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Vibrational spectra and structure of indium and thallium monocyclopentadienyl complexes

O.G. Garkusha*, B.V. Lokshin, R.B. Materikova, L.M. Golubinskaya, V.I. Bregadze

A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., 28 Vavilov Str., Moscow 117813 (U.S.S.R.)

and A.P. Kurbakova

N.S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R., 31 Leninskii Prospekt, Moscow 117907 (U.S.S.R.)

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Abstract

The infrared and Raman spectra of (η^5-C_5H_5)In and (η^5-C_5H_5)Tl in the mid- and low-frequency regions, at temperatures of 12–300 K for the solids, IR spectra in solid argon matrices in addition to the IR spectrum of CpIn in the gaseous state have been studied. The analysis and subsequent discussion of the spectra of the crystals were in line with D_{5h} symmetry of the Cp-ring, which is consistent with the predominantly ionic character of the metal–ligand bond in the crystalline complexes. Two types of crystal vibrations in the low-frequency region could be distinguished, namely, the translation vibrations of ions sensitive to the metal mass and the librations of the $C_5H_5^-$ anions. A study of the IR spectra of argon matrices and gas (C_{5v} symmetry) has shown that monomeric molecules of the complexes studied have a predominantly covalent metal–ring bond. The values of the out-of-plane ρ(CH) frequencies show that the polarity of the M–Cp bond increases upon transition from the isolated molecule to the crystalline polymeric structure.

Introduction

The noticeable difference in structure of the indium and thallium monocyclopentadienyl complexes, depending on their crystalline and gaseous states is of particular interest. X-Ray structural data [1] show that polymeric structures of CpIn and CpTl (Cp = η^5-C_5H_5) in crystal are similar to each other and consist of infinite zig-zag chains of alternating metal atoms and Cp-rings, to give a metal–ring distance of 3.19 Å. On the other hand, by use of electronography in the gas phase for CpIn [2] and of microwave spectroscopy in the gas phase for CpTl [3], it was shown that these compounds are monomeric half-sandwiches (the C_{5v} symmetry point group) in gaseous state with a metal–ring distance of 2.32 and 2.42 Å for CpIn and CpTl, respectively. The nature of the coordination bond in these compounds has been described previously [2–4]. Assumptions were made concerning the predominantly ionic bonding of gaseous CpTl [3,4], while in the case of CpIn it was shown that in terms of their values the overlap integrals are closer to those of compounds having predominantly covalent bonding [2].

Studies of the vibrational spectra of CpIn are scarce. Only in Ref. 5 has CpIn been characterized by the IR spectrum in a limited region (3400–700 cm^{-1}) without elaboration. There is much more spectral data available for CpTl [4,6,7].

Here we describe a detailed study on the vibrational spectra of CpIn and CpTl under various conditions and in different aggregate states. Since CpTl does not exist as a liquid and since it is either insoluble in, or reacting with, common organic solvents, and that CpIn decomposes at room temperature even in vacuum, the Raman spectra of these compounds were obtained only for the crystals. The IR spectra of the crystals were recorded in the mid- and far-infrared spectral regions at various temperatures. The IR spectra of CpIn and CpTl in the solid argon matrices at 12 K were also studied. We also succeeded in obtaining the IR spectrum of the very volatile CpIn in the gas phase in the range 4000–100 cm^{-1}. The vibrational spectra of the complexes have been studied and the structure of the complexes and the character of the M–Cp bond in the various aggregate states are discussed.

