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Infrared spectra of triple-decker sandwich complexes $(Ni_2Cp_3)A$ $(A = BF_4, PF_6)$

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Abstract

Infrared spectra (4000–50 cm^{-1}) of triple-decker sandwich cation $[(CpNi)(\mu-Cp)(NiCp)]^+$ (Cp = η-C_5H_5) in solid state and in solutions have been studied. The assignment of terminal and bridged Cp-ring vibrations was proposed by comparison with the spectra of nickelocene. The frequencies of the terminal and the bridged Cp-ring vibrations differ to within 10–25 cm^{-1}. According to the spectral data the terminal Cp-rings are bonded to the metal atoms stronger than the bridged one. The assignment of skeletal vibrations of $(Cp_3Ni_2)^+$ cation is proposed.

Introduction

Since Werner and Salzer prepared the first triple-decker sandwich compound—the 34-electron cation $(Cp_3Ni_2)^+$ [1,2]—this new class of transition metal complex has attracted particular attention from chemists. The structure of the cation in the salt with BF_4 anion has been determined [3,4] (Fig. 1). While the Cp-rings Cp(1) and Cp(2) are nearly coplanar, the ring Cp(3) is tilted by 3.45° from coplanarity. All three Cp-rings are planar to within 0.003 Å. The relative orientation of the three rings is as follows: Cp(1) and Cp(2) are approximately eclipsed, while Cp(3) is staggered with respect to the other two. The average CC distance in the outer two rings is 1.36(3) Å, in the inner ring it is 1.42(1) Å. An extended Hückel molecular orbital calculation on the electron structure of triple-decker sandwiches with idealized D_{5h} geometry has been carried out by Hoffman [5]. He has shown that there are important similarities between triple-decker sandwiches CpMCpMCp and normal triply CO bridged dimers of the $Fe_2(CO)_9$ type. He predicted two series of stable structures of triple-decker sandwiches containing 30 and 34 valent electrons. Recently the first examples of 30-electron triple-decker complexes of the iron group metals $[(\eta\text{-}C_5R_5)M(\mu\text{-}\eta\text{-}C_5Me_5)M'(\eta\text{-}C_5Me_5)]^+$ (R = H, Me; M = M′ or M ≠ M′ = Fe, Ru, Os) have been synthesized by Kudinov and Rybinskaya [6]. Their structures were proved by ^1H- and ^{13}C-NMR spectra as well as by X-ray structural study.

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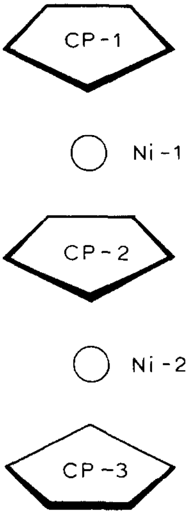


Fig. 1. Simplified molecular structure of $(Ni_2Cp_3)^+$.

Vibrational spectra of these complexes have not been studied before. To eliminate this gap in our knowledge we have undertaken a complete vibrational spectral study of triple-decker complexes with cyclopentadienyl ligands. Here we present an IR spectral analysis of the cation $(Cp_3Ni_2)^+$, the unique stable triple-decker sandwich containing all three cyclopentadienyl rings in an unsubstituted state. The substitution of the anion ($BF_4^- \rightarrow PF_6^-$) and changing the solvent ($CH_2Cl_2 \rightarrow CD_2Cl_2$) allowed us to record the complete spectrum of the cation in the range 4000–50 cm^{-1}. The main purpose of this work was to elucidate the spectral difference between the terminal and bridged Cp-rings.

