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RAMAN SPECTRA OF TRICYCLOPENTADIENYL COMPLEXES OF LANTHANIDES

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Summary

The Raman spectra of some $LnCp_3$ complexes have been obtained at room temperature and at the temperature of liquid nitrogen. The spectra of several complexes have been measured in the molten state, which provided information about the depolarisation of Raman lines. The spectrum of the Cp-ring vibrations is typical of a h^5-coordinated ligand. The intensity distribution reflects the considerably ionic character of the M—Cp bonds in $LnCp_3$ complexes. Assignment of skeletal vibrations is discussed.

The vibrational spectra of lanthanide cyclopentadienyl complexes have been comparatively poorly studied. Until recently the IR spectra of only a few $LnCp_2$ (Cp = cyclopentadienyl), $LnCp_3$ [1,2] and YCp_3 [2] complexes have been recorded and only the region of Cp-ligand vibrations was covered (up to 600 cm^{-1}), i.e. the nature of M—Cp bond in this interesting class of compounds has not been studied. Recently the Raman spectra of several $LnCp_3$ complexes (Ln = La, Pr, Nd, Sm, Gd, Dy and Tm) in the crystalline state were reported [3]. New data on the Raman spectra of $LnCp_3$ complexes are presented in this paper. The spectra of several complexes in the molten state, which provide information about the depolarisation of Raman lines required for the interpretation of Cp-ligand spectra and skeletal vibrations, were also recorded.

$LnCp_3$ complexes (Ln = Pr, Tb, Ho, Gd, Er and Lu) and YCp_3 were prepared by interaction of sodium cyclopentadienide with anhydrous lanthanide chlorides in tetrahydrofuran solution [4,4a]. Compounds were purified by repeated vacuum sublimation and were studied in small capillaries.

Raman spectra were recorded on Coderg PHO and T-800 spectrometers equipped with He—Ne and Ar^+-lasers, respectively. For recording the Raman spectra of molten complexes, capillaries were heated (up to ~300°C) in a special copper holder with the temperature automatically controlled. The spectra of

TABLE 1. RAMAN SPECTRA OF LIQUID TRICYCLOPENTADIENYL COMPLEXES OF THE RARE EARTH ELEMENTS

$ErCp_3$			$TbCp_3$			$HoCp_3$			$GdCp_3$			Assignment
$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	
140	m	dp	135	m	dp	139	m	dp	132	m	dp	
220	m	dp	221	m	dp	218	m	dp	220	m	dp	see text
231	s	p	230	s	p	232	s	p	230	s	p	
			618(br)	vw	?	615	vvw	?				χ(CCC)
			770(br)	m	dp	769	m	dp				
						787(sh)	w	p?				ρ(CH)
			841	vw	dp	840	vw	dp				
			1008	vw	dp	1006	vw	dp				β(CH)
			1064	m	dp	1065(br)	w	dp				β(CH)
			1122	vs	p	1122	vs	p				ν(CC)
			1230(br)	w	p [a]	1229(br)	w	p				overtone
			1350(br)	m	dp	1350(br)	m	dp				ν(CC)
			1435(br)	w	dp	1432	w	dp				ν(CC)
			3075	w	dp	n.m. [b]	n.m.					
			3104	m	dp	n.m.	n.m.					ν(CH)

[a] dp = depolarization ratio; $\rho \cong 0.1$—0.2. [b] not measured.

TABLE 2. RAMAN SPECTRA OF TRICYCLOPENTADIENYL COMPLEXES OF THE RARE EARTH METALS IN THE LOW-FREQUENCY REGION

$PrCp_3$		$TbCp_3$		$LuCp_3$		YCp_3	
$\Delta\nu$	I	$\Delta\nu$	I	$\Delta\nu$	I	$\Delta\nu$	I
						18	w
		24	m	23	m	26	w
		40	w	30	m	38	w
52	w	46	vw	44	m	52	w
		51	w			56	w
62	w	59	vw	58	w		
		65	vw				
72	m	70	vw	74	w	68	w
78	w	79	m	82	w	77	w
87	s	92	w			84	m
				96	m	94	vw
				101	w		
				110	vw	107	w
130	s	123	w	126	w	116	vw
		136	w	133	vw	130	w
				138	m	138	w
		145	w				
		149	m			151	m
		154	w			155	m
		186	w	171	m	183	w
202	m	198	w			198	w
214(sh)	w						
229	m	215	m	220	m	215	m
		225	m			221	w
230(sh)	w	231(sh)	w	230	m	232	m
240	s	237	m	240	m	240	s
						245	s
251	s	249	s	249	s	253	s
		257	sh	253	sh	257	s
263	m	267	s	261	s	270	m
277	m	276	w	278	m	278	w
		280	m				
286	m	287	sh	292	m	286	w

crystalline complexes were recorded at room temperature and at the temperature of liquid nitrogen. In the latter case the capillaries were directly immersed in the coolant kept in a specially designed Dewar flask. The results are presented in Tables 1 and 2.

