±5 ppm. The most paramagnetic peak was assumed to be the resonance of the complexed cation surrounded by eight trapped electrons (or the "pure" electride). The temperature of the sample was calculated from the chemical shift of the pure electride peak by using the established Knight shift parameters. The temperature dependence of each of the peaks corresponding to complexed Cs^+ surrounded by both sodium anions and trapped electrons was measured and fit to the Knight equation, $\sigma(T) = \sigma(\infty) + m/T$. The intercepts were within experimental error of those of the pure sodide and the pure electride. The slope is a measure of the paramagnetic electron density at the cesium nucleus. The peak that corresponds to the doped electride with one sodium anion adjacent to Cs^+ has a slope that is ~85% of the slope for the pure electride; the next peak, with two sodide ions contributing continues the trend with a slope ~70% of that of the pure electride. In the case of the least diamagnetic peak, with three Na^- ions in the anionic sites around a complexed Cs^+ cation, it was difficult to determine accurate values of the chemical shift. The slope indicates that the electron density at Cs^+ for this case is between 45 and 75% of that of the pure electride, depending on whether $\sigma(\infty)$ was fixed or allowed to vary.

Conclusions

^{133}Cs MAS-NMR is a powerful tool for the determination of cationic and anionic species in alkalide salts. Multinuclear NMR techniques can generally be used to fully characterize the stoichiometry of an electride or an alkalide. Moreover, the resonance position in ^{133}Cs NMR may be used as a sensitive probe of local structure about the cesium ion and for the study of interionic interactions. Changes in the Cs–O distances in cesium–crown ether or cryptand complexes brought about by phase transitions, or by changes in the anionic constituent or the temperature, can be monitored by the empirical observation that the paramagnetic Ramsey shift has an inverse relationship to r_{Cs-O}. The resonance position of the Cs^- ion is also sensitive to the size of its anionic cavity. The presence of low-lying excited states apparently causes the resonance position of Cs^- to be paramagnetically shifted from the pure s-state anion. This Ramsey shift is stronger for cavities which are smaller, or which favor a nonspherical anion.

Finally, the NMR data, in combination with structural data on $Cs^+(18C6)_2 \cdot e^-$, may be used to define the nature of the trapped electron. The structure clearly indicates that anionic cavities exist in the lattice in which the electron could be localized by Coulombic attractions to the surrounding cations. The cavity distribution is nearly identical with the distribution of Na^- sites in the salt $Cs^+(18C6)_2 \cdot Na^-$. The trapped electrons interact only very weakly with each other, as evidenced by the absence of any spin pairing or magnetic ordering. They also show only weak overlap with the complexed cations, as evidenced by the very small Knight shift. Further, the mixed alkalide–electride work shows that the interaction of each electron with nearby cations is spread over all of the cations, not just one of them. The electride described here is only one of a growing class of compounds that display rather diverse properties. The strength of electron–electron and electron–cation interactions in other electride systems is of great interest. Undoubtedly solid-state NMR will play a major role in determining the nature of these interactions.

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Registry No. $CS^+(18C6)_2 \cdot Na^-0$, 102086-00-0; $CS^+(18C6)_2 \cdot K^-$, 98481-67-5; $CS^+(18C6)_2 \cdot Rb^-$, 96503-67-2; $CS^+(18C6)_2 \cdot Cs^-$, 87039-74-5; $CS^+(15C5)_2 \cdot Na^-$, 108036-58-4; $Cs^+(15C5)_2 \cdot K^-$, 98481-66-4; $CS^+(15C5)_2 \cdot Rb^-$, 99582-52-2; $CS^+C222 \cdot e^-$, 108036-59-5.

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