Results and discussion

Spectra of C_5H_5-rings

The IR spectra of the salts and nickelocene are presented in Table 1. The assignment of bands is proposed, using the selection rules for D_{5h} symmetry of the bridged Cp-ring and C_{5v} symmetry of the terminal ones. The assignment of two adjacent bands to the vibrations either of terminal or of bridged Cp-rings was made on the basis of their intensity ratio being 2 : 1. The analysis of the spectra leads to the following general conclusions:

1. The vibrational frequencies of the terminal and bridged Cp-rings are distinct by 10–25 cm^{-1}. The frequencies of the terminal Cp-rings can be higher or lower than the frequencies of the bridged Cp-ring. In the spectra of solutions the frequencies of the two terminal Cp-ring coincide. In the spectra of solid salts the splitting of some bands into three components may be explained by the influence of the crystal field or by the distinctiveness of all three Cp-rings of the cation [4]. It should be noted that the intensity distribution between the components of the bands in the spectra of solids depends on the nature of the anion.

2. While the frequency of $\rho(CH)$ vibration of terminal Cp-rings (806 cm^{-1}) is higher than that of the bridged one (781 cm^{-1}), the frequency of degenerate

Table 1

IR frequencies of the cyclopentadienyl rings of nickelocene and of the triple-decker complex of nickel

$NiCp_2$			$(Ni_2Cp_3)BF_4$		$(Ni_2Cp_3)PF_6$		Assignment C_{5v}-terminal D_{5h}-bridged
solid [9]	solution[8]	Assignment [8,9] (D_{5d})	solid	solution (CH_2Cl_2)	solid	solution (CH_2Cl_2)	
3103m [a]		ν(CH) (E_{2u})		3127sh	3122m	3128sh	ν(CH, bridged)
3090w [a]		ν(CH) (A_{2u})	3109m	3116s	3102sh	3116m	ν(CH, terminal)
			3090sh		3092sh		
3078m [a]		ν(CH) (E_{1u})					
			1804w, br	1802vw	1818w		Overtones
			1712w, br	1715vw	1725w	1716w	
			1617w, br	1627vw	1628w	1627w	
1460m							
1450m							
			1418w	1420w	1418w	1420w–m	ν(CC, brid.) (E_1')
1420s	1415m	ν(CC) (E_{1u})	1397m	1398m	1396m	1401m	ν(CC, term.) (E_1)
1375w							
1355vw							
1322m		ν(CC) (E_{2u})					
1255m		β(CH) (A_{1u})	1284w		1260w		
1170m			1180vw		1168w		
1140m					1157w		
			1104c	1105sh			
			1075vs	1072s			BF_4^-
			1047sh	1055sh			
1110s	1110w	ν(CC) (A_{2u})			1106vw		ν(CC, term.) (A_1)
1102w							
1055m		ρ(CH) (E_{2u})			1057sh		
1042m							
1002s	1005s	β(CH) (E_{1u})	1001s	1004s	1007m	1003s	β(CH, term.) (E_1)
			989sh	993sh	1001m	993sh	β(CH, brid.) (E_1')
936w							
896vw							
882vw							
870vw		γ(CCC) (E_{2u})	888w				
					878sh	878m	
					848vs	848vs	PF_6^-
					827vs		
840m	800m	ρ(CH) (E_{1u})	869w	864w			ρ(CH, term.) (E_1)
800 [b]		γ(CCC) (E_{2u})	823sh	825w			γ(CCC, term.) (E_2)
780s	780vs	ρ(CH) (A_{2u})	805sh	806s	807vs	807s	ρ(CH, term.) (A_1)
776vs			797s		797sh		
			780sh	781m	776sh		ρ(CH, brid.) (A_2'')
			764w				BF_4^- ?
					557m	557s	PF_6^-
			520m	520m			BF_4^-

[a] Spectra in ν(CH) range have been recorded for the samples upon 77 K. [b] Data of Ref. 10.

stretching ν(CC) vibration of the terminal Cp-rings (1398 cm^{-1}) is lower than that of the bridged one (1420 cm^{-1}). According to the proposed correlation [7] of the ionicity of the M-ring bond with the frequencies of the Cp-ring vibrations under consideration, such a frequency distribution agrees with a higher polarity (smaller strength) of Ni–Cp (bridged) bonds with respect to the Ni–Cp (terminal) bonds. The same conclusion was made on the basis of X-ray structural study [4]. The Ni–C distances for C atoms belonging to the Cp(2)-ring are somewhat longer than the Ni–C distances of the outer two rings. This is also consistent with the fact that in subsitution reactions on the cation $(Ni_2Cp_3)^+$ with Lewis bases, a preferential cleavage of the Ni-inner-ring bonds was observed [2].

