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# ESR and Optical Studies of the Interaction of Alkali Metal Cryptates with the 9-Fluorenone Anion Radical. Solvent Effect on the Equilibrium between Contact and Cryptand-Separated Ion Pairs

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**Abstract:** ESR and optical spectroscopies of the sodium 9-fluorenone ($F^-$) ketyl in the presence of excess cryptand 222 (C222) show that two species of ion pairs between the $Na^+$–C222 cryptate and the $F^-$ ion coexist in equilibrium in ethereal and aromatic hydrocarbon solvents. One species, (C222 $Na^+$)$F^-$, is a cryptand-separated and the other a contact type, (C222 $Na^+$ $F^-$), in which the carbonyl oxygen atom of $F^-$ is considered to penetrate the molecular framework of C222 and contact the $Na^+$ ion. The optical spectra of (C222 $Na^+$)$F^-$ and (C222 $Na^+$ $F^-$) have $\lambda_{max}$ of 569 and 544 nm, respectively. The carbonyl $^{13}C$ and sodium hyperfine splittings of (C222 $Na^+$ $F^-$) are 4.30 and 0.54 G and those of (C222 $Na^+$)$F^-$ are 1.80 and 0 G, respectively. In the ESR spectrum rapid exchange of the two species gives averaged $^{13}C$ and sodium splittings. Concerning the solvent effect on the concentration ratio of (C222 $Na^+$) to (C222 $Na^+$ $F^-$), the ratio increases with increasing cation solvation power by solvents in ethereal solvents and with increasing size of the $\pi$ orbital on the solvent molecule in aromatic hydrocarbon solvents. Models for the solvent effect are proposed. In the $F^-$–$K^+$–C222 system, the presence of the equilibrium of (C222 $K^+$)$F^-$ and (C222 $K^+$ $F^-$) is also confirmed by ESR spectroscopy. In the $F^-$–$K^+$–cryptand 221 (C221) system, on the other hand, irrespective of the solvent used, the great majority of ionic species in solution is in the form of the contact ion pair (C221 $K^+$ $F^-$).

## Introduction

Macrobicyclic diamines (cryptands), first synthesized by Lehn et al.,[1,2] are known to form very stable inclusion complexes (cryptates) with alkali and alkaline earth metal cations. Among these cryptands, the chemistry of the cryptand 222 (C222), $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$, has been most extensively studied. As to the structure of Na–C222 cryptate, both X-ray studies of the solid[3,4] and $^{23}Na$ NMR studies of the solution[5,6] have proven that the sodium ion is contained within the central cavity of C222, the first coordination sphere consisting of the oxygen and nitrogen atoms of C222. These results indicate that when the cryptand complexed sodium ion forms an ion pair with an anion in low dielectric media, the common species is a cryptand-separated ion pair. The anion is able to contact the sodium ion in the cavity only if the strong cation–anion interaction succeeds in overcoming unfavorable conformational changes of C222 caused by participation of the anion in the first coordination sphere of the cation.

In the course of optical and ESR studies of the interaction of $Na^+$- and $K^+$–C222 cryptates with the 9-fluorenone anion radical (**1**), which has a localized charge on the carbonyl oxygen[7] capable of enhancing the interaction with the cation, we found a solvent-dependent equilibrium between contact and cryptand-separated ion pairs, (C222 $M^+$ $F^-$) and (C222 $M^+$)$F^-$, where $M^+$ and $F^-$ represent an alkali metal ion and the fluorenone anion radical, respectively, in ethereal and aromatic hydrocarbon solvents. In contrast with the results of NMR and X-ray studies, the anion of the contact ion pair can penetrate the molecular framework of C222.

