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A High-Resolution Solid-State ^{23}Na NMR Study of Sodium Complexes with Solvents, Small Ligand Molecules, and Ionophores. ^{23}Na Chemical Shifts as Means for Identification and Characterization of Ion-Ion, Ion-Solvent, and Ion-Ligand Interactions

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We have recorded static and magic angle spinning (MAS) ^{23}Na NMR spectra of a variety of inorganic salts, solvent complexes, and complexes with small ligand molecules and ionophores in the solid state, in order to obtain the ^{23}Na chemical shifts of the ion-ion, ion-solvent, and ion-ligand interactions, respectively. In all cases, MAS resulted in considerable reduction of the linewidths. The observed ^{23}Na chemical shifts were corrected by subtracting the displacements by the quadrupole interaction when the quadrupole coupling constants cannot be ignored. We found that the range of the ^{23}Na chemical shifts found in the solid state is about 60 ppm and the ^{23}Na chemical shift of $NaBPh_4$ appears at the highermost region (−52 ppm). The ^{23}Na NMR chemical shifts of these complexes exhibited their characteristic peak positions, depending on variety of ligand molecules (H_2O, ether, or carbonyl) and Na–O interatomic distances but independent of the type of counterion. Finally, an attempt was made to relate the ^{23}Na chemical shifts to the magnitude of electron transfer from the ligand molecules to 3p orbital of Na^+ ion, by means of an ab initio molecular orbital method.

In recent years, coordination chemistry of alkali and alkaline earth metal ions has gained much interest in relation to understanding the vital role of these metal ions in biological systems and the manner of their specific interaction with naturally occurring ionophores or synthetic analogues such as crown ethers and cryptands.[1] As an excellent means of probing the behavior of the sodium ion in particular, high resolution ^{23}Na NMR spectroscopy has been extensively utilized to analyze the ion–ion, ion–solvent, and ion–ligand interactions in the solution state.[2–16] These ^{23}Na signals, however, cannot be observed separately but are seen as time-averaged single peaks due to rapid chemical exchange processes among several kinds of such short-lived species. Separate ^{23}Na NMR signals of free and complexed states were observed only when BPh_4 was used as a counterion stabilized as a solvent-separated ion pair[8] in solution or ligands of higher association constant such as cryptands were used.[10,12–16]

By contrast, it is expected that high-resolution ^{23}Na NMR studies in the solid state could provide unambiguous ^{23}Na chemical shifts of the individual species of the ion–ion, ion–solvent, and ion–ligand interactions, being free from interference due to chemical exchange processes as encountered in solution state. Undoubtedly, the collection of such data is invaluable because these parameters can be readily used as a diagnostic tool as well as reference data for the interpretation of solution ^{23}Na NMR studies. In addition, these data are very useful as viewed from the theoretical interpretation of the ^{23}Na chemical shifts in terms of electronic structures, because detailed molecular parameters are available from X ray diffraction studies. The displacement of the ^{23}Na chemical shifts was previously interpreted in terms of electron transfer from electron donors such as solvents to the 3p orbital of the Na^+ ion.[17] No detailed study, however, has been done as to the extent of such electron transfer to be compared with the experimental data.

For this purpose, it is known that magic angle spinning (MAS) can be effectively utilized for line-narrowing of the central $1/2 \leftrightarrow -1/2$ transition of quadrupolar nuclei with spin number of half-integer such as ^{23}Na in the solid state, if the line-splitting of the central line by the second-order quadrupole interaction can be neglected.[18] Otherwise, rapid sample spinning about an axis other than the magic angle is more favorable for line-narrowing.[19] In the present paper, we aimed to record ^{23}Na MAS NMR spectra of a number of inorganic salts,[20] solid solvent complexes, and complexes with small ligand molecules or ionophores, to obtain the ^{23}Na chemical shifts of the individual ion–ion, ion–solvent, and ion–ligand interactions, respectively. At the same time, static ^{23}Na NMR spectra were examined with the same samples to evaluate the quadrupole coupling constants, because the quadrupole interaction, if any, would cause the center of gravity in the ^{23}Na MAS NMR signals to shift upfield.[21]

Being consistent with our expectation, all samples studied here which possess octahedral or distorted octahedral arrangement of solvents or ligands gave single resonance lines because of negligible contribution of the quadrupole interaction, although correction of the ^{23}Na chemical shifts by the quadrupole interaction was necessary for crystals of inorganic salts such as rhombohedral, monoclinic and tetragonal structures. Interestingly, the range of the ^{23}Na chemical shifts in the solid state is about 60 ppm and the ^{23}Na NMR signal of $NaBPh_4$ is resonated at the highermost position (−52 ppm) which is very close to the data of the Na^- anion. In addition, the ^{23}Na chemical shifts of a variety of sodium complexes are varied significantly with type of ligand molecules (H_2O, ether or carbonyl group) and stereochemistry of these complexes including the Na–O distances as the most important parameter. Qualitatively, it appears that the extent of electron transfer from the ligand molecules to Na^+ ion, as evaluated by an ab initio molecular orbital method with 6—31 G basis set, is in parallel with the displacement of ^{23}Na chemical shifts.

Experimental

Materials. Inorganic salts were of reagent grade and were used without further purification. The following sodium complexes were purchased from commercial sources: $Na_2SO_4 \cdot 10H_2O$ (Kanto Chemical Inc., Tokyo), sodium deoxyadenosine 5′-monophosphate hexahydrate (Na dAMP$\cdot 6H_2O$, Sigma Chemical Company, MI, USA), $Na_2HAsO_4 \cdot 7H_2O$, $Na(CH_3COO) \cdot 3H_2O$ (Wako Chemicals, Osaka), and trisodium nitrilotriacetate hydrate, sodium L-ascorbate and sodium D-isoascorbate hydrate (Tokyo Kasei Kogyo, Co. Ltd., Tokyo). These complexes were recrystallized from aqueous solution.

