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VIBRATIONAL SPECTRA OF TRIS(CYCLOPENTADIENYL)ZIRCONIUM AND -HAFNIUM HYDRIDES AND DEUTERIDES, Cp_3MX (M = Zr, Hf; X = H, D)

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Summary

The synthesis has been performed of tris(cyclopentadienyl)hafnium hydride and deuteride from Cp_4Hf treated with $LiAlH_4$ and $LiAlD_4$, respectively.

The IR spectra (4000—100 cm^{-1}) and Raman spectra of tris(cyclopentadienyl)zirconium and -hafnium hydrides and deuterides have been studied. The compounds are shown to have the structure $(\eta^5\text{-}C_5H_5)_3MX$ (M = Zr, Hf; X = H, D) with three identically bonded cyclopentadienyl ligands. The spectral characteristics obtained are consistent with metal—ring coordination of the central type. An increase is noted in the strength of the M—H and M—Cp bonds when passing from zirconium to hafnium.

Introduction

Among the hydride derivatives of the π-complexes of zirconium and hafnium with cyclopentadienyl ligands, only complexes of the type Cp_2MH_2 and Cp_2MHX (X = Cl, CH_3, BH_4, AlH_4, OCH_3; Cp = $\eta^5\text{-}C_5H_5$) were known until recently [1—3]. Some time ago we described the synthesis of the zirconium hydride complex of the new type $(\eta^5\text{-}C_5H_5)_3ZrH$, obtained by the reduction of Cp_4Zr under the action of $LiAlH_4$ in THF solution; moreover, the Raman spectra of this complex and its deuterated analogue Cp_3ZrD were outlined briefly [4]. From the Raman spectral data the conclusion was made that all the three Cp rings in these compounds are equivalent.

Cp_3ZrH is interesting as a first representative of zirconium hydrides in which all the three π-bonded ligands are alike. Previously, among the tris(cyclopentadienyl)zirconium complexes, only the monochlorides, Cp_3ZrCl and $(CH_3C_5H_4)_3ZrCl$, had been characterized [5,6]. It is also of interest that the

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known reactions of Cp_4Zr with various reagents, such as acids, alcohols and chelating agents, are accompanied by the replacement of two, three or four Cp ligands. We have, for the first time, eliminated in Cp_4Zr one ring only, the remaining three rings being unaffected.

This paper reports on the synthesis, by a similar method, of the tris(cyclopentadienyl)hafnium hydrides Cp_3HfH and Cp_3HfD. Consideration has been given to the IR and Raman spectra of Cp_3MX (M = Zr, Hf; X = H, D), and the spectra have been interpreted with respect to the structure of the complexes under study. The results obtained are correlated with the data on the spectra of the Cp derivatives of other transition metals.

Results and discussion

The data on the vibrational spectra of the compounds studied are shown in Table 1. Because of the poor solubility, the spectral data were obtained for the solid state only.

Zirconium and hafnium tetracyclopentadienyl derivatives are known [7—10] to contain both *pentahapto*- and *monohapto*-cyclopentadienyl rings and to have different structures, viz., $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$ and $(\eta^5\text{-}C_5H_5)_2Hf(\eta^1\text{-}C_5H_5)_2$.

Comparison of the Cp_3ZrH and Cp_3HfH spectra shows them to be very much alike. The spectra are practically identical both in the middle and in the far IR regions and differ only by the position of the vibration bands of the M—H bond (see below). This fact suggests that in the solid state the Cp_3ZrH and Cp_3HfH molecules have the same structure. Let us now consider the vibrational spectra in more detail.

Vibrations of the cyclopentadienyl ligands.

