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Vibrational spectra of alkali metal (Na, K) cyclooctatetraenides

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Abstract

Infrared spectra (4000–50 cm^{-1}) and Raman spectra of alkali metal cyclooctatetraenides ($C_8H_8M_2$; M = Na, K) solutions in tetrahydrofuran (THF) and crystallosolvates $C_8H_8M_2 \cdot n$THF have been studied, together with Raman spectra of a $C_8H_8K_2$ solution in dimethoxyethane (DME) and of crystallosolvate $C_8H_8K_2 \cdot n$DME. The spectra of ion triads (M^+, $C_8H_8{}^{2-}$, M^+) were compared with the spectra of ion pairs (M^+, $C_5H_5{}^-$) studied earlier. It was found that in THF and DME solutions contact ion triads are formed which, unlike the ion pairs (M^+, $C_5H_5{}^-$), do not form ion aggregates. The out-of-plane ρ(CH) bending vibration frequency is not so dependent on the nature of the metal in the IR spectra of alkali metal cyclooctatetraenides as it is in the spectra of alkali metal cyclopentadienides, which is probably due to the double negative charge on the eight-membered ring. In the range of the skeletal vibrations of the ion triad (K^+, $C_8H_8{}^{2-}$, K^+) (200–100 cm^{-1}) the mutual exclusion rule is followed, indicating the centrosymmetrial structure of this triad. A rather intense line at 169 cm^{-1} of the symmetrical stretching skeletal vibration of the triad (K^+, $C_8H_8{}^{2-}$, K^+) was observed in the Raman spectrum of $C_8H_8K_2$ solutions in THF and DME. The appearance of this line may be connected with high polarizability of the potassium cation or with the presence of the appreciable covalent component of the potassium-ring bonding.

Introduction

The interaction of alkali metals with cyclooctatetraene in ethers and liquid ammonia results in the formation of the plane aromatic cyclooctatetraene dianion with D_{8h} symmetry [1,2]. It is assumed that in weakly polar solvents the dipotassium and disodium salts of cyclooctatetraene dianion exist in the form of the contact ion triad (M^+, $C_8H_8{}^{2-}$, M^+) [3]. The nature of the cation effects on the chemical shift in ^{1}H NMR spectra of the eight-membered ring have been described previously [4]. Thermochemical studies show [5] that the thermodynamic stability of dianion salts with various cations depends on the nature of the cation. Thus, dipotassium salt in

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the solid state is more stable than disodium salt by about 5 kcal/mole. However, the thermodynamic stability of the triad (M^+, $C_8H_8^{2-}$, M^+) in THF solution is greater for Na than for K, which indicates the importance of solvation for the stabilization of the ion triad. Solid salts are crystallized from the saturated solution in the form of crystallosolvates with one [6] or two [7] solvent molecules.

In the present work the vibrational spectra of sodium and potassium cyclooctatetraenides in the solid state and in THF solution were investigated to study the structure, chemical bonding and ionic states in solutions. Raman spectra of the solutions in DME and of solid crystallosolvate with DME were also obtained for the potassium salt. The results were compared with the spectra of the ion pairs ($C_5H_5^-$, M^+) (M = Li, Na) in THF solutions and with the spectra of solid salts C_5H_5M (M = Li, Na, K) [9]. The Raman spectrum of $C_8H_8K_2$ in the solid state and in THF solution has been described [10]. The measurement of the IR spectrum of monotetrahydrofuranate of the dipotassium salt $K_2C_8H_8 \cdot THF$ was reported by Fritz [11], the IR spectra of $M_2C_8H_8$ (M = Na, K), obtained by cocondensation of the metal with cyclooctatetraene on the KBr support at 93 K, were measured by Kuzyanz [12].