Solvent complexes of the Na ions with 1,4-dioxane,[22] methanol,[23] acetone,[24] and *N,N*-dimethylformamide[25] were prepared by the procedure described in the literatures. The sodium complexes with 1,4-dioxane are efflorescent and easily turn into anhydrous powder. By contrast, the complexes with methanol, acetone or *N,N*-dimethylformamide were decomposed very rapidly in air because of lower melting points (25—27°). Accordingly, several kinds of preparations were used to achieve unambiguous assignment of ^{23}Na signals whose relative peak-intensities were varied from sample to sample. For example, the following three kinds of samples were prepared for the complexes of $NaClO_4$ with 1,4-dioxane. $NaClO_4$ dissolved in small amount of water was mixed with 1,4-dioxane (mole ratio 1:3) and allowed to evaporate in air. After separation from solution, sample 3 was obtained by placing the colorless crystals thus obtained in vacuo for 3 h. Plate-shaped crystals were obtained by heating the above-mentioned crystals up to 60° and were allowed to evaporate in air. Sample 1 was obtained by blotting the crystals with a filter paper. Sample 2 was obtained by placing the sample in vacuo for 3 h.

(Ethylene glycol)(1-phenyl-1,3-butanedionato)sodium was obtained from ethanol solution containing sodium 1-phenyl-1,3-butanedionate and 4% ethylene glycol and was crystallized from toluene solution.[26] Glycine–sodium iodide–water (2/1/1) was obtained as crystal from aqueous solution containing glycine and NaI (mole ratio 2:1).[27] In a similar manner, triethanolamine–sodium iodide (1/1) was crystallized from methanol–1-butanol solution containing equimolecular amount of individual components.[28] A solution of acetic acid and half an equivalent of sodium hydroxide in water was allowed to evaporate to give crystals of $NaH(CH_3COO)_2$.[29]

Sodium complexes of valinomycin (Sigma Chemical Company, MI, U.S.A), nonactin (Boehringer-Manheim GmbH, Germany) and tetranactin (Chugai Pharmaceutical Co. Ltd., Tokyo) were obtained from ethyl acetate solution containing 10% excess NaSCN.[30] Complex formation was confirmed by the characteristic change of the ^{13}C chemical shifts in the solid state as determined by cross polarization-magic angle spinning (CP-MAS) NMR.[30,31] Monensin (Na salt) and lasalocid (Na salt) were purchased from Sigma Chemical Company, MI, U.S.A. These compounds were recrystallized from diethyl ether-petroleum ether (1:1) containing small amount of acetone or methanol.

Cryptands [2.2.2], [2.2.1], and [2.2] were purchased from Merck Chemical Company, Germany. 18-Crown-6 was purchased from Aldrich Chemical Company, WI, U.S.A. Sodium complexes with these ligands were prepared by dissolving in methanol, which was allowed to evaporate in air.[32] Complex formation was checked by examination of the ^{13}C CP-MAS NMR spectra.[32]

^{23}Na NMR Spectra. ^{23}Na MAS NMR spectra were recorded on a Bruker CXP-300 spectrometer operating at 79.35 MHz with a Z32DR MAS probe. Solid samples were contained in an Andrew–Beams type rotor machined from Delrin and spun as fast as 2—3 kHz by compressed air. Spectra were accumulated usually less than 200 times. Spectral width was 30 kHz and data points were 4 K. 90° pulse and repetition time were 6 μs and 2 s, respectively. ^{23}Na chemical shifts were referred to the signal of 1 M NaCl in aqueous solution (1 M=1 mol dm^{-3}).

Static ^{23}Na NMR spectra were recorded on the same spectrometer with a Z32vHP high power probe. The spectral width used was up to 500 kHz with 2 K data points. The quadrupole coupling constant was evaluated from the displacement of the satellite lines caused by the first-order (f.o.) quadrupole interaction or from the second-order (s.o.) splitting of the central line.[33]

Ab Initio Molecular Orbital Calculation. We calculated the electronic energies and electron densities of sodium complexes either with solvent molecules or ionophores as a function of the Na–O distance (*R*), by an ab initio molecular orbital method utilizing the IMSPACK program system[34] with a 6—31 G basis set.[35] As a geometry of complex,[36] we postulated an octahedral arrangment of six H_2O or six $H_2C{=}O$ molecules around the central Na^+ ion, representing also an ether (OH) or a carbonyl moiety of these ligand molecules, respectively. For comparison, we also calculated the electronic structure of some sodium complexes containing a single H_2O molecule having various orientations with respect to the sodium ion.

Results

Inorganic Salts. Figure 1 illustrates a typical example of the static ^{23}Na NMR spectrum of $NaClO_3$ in the solid state. The quadrupole coupling constant (e^2qQ/h) 785±2 kHz was readily evaluated either by the

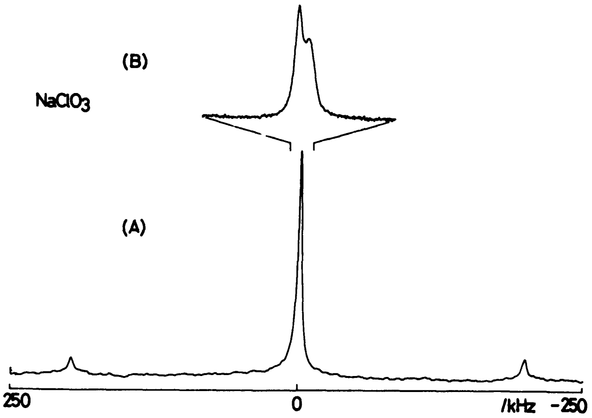

Fig. 1. 79.35 MHz static ^{23}Na NMR spectra of $NaClO_3$ in the solid state. (A) first-order split peaks (197 kHz from the central peak), spectral width 500 kHz. (B) second-order split central peaks (1.01 kHz), spectral width 20 kHz.

