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RAMAN SPECTRA OF CYCLOPENTADIENYL COMPLEXES $(h^5\text{-}C_5H_5)_2M$ (M = Mn, Cr, V, Ru, Os)

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Summary

The Raman spectra of several dicyclopentadienyl complexes Cp_2M of transition metals (M = Mn, Cr, V, Ru, Os) are obtained in the solid and liquid states and are discussed together with the infrared data. The assignment of some Cp-vibrations is revised and a new assignment is proposed. The observed difference between the Raman spectra of the low temperature amber-brown form and the rose form of manganocene is considered as a manifestation of a possible equilibrium between two different isomers of the compound in its low-temperature form.

Due to its unusual magnetic properties, manganocene occupies a special place among dicyclopentadienyl complexes. While being isoelectronic with the ferricinium ion, Cp_2Fe^+, manganocene (Cp_2Mn) exhibits paramagnetism in melt and solutions which corresponds to the presence of five unpaired electrons ($^6A_{1g}$ ground state). The low-temperature amber-brown phase, existing up to 432 K, possesses antiferromagnetic properties (Neel temperature 134 K). However, the field dependence of magnetic susceptibility, although weak, is retained up to 432 K, the point of transition into the paramagnetic rose form which is a normal paramagnetic one and corresponds to the sextet ground state [1]. On the other hand, the existence of stable diamagnetic complexes of manganese enabled M.E. Dyatkina to suggest that the energy difference between the sextet Cp_2Mn state and the possible doublet state, similar to Cp_2Fe^+ (ground state $^2A_{1g}$ or $^2E_{2g}$), is not very great [2]. This suggestion was recently confirmed by the study of the EPR spectra of Cp_2Mn and $(MeC_5H_4)_2Mn$ [3]. Data obtained at 4.2 K were in agreement with a "doublet" ground state. It was proposed that the anomalous magnetic properties of the low-temperature form of Cp_2Mn may be due to an equilibrium between these two forms. We thought it promising to use vibrational spectroscopy for the study of this problem. For the brown form of

TABLE 1

VIBRATIONAL SPECTRA (cm^{-1}) OF DICYCLOPENTADIENYL COMPLEXES Cp_2M (M = Mn, Cr, V, Ru, Os)

Cp_2Mn				Cp_2V		Cp_2Cr			Cp_2Ru	Cp_2Os	Assignment (D_{5d})
Brown form		Rose form	Melt	Solid ~ 90 K		Solid ~ 90 K		Melt	Melt	Melt	
IR	R	R	R	IR	R	IR	R	R	R	R	
										122w	
					183w				160w	159w	$\nu(22)(E_{2u})$
	203m		212m(p)		258m		273s	273s(p)	325s(p)	349vs(p)	$\nu(4)(A_{1g})$
	153m	155m	141m		331m		370vw		396m	419m	$\nu(16)(E_{1g})$
				380s		408m					$\nu(11)(A_{2u})$
				426s		435m					$\nu(21)(E_{1u})$
620w	580m	570vw	620vw	610vw		620vw			590vw	599vw	$\nu(28)(E_{2g}), \nu(34)(E_{2u})$
	750w	758w	749m								
767vs	760w	766w	774w(p)	780vs		765vs			815m(p)	816w	$\nu(2)(A_{1g}), \nu(9)(A_{2u}),$
830w	807w			803(sh)		800(sh)			830w	831m(p)	$\nu(14)(E_{1g}), \nu(19)(E_{1u})$
860m			843w	838m		840(sh)					
		920w	910w	880w(br)						890w	$\nu(27)(E_{2g}), \nu(33)(E_{2u})$
995s 1005s				1005vs		992vs	985w(br)			991w	$\nu(13)(E_{1g}), \nu(18)(E_{1u})$
1055w	1065m	1058m	1060m	1047m 1055m	1055w 1065(sh)	1040w 1055w	1048m 1055m		1060m	1059m	$\nu(24)(E_{2g}), \nu(30)(E_{2u})$
1105w	1108s 1113s	1103s	1109vs(p)	1107s	1106s	1095s	1094vs	1094vs(p)	1098s(p)	1094vs(p)	$\nu(3)(A_{1g}), \nu(10)(A_{2u})$
		1180vw(br)	1234w(p)						1195vw	1180w(p)	$2\,\nu(28)(2\,\nu(34))$
	1230w(br)	1235w(br)		1260m		1252w					$\nu(7)(A_{2g}), \nu(5)(A_{2u})$
1345w	1345m	1337m	1337m	1350m	1345m	1340w(br)	1335m(br)		1360w	1352w	$\nu(26)(E_{2g}), \nu(32)(E_{2u})$
1425w	1405w		1422w	1425m		1408m	1408m(br)		1410m	1401m	$\nu(15)(E_{1g}), \nu(20)(E_{1u})$
3075m	3075m	3075m	3075m	3080w		3086m				3095w	$\nu(12)(E_{1g}), \nu(17)(E_{1u})$
3090m	3095m	3097m	3098m(p)	3090w		3097m	3105m			3110w(p)	$\nu(1)(A_{1g}), \nu(8)(A_{2u})$
						3108w					