Experimental

CpTl and CpIn were synthesized by standard procedures described in [4,5]. Raman spectra (4000–10 cm^{-1}) of the crystalline samples in vacuum-sealed glass capillaries were recorded on a Coderg-PHO and Ramanor-HG2S spectrometers with exciting by He/Ne (6382 Å) and Ar^+ (5145 Å) lasers, respectively. The Raman spectrum of CpIn was recorded in a special optical cryostat at 195 K, the spectra of the CpTl crystals were recorded at 300 and 195 K. The IR spectra (4000–200 cm^{-1}) of the polycrystalline films at 200 and 12 K and those of solid argon matrices at 12 K were recorded on a Hitachi-Perkin–Elmer-225 spectrometer of the samples prepared by high vacuum deposition on a CsI window cooled by a Diplex-CSA-202 closed cycle cryogenic system. The spectra of the argon matrices were recorded for various dilutions: A/M ~ 1/100–1/10000; the initial matrices were annealed in succession at 25, 30, 35 and 40 K for 10 min with subsequent cooling to 12 K. The IR spectra of polycrystalline films at 195 and 77 K were recorded in a liquid nitrogen cryostat with deposition onto a polished copper mirror (reflexion set-up) or onto CsI window (4000–400 cm^{-1}) and onto polyethylene window (500–50 cm^{-1}) on an infrared Fourier-transform spectrometer Bruker IFS-113V. On the same spectrometer were recorded the spectra of CpTl in Nujol and Fluorolube mulls (4000–50 cm^{-1}) as well as the spectra of gaseous CpIn at 300 K in the high-vacuum cell (230 mm optical length) with KRS-5 (4000–400 cm^{-1}) or polyethylene (500–100 cm^{-1}) windows.

Results and discussion

The region of the Cp-ring vibrations

In the case of the M–Cp model with ionic character of the metal–ligand bond, the selection rules for the Cp-ring are determined by D_{5h} point group symmetry, from which it follows that only four vibrations are allowed in the IR spectra: ν(CH), ν(CC), β(CH)-E'_1, and ρ(CH)-A''_2 and seven vibrations are allowed in the Raman spectra: ν(CH), ν(CC)-A'_1, ν(CH), ν(CC), β(CH), γ(CCC)-E'_2, and ρ(CH)-E''_1. In this case the vibrational frequencies appearing in the infrared absorption spectra and those in the Raman spectra may not coincide.

In the case of the covalent metal–ligand bond the molecule follows C_{5v} point group symmetry, and thirteen lines are allowed in the Raman spectrum for the Cp-ring vibrations: ν(CH), ν(CC), ρ(CH)-A_1, ν(CH), ν(CC), β(CH), ρ(CH)-E_1 and ν(CH), ν(CC), β(CH), γ(CCC)-E_2, and seven bands with the same frequencies as the Raman lines are allowed in the IR spectrum: ν(CH), ν(CC), ρ(CH)-A_1 and ν(CH), ν(CC), β(CH), ρ(CH)-E_1.

The data obtained for the vibrations of the Cp-ring are further discussed and assignment of the bands was made by comparison with the spectra of other cyclopentadienyl complexes [8,9]. The spectral data obtained and the assignment of vibrational frequencies are given in Fig. 1 and in Table 1.

The spectra of crystalline CpIn and CpTl agree with the D_{5h} symmetry of the Cp-ring corresponding to predominantly ionic character of the metal–ligand bond, which is characterized by low-frequency of the out-of-plane ρ(CH) bending vibrations and a high intensity of the IR bands of these vibrations. The breathing vibrations of the ring are absent from the IR spectra at 1110–1120 cm^{-1}, with other lines not being allowed in D_{5h} symmetry. The degenerate skeletal ν(CC) vibration band of the ring at 1430 cm^{-1} is absent from the Raman spectrum [8,9]. All of the degenerate vibration bands have an asymmetric shape at 200 K, which is probably due to the static splitting because of reduced symmetry of the molecule in the crystal (the site symmetry of the molecule is lower than D_{5h} symmetry) [1]. The weak and medium bands in the range of 1500–2800 cm^{-1} in the IR spectra are assigned to overtones and combination tones.