Table 1. ^{23}Na Chemical Shifts of Some Inorganic Salts in the Solid State (ppm from 1 M NaCl Soln)

	Static		MAS (ppm)			
	Type of spectrum[a]	$\frac{e^2qQ}{h}$ (kHz)	Obsd chemical shifts	Correction of chemical shifts by quadrupole interaction[b]	Corrected chemical shifts	Crystal structure
NaF	s	0	7.9±6	0	7.9±6	Cubic
NaCl	s	0	7.9±0.3	0	7.9±0.3	Cubic
NaBr	s	0	6.0±0.3	0	6.0±0.3	Cubic
NaHCOO	s	0	−0.2±0.7	0	−0.2±0.7	
NaB[C_6H_4F(p-)]	s	0	−0.5±0.3	0	−0.5±0.3	
$NaBiO_3$	s	0	−0.8±1.3	0	−0.8±1.3	
NaSCN	s	0	−2.1±0.6	0	−2.1±0.6	
NaI	s	0	−2.7±0.4	0	−2.7±0.4	Cubic
NaN_3	f.o.	286±2	−3.5±0.3	0.3	−3.2±0.3	Rhombohedral
$NaHCO_3$	s.o.	700±10	−5.4±0.6	1.9±0.1	−3.5±0.7	Monoclinic
$NaClO_3$	f.o./s.o.	785±2	−6.5±0.6	2.4	−4.1±0.6	
$NaNO_3$	f.o.	332±2	−7.3±0.2	0.4	−6.9±0.2	Rhombohedral
$NaBH_4$	s	0	−8.5±1.7	0	−8.5±1.7	Cubic
$NaIO_4$	f.o.	47±2	−12.5±0.4	0.02	−12.5±0.4	Tetragonal
$NaClO_4$	o	0	−20.0±0.5	0	−20.0±0.5	Tetragonal
$NaBF_4$	s.o.	1200±100	−24.8±1.2	5.7±1	−19.1±2.5	Tetragonal
$NaBPh_4$	s	0	−51.7±1.6	0	−51.7±1.6	

a) s stands for single line; f.o. stands for the first-order split signal; s.o. stands for the second-order split central peak.
b) Estimated errors smaller than 0.1 ppm are not shown.

first-order or second-order quadrupole-split peaks.[33] The quadrupole coupling constants thus obtained are summarized in Table 1, although type of spectrum designated by s gave single lines without quadrupole interaction. In all cases, it was found that these static ^{23}Na NMR spectra were analyzed as being due to a symmetrical field gradient (η=0). In fact, the asymmetry parameter of $NaNO_3$ was reported to be exactly zero[37] and that of $NaBF_4$ was assumed to be negligible.[38] High resolution ^{23}Na MAS NMR spectra were obtained by MAS experiments which resulted in a considerable reduction of the linewidths.[39] The ^{23}Na chemical shifts are summarized in Table 1. The upfield displacements of the ^{23}Na signals by the quadrupole interaction were corrected by the following formula given by Lippmaa and coworkers.[21]

$$\delta = \frac{1}{40}(e^2qQ/h)^2/\omega_L \qquad (1)$$

where ω_L stands for the Larmor frequency.

Solvent Complexes. Table 2 summarizes the ^{23}Na chemical shifts of a variety of solid solvent complexes, together with their bonding features as revealed by X-ray diffraction studies.[22–25,40–43] The static ^{23}Na NMR studies showed that all of these compounds gave single resonance lines, consistent with X-ray diffraction data in which solvent molecules such as H_2O, methanol, acetone, etc. are coordinated to the central sodium ions as an octahedral or a nearly octahedral arrangement.[22–25,40–43]

Figure 2 illustrates the ^{23}Na MAS NMR spectra of some sodium complexes with 1,4-dioxane. Many of

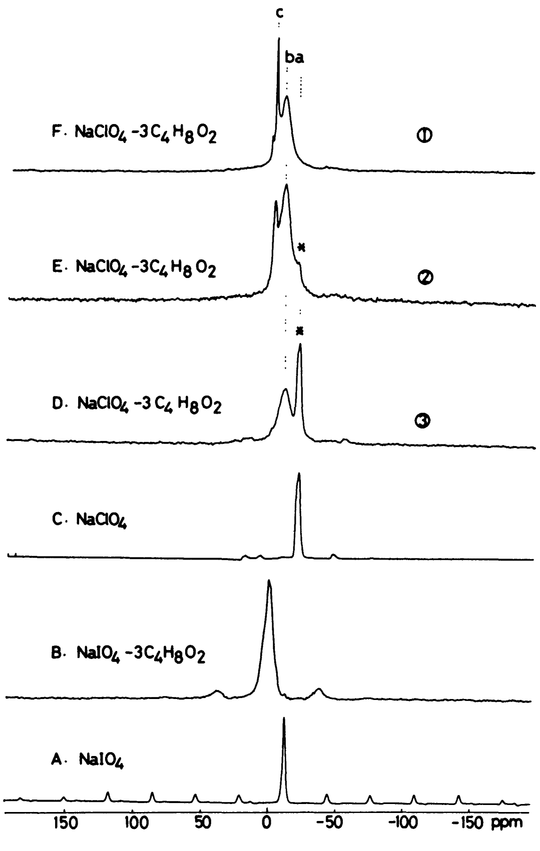

Fig. 2. 79.35 MHz MAS ^{23}Na NMR spectra of the sodium complexes ($NaClO_4$ and $NaIO_4$) with 1,4-dioxane. ①, ②, and ③ in Figure 2D-F stand for the sample number described in the text. The peaks asterisked arose from uncomplexed inorganic salts present in these complexes.

Table 2. ^{23}Na Chemical Shifts of Sodium Ions in Solvent Complexes, Complexes with Small Ligand Molecules and Complexes with Ionophores (ppm from 1 M NaCl Soln.)