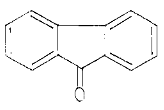

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Table I. Optical and ESR Data for the Solvent Effect on the Equilibrium between (C222 $Na^+$ $F^-$) and (C222 $Na^+$)$F^-$ at 25 °C

| solvent | (569 nm)/ (544 nm)[a] | $a_C$,[b] G | $a_{Na}$,[c] G | $K$[d] |
|---|---|---|---|---|
| DME[e] | 1.20 | 2.00 | 0.1[j] | 11.5 |
| THF[f] | 1.02 | 2.25 | 0.1[j] | 4.6 |
| MTHF[g] | 0.86 | 2.73 | 0.20 | 1.7 |
| THP[h] | 0.73 | 3.00 | 0.23 | 1.1 |
| DMTHF[i] | 0.58 | 3.31 | 0.32 | 0.66 |
| ethyl ether | 0.50 | 3.60 | 0.39 | 0.39 |
| α-methylnaphthalene | 0.55 | 3.43 | 0.36 | 0.53 |
| toluene + naphthalene | 0.56 | 3.46 | 0.36 | 0.51 |
| toluene | 0.40 | 3.84 | 0.43 | 0.23 |
| toluene (2) + hexane (3) | 0.25 | 4.30 | 0.53 | 0 |

[a] The ratio of the absorbancy at 569 nm to that at 544 nm. [b] Carbonyl $^{13}C$ hyperfine splitting. [c] Sodium hyperfine splitting. [d] The concentration ratio of (C222 $Na^+$)$F^-$ to (C222 $Na^+$ $F^-$). [e] 1,2-Dimethoxyethane. [f] Tetrahydrofuran. [g] 2-Methyltetrahydrofuran. [h] Tetrahydropyran. [i] 2,5-Dimethyltetrahydrofuran. [j] Sodium hyperfine lines are not resolved.

## Results and Discussion

**Na–C222 Complexes.** Optical spectra of the sodium fluorenone ketyl in the presence of excess C222 were examined with several solvents. The spectra consist of peaks at 544 and 569 nm, while the bands of the ionic dimer and higher clusters observed in the absence of C222[8] disappear. The intensity ratio of the two peaks is not affected by dilution in the range of $10^{-3}$–$10^{-5}$ M but is dependent upon the solvent used, as shown in Figure 1. This fact suggests that the presence of the two peaks is due to the overlap of two bands, each of which arises from a structurally different ion pair. The absorption maximum in the visible range of the optical spectrum of ketyls has been well correlated to the cationic field acting on the ketyls, being shifted in the bathochromic direction with the increase in the interionic distance.[9-11] The 544-nm

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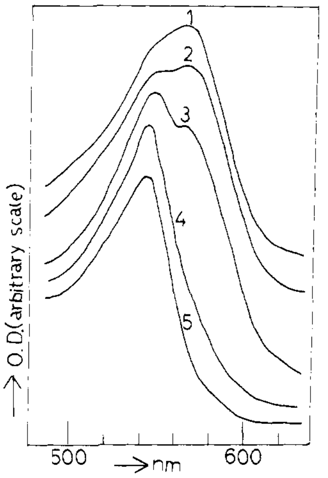

**Figure 1.** Solvent dependence of the visible spectrum of sodium 9-fluorenone ketyl in the presence of excess cryptand C222 at 25 °C. (1) DME, (2) THF, (3) MTHF, (4) toluene, and (5) mixture of toluene (2) and hexane (3); concentration of the fluorenone ion = $(1 \sim 5) \times 10^{-3}$ M; path length of the cell = 0.1 cm.

band has nearly the same position as the spectrum of the K$^+$F$^-$ ion pair in tetrahydrofuran (THF), while the 569-nm band is located near the band of the free F$^-$ ion ($\lambda_{\max}$ = 571 nm) produced in hexamethylphosphoramide (HMPA). Therefore the interionic distance of the ion pair which has the 544-nm band is of the same order of magnitude as that of the contact K$^+$F$^-$ ion pair in THF, while the interionic distance of the ion pair with the 569-nm band is much greater. From this we may assign the ion pair with 544-nm band to the contact ion pair, (C222 Na$^+$ F$^-$), in which the carbonyl oxygen atom penetrates the molecular framework of C222 and contacts the sodium ion, while the ion pair with the 569-nm band can be assigned to the cryptand-separated ion pair, (C222 Na$^+$)F$^-$, in which the F$^-$ ion is located outside of C222. The solvent dependence of the ratio of the absorbance at 569 nm to that at 544 nm is listed in Table I. Greater ratios mean a higher fraction of (C222 Na$^+$)F$^-$. Within the scope of ethereal solvents the ratio increases in the order of solvents of increasing cation solvation, which has also been observed in the usual cases.[12,13] This order is mainly determined by the steric hinderance of the groups at sites adjacent to the ethereal oxygen atom. In aromatic hydrocarbon solvents the ratio increases with an increase in the size of $\pi$ orbital in the order toluene $\approx$ *m*-xylene $\approx$ benzene $<$ $\alpha$-methylnaphthalene, and the steric factor of these solvent molecules does not show any substantial effect. Addition of naphthalene to the toluene solution increases the ratio, while addition of hexane first decreases the ratio until it becomes constant when the fraction of hexane is higher than 0.6. In pure hexane the ion pair is almost insoluble. Thus, even in aromatic hydrocarbons the two species of ion pairs coexist in equilibrium and only when the solvent has a high mole fraction of hexane does the single species (C222 Na$^+$ F$^-$) exist.