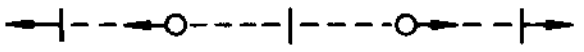
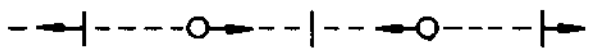
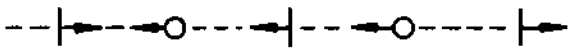
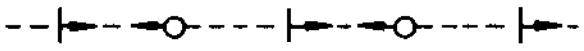
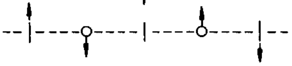
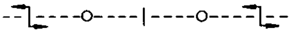
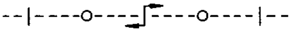
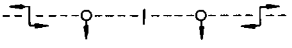
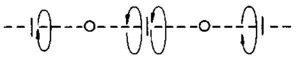
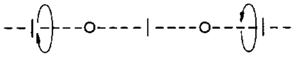
3. The frequencies of the terminal Cp-rings in the spectra of the cation $(Ni_2Cp_3)^+$ and nickelocene are close. On transition from nickelocene to the cation a small increase in the frequencies of out-of-plane ρ(CH) modes and a decrease in the frequency of degenerate ν(CC) modes were observed. The intensity of the ring-breathing mode band at 1110 cm^{-1} in the spectra of solid cation became very weak and this band was not observed in the spectrum of $(Ni_2Cp_3)^+PF_6^-$ in CH_2Cl_2 solution. In the spectra of $(Ni_2Cp_3)^+BF_4^-$ this region (1050–1150 cm^{-1}) is overlapped by intensive bands of the BF_4^- anion. In the spectrum of nickelocene solution the absolute intensity of the band at ~1110 cm^{-1} is low $(0.01 \cdot 10^{-4}$ $l \cdot mol^{-1} \cdot cm^{-2})$ [8], but in the spectrum of solid nickelocene the intensity of 1110 cm^{-1} band is close to that of 1420 cm^{-1} band and this band has been noted [9] as strong. Thus upon transition from nickelocene to cation an increase in the ρ(CH) frequencies and simultaneously decrease in the intensity of ring-breathing mode band were observed. The same spectral changes upon transition from solid ferrocene to ferricenium tetrachloroferrate have been observed but in this case the increase in the frequency of ρ(CH) mode was larger (816–852 cm^{-1}). Very low intensity of the ring-breathing band at 1110 cm^{-1} in the IR spectra of ferricenium salts was noted also by Maitlis [11]. The comparison of IR spectra of cobaltocene [8] and cobalticenium chloride [12] in solution shows that as in the case of iron-derivatives the frequency of ρ(CH) mode increases from 780 to 860 cm^{-1} and the intensity of the ring-breathing mode band at 1113 cm^{-1} decreases upon the transition from neutral complex to the cationic one. Apparently, relatively high values of ρ(CH) frequencies and low intensities of the ring-breathing band are typical for cationic Cp-complexes of the transition metals.

Low-frequency region

The skeletal vibrations and their activity in the IR and Raman spectra for idealized symmetry D_{5h} of CpMCpMCp unit are presented in Table 2. According to these data we expect in the far-infrared spectrum of the cation the appearance of five bands corresponding to two stretching, one tilting and two bending metal–ligand modes. In the solid state the symmetry of the cation is lower than D_{5h} (C_5 or C_1) [4]. Hence in the spectra of solids all ten skeletal vibrations can occur. To first appearances, the IR spectra of solutions and solids contain two broad bands at 300 and 210 cm^{-1}. However the shapes of these bands are complex. The profiles of these bands are formed by the superposition of two and three overlapping subbands respectively (Table 3). The assignment of the low-frequency bands is problematic. By analogy with the far infrared spectrum of nickelocene the following arrangement of M–Ligand frequencies is assumed: stretch > tilt > bending. Then the bands at 306 and 301 cm^{-1} can be assigned to the stretching ν_3 and ν_4 modes. To verify this assumption the normal coordinate calculation of the stretching skeletal vibrations for the CpMCpMCp five-mass approximation model has been carried out. The diagonal and interaction force constants of the Cp(terminal)–Ni–Cp(bridged) frag-