Experimental

Potassium and sodium cyclooctatetraenides were synthesized by the reaction of cyclooctatetraene in THF and DME solutions with a metal mirror in a vessel connected to a vacuum line. Synthesis of the dipotassium salt has been previously described in detail [4,10]. Dipotassium salt dissolves readily in THF but not so well in DME. White polycrystals of dipotassium salt were obtained by refreezing the solvent in vacuum upon concentration of the solutions. Solutions of dipotassium and disodium salts are yellow. Disodium salt dissolves poorly in THF and forms the precipitate (white polycrystals). The Raman spectra of solid salts and their solutions were recorded with a spectrometer (Ramanor-HG-2S) equipped with a Ar^+ laser (5145 Å, W 100 mW) directly in a reaction vessel with thin glass walls. The samples for the IR spectra were prepared in a special box and repeatedly flushed with high-purity grade argon. The IR spectra of solutions in KBr window cells of 0.028–0.09 mm thickness (4000–400 cm^{-1}) and in polyethylene (PE) window cells of 0.5–0.8 mm thickness (500–50 cm^{-1}), as well as the IR spectra of solid samples in Nujol mull between the PE films of 80 μ thickness (4000–50 cm^{-1}) were recorded on a Fourier transform spectrometer (Bruker IFS-113 v) with a resolution of 2 cm^{-1}.

Results and discussion

Cyclooctatetraene dianion vibration region

The Raman and IR spectra of dipotassium and disodium salts in the solid state and in solutions, the bands of the solvent being subtracted in the latter case, are given in Table 1. The assignments of vibrational frequencies are given at the right hand side of the table. In accordance with D_{8h} symmetry of the free dianion and the ion triad (M^+, $C_8H_8^{2-}$, M^+), 42 vibrations of the eight-membered ring may be divided into the following symmetry groups: $\Gamma_V = 2A_{1g}(R) + A_{2g}(n.a.) + A_{2u}(IR) + 2B_{1g}(n.a.) + 2B_{1u}(n.a.) + 2B_{2g}(n.a.) + E_{1g}(R) + 3E_{1u}(IR) + 4E_{2g}(R) + 2E_{2u}(n.a.) + 2E_{3g}(n.a.) + 4E_{3u}(n.a.)$.

Vibrational frequency assignments in the Raman spectrum of dipotassium salt can be found in the literature [10]. There is a discrepancy in the assignment of the bands in the IR spectra. The question is which of the two weak bands at 1290 or 1430 cm^{-1} should be assigned to degenerate vibrations $\nu(CC)$ of class E_{1u}. Frits [11] assigns the band at 1430 cm^{-1} to this vibration, whilst Kuzyanz [12] assigns the band at 1290 cm^{-1} to the same vibration considering the band at 1430 cm^{-1} to be an oxidation product since the intensity of this band increases after treating the sample with dry air. In the spectra of solutions and solid salts we failed to observe the bands at 1290 cm^{-1} on the background of the THF or PE and Nujol absorption, but the band at 1424 cm^{-1} can be distinctly observed in the spectra in the form of a shoulder on the intense band of THF or PE and Nujol absorption. We also failed to observe an increase of this band intensity upon the contact of the substance with the air. We suggest that the band at 1424 cm^{-1} can be assigned to $\nu(CC)$, (E_{1u}) following the analogy with the spectra of other aromatic compounds where the bands in the range of 1440–1480 cm^{-1} correspond to this vibration [13].

