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RAMAN SPECTRA OF POTASSIUM CYCLOOCTATETRAENIDE *

V.T. ALEKSANYAN *, I.A. GARBUZOVA, T.M. CHERNYSHOVA and Z.V. TODRES
Institute of Organo-Element Compounds, Academy of Science, 28 Vavilova st., Moscow (U.S.S.R.)

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Summary

Raman spectra of the crystalline solvate $K_2COT \cdot n THF$ (COT = cyclooctatetraene) and its solution in THF have been recorded. An assignment of the vibration frequencies has been made. A rather strong line has been assigned to the symmetric stretching vibration of potassium cations relative to the 8-membered ring.

Dicyclooctatetraene-uranium(IV) (uranocene), obtained by Steitwieser in 1968 [1], was the first example of a π-complex wherein the cyclooctatetraene dianion, an 8-membered aromatic carbocycle with 10 π-electrons, serves as the ligand. To date, the chemical and physical properties of a large variety of cyclooctatetraene dianion (COT) complexes with transition metals [2] have been studied. The COT complexes with lantanides and actinides are of special interest in view of the possibility of interaction between the π-orbitals of the ligand and the *f*-orbitals of the coordinating atom [3,4]. The vibrational spectra of COT complexes have been studied in a number of cases [3—11] but complete Raman and IR spectra have been reported only for thorocene, $ThCOT_2$ [6]. An attempt to analyse the IR spectra of COT complexes is given in ref. 7. Since there are no complete data on the vibrational spectra of the "free" COT dianion, it is difficult to judge the reliability of the suggested assignment: at the present time only IR active vibration frequency values for K_2COT and Na_2COT complexes are known [12,13]. The purpose of this work was to obtain and analyse the Raman spectrum of the dipotassium salt of the COT dianion, K_2COT, and to compare the results with those in the literature on the spectra of COT complexes with transition metals.

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Experimental section

Potassium cyclooctatetraenide was prepared as a crystalline solvate, $K_2COT \cdot nTHF$ and in solution in THF, according to procedures described in ref. 14. The solution and crystal spectra measurements were made with a Ramanor-HG 2S spectrometer; the 514.5 nm line of a Spectra Physics-164 argon laser was used for excitation. The laser power varied from 50 to 200 mW. The salt solution in THF was sealed under argon in a glass cuvette with two outlets. Subsequent recording of the spectrum of the solution accompanied by a gradual removal of the solvent via one of the outlets was carried out so as the separate the COT^{2-} lines from the spectrum of the solvent. Soon after the removal of the solvent transparent, yellow solvate crystals appeared on the bottom and on the walls of the glass cuvette. The THF lines in the solvate spectrum are relatively weak and do not mask the dianion lines.

Results and discussion

Potassium cyclooctatetraenide in THF exists in the form of a neutral ion aggregate (K^+, COT^{2-}, K^+)- in which the solvated K cations are bonded to the dianion in a contact triple ion [15,16]. According to X-ray analysis of K_2COT-(diglime) [17] and K_2(1,3,5,7-tetramethylCOT)(diglime)$_2$ [18], a sandwich structure is realized in the crystal: the potassium atoms are located on the C_8-axis on both sides of the rings. In the case of potassium cyclooctatetraenide one of the potassium atoms is solvated by a diglime molecule, whereas in the case of the methyl derivative both potassium atoms are solvated.

The structure of $K_2COT \cdot nTHF$ has not been determined. However, it is known that the THF can be completely removed from the solvate under vacuum without heating, which indicates that the interaction of the THF molecule with the salt is rather weak [16].

The Raman spectrum of K_2COT is consistent with the presence of a planar aromatic ring with a D_{8h} symmetry in the crystal and in solution. The 42 modes of COT^{2-} belong to a reducible representation giving rise to the following symmetry species: $\Gamma_{vibr} = 2A_{1g} + A_{2g} + 2B_{1g} + 2B_{1u} + 2B_{2g} + E_{1g} + 3E_{1u} + 4E_{2g} + 2E_{2u} + 2E_{3g} + 4E_{3u}$, thus the Raman spectrum must reveal seven lines of the following modes: $2A_{1g}(\nu(CH), \nu(CC))$; $E_{1g}(\rho(CH))$, $4E_{2g}(\nu(CH), \beta(CH), \gamma(CCC), \nu(CC))$.