The assignment of the Cp-ring vibrational frequencies based on D_{5h} symmetry is given in Table 1, from which it can also be seen that frequencies of some normal vibrations have been reassigned as compared with those given in ref. 6. The intensities of the lines 1181 and 1207 cm^{-1} in the Raman spectra in those of CpIn and CpTl, respectively, are unexpectedly high. Weak bands in this region are observed for many metallocenes, the latter being assigned either to the in-plane β(CH) bending vibration of the E'_2 class as in ref. 6 or to the overtone of the out-of-plane χ(CCC) bending vibration of the ring of the E_{2g} class [8,9]. The latter assignment is confirmed by the fact that this line is polarized in the Raman spectra of solutions and melted sandwich metallocenes [10,11] and it should be depolarized for the β(CH) vibrations. The overtone is completely symmetrical ($2E''_2 = A'_1 + A'_2 + E'_1$) and thus is polarized. The fundamental χ(CCC) vibration of the E''_2 class for D_{5h} symmetry is forbidden both in Raman and IR spectra. The overtone because of the symmetry is allowed in the Raman spectrum, and an increase in its intensity for CpIn and CpTl can be explained by Fermi resonance with the strongest line in the Raman spectrum, that is, due to the breathing vibration ν(CC),A'_1 of the ring.

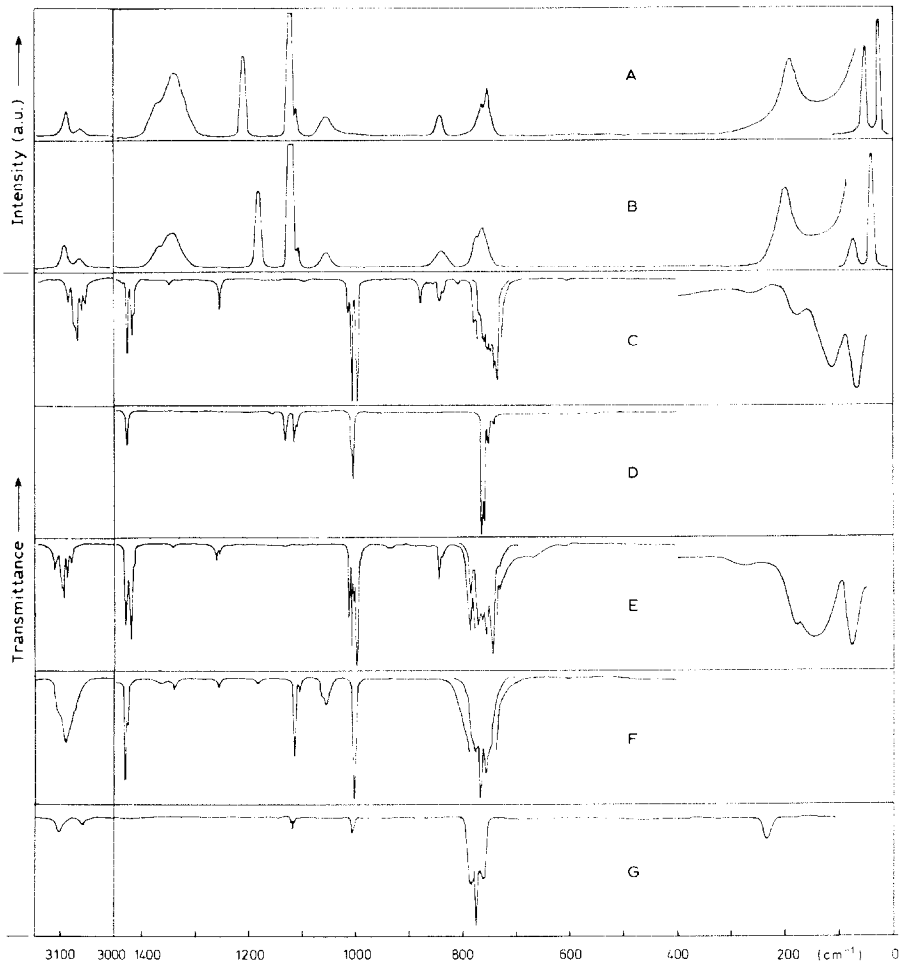

Fig. 1. Vibrational spectra of CpTl and CpIn. Raman spectra of CpTl (A) and CpIn (B) crystals at ~195 K; IR spectra of polycrystalline films of CpTl (C) and CpIn (E) at ~12 K (mid-IR region) and ~77 K (far-IR region); IR spectra of CpTl (D) and CpIn (F) in argon matrixes at ~12 K; (G) IR spectrum of gaseous CpIn.