Of all the spectra of cyclopentadienyl complexes of metals the most sensitive to the metal–ligand bond polarity appear to be the frequencies of out-of-plane $\rho(CH)$ bending modes in the range 690–890 cm^{-1}. The frequencies of $\rho(CH)$ modes decrease with an increase of metal–ring bond polarity [14]. The frequency range of $\rho(CH)$ in the IR spectra was found to be very informative when the ionic states of alkali metal cyclopentadienide solutions were investigated [8,9]. In the IR spectra of solid cyclopentadienides of alkali metals and their solutions in THF the frequency of the $\rho(CH)$ band shifted by ~ 27 cm^{-1} to the low-frequency range upon transition Li → Na → K. In addition, the $\rho(CH)$ band in the IR spectra of the C_5H_5M ($M = Li$, Na) has a complicated contour depending on the solution concentration, which may be due to the formation of ion pair aggregates in this solvent [8]. The peculiarities of the spectra of alkali metal cyclooctatetraenides in the frequency range of the $\rho(CH)$ mode (650–680 cm^{-1}) are of another character are shown by two observations. Firstly, the single $\rho(CH)$ band is observed in the IR spectra of the $C_8H_8M_2$ ($M = Na$, K) solutions in THF independent of the solution concentration. Secondly, the $\rho(CH)$ frequency is only slightly sensitive to the nature of the alkali metal cation, shifting only by 6 cm^{-1} to low frequency range upon transition Na → K. The first observation indicates that alkali metal cyclooctatetraenides in solution contain the species of only one type, namely, the contact ion traids (M^+, $C_8H_8{}^{2+}$, M^+) which in contrast to the ion pairs (M^+, $C_5H_5{}^-$) do not form the ion pair aggregates. Indeed, the ion triad (M^+, $C_8H_8{}^{2-}$, M^+) is a closed structural unit with the positively charged metal atoms at the ends, presenting an obstacle to the formation of aggregates. The second observation shows that the polarity of the metal–ring bond changes only slightly when the metal is changed. The $\rho(CH)$ band frequency in the spectra of alkali metal cyclooctatetraenides depends only slightly on which metal is present; this can be explained by the fact that the dianion carries on itself the double negative charged and, consequently, a small redistribution of the electron density upon the metal substitution results in relatively small changes in the polarity of the metal–ring bond. It should be noted that in the spectra of the complexes of the cyclooctatetraene dianion with lanthanides (Ln) and actinides (An) $An(\eta^8\text{-}C_8H_8)_2$ and $K[Ln(\eta^8\text{-}C_8H_8)_2]$ the dependence of the $\rho(CH)$ band frequency on the metal is much weaker (690–730 cm^{-1}) than in the spectra of cyclopentadienyl metal complexes (690–890 cm^{-1}). However there is still

Table 1

Vibrational spectra of potassium and sodium cyclooctatetraenides

$C_8H_8Na_2$ (cm^{-1})				$C_8H_8K_2$ (cm^{-1})						Assignment symm. D_{8h}
Raman		IR		Raman		Raman		IR		
THF soln.	crystal	THF soln.	cryst.	THF soln.	DME soln.	cryst. 1 [a]	cryst. 2 [a]	THF soln.	cryst. 1	
	100m					90w	47m			
	113sh						95w			
								139m	114m	ν_{18}, E_{1u} δ(MLM)
				169m(p)		157sh				ν_3, A_{1g} ν(ML)
	173w,br		172w	173s(dp)	170w,br	180m	176m,br			ν_{14}, E_{1g} (Tilt)
			214w							
		236vw,br	244m					196m	209m	ν_6, A_{2u} ν(ML)
			278sh						282w	THF
330m(dp)	331m			342s(p)	344s	343s	344s			ν_{22}, E_{2g} γ(CCC)
							372vw			DME
			648w							?
		659m	686s					653s	681s	ν_5, A_{2u} ρ(CH)
715m(dp)	711m		[b]	711m(dp)	710w	709w	709m		[b]	ν_{13}, E_{1g} ρ(CH)
						718sh	717sh			
738s(p)	740s		[b]	736s(p)	738s	736s	737s		[b]	ν_2, A_1 ν(CC)
									808vw	?
			874sh							
		881sh	883s					883s	881s	ν_{17}, E_{1u} β(CH)

	889w		888s			905w	847w		887s	THF or DME
	930w	^{c}				919w	860w	^{c}	914sh	THF or DME
	1037w		1033w			1032w	1027w			ν_{21}, E_{2g} β(CH)?
		^{c}	1057			1055w		^{c}	1059w	THF
			1140vw					1133w	1141w	
	1252w					1240vw				
								1423w	1427w	ν_{16}, E_{1u} ν(CC)
			^{b}						^{b}	
	1450vw					1450vw	1445w			THF or DME
1487w	1489m			1488(dp)	1488m	1492s	1492m			ν_{20}, E_{2g} ν(CC)
									1535vw	
						1577vw	1574w			
								1624w	1675vw	
								1736w	1802vw	
							2820w			DME
						2860sh				THF
	2878w					2878m				THF
						2910w				THF
		^{c}	^{b}			2940w		^{c}	^{b}	THF
						2979m				ν_{19}, E_{2g} ν(CH)
	2985w					2985sh				THF
	3011w					3011m	3012w			ν_1, A_{1g} ν(CH)