Discussion

General description

Comparison of the results obtained shows that the spectra of molten complexes contain fewer lines than the spectra of crystalline complexes. This is due not only to the higher temperature of measurement (260—300° C) but also to the complex structure of the crystal lattice, which has been studied for $SmCp_3$ [4] and $ScCp_3$ [5]. The metal atom is surrounded by four tetrahedrally arranged Cp rings, two of which are symmetrical in relation to the metal ("h^5-coordination") and two have different "h^1-coordination". However, the spectra of the complexes studied do not display any features characteristic of true h'-coordination of two Cp rings, the spectra are typical of complexes with symmetrical coordination of Cp rings. The inequality of the Cp rings is revealed in the more complex, as compared for instance with $FeCp_2$, $RuCp_2$, and $OsCp_2$ complexes [6], structure of multiplets, observed at frequencies at which melt spectra display single relatively wide lines. The structure is especially complex at frequencies of skeletal vibrations. Ten lines and more are observed in the 200—270 cm^{-1} range (Table 2) *. Similarity in the number, relative intensities of components and their arrangement indicates the identity of the lattice structures of the complexes.

It was assumed that the lines arising solely from electron transitions, observed in the Raman spectra of numerous lanthanide salts [7,8], may be present in the $LnCp_3$ spectra. However, comparison of paramagnetic $LnCp_3$ with diamagnetic $LuCp_3$ and YCp_3 did not reveal such transitions. The structure of the $LnCp_3$ spectra at low frequencies, the most probable region of electron transitions (within the J-manifold split in the crystalline field), is practically the same. Certain differences observed below 120—150 cm^{-1} may be due to changes in the spectra of lattice vibrations.

The spectra of the Cp-ligand

As mentioned above, the spectra of Cp-ring vibrations are typical of a h^5-coordinated ligand. The intensity distribution however, differs considerably from that of covalent complexes, for instance of ferrocene [6,9]: on average the lines of vibrations allowed in the Raman spectra for the free $C_5H_5^-$ ion are stronger whereas lines of vibrations, analogues of vibrations forbidden in the $C_5H_5^-$ spectrum, are weaker, for example, the ~1000 (β(CH)) and ~1440 cm^{-1} (ν(CC)) lines. Evidently these features of the Raman spectra, previously discussed in [10], reflect the considerably more ionic character of M—Cp bonds

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* Only data of the low-frequency region measured at the temperature of liquid nitrogen are presented here. The general structure of spectra in the entire frequency range is the same as described in [3] for all complexes studied in the present work.

in $LnCp_3$ complexes. Similar intensity distributions in the Raman spectra were reported for $MgCp_2$ [11], $MnCp_2$ [12], and CpBeCl [13].

The assignment of vibration frequencies given in Table 1 are made in accordance with analysis of vibrational spectra of Cp-complexes described in [10]. It should be noted that the weak line at ~1230 cm^{-1}, as in the complexes studied previously [11—13], is polarised and is therefore interpreted as the overtone of an out-of-plane bending vibration of the Cp ring, strengthened by resonance interaction with the breathing Cp-ring vibration (~1120 cm^{-1} line).

Skeletal vibrations

It is known that tricyclopentadienyl complexes of rare earth metals have a slight dipole moment in solution (0.86 D for $LuCp_3$ [2] and 1.46 D for YCp_3 [15]). A symmetrical trigonal structure with the Cp rings slightly tilted towards the third order axis (C_{3v} symmetry model) was inferred from this. We shall base our assignment on this model, bearing in mind that the actual selection rules may practically coincide, due to the apparently small tilting angle, with the selection rules of the more symmetrical D_{3h} model *.

Group theory predictions for Raman and IR absorption spectra are presented in Table 3. Three M—Cp stretching vibrations were taken into account: one symmetrical and one doubly degenerated tilting vibration.