	Static		MAS		Bonding features			
	Type of spectrum[a]	$\frac{e^2qQ}{h}$ (kHz)	Chemical shifts	Correction of chemical shifts by quadrupole interaction	Type of ligands[b]	Bond distance (Na–O, Å)	Coordination number	Ref
A. Solvent complexes								
$Na_2SO_4 \cdot 10H_2O$	s	0	2.3±1.5	0	H_2O	av. 2.43	6(Octahedral)	40
$Na_2HAsO_4 \cdot 7H_2O$	s	0	1.0±1.5	0	H_2O	2.35—2.48	6(Octahedral)	41
$NadAMP \cdot 6H_2O$	s	0	1.9±1.3	0	H_2O	2.37—2.45	6(Nearly octahedral)	42
$Na(CH_3COO) \cdot 3H_2O$	s	0	−0.2±1.7	0	$5H_2O$, COO	2.35—2.56	6(Distorted octahedral)	43
$NaI \cdot 3CH_3OH$	s	0	−2.9±0.4	0	CH_3OH	av. 2.47	6(Octahedral)	23
$NaClO_4 \cdot 3DX$	s	0	−11.3±1.5	0	DX	av. 2.43	6(Elongated octahedral)	22
$NaIO_4 \cdot 3DX$	s	0	−1.2±1.0	0	DX			
$NaBF_4 \cdot 3DX$	s	0	−11.6±1.6	0	DX	av. 2.43	6	22
$NaI \cdot 3DX$	s	0	−9.4±1.6	0	DX	av. 2.43	6	22
$NaSCN \cdot 3DX$	s	0	−10.0±1.0	0	DX			
$NaI \cdot 3DMF$	s	0	−11.7±1.0	0	DMF	av. 2.40	6(in between trigonal prism and octahedral)	25
$NaI \cdot 3(CH_3)_2C{=}O$	s	0	−6.2±0.9	0	$(CH_3)_2C{=}O$	av. 2.46	6(Octahedral)	24
B. Complexes with small ligands								
(Ethylene glycol)(1-phenyl-1,3-butanedionate)sodium	s	0	−8.7±2.8	0	3C=O, 2OH	2.29—2.36, 2.32—2.33	5(Tetragonal pyramid)	26
Trisodium nitrilotriacetate hydrate	s	0	−8.7±0.4	0	COO, H_2O	2.28—2.67	6(Distorted octahedron)	44
Sodium L-ascorbate	s	0	−9.6±1.9	0	4OH, C=O ether	2.42—2.72	6(Distorted octahedron)	45
Sodium D-isoascorbate hydrate	s	0	−0.6±1.5	0	3OH, 2 ether H_2O	2.30—2.39	6(Distorted octahedron)	46
$NaI\ 2(NH_2CH_2COOH)H_2O$	s	0	0.4±0.2	0	COO, H_2O	2.32—2.64	6(Octahedral)	27
$NaI\ N(CH_2CH_2OH)_3$	f.o.	464	−3.8±1.9	0.9	OH	2.45—2.62	7(Irregular)	28
$NaH(CH_3COO)_2$	s	0	−0.6±0.9	0	COO	2.40—2.44	6(Trigonal prism)	29
C. Ionophores								
NaSCN-valinomycin	s	0	−23.3±4.7	0	C=O	2.69—2.83[c]	6(Octahedral)	47
NaSCN-nonactin	s	0	−18.2±1.0	0	C=O, ether	2.36—2.80	8(Distorted cubic)	48
NaSCN-tetranactin	s	0	−24.0±1.2	0	C=O, ether	2.43—2.95	8(Distorted cubic)	49
Lasalocid	s	0	−11.6±3.3	0	Ether	2.28—2.77	6(Monocapped pentagon)	50
Monensin	s	0	−14.2±3.4	0	Ether	2.35—2.52	6(Distorted octahedron)	51
NaSCN-[2.2.1]	s	0	−16.4±2.8	0	Ether	2.45—2.52	7	52
NaI-[2.2.2]	s	0	−16.2±1.7	0	Ether	2.57—2.58	8	53
NaSCN-[2.2]	s	0	−18.3±3.5	0	Ether		7	
NaSCN-18-crown-6	s	0	−16.0±0.9	0	Ether	2.45—2.62	7(Distorted pentagonal bipyramid)	54

a) s stands for single line; f.o. stands for the first-order split signal. respectively. b) DX and DMF stand for 1,4-dioxane and *N,N*-dimethylformamide. c) Data from potassium complex.

these complexes are efflorescent. In fact, the ^{23}Na MAS NMR spectra of $NaClO_4$–$3C_4H_8O_2$ complex gave three kinds of peaks whose relative peak intensities are significantly varied among three kinds of preparations (Figure 2D—F). The peak a is readily ascribed to the ^{23}Na NMR peak of uncomplexed $NaClO_4$, as compared with the peak position of $NaClO_4$ crystal (Fig. 2C). The peak c is assigned to the presence of Na^+ ion dissolved in a concentrated solution, because this peak is visible only for samples containing a wet fraction. In addition, it is emphasized that this sharp signal is still present in the static ^{23}Na NMR spectra. Accordingly, the peak b is unambiguously ascribed to the Na^+ ions complexed with 1,4-dioxane. By contrast, $NaIO_4$–$3C_4H_8O_2$ complex gave no residual peaks corresponding to the peaks a and c of $NaClO_4$–$3C_4H_8O_2$ complex (Fig. 2B). It is noteworthy that the ^{23}Na chemical shifts of these complexes are significantly displaced as compared with those of uncomplexed inorganic salts (Table 2).

Complexes with Small Ligand Molecules. In contrast to the cases of the solvent complexes described above, the sodium ions of the present complexes are coordinated to hydroxyl, carbonyl or ether moieties of small ligand molecules. The electric field gradient around the sodium ions is virtually zero as viewed from the appearance of single lines in the static ^{23}Na NMR, except for the case of 2-aminoethanol–sodium iodide(1/1) in spite of different type of oxygens around the sodium ions. For the latter, the bonding feature is that of an irregular geometry of 7 coordination which would cause non-zero quadrupole coupling constant (see Table 2).[28]

Complexes with Ionophores. Figure 3 illustrates the ^{23}Na MAS NMR spectra of crystalline sodium complexes with a variety of naturally occurring ionophores whose chemical structures differ substantially among them (see Fig. 4, for chemical structure[55]). Clearly, the ^{23}Na NMR signals of NaSCN complexes of nonactin, tetranactin, and valinomycin were displaced upfield by 16, 22, and 21 ppm, respectively, upon complex formation as compared with those of uncomplexed NaSCN, and the extent of the displacements