However, it should be noted that in the Raman spectra of alkali metal cyclopentadienides with an ionic metal–ligand bond the band at 1200 cm^{-1} was not observed [12].

The IR spectra of CpIn and CpTl crystals at 12 K are also very similar. The spectra are more complicated owing to splitting of some of the bands into their components (Davydov splitting), a phenomenon which is connected with the presence of the four entities making up the unit cell of the crystal [1]. Thus, the band of the in-plane bending vibrations β(CH),E_1' at 1000 cm^{-1} splits into four components, and the bands of the out-of-plane ρ(CH) bending vibrations split yet again into eight components. At 12 K, weak bands at 840 and 1340 cm^{-1} of the vibrations forbidden in the IR spectra for the D_{5h} symmetry coinciding with Raman lines and the band at 1250 cm^{-1} of the vibration forbidden in the IR and Raman spectra are observed, which can be due to a lower site symmetry of the ring in the crystal compared with that of free Cp-anion.

The data obtained from the IR spectrum of gaseous CpIn are of particular importance and require special mention. Since the pressure of the CpIn vapour is comparatively low at room temperature, the bands in the IR spectrum of the gaseous phase are weak and only five out of seven IR-active vibrations of the Cp-ring could be observed. The spectrum clearly exhibits the bands of stretching ν(CH) vibrations at 3103 and 3058 cm^{-1} of A_1 and E_1 symmetry classes, respectively; breathing of the ring ν(CC),A_1 at 1117 cm^{-1}; in-plane bending β(CH),E_1 vibration at 1009 cm^{-1} and out-of-plane bending ρ(CH),A_1 vibration at 773 cm^{-1}. Two bands exhibit a distinctly rotational PQR structure. The appearance (in the gas spectrum) of the totally symmetrical vibration band of the ring forbidden for the D_{5h} symmetry exposes the covalent nature of the metal–ring bonding (the C_{5v} symmetry). This is also confirmed by the presence of two ν(CH) stretching vibrations in contrast to the ionic structure, for which only one ν(CH) band should be observed for D_{5h} symmetry.

Analysis of the PQR structure of the absorption bands shows that the CpIn molecule in the gaseous phase is monomeric. The CpIn monomeric molecule is a prolate symmetric top and the values of its rotational constants calculated on the basis of electronographic data [2] are: $A = 0.147$ and $B = C = 0.075$ cm^{-1}. On the basis of these we obtained the splitting value $\Delta\nu$(PR) 14.5 cm^{-1} for the parallel-type bands which are A_1 vibrations. In the spectrum of the gas recorded by us, these values are equal to 12 and 14 cm^{-1} for the out-of-plane bending vibration ρ(CH) and breathing ring vibration ν(CC), respectively, i.e., these values are very close to those calculated. The expected increase in the moment of inertia and the concomitant decrease in the PR-splitting value upon formation of associates did not occur.

The IR spectra of CpIn in solid argon matrices are also consistent with covalent structure. These spectra are more complicated then is expected for ionic structure. In the IR spectra all bands which are allowed for the C_{5v} symmetry vibrations of the A_1 and E_1 classes, but also weak bands of forbidden vibrations of the E_2 class at of 1060, β(CH); 1338, ν(CC); 1257, β(CH) and weak bands at 1185 cm^{-1}, 2χ(CCC) were observed. The appearance of forbidden bands can be due to a partial formation of associates in the matrix, which results in a decrease in the symmetry. The matrices of CpTl were obtained under much higher dilutions and their IR spectra did not exhibit the bands described above (see Fig. 1 and Table 1). Moreover, the frequencies of these bands correspond to those in the spectra of the crystals.

