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VIBRATIONAL SPECTRA OF ALKALI METAL CYCLOPENTADIENIDES

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Summary

The vibrational spectra of crystalline alkali metal cyclopentadienides (C_5H_5M; M = Li, Na, K) and the Raman spectra of C_5H_5Li and C_5H_5Na solutions in tetrahydrofuran (THF) have been obtained. The Raman spectra of C_5H_5M solids have been measured both at room and liquid nitrogen temperatures. The spectra obtained were very similar to those of η^5-cyclopentadienyl (Cp) complexes with predominantly ionic character of the metal–ligand bond. According to the position of the ρ(CH) bands, the polarity of the M–C_5H_5 bond increases upon transition from the solids to their solutions in THF. In the low-frequency range of the Raman spectra of C_5H_5Li and C_5H_5Na solutions in THF, a weak line assigned to the tilt vibration of the anion in a tight ion-pair (M^+ $C_5H_5^-$) was revealed. The dependence of the low-frequency Raman spectra of η^5-Cp complexes on the nature of the metal–ligand bonding is discussed.

Introduction

Recently, considerable attention has been given to the study of the vibrational spectra of metallocenes. The problems concerning the spectroscopy and structure of cyclopentadienyl complexes have been discussed in a number of reviews and monographs [1–3]. However, there is still no complete spectral data on the vibrational spectra of the $C_5H_5^-$ anion in ionic monocyclopentadienides of alkali metals. IR data are limited to a medium frequency region [4–6]. Up to now, the only measurement of the Raman spectrum of the $C_5H_5^-$ anion has been reported in Fritz's reviews [4,5], from which it follows that the vibrational frequencies of the $C_5H_5^-$ anion can be substantially distinguished from those of the cyclopentadienyl (Cp) ring in the spectra of the η^5-Cp complexes. Earlier, it was shown that in spite of the large variety of η^5-Cp complexes with different bonding characters, the spectrum

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of the Cp ligand exhibits comparatively small changes: most of the ligand frequencies vary in a rather small range (10 ± 30 cm^{-1}) [1,2], therefore the data presented in refs. 4 and 5 appear doubtful; at any rate, it required a re-investigation. New data on the IR and Raman spectra of the C_5H_5M (M = Li, Na, K) salts are presented in this paper. It is known [7,8] that alkali metal cyclopentadienides in solution are dissociated into ions to form tight or solvent-separated ion-pairs depending on the solvent and cation. C_5H_5Li and C_5H_5Na in solution in THF form a tight ion-pair [7,8]. Earlier, we detected in the low-frequency region of the Raman spectrum of potassium cyclooctatetraenide in THF the line at ~ 170 cm^{-1} assigned to the cation-anion stretching vibration in a contact ion triad, K^+ $C_8H_8^{2-}$ K^+ [9]. Since the intensity of the Raman line of such a vibration should be close to zero for an ionic bond [10], the result obtained requires a more detailed investigation with respect to other similar objects. In this connection, particular attention is focused, in this paper, on the assignment in a low-frequency range of the Raman spectra.

Experimental

Lithium, sodium and potassium cyclopentadienides were prepared by metallation of cyclopentadiene in pure THF solution. The glass set-up used for the synthesis consisted of two vessels connected to each other by means of a porous glass filter, which allowed, after metallation of the cyclopentadiene, repeated recrystallization of the resulting product to be performed in the starting THF. As a result of recrystallization, the samples were completely free of impurities, especially of the dyed products of cyclopentadienide oxidation.

To prepare the alkali metal cyclopentadienides, an appropriate amount of metal in 20–25% excess with respect to the stoichiometric quantity required was placed in one of the vessels. After pumping out, a measured amount of THF together with cyclopentadiene was frozen in the same vessel. Then high-purity grade argon was added to the mixture under a pressure slightly higher than atmospheric. Metallation was carried out below 0°C, the resulting hydrogen being released periodically through a tap. After completion of the reaction and repeated recrystallization of the product, the THF was removed by freezing. One of the vessels containing purified, white cyclopentadienide crystals was sealed and evacuated at 100–120°C by a sorption pump to a pressure of 1×10^{-3}–5×10^{-4} Torr in order to remove possible volatile impurities.

The melting points of the obtained cyclopentadienides of potassium and sodium were equal to 325 ± 2 and 393 ± 2°C, respectively. Both compounds melt with slight decomposition. We failed to determine the melting point of lithium cyclopentadienide because this compound underwent thermal decomposition before melting when it was heated to 450°C.