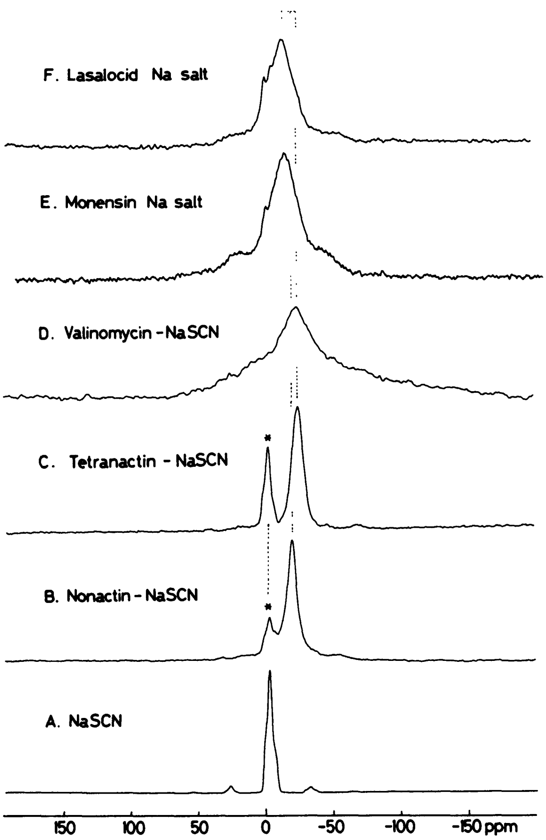

Fig. 3. 79.35 MHz MAS ^{23}Na NMR spectra of the sodium complexes with naturally occurring ionophores in the solid state. The peaks asterisked in Fig. 3B and C are from uncomplexed NaSCN.

of peaks in these cases is much larger than that of the solvent complexes described above (Table 2).

Figure 5 shows the ^{23}Na MAS NMR spectra of the sodium complexes with cryptands in the solid state (see Fig. 4). Again, it is clear that the ^{23}Na signals are displaced upfield by complexation with these cryptands and 18-crown-6 (spectrum not shown), consistent with the data of the naturally occurring ionophores (Table 2).

Ab Initio Calculation. Figure 6 summarizes the interaction energies and gross orbital charges of Na^+ ions complexed with H_2O or $H_2C{=}O$ molecules to form octahedra (a) and (b), respectively, or to form the plane (c). We consider the complexes (a) and (b) as models of the solvent complexes and complexes with ionophores, and the complex (c) as crown ethers. The total interaction energy (ΔE) was decomposed into the terms of polarization (PL), electrostatic (ES), charge transfer (CT), exchange (EX), and mixed term (mix) by the procedure of Morokuma et al.[56] Obviously, the interaction energy arises mainly from the electrostatic (ES) interaction and achieves the minimum value at about the Na–O distance of 2.4 Å, consistent with the experimental finding. The achieved stabilization energy increases in the following order: octahedral H_2CO<planar H_2O<octahedral H_2O. The largest amount of electron transfer from the ligand molecules to the 3p orbital of the Na^+ ion occurs at the bond length larger than 2.4 Å, and decreases with the following order: octahedral H_2O>octahedral $H_2C{=}O$>planar H_2O. Figure 7 summarizes the interaction energy and gross orbital charge of the Na^+ ion complexed with a H_2O molecule with various orientation. Similar results were obtained for the interaction with $H_2C{=}O$ molecule (data not shown).

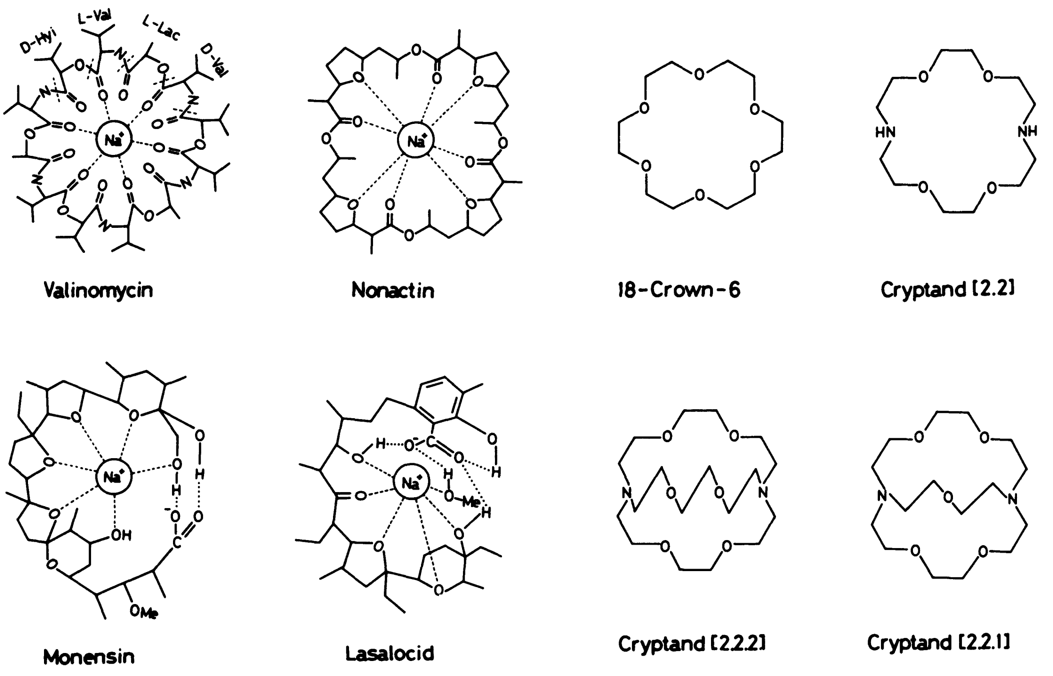

Fig. 4. Chemical structure of naturally occurring ionophores, 18-crown-6 and cryptands.

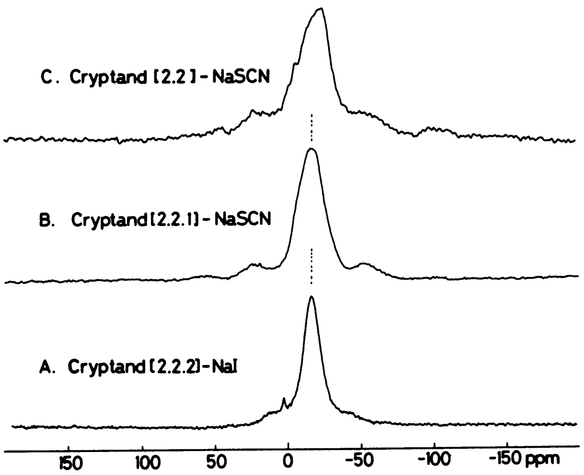

Fig. 5. 79.35 MHz ^{23}Na MAS NMR spectra of the sodium complexes with various types of cryptand molecules.