The two A_{1g} symmetry modes should be present in the Raman spectrum of the solution (Fig. 1) as polarized lines: the strong, polarized line, at ~740 cm^{-1}, is undoubtedly due to the totally symmetrical mode of the ring. Identification of the second A_{1g} mode in the spectrum of the solution proved difficult due to strong scattering of the solvent in the range 2800—3100 cm^{-1}. Two new lines at 3011 and 2979 cm^{-1} were detected in the spectrum of the crystal (Fig. 2) in the ν(CH) range. Similar to the spectra of other aromatic carbocycles [19,20], we can assign the high-frequency 3011 cm^{-1} line to the ν(CH) (A_{1g}) mode and the low-frequency one to the ν(CH) (E_{2g}) mode.

The only E_{1g} symmetry mode is recorded in the Raman spectrum as a relatively weak line at 711 cm^{-1}, depolarized in the Raman spectrum of the solution. Its assignment is reliable as the ρ(CH) vibration lines in the spectra of other arom-

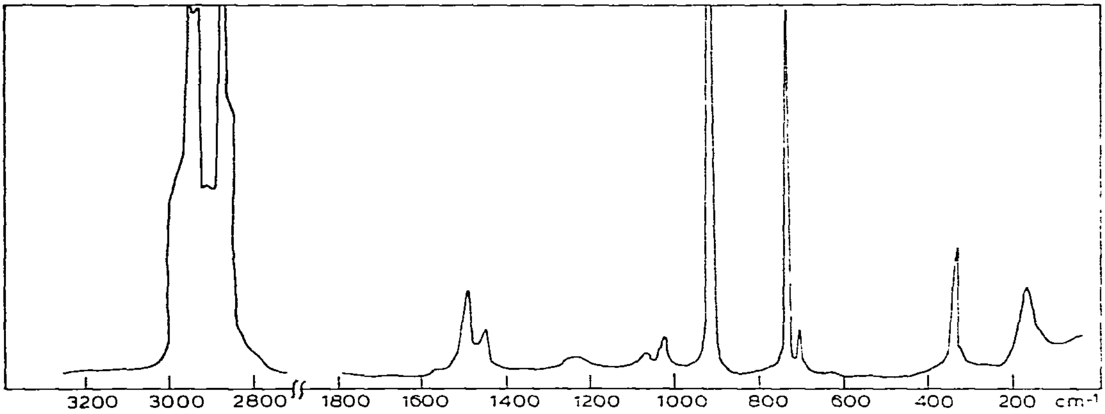

Fig. 1. Raman spectrum of THF solution of K_2COT.

atic carbocycles appear in the same region. The low frequency depolarized line in the Raman spectrum at 343 cm^{-1} can be assigned to the in-plane ring bending, $\gamma(CCC)(E_{2g})$. The frequency of this mode tends to decrease with increase in the carbocycle size for a number of aromatic carbocycles from 606 cm^{-1} in the spectrum of benzene [19] to 433 cm^{-1} in the spectrum of the tropilium cation [20]. A further decrease in the frequency in the case of COT^{2-} is reasonable.

The frequency of the degenerate C—C ring stretching mode, $\nu(CC)(E_{2g}$, 1488 $cm^{-1})$ is considerably lower than that of the corresponding mode in the benzene and tropilium cations (~1600 cm^{-1}). The corresponding IR band of the E_{1u} mode is also as low as 1295 cm^{-1} [13]. In the spectra of other aromatic carbocycles the band in the 1450—1490 cm^{-1} region corresponds to this mode [19—21].

We failed to find lines which could be assigned with certainty to the in-plane C—H bending mode ($\beta(CH)$, E_{2g}). Two candidates for such an assignment occur in the spectrum of the crystal: they are the weak lines at 905 and 1055 cm^{-1}.