The IR spectra (4000–50 cm^{-1}) of the solid samples in Nujol mull were recorded on an infrared Fourier-transform spectrometer (Bruker IFS-113 V). The samples were prepared in a specially constructed vacuum-tight box, in a continuous flow of high-purity argon and measured in special hermetic cells which had polyethylene and CsI windows. Raman spectra were measured on a Ramanor-HG-2S spectrometer equipped with a Spectra-Physics 164 Ar^+ laser; the exciting line was 5145 Å. The spectra were recorded for the solid samples in glass capillaries at room and liquid nitrogen temperatures in an optical Dewar vessel [11]. The Raman spectra of the solutions in THF for C_5H_5Li and C_5H_5Na providing information about the depolarization of Raman lines were also recorded. The solubility of C_5H_5K in THF (less than 1%) proved to be insufficient for recording the Raman spectra. The Raman spectral measurements of the solutions were hindered by the fluorescence of the samples, the intensity of which increased in the high-frequency range.

The results are presented in Table 1.

Results and discussion

The spectra of the $C_5H_5^-$ anion

The vibrational spectra of the salts (Figs. 1 and 2) in this region were, as expected, very similar to the spectra of η^5-Cp complexes with considerably ionic character of the metal–ligand bond, which is characterized by low-frequency values of the

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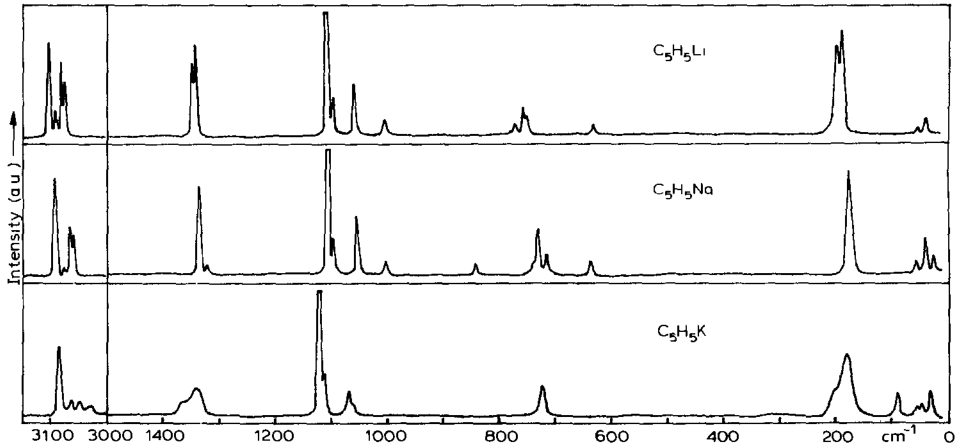

Fig. 1. Raman spectra of polycrystalline alkali metal cyclopentadienides at ~ 77 K.

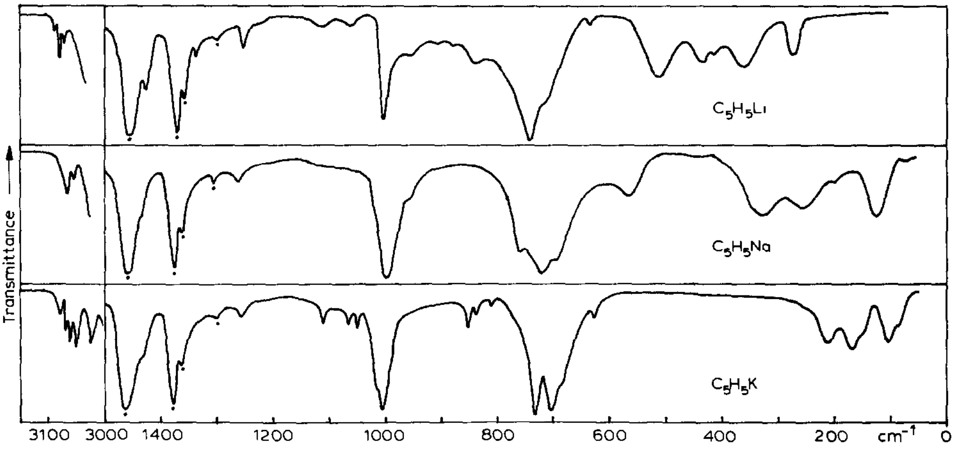

Fig. 2. Infrared spectra of solid alkali metal cyclopentadienides in Nujol mull. • Nujol bands.