In studying the vibrational spectra of cyclopentadienyl compounds much attention was given to the determination of the frequency of out-of-plane bending ρ(CH) vibrations of the A_1 class (for C_{5v} symmetry) since these vibratrions are most sensitive to the character of the metal–ligand bond [8,9]. The band of these vibrations in the IR spectrum is the most intense and is a convenient indicator of the degree of ionic character of the metal–ring bond [12,13]. At 12 K in the argon matrix spectra of CpTl and CpIn a more complicated structure which depends upon the degree of dilution and the conditions of deposition (Fig. 2) is observed in this region. In order to obtain a clearer picture of the out-of-plane ρ(CH) bending vibration band of the CpTl monomeric molecule was carried out a more detailed

(*Continued on p. 288*)

Table 1

Vibrational spectra of indium and thallium monocyclopentadienyl complexes

C_5H_5In					C_5H_5Tl				Assignment		
Raman	IR				Raman	IR			D_{5h} symmetry for $C_5H_5^-$	C_{5v} symmetry for M–Cp	Vibrations
solid 195 K	solid 200 K	solid 12 K	Ar-matrix 12 K	gas 300 K	solid 195 K	solid 200 K	solid 12 K	Ar-matrix 12 K			
38vs					26vs				Lattice translational vibrations		
73s					54vs						
	78m					68m					
	147m					130m					
	178w					181w			Cp-ring librations		
198m(br)					191m(br)						
				230m						ν_4,A_1	ν(M–Cp)
	612vvw	612vvw	612vw			612vw	612vvw		ν_{14},E''_2	ν_{16},E_2	χ(CCC)
			754sh					743vw			
			759s					751m			
			770sh	767 (P)				756vs			
	741vs	742vs	772vs	773vs (Q)		732vs	731vs	759vs	ν_4,A''_2	ν_3,A_1	ρ(CH)
		745sh		779 (R)			736sh				
		754vs					742m				
		757sh					747m				
761m(br)	768sh	762s	780s		751m	752sh	754m	765m	ν_8,E''_1	ν_9,E_1	ρ(CH)
		769sh	785sh				757sh	768w			
775sh		772s			762m(br)		763sh				
		785m					774sh				
	804vvw	803vvw				804vvw	804vvw		ν_{13},E''_2	ν_{15},E_2	ρ(CH)
		836sh					835vw				
840w(br)	838vvw	839w	841w		840m	836vvw	838vw		ν_{12},E'_2	ν_{14},E_2	γ(CCC)
		852vvw					856vvw				
		867vvw	864w				862vvw				
		879vvw					877vw				
								1002sh			
	1000s	998s	1005s	1009m		999s	997s	1005s	ν_7,E'_1	ν_8,E_1	β(CH)
		1002w					1002sh				
	1005sh	1007s				1003s	1005s	1008m			
		1012w					1010w	1010sh			

1060w(br)			1057m		1058m(br)				ν_{11},E_2'	ν_{13},E_2	$\beta(CH)$
			1061sh								
	1090vw	1090vw	1091vw			1090vw	1090w(br)				
					1108vw						
1111sh			1108w	1109 (P)	1114sh			1113w	$\nu_2{}^{13}C$	$\nu_2{}^{13}C$	
1116vs			1115m	1117w (Q)	1118vs			1115m	ν_2,A_1'	ν_2,A_1	$\nu(CC)$
				1125 (R)				1124w			
								1131m			
1181m			1185vw(br)		1207m			1158w	2 ν_{14}	2 ν_{16}	
		1256vw	1257w			1254vvw	1256w		ν_3,A_2'	ν_5,A_2	$\beta(CH)$
		1259w									
1344m(br)		1346vw	1338w		1342s(br)		1346vw		ν_{10},E_2'	ν_{12},E_2	$\nu(CC)$
1369sh			1360vvw		1371m(br)						
	1417sh	1417sh					1417sh				
		1419sh	1418sh			1419sh	1419sh				
	1422m	1421m	1422sh			1422w	1420m				
	1427m	1428m	1429m			1426m	1427m	1428m	ν_6,E_1'	ν_7,E_1	$\nu(CC)$
			1437sh				1437vvw				
			1505sh				1457vvw				
	1515vw(br)	1515vw	1528w			1500vw(br)	1500vw(br)	1501w			
			1543w								
			1590sh					1603sh			
	1610w(br)	1610w(br)	1602w			1600w(br)	1600w(br)	1606m	Overtones		
			1623w					1622m			
			1632sh								
			1712sh				1715vw(br)				
			1725w								
		3057vw					3054w				
3068w	3062sh	3064w	3076sh	3058w	3065w(br)	3060sh	3062w		ν_9,E_2'	ν_{11},E_2	$\nu(CH)$
	3076m	3071m	3088m			3072m	3070m		ν_5,E_1'	ν_6,E_1	$\nu(CH)$
		3075sh					3074sh				
3094m		3088vw	3104sh	3103m	3092m		3085w		ν_1,A_1'	ν_1,A_1	$\nu(CH)$