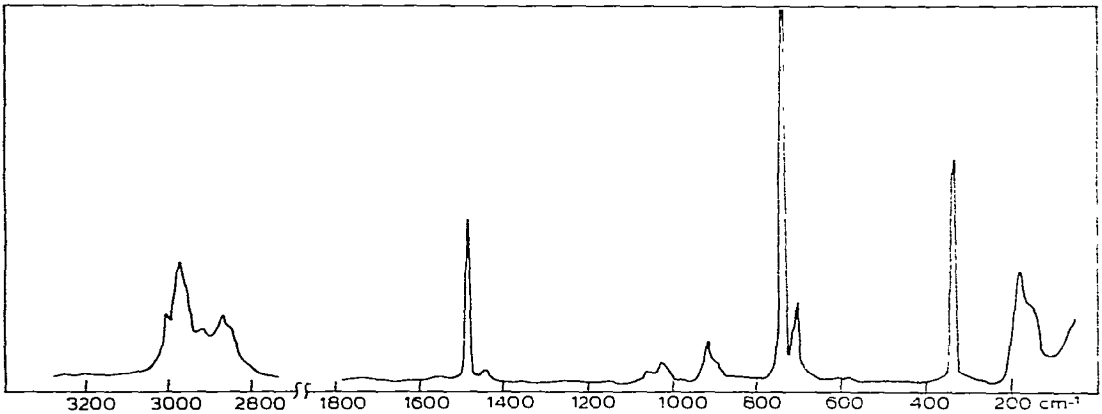

Fig. 2. Raman spectrum of the crystalline solvate $K_2COT \cdot n$ THF.

The corresponding IR band of the E_{1u} mode is at 880 cm^{-1}. If we assume that the E_{2g} line is in almost the same region of the spectrum, we may regard the 905 cm^{-1} line as the most suitable candidate for this assignment. However, we cannot exclude the possibility that the 905 and 1055 cm^{-1} lines may appear as a result of crystal effects.

A rather strong and polarized line at 170 cm^{-1} with a halfwidth of around 30 to 40 cm^{-1} was observed in the low-frequency Raman spectrum. In the spectrum of the crystal this line has a weak satellite at 157 cm^{-1} (Fig. 2). Such wide bands are typical for the IR spectra of salt solutions of alkali metals in solvating solvents. These bands are assigned either to cation vibrations in a solvent cage, in the case of formation of solvated ions or of a solvent-separated ion pair [22—24], or to the internal cation—anion stretching vibration in the case of formation of a contact ion pair [25,26]. In the first case the position does not depend on the nature of the anion, in the second case such a dependence is observed. We assume that the line observed at 170 cm^{-1} in the Raman spectrum of K_2COT in THF is due to the symmetric stretching of potassium cations relative to the 8-membered ring, from the following arguments: (a) K_2COT in THF solution exists in the form of a contact triple ion; (b) A line with similar characteristics is seen in the spectrum of the crystal where THF is not in excess; (c) the frequency of this vibration is higher than that of the potassium ion vibration in a solvent cage of THF

TABLE 1

RAMAN FREQUENCIES AND ASSIGNMENTS FOR POTASSIUM CYCLOOCTATETRAENIDE [a]

THF soln. $\Delta\nu$ (cm^{-1}) (ρ)	crystal-phase $\Delta\nu$ (cm^{-1})	assignment
	78w	
	157(sh)	
170m(br) (p, $\rho \simeq 0.5$)	180m(br)	$\nu[K^+COT^{2-}K^+]$
280vw(br)		THF
342m(dp)	343s	γ(CCC)E_{2g}
711w(dp)	709w	ρ(CH)E_{1g}
	718(sh)	
736s(p)	737s	ν(CC)A_{1g}
	905(sh)	β(CH)E_{2g}?
918vs	919w	THF
1030w	1032w	THF
1057vw	1055w	β(CH)E_{2g}?
1075vw		THF
1230w(br)		THF
1450w	1450vw	THF
1488m(dp)	1492s	ν(CC)E_{2g}
1570w	1570vw	impurities
2860(sh)	2860(sh)	THF
2878s	2878m	THF
2915w	2910w	THF
2942s	2940w	THF
2963s	2979m	ν(CH)E_{2g}
2983(sh)	2985(sh)	THF
	3011m	ν(CH)A_{1g}

Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad; ρ, depolarization degree.

molecules (142 cm^{-1}) (observed, e.g. in the IR spectrum of $K^+Co(CO)_4^-$ in THF [24]).