Cp_2Mn, IR absorption spectra in the region of 4000—400 cm^{-1} have been described [1,4], to our knowledge the Raman spectra have not previously been recorded.

In the present work we have recorded the Raman spectra of Cp_2Mn in two crystalline modifications and as a melt, and the IR spectra of the low-temperature form in the 4000—250 cm^{-1} region. The data obtained are compared with the spectra of chromocene, vanadocene, ruthenocene, and osmocene. For Cp_2Cr and Cp_2V only the IR spectra have been described [4,5]. Analysis of available IR spectra of Cp_2Cr and Cp_2V shows that decomposition products (for example, cyclopentadiene) were present in the studied samples. Raman spectra of these compounds have not been previously recorded. For Cp_2Ru and Cp_2Os, Raman spectra have been obtained only for solid state and solutions, and the degree of Raman line depolarization, due to low solubility, has only been measured for the strongest lines [6—9]. We have recorded the Raman spectra of melts and determined the line polarization.

Experimental

IR spectra were recorded on Perkin—Elmer 457 and UR-20 Zeis spectrophotometers. Preparation of samples and recording of spectra were carried out in the absence of oxygen and moisture. Compounds were deposited in a vacuum glass cryostat onto a KRS-5 window cooled to 90 K. Before evacuating, a small capillary containing the substance to be studied was crushed in a side arm of the cryostat in an Ar atmosphere. During deposition the side arm washeated to 60—100°C in a heating jacket. Despite these precautions weak bands of cyclopentadiene were sometimes observed in the IR spectra.

Raman spectra were obtained on Coderg PHO and T-800 spectrophotometers with a He—Ne laser (6328 A line). Samples were placed in capillaries which were vacuum sealed. To measure the spectra at elevated temperatures the capillaries were heated in a special copper holder connected to a furnace. The temperature was automatically controlled and was maintained within several degrees. Despite strong absorption satisfactory spectra of the amber-brown form of Cp_2Mn were obtained. We were not able to record several weak lines of Cp_2Cr and Cp_2V. No difficulties were encountered while measuring the spectra of Cp_2Mn melts, the rose form and the spectra of Cp_2Ru and Cp_2Os melts. The data obtained are presented in Table 1.

Discussion

Vibrational spectra and assignments of the compounds studied are given in Table 1. Raman spectra of Cp_2Mn, Cp_2Cr and Cp_2V have not been previously recorded. IR spectra obtained at —196°C differ noticeably from those previously reported. The recorded Raman spectra of the Cp_2Ru and Cp_2Os melts made it possible to perform polarization measurements on several weak lines. Comparison of the spectra shows that in the region of cyclopentadienyl ring vibrations (above 600 cm^{-1}), regardless of the significant differences in the nature of metal—ligand bonds, spectra of all the compounds studied are very similar. Assignment was performed on the basis of D_{5d} molecular symmetry. The eclipsed conformation with D_{5h} symmetry possible for these compounds does not change the selection rules and only leads to changes in the designations of the corresponding vibrations. Numeration of frequencies is the same as in [5]. Assignment of most of the frequencies is not discussed here since it corresponds to the accepted assignment for h^5-Cp compounds. Only new assignments and specific features of spectra are discussed below.