The results of ESR spectroscopy are quite parallel to those of optical spectroscopy, although the high exchange rate between the two species of ion pairs (in the sense of the ESR time scale) gives only averaged carbonyl $^{13}$C and sodium hyperfine splittings (fluorenone with 90.9% enriched carbonyl $^{13}$C was used). Since the $^{13}$C splitting is known to increase with decrease in interionic distance[8] and the sodium splitting of (C222 Na$^+$)F$^-$ is expected to be zero, the observed $^{13}$C and sodium splitting are increased in solvents which give higher fractions of (C222 Na$^+$ F$^-$) as listed in Table I. In agreement with the results of optical spectroscopy, the $^{13}$C splitting in a mixture of toluene and hexane is near that of the K$^+$F$^-$ ion pair (4.20 G) in THF. In 1,2-dimethoxyethane (DME) and THF the $^{13}$C splittings approach that of the free F$^-$ ion (1.75 G) in HMPA and the sodium hyperfine lines disappear. The equilibrium constant, *K*, of eq 1 can be calculated on the basis

$$(\text{C222 Na}^+\ \text{F}^-) \rightleftarrows (\text{C222 Na}^+)\text{F}^- \qquad (1)$$

of both the optical and the ESR data by simple procedures, assuming that for the optical method the spectral shapes of both (C222 Na$^+$ F$^-$) and (C222 Na$^+$)F$^-$ are identical with the shape of the 2:3 mixture of toluene and hexane, while for the ESR method the $^{13}$C splitting constants of (C222 Na$^+$ F$^-$) and (C222 Na$^+$)F$^-$ are 4.30 and 1.80 G, respectively.[14] The values of *K* listed in Table I were obtained by the ESR method and accord well with those obtained by the optical method (within 10%).[15] The conversion of (C222 Na$^+$ F$^-$) to (C222 Na$^+$)F$^-$ is slightly exothermic or nearly thermoneutral. Plots of ln *K* vs. 1/*T* for DME, THF, and 2-methyltetrahydrofuran (MTHF) give $\Delta H°$ values of −2.4, −1.4, and −0.6 kcal/mol, respectively. These values of $\Delta H°$ are appreciably smaller than the enthalpy changes from contact to solvent-separated ion pairs observed so far.[13,16,17] In the other solvents *K* appears to be independent of temperature.