In ref. 27 it was shown that the contact ion pair or the triple ion is created largely under the influence of ionic forces, therefore, the appearance of a rather strong line due to cation—anion stretching in the Raman spectrum of K_2COT was quite unexpected. We failed to find any examples of Raman spectra showing cation—anion stretching lines of contact ion pairs or triple ions in the literature. All attempts to assign the stretching mode of the cation relative to the solvent molecules in the Raman spectrum of the solvated alkali metal cation or the solvent-separated ion pair were unsuccessful [24,23,28]. However, examples are available in the literature of ionic compounds with strong cation—anion stretching in the low-frequency range of the Raman spectra. These are the ionic-bonded cyclopentadienyl complexes of alkaline-earth and rare-earth metals and manga-

TABLE 2

VIBRATIONAL SPECTRA OF POTASSIUM CYCLOOCTATETRAENIDE AND THOROCENE ^{a}

K_2COT (cm^{-1})		$ThCOT_2$ (cm^{-1}) [6,7]		Assignment for thorocene (D_{8h})	
Infrared [13]	Raman	Infrared	Raman	ref. 7	this work
	170m		188vw		
			200vw		
			225 } s		
			228		
		250vs	242s	ν(M—L)$_{as}$	
			270w		
		375m			
	343m		391m		γ(CCC)E_{2g}
		525w			
		565w			
		608w			
		642m			
675vs		695vs		ν(M—L)$_{tilt}$ E_{1u}	ρ(CH)A_{2u}, A_{1g}
	709w				
		742s	726w	ρ(CH) } A_{2u}, E_{1u}	ρ(CH)E_{1g}, E_{2u}
	737s	775s	775s	ρ(CH)	ν(CC)A_{1g}, A_{2u}
		790w	790w		
		810w			
		848w	860vw		
880s		895s	901vw	β(CH)E_{1u}	β(CH)E_{1g}, E_{1u}
1295w		1315m	1320vw	ν(CC) } A_{2u}, E_{1u}	ν(CC)E_{1g}, E_{1u}
				ν(CC)	
		1430m			
		1450w			
	1492m		1505w		ν(CC)E_{2g}
		2830w	2855vw		
		2880w			
			2905m		
		2920m	2928vw	ν(CH) } A_{2u}, E_{1u}	
	2979m		2982w		ν(CH)E_{2g}
2994s		3005m		ν(CH)	ν(CH)E_{1g}, E_{1u}
	3011m		3022m		ν(CH)A_{2u}, A_{1g}
			3045m		

^{a} Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

nese [29]. The results obtained have not yet been theoretically treated and requires a more detailed analysis.

The assignment of the Raman spectra of K_2COT is given in Table 1. The complete vibration spectrum of K_2COT is presented in Table 2, along with the literature data on the thorocene spectra [6,7]. Table 2 also gives a partial assignment of vibrational frequencies in the spectrum of thorium complexes as well as a comparison of the assignments for the K_2COT and $ThCOT_2$ spectra [7].

Analysis of these data allows us to make the following tentative remarks.

1. The thorocene spectra maintain the features seen in the spectrum of the COT^{2-} ion. Practically all the COT^{2-} frequencies rise slightly with coordination.

2. A number of assignments for vibration frequencies suggested in ref. 7 should be recognized as invalid. Thus, not all the bands in the 700—800 cm^{-1} region of the IR spectrum of thorocene are due to the out-of-plane C—H stretching: one of them is due to antiphase ring breathing. In ref. 7 the IR band in the 1300—1400 cm^{-1} region is assigned to this mode. We consider this assignment to be invalid, since the frequency of this vibration should be close to or coincide with that of the synphase ring breathing at 775 cm^{-1}.

3. The IR bands in the range below 2950 cm^{-1}, do not belong to the fundamental modes and are, therefore, due to transitions of higher order.

4. The assignment given in ref. 7 of the strong bands at ~700 cm^{-1} in the IR spectrum of thorocene to the asymmetric metal—ring tilt is invalid. In fact, these bands should be assigned to the out-of-plane C—H bending modes.

A more complete discussion of the data obtained requires further investigation of the spectra of COT complexes.

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