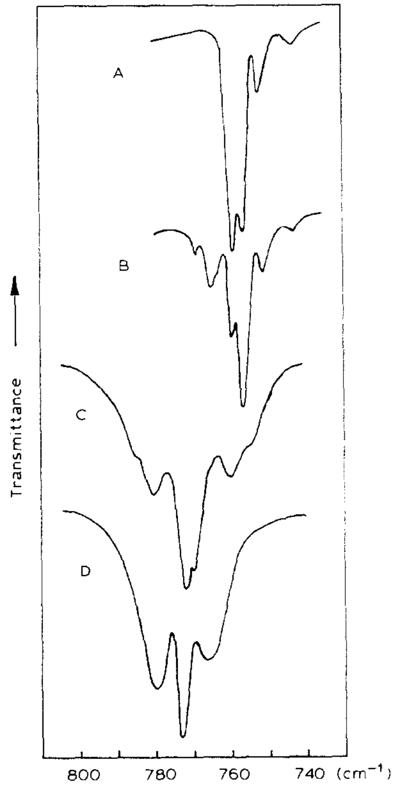

Fig. 2. IR spectra of CpTl (A,B) and CpIn (C,D) in the region of the out-of-plane ρ(CH) bending vibrations. (A) the initial argon matrix ($A/M \sim 1/10000$) at ~ 12 K; (B) the same matrix after two successive annealings at ~ 30 K × 10 min, and ~ 35 K × 10 min; (C) the initial argon matrix ($A/M \sim 1/300$) at ~ 12 K; (D) the IR spectrum of CpIn in the gas phase.

study of this region in the IR spectra of the argon matrices. In the case of highly diluted matrices ($M/A \sim 10000$) and vacuum deposition of CpTl at room temperature, the spectrum revealed a very intense doublet at 759/756 and a weak line at 751 cm^{-1} (Fig. 2). In the case of successive annealments of the diluted matrix (see Experimental) the intensity of the central doublet gradually decreases with a change in the relative intensities of its components, the bands at 743, 751 and 765, 768 cm^{-1} which appear on the both sides of the doublets and with increased intensity. From these experiments we assign to the monomer the bands at 759 and 756 cm^{-1}, but not the band at 768 cm^{-1} as in Ref. 7. The appearance of two bands in the spectrum can be explained in terms of the presence of two non-equivalent positions in the unannealed matrix (the matrix effect), with the component at 759 cm^{-1}, which is retained when it is annealed for a longer time, to give a more stable orientation of the monomer in the argon matrix.

In the region of the out-of-plane ρ(CH) vibrations in the IR spectrum of CpIn in solid argon matrix, a complicated structure is also observed. But even in this case the intensest central band, at 772, having the shoulder at 770 cm^{-1} should be assigned to the absorption of the CpIn monomer. This is also confirmed by the similarity of the spectra of CpIn and CpTl in argon matrices as well as by almost complete coincidence of the frequency of this band and that of the band of the Q-branch of the out-of-plane ρ(CH) vibrations in the spectrum of gaseous CpIn (Fig. 2).

It should be noted that the values obtained for the frequencies of the out-of-plane bending vibrations ρ(CH) of CpIn and CpTl in the monomeric state at 772 and 759 cm^{-1} are about 30 cm^{-1} higher than the same frequencies of ρ(CH) for the crystals at 742 and 731 cm^{-1}. This is consistent with the well-known tendency of the ρ(CH) vibration frequency to decrease with an increase in the ionic character of the metal–ring bond [8,9]. Thus it follows that the covalent component of the M–Cp coordination bond increases progressively on going from the crystalline polymeric structure to the isolated molecule (gas, matrix), which is confirmed by a corresponding decrease in the metal–ring distance upon transition from crystal to gas. The frequencies of the out-of-plane ρ(CH) vibrations for crystalline CpIn at 742 and CpTl at 731 cm^{-1} approach the values found for the crystalline alkali metal cyclopentadienides CpLi (735 cm^{-1}), CpNa (722 cm^{-1}) and CpK (719 cm^{-1}) [12]. For the free $C_5H_5^-$ anion the respective frequency is equal to 686 cm^{-1} [13].