TABLE 1

VIBRATIONAL SPECTRAL DATA OF LITHIUM, SODIUM AND POTASSIUM CYCLOPENTADIENIDES[a]

C_5H_5Li				C_5H_5Na				C_5H_5K			Assignment
Raman solid, 300 K	Raman solid, 77 K	Raman solution	IR solid	Raman solid, 300 K	Raman solid, 77 K	Raman solution	IR solid	Raman solid, 300 K	Raman solid, 77 K	IR solid	
				29w	30vw			30w	28w		
37w	44w				43w				46w		
57w	60vw				62vw			53vw	52vw		
								88w	88w		
										95sh	
							119m			107m	
										156sh	
194vs	198vs	154w(dp)		171s	178vs	139w(dp)		179m	180m	173m	See text
	205vs							200sh	200sh	213m	
							252m				
			273m								
							323m				
			365m								
			420m								
			439m								
			515m								
	643vw		642vw		643vw		566w				
	759m		723sh		722m		691sh			697sh	
759w	763m	719w(dp)	747s	730w	737m	715w(dp?)	722s	719w	719w	704s	ν_3,ν_9
					745sh		758m			733s	
776vw	780vw									814vw	

854vw	855vw		850vw		848vw					854w	ν_{14}
			877vw				956vw				
			1006s				998s			1008s	ν_8
1015vw	1015vw									1015sh	
									1055w	1053w	
1067m	1068m		1066vw	1062w	1064m			1070w(br)	1069w	1071vw	ν_{13}
1106sh	1108sh			1106sh	1104sh			1110sh	1109sh		$\nu_2{}^{13}C$
1114vs	1115vs	1121vs(p)	1114vw	1112s	1112s	1119vs(p)		1119vs	1120vs	1116vw	ν_2
			1258w				1260vw			1260vw	
										1265vw	
1348m	1348m	1346w(dp)	1345vw	1342m	1342m			1346w	1340m		ν_{12}
	1352m							1375sh	1370sh		
			1433m							1440m	ν_7
			1530vw(br)							1556w(br)	
			1640w(br)				1594w(br)			1570w(br)	
			1756w(br)				1710w(br)			1675w(br)	$\nu_3 + \nu_8$
										1705w(br)	
										3022m	
	3077m				3058m			3054w	3054w		
3080m	3080m			3060m	3064m			3068w	3068w		ν_{11}
			3077sh				3055sh			3051m	
			3082m				3067m			3061m	ν_6
	3090w									3070sh	
3104s	3104s	3088m(p)	3092m	3090s	3089s	3086m(p)		3088m	3084m	3081w	ν_1

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[a] Abbreviations: vs-very strong, s-strong, m-medium, w-weak, vw-very weak, sh-shoulder, br-broad, p-polarized, dp-depolarized.

out-of-plane ρ(CH) bending modes (700–780 cm^{-1}), a high intensity of the IR bands of these modes, a very weak intensity of the IR band of the ring-breathing vibration at 1110–1120 cm^{-1}, and the absence or low intensity of the Raman line of the degenerate ν(CC) vibration at 1400–1450 cm^{-1} [1,2]. The spectra are interpreted using the selection rules for the D_{5h} point group symmetry of the "free" $C_5H_5^-$ anion (four vibrations are allowed in the IR spectra and seven in the Raman spectra). The appearance of additional weak bands is probably due to the effective reducing of the real symmetry of the $C_5H_5^-$ anion because of the perturbing action of the metal atom or the influence of the crystal field. The weak and medium bands in the range of 1500–2000 cm^{-1} in the IR spectra are likely due to the second-order transitions (overtones and combination tones). The assignments of the $C_5H_5^-$ anion vibrations based on D_{5h} symmetry are given in Table 2. These assignments are compared with those presented by Fritz for C_5H_5K in refs. 4 and 5 and with those in the spectra of covalent ferrocene [12] and in the spectra of complexes with considerably ionic character of the metal–ring bond, such as dicyclopentadienylmagnesium [13] and monocyclopentadienylthallium [14]. As can be seen in Table 2, the spectral data obtained by us are inconsistent with those recorded by Fritz [4,5] and show stability of the C_5H_5-ring modes, whose frequencies, on the whole, depend comparatively little on the nature of the metal. The greatest distinction, as was noted earlier in refs. 1 and 2, is found in the region of the out-of-plane ρ(CH) modes, whose frequencies decrease regularly with increasing metal–ring bond polarity.