1. Frequencies of the out-of-plane CH ring vibrations in the 700—850 cm^{-1} region are significantly affected by the metal atom. It is usually accepted [5] that these frequencies decrease with an increase in the ionic character of the M—Cp bond. This is confirmed by the position of the ρ(CH) frequencies in spectra of melt and the rose form of Cp_2Mn and other ionic Cp complexes [10,11]. However, the dependence is apparently of a more complex nature. Thus, the ρ(CH) frequencies of Cp_2Fe^+ are higher than for ferrocene. For Cp_2V and Cp_2Cr a band near 840 cm^{-1} is observed along with very intensive IR bands at 765—780 cm^{-1}. It is of interest that the spectra of the low temperature manganocene form is more complex than the spectra of the rose form and of the melt; in addition to lines in the 750—780 cm^{-1} region, bands appear near 830 and 860 cm^{-1}. Their appearance can hardly be explained by the crystalline effects and their position is similar to that of the ρ(CH) frequencies in the ferricinium ion spectrum. It may be assumed, in accordance with [3], that in the brown form of Cp_2Mn along with "sextet" molecules, "doublet" Cp_2Mn is present, an electron analogue of the ferricinium ion. This may be the cause of anomalous magnetic properties of the low-temperature form.

Results of polarization measurement of ρ(CH) lines in the melt made it necessary to reverse the symmetry assignment of the 816 and 831 cm^{-1} lines of osmocene. Unlike ferrocene [12], the line with higher frequency corresponds to the symmetrical vibration. It should be noted that in both cases the more intensive line in the IR spectra corresponds to ν(9) vibration.

2. We have proposed a new assignment of the line in the 1050 cm^{-1} region to the in-plane bending vibration β(CH)ν(24) of E_{2g} class. This line is usually assigned to out-of-plane bending vibration ρ(CH)ν(25) of E_{2g} class. This assignment was first proposed by Lippincott and Nelson [13] while comparing spectra of metallocene compounds with benzene and tropylium ion spectra. The ρ(CH) (E_2'') vibration in the free $C_5H_5^-$ ion (D_{5h} symmetry) is not active in the IR spectrum or in the Raman spectrum. It can be expected that, in the case of ionic Cp complexes, this line should be weak in the Raman spectra, however, for metallocenes, in which the ionic character of the bond is beyond all question (Cp_2Mn in the present work, tricyclopentadienyl complexes of lanthanides [11], Cp_2Mg [10]), this line is sufficiently intense and consequently, should be assigned to one of the allowed vibrations of the $C_5H_5^-$ ion. The only suitable candidate seems to be the in-plane bending vibration β(CH)(E_2') which in the Cp_2M model corresponds to ν(24) and ν(30) vibrations (E_{2g} and E_{2u}). Other arguments in favour of this assignment will be discussed in a paper devoted to the analysis of vibrational spectra of the Cp-ligand in various cyclopentadienyl compounds [14].

3. The line in the 1230 cm^{-1} region for Cp_2Mn and in the 1180 cm^{-1} region for Cp_2Os is polarized. Previously we established that the corresponding line in the Raman spectra of Cp_2Fe [12] and $CpMn(CO_3)$ is polarized [15]. This line is

usually assigned to an in-plane bending β(CH) vibration (ν(24), E_{2g}). In [12] we suggested that this line corresponds to the overtone of the out-of-plane bending vibration of the ring ν(28) strengthened by Fermi resonance with the ν(3) vibration (A_{1g}). Another important argument in favour of this assignment is the parallelism of frequency variation in the 600 and 1200 cm^{-1} regions of Cp_2Ru, Cp_2Os and Cp_2Mn spectra depending on the metal, the frequency of the latter taking into account the anharmonicity is equal to the doubled frequency of the ν(28) vibration. This line was not observed in the Raman spectra of Cp_2Cr and Cp_2V, apparently owing to its very low intensity. In the solid state IR spectra of these compounds rather strong bands are observed in the 1250—1260 cm^{-1} range. Their frequencies exceed 2 ν(28) and, therefore they can not be assigned to the corresponding overtone. By analogy with Cp_2Fe [16] they probably correspond to the forbidden in-plane bending β(CH) vibration (ν(5), A_{1u}, ν(7), A_{2g}) which appears in the spectrum as a result of crystalline effects.