The internal vibrations of the Cp ligands lie in the region above 600 cm^{-1} [11]. The same region includes a number of vibrations of the M—H bond, but these can be readily distinguished from those of the Cp rings using the data for the shift of frequencies on deuteration. Analysis of the spectra shows them to contain all the bands typical of the π-bonded $\eta^5\text{-}C_5H_5$ ring and no bands that could be assigned to the vibrations of Cp rings bonded by other than η^5-coordination [7,11]. Vibrations of $\pi\text{-}C_5H_5$ ligands are usually well described on the basis of the C_{5v} local symmetry, since the internal vibrations of the Cp ligands at the metal atom are weakly coupled. For this reason the assignment of the frequencies of the Cp rings in Table 1 is based on C_{5v} symmetry. The assignment is similar to that available for other Cp complexes [11] and therefore will not be discussed in this paper. The splitting of frequencies of some degenerate vibrations may be connected with the removal of degeneracy due to the lower molecular symmetry (C_{3v}) and/or crystalline effects. Thus the data on the vibrational spectra lead to the conclusion that the complexes studied have the same structure, $(\eta^5\text{-}C_5H_5)_3MX$ (M = Zr, Hf; X = H, D), with three π-bonded cyclopentadienyl ligands.

Let us consider some features of the Cp ligand spectra in these compounds. It is accepted that in the covalent π-complexes the bond of the π ligand to the transition metal atom incorporates two components, viz., a donor-acceptor

TABLE 1. FREQUENCIES (cm^{-1}) IN VIBRATIONAL SPECTRA OF Cp_3MH AND Cp_3MD (M = Zr, Hf)

Cp_3ZrH		Cp_3ZrD		Cp_3HfH		Cp_3HfD		Assignment
R	IR	R	IR	R	IR	R	IR	
3125m	3129m	3126m	3127m	3124m	3127w	3124m	3126w	νCH
3111vw	3118w	3113vw	3116w		3118vw	3112w	3117vw	
3104w	3106w	3105w	3108w	3103w		3104w	3107vw	
3083vw	3090w	3085w	3088w	3087w	3090vw	3088w	3089vw	
				3081w		3082w		
1608s	1609m	1161m	1161m	1669m	1670m	1193m	1196m	
		1144m	1143m					νMH
1457m	1453m	1457w	1453m	1457w	1456m	1456w	1454m	$\nu CC(E_1)$
1443m	1439m	1442w	1436m	1442w	1439m	1442w	1435m	
1372s	1372m	1370m	1370m	1370m	1372m	1370m	1372m	$\nu CC(E_2)$
	1278w		1278w		1278w		1278w	$\beta CH(A_2)$
1134vs	1134w	1131vs		1132vs	1130vw	1131vs	1130vw	$\nu(\text{ring})(A_1)$
1086m	1087w	1086m	1079w	1084m	1084w	1085m	1081w	$\beta(CH)(E_2)$
1079m	1069m	1079m	1062m		1065w	1075m	1064w	
1028w	1031s	1031vw	1026s	1025w	1027s	1026vw	1025s	$\beta(CH)(E_1)$
	1019s	1026vw	1031s		1023s		1014s	
935vw	926s		920m		923s	926vw	922s	$\gamma(CCC)(E_2)$
904vvw								
848w	851s	846w	846m	847w	845s	846w	846s	ρ(CH)
	838vs				833vs	826w	831vs	
823w		823w	828s	818m		814w		
805w	807vs	795w	799vs	808m	803vs	799w	806vs	
753s	752s	538s	538m	765m	764s	551m	551s	β(MH)
622w		620vw						
614m	612w	615w	617w			615w	616m	χ(CCC)
		611m		610w	610w	608w		
285vs	290s	284vs	290s	286vs	284m	283vs	283m	$\nu(MCp)(A_1)$
267s	264s	264s	263s	255s	250m	252s	250m	tilt MCp
252vs	247s	249vs	246s	228vs(br)	226s(br)	225vs(br)	226s(br)	ν(MCp)(E)
221w		222w						tilt MCp
185vs	182vw	184vs	188m	172vs	165m	169vs	165m	δ(CpMCp)
	157m		156m		140m		140m	
116w	121vw	116vw	122vw		102w		106vw	
90m		91m		94w	93w	91w	92w	
73s		73s		74m	77w	71m		torsion(?)
46w		45w		43w		38w		