On transition from the solid sample spectra to the spectra of their solutions in THF, a small increase in the ring-breathing mode ν(CC) was observed, the remaining frequencies being shifted to the low-frequency range. Maximal shifts are seen for the ρ(CH) line (up to 39 cm^{-1}) in the spectrum of C_5H_5Li. The spectra of the C_5H_5Li and C_5H_5Na solutions are close in frequency to the solid C_5H_5K spectrum. According to the position of the ρ(CH) line, the $C_5H_5^-$ M^+ bond polarity increases upon transition from solid to solution compounds.

TABLE 2

COMPARISON OF THE C_5H_5-RING FUNDAMENTAL FREQUENCIES OF VARIOUS CYCLOPENTADIENYL COMPOUNDS

ν_i	Symmetry C_{5v} model MCp	Symmetry D_{5h} free $C_5H_5^-$	Assignments	C_5H_5K [4,5]	C_5H_5K	C_5H_5Na	C_5H_5Li	C_5H_5Tl [14]	$(C_5H_5)_2Mg$ [13]	$(C_5H_5)_2Fe$ [1,12]
ν_1	A_1	A_1'	ν(CH)	3043	3088	3090	3104	3096	3102	3100
ν_6	E_1	E_1'	ν(CH)	3048	~3061 [a]	3067	3082	3070	3076	3080
ν_{11}	E_1	E_2'	ν(CH)	3096	~3061	3060	3080	3065	3064	3090
ν_7	E_1	E_1'	ν(CC)	1445	1440	–	1433	1425	1425	1410
ν_{12}	E_2	E_2'	ν(CC)	1447	1346	1342	1346	1350	1342	1350
ν_2	A_1	A_1'	ν(CC)	983	1119	1114	1114	1120	1113	1110
ν_{13}	E_2	E_2'	β(CH)	1020	1070	1062	1067	1060 [b]	1060	1060
ν_8	E_1	E_1'	β(CH)	1008	1008	998	1006	1008	1007	1000
ν_{14}	E_2	E_2'	γ(CCC)	565	854	848	854	843	~871	900
ν_9	E_1	E_1''	ρ(CH)	625	719	730	759	754 [b]	~750	830
ν_3	A_1	A_2''	ρ(CH)	702	~719	~722	~735	727	~768	800

[a] Average frequency values for crystal splitting. [b] These frequencies are reassigned.

Low-frequency region

Solid cyclopentadienides of lithium, sodium and potassium are characterized by their rather high melting points, their non-volatility and their capability of dissociating into ions in polar solvents. All these physico-chemical properties presuppose an ionic polymer-chain structure of crystals of these salts *. In a predominantly ionic complex, the discrete metal–ring vibrations will be incorporated into the "lattice" modes which involve the co-operative motion of all the cation atoms and cyclopentadienyl rings in the polymer chains.

Because of the absence of X-ray structural data, it is impossible to make strict assignments in the low-frequency region of the solid cyclopentadienide spectra. We can discern two groups of bands: bands which are regularly displaced upon replacement of the cation; and bands whose frequencies are weakly dependent on the cation mass. The former group of bands is seen in the IR spectra, the latter in the Raman spectra (Figs. 1 and 2). The bands in the IR spectra at 515, ~ 430, 365 cm^{-1} (Li), 323, 253 cm^{-1} (Na), 213, 173 and 156 cm^{-1} (K) may be assigned to the translation modes of the M^+ cations in the crystal lattice, as the ratio of the frequency squares of these modes is approximately equal to the ratio of the inverse masses of the lithium, sodium and potassium atoms.

In the Raman spectra of all the samples in the 170–200 cm^{-1} range, we observe a broad line with half-band widths at 20–36 cm^{-1} whose integrated intensity, according to an approximate estimation as $I_{max} \cdot \Delta\nu^{1/2}$, is comparable with that of the ring-breathing mode line at ~ 1115 cm^{-1}. The maximal half-band width reveals a line of 180 cm^{-1} ($\Delta\nu_{1/2} = 36$ cm^{-1}) in the C_5H_5K spectrum; the line is asymmetrical and has a non-resolved, high-frequency shoulder at ~ 200 cm^{-1}. On transition from the spectra of C_5H_5Li and C_5H_5Na solid samples to those of their solutions we can see a displacement of this line to ~ 30 cm^{-1} in the low-frequency range and a notable decrease in its intensity (in comparison with the intensity of the ring-breathing mode line). This line is depolarized or weakly-polarized too **.