Discussion

Tables 1 and 2 show that the range of the ^{23}Na chemical shifts of inorganic salts and sodium complexes so far studied is about 60 ppm and these chemical shifts can be used as a diagnostic means of characterization of these compounds. These characteristic shifts, however, cannot be obtained by solution NMR spectra, because dissolution of these solid samples in solvents results in the disruption of the crystalline structure formed by ionic interactions.

It is noteworthy that the ^{23}Na NMR peak of $NaBPh_4$ resonates at −51.7 ppm (Table 1). This peak position is surprisingly high for a Na^+ ion. In contrast to Na^+ ions, the ^{23}Na chemical shift of Na^- ion is solvent-independent:[14–17] −61.9 ppm in $MeNH_2$, −61.8 ppm in 12-crown-4 and −63.1 ppm for the gas state. In

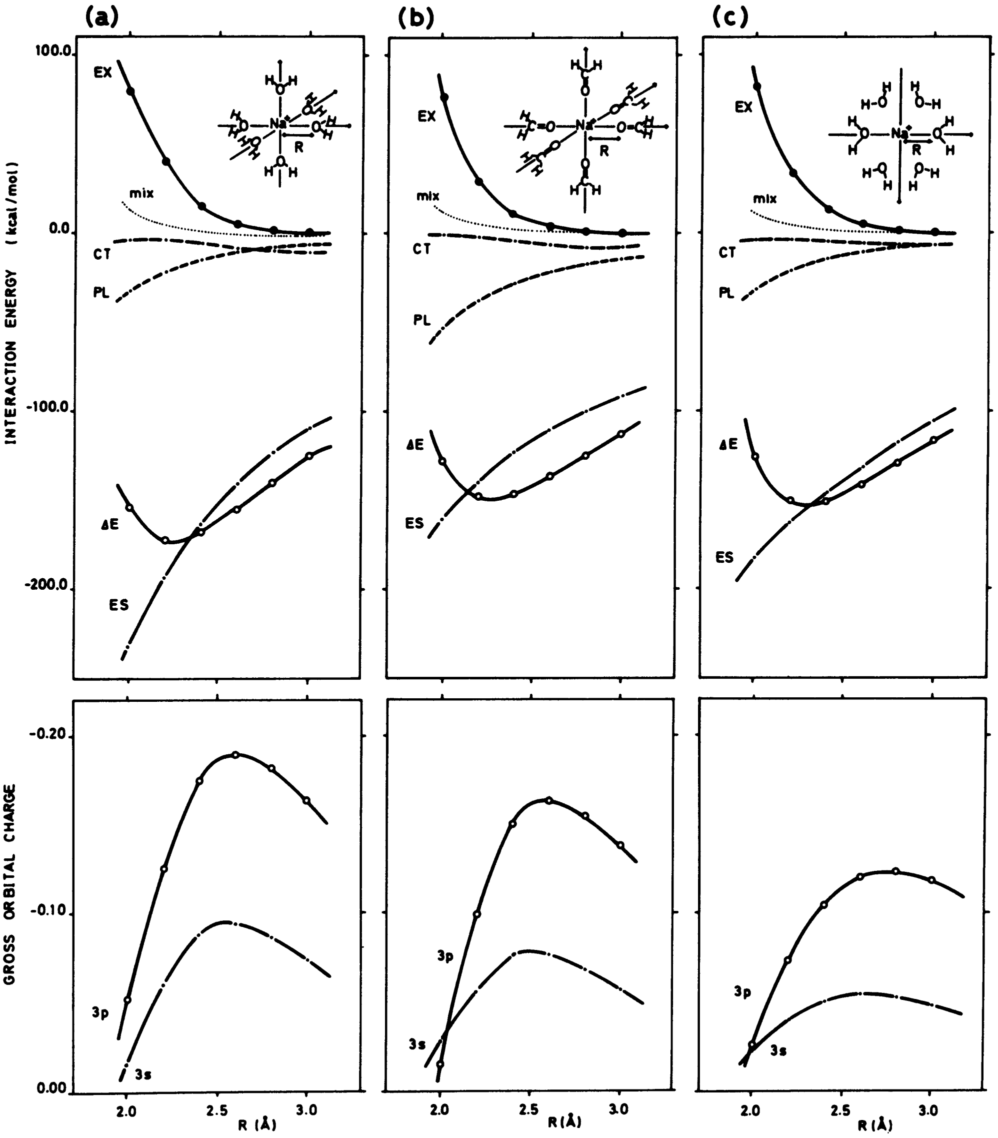

Fig. 6. The interaction energies and gross orbital charges of Na^+ ions complexed with H_2O and $H_2C{=}O$ molecules to form octahedron (a) and (b), respectively, or to form plane (c) as a function of the Na–O distance R (Å).