[a] Crystal 1 = crystallosolvate $C_8H_8K_2 \cdot n$THF, crystal 2 = crystallosolvate $C_8H_8K_2 \cdot n$DME; p, polarized; dp, depolarized; s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad. [b] Strong absorption of PE and Nujol. [c] Strong absorption of THF.

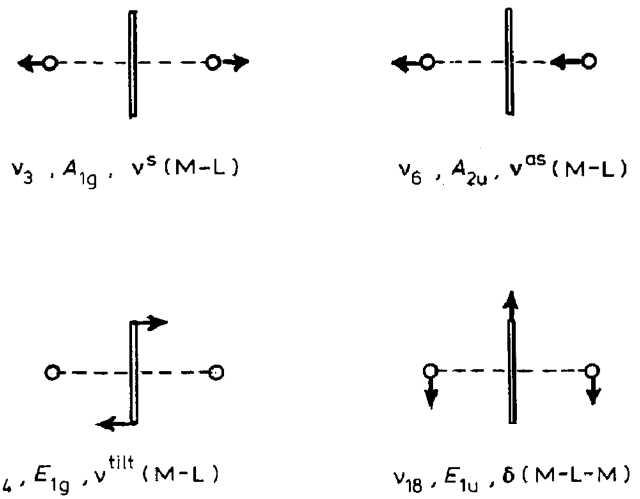

Fig. 1. Skeletal vibrations of the ion triad (M^+, $C_8H_8^{2-}$, M^+).

a tendency for ρ(CH) band frequency to decrease with an increase in the polarity of the metal–ring bond [15,16].

The region of skeletal vibrations

The low-frequency region of the alkali metal salts spectra is most informative about the type of ionic states in solutions and the character of bonding in them, since it is in this region where the interionic (skeletal) vibrations are situated. There are four skeletal vibrations for the ion triad (M^-, $C_8H_8^{2-}$, M^-) with the D_{8h} symmetry (Fig. 1).

Among the four vibrations only the frequency of the tilt vibration ν_{14} does not depend on the cation mass, since the metal atoms are not involved in this vibration.

Due to weak solubility of the disodium salt the complete spectra of solutions of this salt were not obtained. We also failed to observe the lines in the low-frequency range (< 300 cm^{-1}) in the Raman spectrum of the saturated solution in THF, whilst only one line at 173 cm^{-1} was observed in the spectrum of the solid salt, which we assigned to the ν_{14} vibration. A weak broad band with the maximum at 236 cm^{-1}, probably corresponding to the ν_6 vibration, was observed in the IR spectrum of the solution, in the spectrum of the solid salt the same broad band with the maxima at 278, 244, 214 and 172 cm^{-1} corresponds to it.

Only one broad line at ~ 170 cm^{-1} at first glance is present in the Raman spectra of the dipotassium salt solutions in THF and DME. The degree of depolarization of this line is approximately 0.5 and, consequently, it has been assigned to the symmetrical stretching vibration [10]. However, a more precise measurement of the depolarization ratio of this line has shown that it appears to be the overlapping of two adjacent lines: polarized at 169 cm^{-1}, ν_3, and depolarized at 173 cm^{-1}, ν_{14} (Fig. 2). In the IR spectra of the $C_8H_8K_2$ solutions in THF two rather narrow bands with $\Delta\nu_{1/2}$ 30 cm^{-1} at 196 and 139 cm^{-1} were observed. There are rather-narrow bands at 209 and 114 cm^{-1} in the spectrum of the solid salt. We assigned these bands to the ν_6 and ν_{18} vibrations, respectively. In contrast to the spectra of the alkali metal cyclopentadienides in solution the spectrum of the