Table 2

Diagram of the skeletal vibrations for the CpMCpMCp sandwiches with D_{5h} symmetry [a]

ν_i	Mode	Symmetry	Activity	Description
ν_1		A'_1	Raman	Stretch
ν_2		A'_1	Raman	Stretch
ν_3		A''_2	IR	Stretch
ν_4		A''_2	IR	Stretch
ν_5		E'_1	IR	Deformation
ν_6		E'_1	IR	Deformation
ν_7		E''_1	Raman	Deformation
ν_8		E''_1	Raman	Tilt
ν_9		E''_1	Raman	Tilt
ν_{10}		E'_1	IR	Tilt
ν_{11}		A'_2	inactive	Torsion
ν_{12}		A''_1	inactive	Torsion

[a] | = cyclopentadienyl ring.

ment were assumed to be equal to those for nickelocene, e.g. 2.22 and 0.55 mdyn/Å. The diagonal and interaction force constants of the Ni–Cp(bridged) –Ni fragment were diminished in proportion to the lengthening of the Ni–Cp distances upon

Table 3

Far-IR spectra of nickelocene and the triple-decker complexes of nickel

$NiCp_2$			$[Ni_2Cp_3]BF_4$		$[Ni_2Cp_3]PF_6$
solid [9]	solution [8]	assignment (D_{5d}) [9]	solid	solution	solid
			354w		312sh
358m	345m	ν_{as}(M–Cp) (A_{2u})			
			310m	306sh	305m
			296sh	301m	301m
270w	280w	ν_{tilt} (E_{1u})			
			221sh	221sh	217sh
			216w	212w	215w
			208sh	209sh	207sh
132w	170vw	δ(CpMCp) (E_{1u})			
					80w, br

transition from the terminal to the bridged Cp-ring and were taken to be equal to 2.10 and 0.52 mdyn/Å. The calculated frequency values were equal to 168 (ν_1), 352(ν_2), 290(ν_3) and 335(ν_4) cm^{-1}. The difference between Raman-active mode frequencies ν_1 and ν_2 (184 cm^{-1}) is larger than for IR-active modes ν_3 and ν_4 (45 cm^{-1}). The small theoretical value of the difference between ν_3 and ν_4 does not exclude their practical coincidence in the real spectrum (301 and 306 cm^{-1}). The frequency of the IR-active tilt vibration, ν_{10}, was estimated as follows. In the spectra of nickelocene the frequencies of asymmetrical (E_{1u}) and symmetrical (E_{1g}) tilt vibrations lie at 270 and 210 cm^{-1} respectively [10]. The average value (240 cm^{-1}) will be the frequency of the tilt mode of nickelocene in the absence of Cp–Cp interaction. Since for ν_{10} vibration the interaction between two terminal Cp-rings is minor (Table 2) we suppose that the frequency of ν_{10} vibration will be close to the average value of two tilt vibrations of nickelocene (from the assumption of the coincidence of force constants). Probably one of the subbands in the region 200–220 cm^{-1} corresponds to this ν_{10} vibration.

Experimental

The salts of the cation were synthesized by the method described previously [1,2]. The salts are dark-brown polycrystals stable in an inert atmosphere. Raman spectra measurements were unsuccessful due to the dark colour of the samples. IR spectra of solutions and solids in Nujol mulls between KBr and polyethylene windows were recorded on the Bruker IFS-113v FT-IR spectrometer. For the spectra of solutions the KBr cells with 0.09 and 0.028 mm thickness and polyethylene cells with 0.7 and 0.3 mm thickness were used.

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