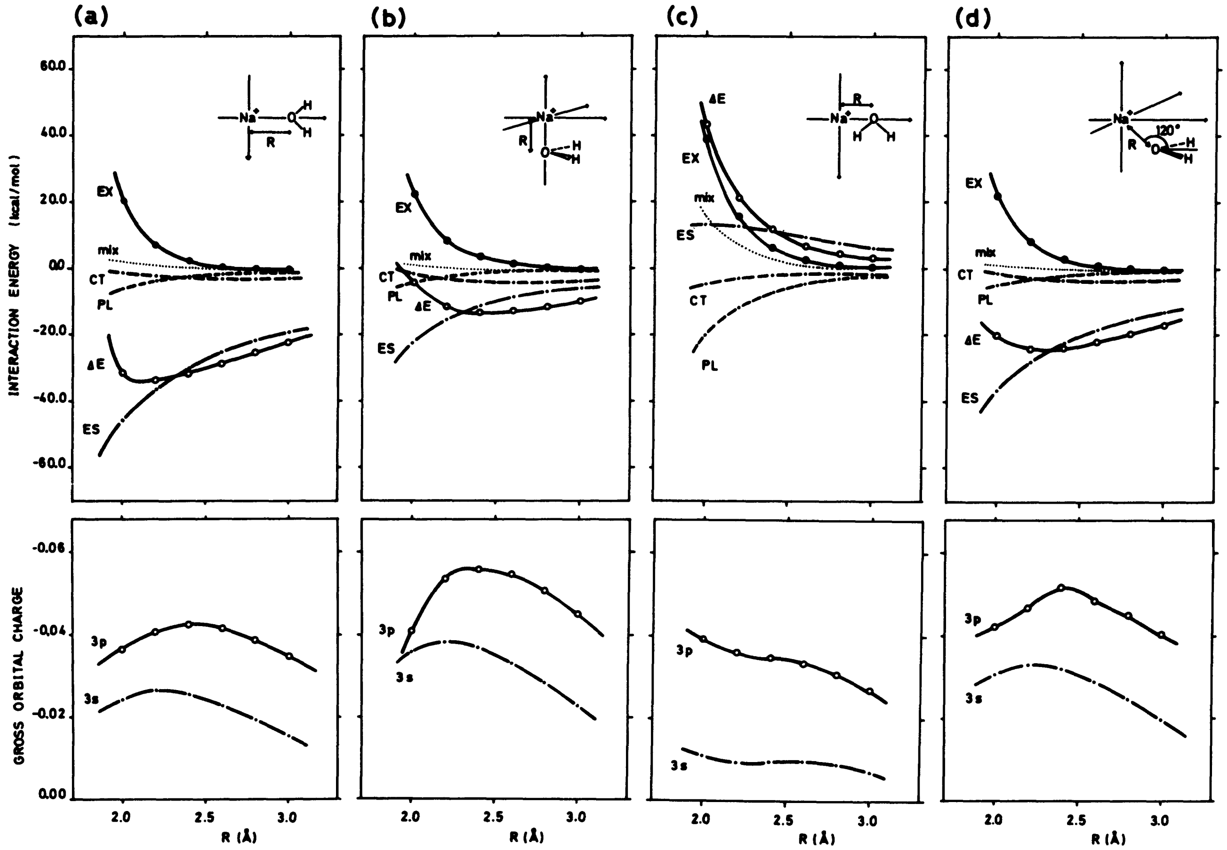

Fig. 7. The interaction energies and gross orbital charges of Na^+ ions complexed with a H_2O molecule with various orientation.

connection with this, Malli and Fraga⁵⁷⁾ showed that the changes in nuclear shielding constants of Na^-(gas) with respect to Na^+(gas) are relatively small, amounting to a shielding of only 7.7 ppm for the addition of two 3 s electrons to gaseous Na^+ to form Na^-(gas). Thus, it is possible to estimate the ^{23}Na chemical shift of Na^+(gas) as −55.4 ppm, on the basis of the data mentioned above. Accordingly, the electronic structure of the Na^+ cation in $NaBPh_4$ crystal seems to be very similar to that of the gaseous Na^+ ion, as manifested from a very small deshielding (+3 ppm). On the contrary, the large downfield shifts ($\approx$+60 ppm) of a number of inorganic salts could be interpreted in terms of a large paramagnetic shielding contribution due to the presence of the 3 p electron transferred from the counteranions, by analogy with the case of the ion-solvent interaction. As to the latter, the ^{23}Na chemical shifts can be correlated with the Gutmann donor strength of the solvents over a range of almost 20 ppm.⁵⁸⁾

In Figure 8, we summarized the range of the ^{23}Na chemical shifts of various sodium complexes as a function of the type of ligand molecule. For the complexes with mixed ligands, we plotted the range of the ^{23}Na chemical shifts by the type of ligands whose bonding numbers are larger than 3. In addition, we expressed the ^{23}Na chemical shifts of these complexes whose Na–O distances are in the normal range (2.3—2.5 Å) and are larger than this range by the thick and dotted lines, respectively. The following three features emerge from closer examination of Fig. 8 and Table 2.

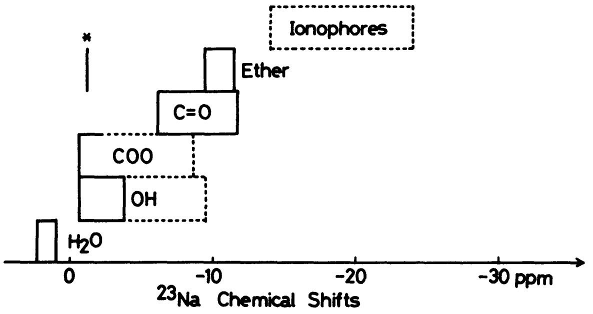

Fig. 8. Schematic representation of the displacements of the ^{23}Na chemical shifts as related to the type of ligand molecules. The data shown by the thick and dotted lines correspond with the complexes whose Na–O distance is in normal region (2.3—2.5 Å) and is larger than this range, respectively. The diagram asterisked arose from $NaIO_4$-$3C_4H_8O_2$ whose chemical shift is significantly lower than that of the other complexes indicated by the "ether".

First, the ^{23}Na chemical shifts of $Na_2SO_4 \cdot 10H_2O$, $Na_2HAsO_4 \cdot 7H_2O$, and NadAMP$\cdot 6H_2O$ are the same, 1.0—2.3 ppm, within the experimental error, regardless of the variety of the counter-anions. Further, the ^{23}Na chemical shifts of four sodium complexes ($NaClO_4$, $NaBF_4$, NaI, and NaSCN) with 1,4-dioxane are the same, regardless of the different kinds of counteranions. These findings are rationalized by assuming that the Na^+ ions of these complexes are complexed with six (octahedral) H_2O molecules with Na–OH_2 distance 2.35—2.48 Å for the former,[40—42] and are complexed by six dioxane molecules with an average Na–O distance of 2.43 Å for the latter.[22] Accordingly, the counteranions have no direct effect upon the ^{23}Na chemical shifts because they are not directly coordinated to the sodium ions. It is not clear, however, why the ^{23}Na signal of the $NaIO_4$ complex appears at such a surprisingly lower field (−2.9 ppm). It is probable that the Na–O distance of this crystal might be different from the others, although no X-ray diffraction study is available. In a similar manner, the ^{23}Na chemical shift of $Na(CH_3COO)3H_2O$ is very close to the value of the sodium ions coordinated by six aqua ligands, because the Na ion in this case is coordinated by five H_2O molecules and one COO moiety.