In ordinary cases the change from a contact to a separated ion pair requires a large amount of solvation energy in order to compensate for the loss of interionic energy. In the present case, however, a relatively small increase in solvation energy will be enough to provide the driving force for the change, because (C222 Na$^+$ F$^-$) is already destabilized by unfavorable conformational changes of C222. The following model is proposed for the present solvent effect. In aromatic hydrocarbon solvents the ion-induced dipole interaction between F$^-$ and solvent molecules is assumed to play a dominant role for the change of the structure of the ion pair. This interaction is rather a short-range force, with the energy proportional to $r^{-4}$, where *r* is the distance between an ion and a solvent molecule. Since a large part of the negative charge of F$^-$ ion is localized on the carbonyl oxygen atom, *r* for this case can be approximately regarded as the distance between the oxygen atom and a solvent molecule. In (C222 Na$^+$ F$^-$) the penetration of the carbonyl oxygen atom in the molecular framework of C222 prevents solvent molecules from approaching the oxygen atom until such a distance as the ion-induced dipole interaction becomes effective, while in (C222 Na$^+$)F$^-$ such an approach will be possible. Thus the solvation energy increases from (C222 Na$^+$ F$^-$) to (C222 Na$^+$)F$^-$. This increase of solvation energy may work effectively for the change of unstable (C222 Na$^+$ F$^-$). The easily polarizable $\pi$ cloud of aromatic hydrocarbons gives a major contribution to the ion-induced dipole interaction, and the wider spread of the $\pi$ cloud gives it greater polarizability. Therefore, the present solvent effect can be reasonably explained. In ethereal solvents, the fact that the fraction of (C222 Na$^+$)F$^-$ increases in a solvent of better cation solvation suggests the possibility of contact interaction between the cation and solvent molecules. This interaction was found in a $^{133}$Cs NMR study of Cs$^+$–C222 cryptates[18] and was reasonably assumed for planar crown ether complexes of alkali metal ions by Smid et al. in order to explain the effect of ethereal solvents on the equilibrium between contact and crown-separated fluorenylsodium and -potassium ion pairs.[19] The NMR studies of Na$^+$–C222 cryptate, however, showed that solvent molecules can not come into direct contact with a C222 cryptand-complexed sodium ion,[5,6] and the solvent effect of aromatic hydrocarbons reveals that a minor change in the solvation energy affects the equilibrium of the two species of ion pairs. The following explanation would be adequate. In (C222 Na$^+$)F$^-$ the wide

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[14] A value of 4.30 G for (C222 Na$^+$ F$^-$) is obtained from the $^{13}$C splitting in a toluene and *n*-hexane mixture, and a value of 1.80 G for (C222 Na$^+$)F$^-$ is estimated from the low-temperature value of the $^{13}$C splitting in THF and DME solutions.

[15] *K* can be also calculated by using the sodium hyperfine splittings of (C222 Na$^+$ F$^-$) and (C222 Na$^+$)F$^-$, 0.53 and 0 G, respectively. The obtained values agree well with those listed in Table I.

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Table II. ESR Data for C222- and C221-Complexed Potassium 9-Fluorenone Ketyl

| | C222 | | | C221 |
|---|---|---|---|---|
| solvent | $a_C$, G | $K$ | $\Delta H°$,[a] kcal/mol | $a_C$, G |
| DME | 1.97 | 9.65 | −3.8 | 3.70 |
| THF | 2.20 | 3.53 | −1.7 | 3.72 |
| MTHF | 2.50 | 1.59 | −0.7 | 3.72 |
| DMTHF | 2.86 | 0.71 | b | 3.80 |
| toluene | 3.16 | 0.33 | b | 3.90 |
| toluene + hexane | 3.61 | 0 | b | |

[a] Enthalpy change for conversion of (C222 $K^+$ $F^-$) to (C222 $K^+$)$F^-$. [b] The $^{13}C$ hyperfine splitting is independent of temperature.

space between the $-(CH_2CH_2O)_2CH_2CH_2-$ bridges of C222 permits the ethereal oxygen atom to a considerable extent to approach the sodium ion, although the oxygen atom still behaves as a member of the second sphere of the solvation shell. The extent of this approach depends on the steric factor of ethereal molecules. In (C222 $Na^+$ $F^-$), on the other hand, the bridges are packed together more closely, so that the ethereal oxygen atom is squeezed out of the interstitial space. Thus the separation between the sodium ion and solvent molecules is increased from (C222 $Na^+$)$F^-$ to (C222 $Na^+$ $F^-$). The change in the solvation energy of the sodium ion in this process will be of comparable order of magnitude to the aforementioned change in the solvation energy of the $F^-$ ion in aromatic hydrocarbons and should be able to become the dominant factor for the observed changes in the ion pairs.

**K-C222 Complexes.** The results of ESR studies of the interaction between the C222-complexed potassium ion and the fluorenone anion are summarized in Table II. In analogy with the Na-C222 complex, a large solvent dependence of the $^{13}C$ splitting can be explained in terms of the equilibrium between (C222 $K^+$ $F^-$) and (C222 $K^+$)$F^-$. The low-temperature value of the $^{13}C$ splitting in DME or THF (1.80 G) is identical with that obtained with the C222-complexed sodium keyl in DME or THF at low temperatures. This suggests that in the cryptand-separated ion pair the value of the $^{13}C$ splitting is independent of alkali metal ion in the cavity. The concentration ratio, $K$, of (C222 $K^+$)$F^-$ to (C222 $K^+$ $F^-$) was calculated by assuming that the $^{13}C$ splitting of (C222 $K^+$ $F^-$) is 3.61 G which is the value in a 1:1 mixture of toluene and hexane, and the $^{13}C$ splitting of (C222 $K^+$)$F^-$ is 1.80 G. In the same solvent, $K$ and $\Delta H°$ values of the potassium complex are of comparable order of magnitude to those for the sodium complex.