(L → M) and a dative (M → L) one, which is responsible for its enhanced multiplicity and higher strength. The donor-acceptor bond has an axial symmetry and therefore can be described as "a central σ bond" [10]. The dative bonds possess a plane of symmetry so they belong to the π-type bonds. In the Zr and Hf complexes back-donation is impossible, because the transition metal atom has no appropriate *d* electrons for the formation of such a bond. As a result, the M—Cp bond multiplicity in these compounds will be lower as compared with that in classical Cp complexes (e.g., ferrocene). In the vibrational spectra of Cp_3MH (M = Zr, Hf) this leads to the following features: (1) the frequencies of the breathing mode of the Cp rings (1130—1134 cm^{-1}) and of the degenerate mode of the rings (1440—1460 cm^{-1}) have higher values (for Cp_2Fe these are 1105 and 1408 cm^{-1}, respectively); (2) the breathing mode is not observed or is very weak in the IR spectra (in the Raman spectra the corresponding line is very strong); (3) the band intensity of the degenerate (E_2) mode (ca. 1370 cm^{-1}) in the Raman spectra is substantially higher as compared with that of the E_1 ring mode (ca. 1450 cm^{-1}). All these features are typical of complexes with a weak metal—ring bond. In particular, the same features can be observed in the spectra of the ionic η^5-Cp complexes, viz., Cp_2Mg, Cp_2Mn, Cp_3Ln (Ln = lanthanoid) [11]. However, in contrast to the ionic complexes, where the frequencies of the out-of-plane C—H vibrations are observed below 800 cm^{-1}, in the complexes studied they lie in the region 800—850 cm^{-1}, typical of covalent-type complexes. The covalent nature of these complexes is proved by the high intensity of the Raman lines corresponding to the metal—ligand bond vibrations, although their frequencies are somewhat lower than those of typical cyclopentadienyl π-complexes and lie in the region 200—300 cm^{-1} (see below).

These data as a whole are consistent with the presence of a relatively weak metal—ring covalent bond in these compounds.

M—H bond vibrations

The Cp_3MH molecules have C_{3v} symmetry with an axial arrangement of the M—H bond, for which one can expect two modes only, viz., stretching (A_1) and bending (E). In fact, in the vibrational spectra in the region above 300 cm^{-1}, in addition to the vibrations of the Cp rings, only two bands are observed: at 1603 and 753 cm^{-1} for Cp_3ZrH, and 1669 and 765 cm^{-1} for Cp_3HfH. On deuteration these bands shift to the low frequency region. The frequency ratio of the hydrides and the deuterides is within 1.38—1.40, which suggests that these vibrations are not coupled with the other ones and allows one to consider the M—H bond as a pseudodiatomic molecule. It is interesting to note that there is an increase in the frequencies of the stretching M—H vibrations when passing from Zr to Hf. Such a frequency increase can only be associated with a high force constant of the M—H bond (K_{MH}). Calculations using a simple diatomic model give a value of 2.57×10^6 cm^{-2} for K_{ZrH} and 2.78×10^6 cm^{-2} for K_{HfH}. The increase in the force constant can be attributed to a higher strength of the M—H bond when passing from Zr to Hf. Such an increase appears not only to be typical of the transition metals of Group IV. The hydride π-complexes of the transition metals belonging to the other groups of the Periodic System show the same behaviour, when passing from the 4*d*- to the 5*d*-elements. Such a situation is exemplified by complexes of the metals of

Group V: Cp_2NbH_3 (1710 cm^{-1}) and Cp_2TaH_3 (1735 cm^{-1}), $Cp_2Nb(CO)H$ (1695 cm^{-1}) and $Cp_2Ta(CO)H$ (1750 cm^{-1}) [12]; of Group VI: Cp_2MoH_2 (1847 cm^{-1}) and Cp_2WH_2 (1912 cm^{-1}), $CpMo(CO)_3H$ (1808 cm^{-1}) and $CpW(CO)_3H$ (1828 cm^{-1}) [13]; of Group VII: Cp_2TeH (1984 cm^{-1}) and Cp_2ReH (2016 cm^{-1}) [14]. It is important that for the hydrides of nontransition elements an inverse dependence is observed, i.e. the frequencies and strength of the M—H bond decrease with the atomic element number in a group. Numerous examples can be found in ref. 15.