The Raman spectra of molten complexes display at least three lines, one of which is strongly polarised (Table 3). This structure of the spectra indicates high symmetry of the complexes in melt form although the considerable width of the line (up to 30—40 cm^{-1}) does not exclude possible superposition of three or more transitions in the 200—250 cm^{-1} region. The similarity of the spectra of all four complexes not only in the frequency values but also in the intensity distribution, points to the identical structure of the molten complexes.

TABLE 3

DISTRIBUTION OF SKELETAL VIBRATIONS OF $LnCp_3$ COMPLEXES AMONG SYMMETRY TYPES OF GROUPS C_{3v} AND D_{3h}

Type of symmetry	C_{3v}	A_1		A_2		E	
	D_{3h}	A_1'	A_2''	A_1''	A_2''	E'	E''
Stretching M—Cp		1	—	—	—	1	—
Tilting M—Cp, in plane		—	—	—	1	1	
Tilting M—Cp, out of plane		—	1	—	—	—	1
Rocking, in plane		—	—	—	rotation	1	—
Rocking, out of plane		—	1	—	—	—	rotation
Twisting		—	—	1	—	—	1
Selection rules	C_{3v}	Raman, IR		—		Raman, IR	
	D_{3h}	Raman	IR	—	—	Raman, IR	Raman

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* This model does not take into account the asymmetry of the Cp ring in relation to the coordination plane. However, this will hardly cause any distortions as practically free rotation of Cp rings around the Cp—M bond may be assumed for the temperatures used in our study.

The polarised line, obviously, corresponds to a A'_1 (D_{3h})-type vibration. The C_{3v} model involves another polarised line, however it can be assumed that it should be weak and that it may be displayed at another frequency since it is due to tilting movement of Cp rings.

Assignment of the two depolarised lines is not so obvious. The most likely assignment of the 220 cm^{-1} line is the E vibration which is a degenerated combination of symmetrical stretchings of the three M—Cp coordinates (first line in Table 3). Then, the two remaining allowed vibrations, the linear combinations of tilting movements of three Cp rings (E' and E'') may be associated with the 140 cm^{-1} line (second and third lines in Table 3).

It is possible, however, that the 140 cm^{-1} line is due to an E'-type rocking vibration and that all ν(M—Cp) vibrations are located in the 200—250 cm^{-1} region.

References

1 G. Wilkinson and J.M. Birmingham, J. Amer. Chem. Soc., 78 (1956) 42.
2 E.O. Fischer and H. Fischer, J. Organometal. Chem., 3 (1965) 181.
3 V.T. Aleksanyan, G.K. Borisov, G.G. Devyatikh and J.A. Koningstein, J. Raman Spectrosc., 2 (1974) 345.
4 Wong Chi-Hsiang, Lee Tseng-Yu and Lee Yuen, Acta Cryst., B25 (1969) 2580.
4 a S.G. Krasnova, G.K. Borisov and G.G. Devyatykh, J. Inorg. Chem. (USSR), 16 (1971) 1733.
5 J.L. Atwood and K.D. Smith, J. Amer. Chem. Soc., (1973) 95.
6 Ya.M. Kimel'fel'd, E.M. Smirnova and V.T. Aleksanyan, J. Mol. Struct., 19 (1973) 329.
7 J.A. Koningstein, Spectroscopy in Inorganic Chemistry, Vol. 2, Academic Press, N.Y., 1971.
8 J.A. Koningstein, Usp. Khim., 42 (1973) 1810.
9 E.R. Lippincott and R.D. Nelson, Spectrochim. Acta, 10 (1958) 307.
10 V.T. Aleksanyan and B.V. Lokshine, J. Organometal. Chem., in press.
11 V.T. Aleksanyan, I.A. Garbuzova, V.V. Gavrilenko and L.I. Zakharkin, J. Organometal. Chem., in press.
12 V.T. Aleksanyan, B.V. Lokshine, G.K. Borisov, G.G. Devyatykh, J.A. Koningstein and B.F. Gächter, J. Organometal. Chem., in press.
13 D.A. Coe, J.W. Nibler, T.H. Cook, D. Drew and G.L. Morgan, J. Chem. Phys., 63 (1975) 4842.
14 B.V. Lokshine, V.T. Aleksanyan and E.B. Rusach, J. Organometal. Chem., 86 (1975) 253.
15 E.O. Fischer and H. Fischer, J. Organometal. Chem., 6 (1966) 141.