**K-C221 Complexes.** In contrast with the $^{13}C$ splitting of the C222-complexed sodium or potassium ketyl, that of the cryptand 221-complexed (C221) potassium ketyl exhibits only a small solvent dependence, as listed in Table II, and is independent of temperature in the range +60 to −60 °C. Furthermore, the $^{13}C$ splitting in the DME or THF solution is even greater than the value assumed for the $^{13}C$ splitting of (C222 $K^+$ $F^-$) (3.61 G). On the basis of these facts, we can conclude that, within the scope of solvent used, the vast majority of the ionic species in solution is a contact ion pair (C221 $K^+$ $F^-$) although a slight solvent dependence of the $^{13}C$ splitting suggests the existence of the equilibrium of (C221 $K^+$ $F^-$) and (C221 $K^+$)$F^-$. The X-ray study of the crystal structure of C221-complexed potassium thiocyanate[20] has shown that the $K^+$ ion lies not in the center of the cavity of C221 but between the two $-(CH_2CH_2O)_2CH_2CH_2-$ bridges and the $SCN^-$ ion comes in contact with the $K^+$ ion. The present results indicate that the structure of the K-C221 complex in the solid will be held in solution and the fluorenone anion can easily approach the potassium ion to form a contact ion pair.

## Experimental Section

Optical spectra were obtained on a Shimazu MPS-5000 spectrometer. ESR spectra were obtained on a JES-PE ESR spectrometer. The anion radical was prepared by reduction of 9-fluoroenone with a sodium or potassium mirror in a solution containing an excess of cryptand. All operations were carried out under high vacuum.

Cryptand 222, cryptand 221, and 9-fluorenone containing 90.9% enriched carbonyl $^{13}C$ were purchased from E. M. Merck and used without further purification. Ethereal and hydrocarbon solvents were used after being dried with sodium hydride or Na-K alloy.

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# Gear Effect. 9.[1] Steric Anisotropy of Space through "Januslike" Substituents. A Dynamic $^1H$ and $^{13}C$ NMR Study of 1,3-Dibenzyl-4,5-diisopropylimidazoline-2-thione

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**Abstract:** A molecule has been designed which clearly demonstrates the steric anisotropy of space created by two geared isopropyl groups: 1,3-dibenzyl-4,5-diisopropylimidazoline-2-thione (A). A dynamic $^1H$ and $^{13}C$ NMR spectroscopy study of A gives evidence of three rate processes. The high-energy process ($\Delta G^{\ddagger}_{229K}$ = 11.5 ± 0.1 kcal mol$^{-1}$) has been identified as the exchange of the isopropyl groups between two geared conformations. The two other processes arise from slow rotation of the two benzyl groups, but the magnitudes of the barriers, in this apparently symmetrical ($C_{2v}$) molecule, are quite unequal, $\Delta G^{\ddagger}_{205K}$ = 10.6 ± 0.1 and 8.5 ± 0.1 kcal mol$^{-1}$, respectively. The reason for these unequal barriers is found in the geared conformational state of the isopropyl groups in which they have one bulky and one nonbulky face. The comparatively complex exchange system of the benzylic methylene protons, the conformations of the isopropyl and benzyl groups, and the mechanism for the conformational interconversions are analyzed. The implications of these results for other unsymmetrical substituents and for the possible role of such groups in the steric control of the selectivity of enzymes is emphasized.

From a steric point of view, the isopropyl group is very versatile since it can be as bulky as a *tert*-butyl group when it is viewed from the side of the two methyl groups or as small as a methyl group when it is considered from the opposite side. Thus, conformational control of reactivity (and selectivity) may be generated from this "januslike"[2] group depending on its induced confor-

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(1) Part 8: B. Blaive, C. Roussel, J. Sandström, and J. Metzger, *Can. J. Chem.*, in press.

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