Skeletal vibrations

For the MCp_3 moiety (C_{3v} local symmetry) one expects the following modes: two stretching M—Cp vibrations ($A_1 + E$), four tilting vibrations ($A_1 + A_2 + 2E$), two bending CpMCp vibrations ($A_1 + E$) and two torsion vibrations ($A_2 + E$). The A_1 and E modes are active in both the IR and Raman spectra, whereas the A_2 modes are forbidden in both types of spectra. Coincidence of frequencies of the IR and Raman spectra for most bands in the region below 300 cm^{-1} allows one to discard a more symmetrical structure of the MCp_3 moiety (D_{3h} symmetry) since in this case, because of the more severe selection rules, some of the bands would be expected to be observed in the IR spectrum only (A_2'') and some of them in the Raman spectra only (A_1', E''). A similar statement is valid for C_{3h} symmetry. The exact band assignment by symmetry presents a problem because of the lack of Raman line polarization data, which could not be obtained in view of the poor solubility of the complexes. Therefore, the assignment presented below is tentative.

Comparison with the spectra of other Cp complexes allows one to assume that a group of bands in the region 200—300 cm^{-1} relates to the stretching and tilting M—Cp vibrations, whereas the bands in the region 140—185 cm^{-1} relate to the bending CpMCp vibrations. In the region 200—300 cm^{-1} for Cp_3ZrH and Cp_3ZrD one can observe four bands instead of the expected five, which seems to be due to band overlapping. The frequencies of the skeletal modes show practically no shift on deuteration but, if Zr is replaced by Hf, the bands shift to the low frequency region by 10—30 cm^{-1} as a result of an increase in the mass of the metal atom. An exception to this is the highest frequency band whose position remains virtually unchanged. Theoretical analysis reveals that the bands of the symmetrical vibrations of the Cp_3M moiety are expected to be less dependent on the mass of the metal atom than those of the antisymmetrical vibrations. A weaker dependence of the symmetric vibrations on the mass of the metal atom was also noted for the compounds Cp_2MX_2 (M = Ti, Zr, Hf; H = Cl, Br, I) [16,17]. Considering this situation and also the fact that, as a rule, the fully symmetric vibrations correspond to the most intense Raman lines, we assign the strongest Raman line in the region 283—290 cm^{-1} to the A_1 mode of M—Cp.

Such an assignment suggests that the frequency of the stretching M—Cp mode is higher than the frequencies of the tilting modes. The inversion of frequencies as compared with those of the typical covalent complexes where the tilting vibrations usually lie above the stretching ones, is characteristic of π-complexes with a central or ionic bond type, such as Cp_2Ni, Cp_2Mn, Cp_2Mg, Cp_3Ln [11], and it is consistent with the conclusion concerning the bond type in Cp_3MH (M = Zr, Hf) made above from the data on the vibrations of the Cp rings.