4. The relative intensity of the degenerate in-plane ring vibrations ν(26)(E_{2g}) and ν(15)(E_{1g}) in the Raman spectra are strongly affected by the metal. This fact is of special interest since for corresponding vibrations of the $C_5H_5^-$ anion (E'_2 and E'_1), the first is allowed in the Raman spectra, whereas the second is forbidden and may appear in the spectrum only as a result of the perturbation effect of the metal. In the spectra of covalent Cp_2Ru and Cp_2Os the intensity of the ν(15) line is considerably higher than that of the ν(26) line. For Cp_2Mn and Cp_2V the ν(26) line intensity by far exceeds that of ν(15), indicating strong ionic character of the M—Cp bond in these compounds. In Cp_2Cr spectra these lines have approximately the same intensity. It has been noted that the IR band frequency of the ν(20) vibration (E_{1u}) increases with the ionic character of the metal—ring bond [5]. The corresponding ν(15) vibration has a lower frequency (1400—1410 cm^{-1}) in the Cp_2Ru, Cp_2Os and Cp_2Cr Raman spectra than in the spectra of Cp_2V and Cp_2Mn (rose form and melt) which is in agreement with this conclusion. For the low-temperature form of Cp_2Mn, 1405 and 1425 cm^{-1} frequencies are present in the vibrational spectra. This may also serve as an argument in favour of the presence of two "electron isomers" in the crystal of this compound.

5. The frequencies of the CH stretching vibrations in all compounds studied are above 3000 cm^{-1}. Bands in the 2900—3000 cm^{-1} region reported in [4,5] for the same compounds have not been observed in the IR or Raman spectra, and therefore, should be attributed to the decomposition products or to impurities.

We shall restrict ourselves to these comments on the vibrations of the Cp— ring. Assignment of these vibrations and the effect of the metal—ring bond on them will be discussed in a separate paper.

The low-frequency region which includes metal—ligand vibrations is of considerable interest for comparing various dicyclopentadienyl compounds. For the D_{5d} model only two vibrations are allowed in the Raman spectra: $\nu_4(A_{1g})$ and ν_{16} (E_{1g}). Assignment of low-frequency vibrations of Cp_2Ru and Cp_2Os has been carried out in [12]. In the Raman spectra of liquid Cp_2Mn we observed lines at 212 and 141 cm^{-1}, the frequencies of which are lower than those for ionic Cp_2Mg (218 and 189 cm^{-1}). Two features of the Cp_2Mn spectrum in this region should be noted:

(a) Although the ionic character of Mn—Cp in the rose and melt forms of Cp_2Mn is beyond doubt and is in good agreement with the existence of five unpaired electrons [1], the Mn—Cp line intensities are very high in relation to breathing ring $\nu(3)$ vibrations and are close to line intensities in Cp_2Ru and Cp_2Os.

(b) The $\nu(4)$ line has unexpectedly a higher frequency than $\nu(16)$. Such frequency inversion in relation to most metallocenes is also observed for dicyclopentadienylmagnesium [10] and nickelocene [17], but unlike the latter, in Cp_2Mn and Cp_2Mg the intensity of the $\nu(4)$ line is higher, not lower, than $\nu(16)$. Frequency inversion can be considered as another argument in favour of the ionic structure of Cp_2Mn. If the contribution of the electrostatic interaction to the metal—ring bond is considerable, it can be expected that the force constant determining the frequencies of symmetrical vibrations (A_{1g}) should be higher than the force constant for tilting vibrations (E_{1g}).

Mn—Cp frequencies of the brown (153 and 203 cm^{-1}) and the rose (155 cm^{-1}) forms are quite close to the frequencies in the melt spectra. We were unable to observe new lines in the low frequency region of the Raman spectrum, corresponding to vibrations of the "doublet" form of Cp_2Mn (for Cp_2Fe^+ the $\nu(4)$ and $\nu(16)$ lines are near 300 and 400 cm^{-1} respectively). In view of the absence of such lines in the spectra studied no final conclusion can be made about this problem. Another interesting feature of the brown form of Cp_2Mn as well as of Cp_2Fe^+ is the absence, in the IR low-frequency region, of bands that could be assigned to antisymmetrical metal—ligand vibrations ($\nu(11)$ and $\nu(21)$). This fact so far has no adequate explanation.

Assignment of the low-frequency of Cp_2V and Cp_2Cr does not present any difficulties; strong lines of symmetrical M—Cp vibrations are observed in the Raman spectrum, and bands of antisymmetrical vibrations in the IR spectra. Low frequency shift in relation to ferrocene frequencies is in agreement with the weaker metal—ring bond in these compounds.

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