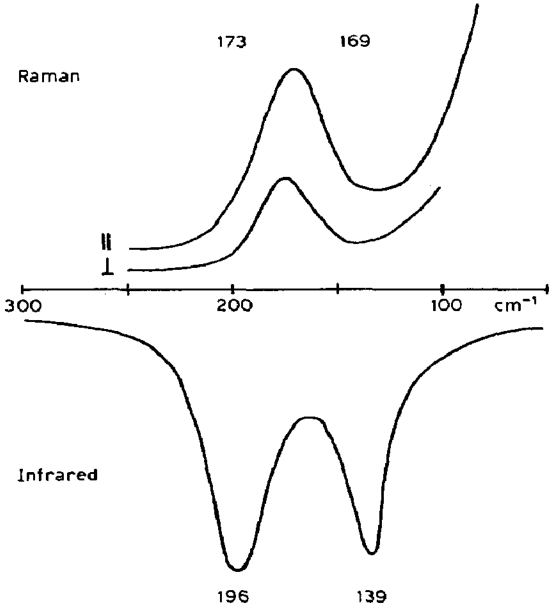

Fig. 2. Low-frequency infrared and Raman spectra of $C_8H_8K_2$ in THF solution.

dipotassium salt solution does not show any dependence on concentration, which is additional evidence of the absence of ionic aggregates. Thus it follows that in the spectra of the dipotassium salt the bands of all four (skeletal) vibrations, ν_3, ν_{14}, ν_6 and ν_{18}, were observed. There are no coincidences between the infrared and Raman frequencies, the rule of mutual exclusion is held for the skeletal modes, confirming the centrosymmetrical structure (D_{8h}) for ion triad (K^+, $C_8H_8^{2-}$, K^+) both in solution and in the crystalline state. We estimate the force constant of the potassium–ring bond as 0.64 mdyn/Å in terms of the three-mass model.

The character of bonding in the ion triad (K^+, $C_8H_8^{2-}$, K^+) is worthy of consideration. It is assumed that the ion triad or ion pair are mainly stabilized by the forces of electrostatic nature, the forces of the covalent nature are relatively weak [17]. It is well known that in the Raman spectrum intensity of the line representing the stretching mode of the bond decreases with an increase in its polarity. This may be the reason for the absence or a weak intensity of the lines of the cation–anion or cation–solvent vibrations in the Raman spectra of the alkali metal salts in solution [18]. In a number of cases these lines were detected by using special techniques of difference Raman spectroscopy [19,20]. We failed to observe the lines of the stretching symmetrical skeletal vibrations in the Raman spectra of alkali metal cyclopentadienides in solution (Li, Na) [9] and in the spectrum of sodium cyclooctatetraenides (this work). In this respect, the triad (K^+, $C_8H_8^{2-}$, K^+) is an interesting exception. There is in the Raman spectrum of this triad a rather intense line representing the symmetrical stretching skeletal vibration, which might be due either to a high polarizability of the potassium cation, (four times greater than that of the sodium cation), or to the presence of an appreciable covalent component of the potassium–ring bond. It was shown by ESR spectroscopy using the cation dependence of the disproportionation equilibrium constant [2] that the triad (K^+, $C_8H_8^{2-}$, K^+) does not completely dissociate on the ions even in HMPA solution in contrast to the triad (Na^+, $C_8H_8^{2-}$, Na^+). The charged ion pair ($C_8H_8^{2-}$, K^+) and the cation K^+ are formed in the HMPA solution [2].

The dimension of the potassium cation seems to be more favourable for covalent overlapping of its orbitals with the orbitals of the dianion. In fact, the ionic radius of potassium (1.33 Å) is quite close to the radius of an eight-membered cycle with sides of 1.40 Å [6] (1.81 Å), whereas the ionic radius of sodium is much less (0.95 Å). The assumed difference in the electron structure of the dipotassium and disodium salts resulting from the difference in the character of low-frequency IR and Raman spectra of these salts should have effects on their electronic absorption spectra which will be our subject of study in the near future.

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