Second, the ^{23}Na NMR signals of sodium complexes coordinated to COO or OH groups apprears at almost the same position (or slightly at higher field by 1—2 ppm) as those of the sodium complexes with H_2O (see Fig. 8). On the contrary, the ^{23}Na chemical shifts are displaced upfield by 5—10 ppm when the sodium ions are complexed with ether or the C=O moieties of ligands. Third, the ^{23}Na chemical shifts are significantly displaced upfield when the Na–O distances of the complexes are increased, as encountered for a variety of complexes with ionophores whose size of cavity is more preferrable to cations of larger ionic radii like potassium ions. In addition, the observation of the ^{23}Na chemical shift of trisodium nitrilotriacetate hydrate at rather higher field (−8.7 ppm) as H_2O and COO ligands could be interpreted in terms of the presence of a longer Na–O distance as compared with that of the other complexes.

A theoretical interpretation of the chemical shifts for alkali halide crystals was successfully performed by Kondo and Yamashita[59] and Ikenbery and Das[60] who took into account the overlap between the np-orbital of the metal and the outermost s- and p-orbitals of the halide ions. This approach, however, is not convenient for our purpose, because we are mainly concerned with a relation between the ^{23}Na chemical shifts and the magnitude of electron transfer from the ligand molecules. Alternatively, Bloor and Kidd showed that the paramagnetic term of the ^{23}Na chemical shifts amounts to ca. −270 ppm per electron donated to a 3p orbital of the sodium atoms,[17] using Schneider and Buckingham's "atom in a molecule" method.[61] The calculated electron density of 3p orbital at R=2.5 Å is 0.19, 0.16, and 0.11 for the coordinations of octahedral six H_2O (a), octahedral six H_2C=O (b) and planar six H_2O (c) molecules, respectively, as illustrated in Fig. 6. The resultant ^{23}Na chemical shifts for the models (a), (b), and (c) are −4, −12, and −25 ppm, respectively, by taking into account the fact that the paramagnetic shielding constant for the cases (a), (b), and (c) are −51, −43, and −30 ppm, respectively, following the formula of Bloor and Kidd[17] and the ^{23}Na chemical shift of the gaseous Na^+ ion is estimated as −54 ppm when referred to 1 M NaCl, as described already. The calculated ^{23}Na chemical shifts thus obtained are in good agreement with the experimental data, if the models (a), (b), and (c) are considered as representing the sodium complexes with ligands of H_2O, acetone or DMF, and 18-crown-6, respectively. Obviously from the data of Fig. 6, the electron density in the 3p orbital is decreased when the Na–O distance is increased further from 2.5 Å as in the cases of the complexes with ionophores, resulting in the upfield displacements of the ^{23}Na signals as a result of a reduction in the paramagnetic shielding contribution.

The extent of the electron transfer would be much influenced by the relative orientation of the lone-pair orbitals with respect to the direction of the Na–O vector, as shown in Fig. 7. Accordingly, the electron transfer is minimal for the arrangement of Na–H_2O as shown in Fig. 7(c), in which the lone-pair orbitals are perpendicular to the Na–O vector. On the contrary, the magnitude of the electron transfer is maximum for the arrangement of Fig. 7(b), although stabilization is not fully achieved. Similar results were obtained for the case of the Na–O=CH_2 system. For this reason, the relative orientation of the ligand molecule is a very important factor in the determination of the ^{23}Na chemical shifts in addition to the Na–O distance, because the magnitude of electron transfer is dependent on this separation. It is now obvious that the ^{23}Na chemical shifts of the sodium complexes can be well related to the extent of the electron transfer from the ligand molecules, although a more elaborate treatment is required to achieve a quantitative interpretation of the ^{23}Na chemical shifts in terms of electronic structure.[62]

Concluding Remarks

We have demonstrated that the ^{23}Na NMR signals of inorganic salts as well as a variety of sodium complexes in the solid state exhibit displacements of chemical shifts as large as 60 ppm and provide a convenient means of analyzing the following individual species, ion-ion, ion-solvent, and ion-ligand interactions which are present in the solution state. We found that these variations of the ^{23}Na chemical shifts are well related to the extent of electron transfer from the ligand molecules to the 3p orbital of the sodium ions which results in substantial deshielding due to a significant paramagnetic contribution. Accordingly, the ^{23}Na chemical shifts in the solid state are proven to be a very useful means for the characterization of these complexes as viewed from the type of ligand molecules, their relative orientation, and the Na–O distances as well as reference data for solution NMR spectra.

The numerical calculations were carried out with a HITAC M-240H in the National Cancer Center and a HITAC M-200 H in the Institute for Molecular Sciences. This work was supported, in part, by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan. Finally, we thank Dr. G. A. Webb, University of Surrey, England, for helpful discussion.

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be completely removed by MAS experiments. In fact, the following complexes gave larger linewidths than 1500 Hz: Valinomycin (3000 Hz), monensin (2800 Hz), lasalocid (2100 Hz), [2.2.1] (1700 Hz) and [2.2] (2200 Hz). We found that the linewidths were in some instances significantly decreased by proton decoupling or removal of water molecules (Ref. 20). Further, the linewidths of $Na_2SO_4 \cdot 10H_2O$ and $Na_2HAsO_4 \cdot 7H_2O$ were decreased from 600 and 430 to 400 and 160 Hz, respectively, by recrystallization from D_2O solution. In this connection, it is mentioned that these linewidths studied herein were not affected by the second-order quadrupole interaction, because the quadrupole coupling constants from the static ^{23}Na NMR spectra were zero. Further, the linewidths of $NaBH_4$, $NaBPh_4$, and $NaBF_4$ are 1000, 1010, and 740 Hz, respectively, although the quadrupole coupling constants of the former two are zero and are 1.2 MHz for the latter.

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