As already mentioned in the Introduction, we observed the same line at 170 cm^{-1} in the Raman spectrum of the $K_2C_8H_8$ solution in THF and assigned it to the cation-anion stretching mode in a contact ionic triad, K^+ $C_8H_8{}^{2-}$ K^+ [9]. However, the frequency of such a vibration should depend strongly on the cation mass [16]; this is not observed in the experiment. If we suppose that the mass effect is compensated by a change in the force constant of the M–C_5H_5 bond, then on the basis of the two-mass approximation model, we obtain a force constants for the Na–C_5H_5 bond which is twice as high as that of the Li–C_5H_5 bond. This is not in agreement with the literature data [16–18], according to which the force constant of the cation–anion bond increases in the opposite direction, i.e. from Na to Li, which agrees with the greater capability of lithium to form covalent bonds. Taking into account the degree of depolarization of the line around 150–130 cm^{-1} in the Raman

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* There are X-ray structural data for the adduct of C_5H_5Na with tetramethylethylendiamine [15]. The orthorhombic crystals with $Z = 8$ contain zigzag-like chains, –M–C_5H_5–M–C_5H_5–M, with a mean distance r(Na–C) equal to 2.92 Å. The distance r(C–C) (1.38 Å) is shorter than that in the other Cp complexes.

** Precise measurement of the degree of depolarization is hindered by the weakness of this line and the Rayleigh wing nearness.

spectra of the C_5H_5Li and C_5H_5Na solutions, as well as the weak dependence of the frequency of this mode on the cation mass both in the spectra of the solid samples and in those of the solution samples, we assigned this line to the degenerate "tilt" mode in the M^+ $C_5H_5^-$ contact ion-pair or to the libration mode of the $C_5H_5^-$ anions in the crystal lattice. An additional argument in favour of this assignment is the significant half-band width of this line both in the spectra of the solid salts and in those of their solutions, which is characteristic of the asymmetric (degenerate) vibrations.

The suggested assignment allows one to follow logically the change in the low-frequency Raman spectrum of the cyclopentadienyl metal complexes with a change in the polarity of the metal–ring bond.

In the low-frequency region of the Raman spectra of the Cp_2M complexes, we see two closely-lying lines of the skeletal vibrations of the metal–ring bond: one line is a symmetric stretching mode, the other is a degenerate tilt mode [1–3]. In the spectra of Cp_2M complexes with a covalent metal–ligand bond, the intensity of the symmetric stretching mode is stronger than that of the "tilt" mode [1,2]. In the Raman spectra of complexes with a predominantly ionic metal–ring bond such as Cp_2Mg [13] and Cp_2Mn [19], inversion of the intensities is observed: the "tilt" mode line is more intensive than that of the stretching mode.

According to our assignment, the intensity of the stretching line in the spectra of the ionic cyclopentadienides should reduce practically to zero and we should observe only a "tilt" mode line in the spectra. Thus, the intensity of the stretching line of the metal–ring bond decreases with an increase in its polarity, which is in agreement with the theoretical considerations [10]; this reasonably leads us to expect a decrease of the line intensity of the stretching mode of the bond with an increase in its polarity.

Temperature effects in the Raman spectra of cyclopentadienides

If the C_5H_5Li sample is cooled to liquid nitrogen temperature, the majority of the lines in the Raman spectrum narrow and split into two components. Since only the degenerate mode lines are split, this may be due to a site splitting. In the case of C_5H_5Na, we observe a narrowing of the majority of lines when the sample is cooled. We may also see the splitting of some of them, but the $\sim 170^{-1}$ line, however, remains unchanged. As far as the C_5H_5K compound is concerned, the cooling of the sample will exert a slight influence on the width of the Raman spectral lines, and the lines remain broad. The appreciable width of the low-frequency vibration lines in the C_5H_5K spectrum and the almost total absence of a temperature dependence apparently indicate statistical disorder in the C_5H_5K crystals which, in turn, may be related to the arbitrary rotation of the C_5H_5 ring about the highest order axis of the crystal.

Both the IR spectra at room temperature and the Raman spectra at liquid nitrogen temperature for different cyclopentadienides are characterized by the different number of components of the crystal splitting of the bands which are clearly seen in the ν(CH) and ρ(CH) regions. Different numbers of the bands are also seen in the low-frequency range, whereas no coincidence of the frequencies is observed in the IR and Raman spectra. This leads us to suppose different centrosymmetric crystal structures for lithium, sodium and potassium cyclopentadienides.

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