To the antisymmetric stretching M—Cp mode in the Cp_3ZrH spectrum one can assign either a frequency of 267 cm^{-1} or 252 cm^{-1}, shifting, when passing to Cp_3HfH, to 255 cm^{-1} and 228 cm^{-1}, respectively. The second case seems to be preferred due to the higher intensity of the low-frequency line in the Raman spectra. Irrespective of the type of assignment, the M—Cp frequency shift, when passing from Zr to Hf, is somewhat smaller than could be expected taking into account the increase in the mass of the metal atom, which appears to be associated with a larger force constant of the Hf—Cp bonds as compared with that of the Zr—Cp bond. We calculated the force constants of the M—Cp bond for the MCp_3 moiety in an approximation of a simple tetraatomic model, considering the Cp ligands as point masses and the CpMCp angles as being tetrahedral. For the assignment variant $\nu(ZrCp)_{sym}$ 285 cm^{-1}, $\nu(ZrCp)_{asym}$ 267 cm^{-1}, $\nu(HfCp)_{sym}$ 286 cm^{-1} and $\nu(HfCp)_{asym}$ 255 cm^{-1} the following force constants (10^6 cm^{-2}) were obtained: $K(ZrCp) = 2.85$, $K(HfCp) = 3.29$. For the second assignment variant, $\nu(ZrCp)_{sym}$ 285 cm^{-1}, $\nu(ZrCp)_{asym}$ 252 cm^{-1}, $\nu(HfCp)_{sym}$ 286 cm^{-1}, $\nu(HfCp)_{asym}$ 228 cm^{-1}, the corresponding values are as follows: $K(ZrCp) = 2.68$, $K(HfCp) = 2.93$. In these two cases the force constant for HfCp is larger than that for ZrCp, i.e. the strength of both the M—Cp and the M—H bond increases when passing from Zr to Hf. The trend observed for the transition elements of Group IV is similar to that found earlier for the elements of Group V, V and Nb [18], Group VI, Cr, Mo and W [19], Group VII, Mn and Re [20], and Group VIII, Fe, Ru, Os [21], where one can also observe a metal—ligand bond strengthening with increasing atomic number of the element in a group.

The assignment of the torsion vibrations remains unclear. From an analysis of the Raman spectra of gaseous Cp_2MCl_2 (M = Zr, Hf), the lines in the region 106—120 cm^{-1} showing a small shift when passing from Zr to Hf, were assigned to the torsion vibrations [22]. In the Raman spectra of the compounds studied fairly strong lines at 71—74 cm^{-1} are observed. However they are in the frequency region where the crystal lattice vibrations may also lie, so that their assignment to the torsion vibrations can only be tentative.

Experimental

The Raman spectra were obtained on solid samples, sealed in vacuo in glass capillaries, with the aid of a Ramanor HG2S spectrometer, when excited with the 5145 Å line of an Ar^+ laser, and of a Coderg PHO spectrometer, when excited with the 6471 Å line of a Kr^+ laser. The IR spectra were recorded on an Zeiss UR-20 spectrometer and an Bruker IFS-113v Fourier spectrometer in Nujol and hexachlorobutadiene. The samples were prepared under dry argon.

$(C_5H_5)_3ZrH$ and $(C_5H_5)_3ZrD$ were synthesized by the published method [4]. $(C_5H_5)_3HfH$ and $(C_5H_5)_3HfD$ were prepared under dry argon by using perfectly dry freshly distilled solvent without any access of oxygen and air moisture. The starting compound $(C_5H_5)_4Hf$ was obtained by the method described elsewhere [23].

Tris(cyclopentadienyl)hafnium hydride $(C_5H_5)_3HfH$

To a solution of freshly prepared $(C_5H_5)_4Hf$ (2.19 mmol) in THF (10 ml) was added, on constant stirring at 20°C, a solution of $LiAlH_4$ (1.21 mmol) in THF (10 ml). The mixture was magnetically stirred at room temperature for 5 h. After cooling the mixture to —5°C overnight the precipitated white crystals were filtered off on cooling and dried in vacuo under argon. The yield of $(C_5H_5)_3HfH$ was 0.31 g (38%). Found: C, 47.64; H, 4.30; Hf, 48.28. Calcd. for $C_{15}H_{16}Hf$: C, 48.07; H, 4.30; Hf, 47.62%.

Tris(cyclopentadienyl)hafnium deuteride $(C_5H_5)_3HfD$

Similar to the above-described method, $(C_5H_5)_4Hf$ (1.84 mmol) and $LiAlD_4$ (0.93 mmol) gave 0.2 g (30%) of $(C_5H_5)_3HfD$. Found: C, 47.57; Hf, 47.87. Calcd. for $C_{15}H_{15}DHf$: C, 47.94; Hf, 47.50%.

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