Low-frequency region

As stated before, CpIn and CpTl in the crystalline state produce polymeric structures in the form of infinite zig-zag chains of alternating metal atoms and Cp-rings [1]. In general, various types of vibrations of such a zig-zag can be classified as symmetric and asymmetric M–Cp stretching vibrations, tilt vibrations of the Cp-ring and Cp–M–Cp and M–Cp–M deformation vibrations. The M–Cp stretching vibrations and Cp–M–Cp and M–Cp–M deformation vibrations can be described in terms of longitudinal and transverse translation vibrations of the ions in the polymer chain. The frequencies of such vibrations should depend strongly on the atomic mass of the metal. The tilt vibrations of the Cp-rings correspond to the libration modes of the Cp-anions and their dependence upon the atomic mass of the metal should be considerably weaker. In accordance with these assumptions we should then assign both lines at 198 and 191 cm^{-1} in the Raman spectrum, and the bands at 178 and 181 cm^{-1} in the IR spectra of CpIn and CpTl to the libration modes. The frequencies of the bands at 38,73 and 78, 147 cm^{-1} for CpIn and those at 26,54 and 68, 130 cm^{-1} for CpTl, dependent on atomic mass of the metal are assigned to translation vibrations of ions in the polymer chain (Table 1).

As in ref. 6, in the case of CpTl we observe high-frequency shifts of all low-frequency vibrations with decreasing temperature. This may be due not only to the temperature-dependent changes in dimensions of the crystal lattice, but also to phase transition. The needle-like crystals of CpTl and CpIn which are yellow at room temperature turn white when cooled slightly. The IR spectrum of the CpTl in Nujol mull reveals three bands of 67,112 and 178 cm^{-1} at 300 K. In the spectra of the polycrystalline films at 77 K these bands are shifted, and the low-frequency band splits into three components, namely, 68/71/74, 130, and 185 cm^{-1}. It is interesting to note that heating the sample in the cryostat up to 300 K does not result in a frequency shift, which is probably due to a prolonged phase transition because the white colour of the film remains.

Similarity of the low-frequency spectra (once differences in the metal atom masses are taken into account) in addition to the similar character of Davydov splitting of the bands observed at 12 K, indicate the analogous structures of the crystal lattices of CpIn and CpTl.

The monomeric half-sandwich molecules (C_{5v}) should have two skeletal vibrations: stretching vibration of the metal–ring ν_4,A_1 and tilt vibration ν_{10},E_1. Unfortunately, we failed to obtain spectra of the solid argon matrices which covered the skeletal vibration region. The spectrum of gaseous CpTl was not obtained either because of the low pressure of the vapour at room temperature. On the basis of data from the microwave spectra of CpTl [14] the frequencies of 160 ± 20 and 290 ± 40 cm^{-1} were assigned to the stretching vibrations (ν_4,A_1) and tilt vibrations (ν_{10},E_1), respectively. In the IR spectrum of gaseous CpIn we recorded one absorption band at 230 cm^{-1} which is certainly attributable to skeletal vibration. The second band was not recorded probably owing to its low intensity. The 230 cm^{-1} band may be assigned to the stretching vibration ν(In–Cp) because the value for ν(Tl–Cp) calculated on the basis of this frequency taking into consideration the masses of In and Tl atoms, is 172 cm^{-1}, which is close to that from the data of the microwave spectra [14]. The force constant of the In–Cp bond calculated using a two-mass approximation is 1.41 mdyn $Å^{-1}$, which is slightly less than of the force constant of the Mg–C_5H_5 bond in Cp_2Mg of 1.73 mdyn $Å^{-1}$.

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