

Vibrational Spectroscopic Investigation of Some Hofmann-T_d Type Complexes: Ni(1-Phenylpiperazine)₂M(CN)₄ (M = Cd or Hg)

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Summary: New Hofmann-T_d type complexes in the form of Ni(pp)₂M(CN)₄ (where pp = 1-Phenylpiperazine and M = Cd or Hg) have been prepared in powder form and their infrared (4000-100 cm⁻¹) and Raman (2800-1650 cm⁻¹) spectra have been reported. The results suggest that these compounds are similar in structure to the Hofmann-T_d type complexes, in which the M atom is tetrahedrally coordinated to the carbon atoms of the four cyanide groups, while the Ni atom is octahedrally surrounded by six nitrogen atoms, two of which are from pp ligands which have been coordinated as a unidentate ligand coordinating only through the NH nitrogen and the rest are from cyanide groups. In this host structure, the M(CN)₄ groups have been linked by the Ni(pp)₂ moieties to form a three-dimensional network.

Introduction

Vibrational spectroscopy has long been recognized as a tool for revealing the structural properties of Hofmann-T_d type complexes [1-7]. Hofmann-T_d type host structures are defined with the general formula of M(L)₂M'(CN)₄ where the M is one of the first-row transition metals, the L corresponds to a bidentate or a pair of unidentate ligand molecules and the M' is Cd, Hg or Zn. The host structure is formed by the chains of -M-L₂-M-L₂- extending along the *a*- and *b*-axes alternately and the tetrahedral M'(CN)₄ ions are arranged between the consecutive crossing chains with the N-ends bonded to the M atoms [5-7]. This structure possesses two kinds of cavities, namely α and β. The α cavity with the rectangular box is similar to those in the Hofmann type hosts while the β cavity is a twisted biprism [1-4]. The cavities within the structure can act as hosts for the guest molecules.

In our previous study, we reported the infrared spectroscopic study of Hofmann type complexes of pp [8]. In the present work, we have synthesized two new Ni(pp)₂M(CN)₄ Hofmann-T_d type complexes (abbreviated hereafter as Ni-pp-Cd or Ni-pp-Hg), where M = Cd or Hg, for the first time and have investigated their FT-IR and Raman spectra.

Results and Discussion

The infrared and Raman spectra obtained for the Ni-pp-Cd and Ni-pp-Hg complexes are similar.

This indicates that the compounds have almost same spectral features. The infrared and Raman spectra of the compounds are given in Figs. 1-4. The spectral analysis of each compound have been performed by taking into account the pp molecule and M(CN)₄ (M = Cd or Hg) ions individually.

1-Phenylpiperazine vibrations

The free pp consists of a bulky phenyl group (-C₆H₅), with high basic strength, attached to one of the nitrogens of piperazine (C₄H₁₀N₂). This molecule has been used as a ligand in various complexes [8-11]. The free pp exists in a chair conformation because of the steric crowding present in the boat form [9]. However, as it can be seen from Fig. 5 [9], this molecule can coordinate in the boat form as a bidentate ligand (a) [10], in the chair form as a bidentate ligand (b) [11] or as a unidentate ligand coordinating only through the NH nitrogen (c) [8, 9]. In our previous study, we reported the vibrational assignments and the frequencies of the free pp molecule both theoretically and experimentally in the region of (4000-400) cm⁻¹ [12]. The assignments and the frequencies of the fundamental bands observed in the infrared spectra of the compounds under study have been given in Table-1, together with our previous data, for comparison.

The spectral data for pp in the complexes exhibit characteristics of a coordinated ligand (Table-1, Figs. 1, 2). On coordination, the NH and CH₂

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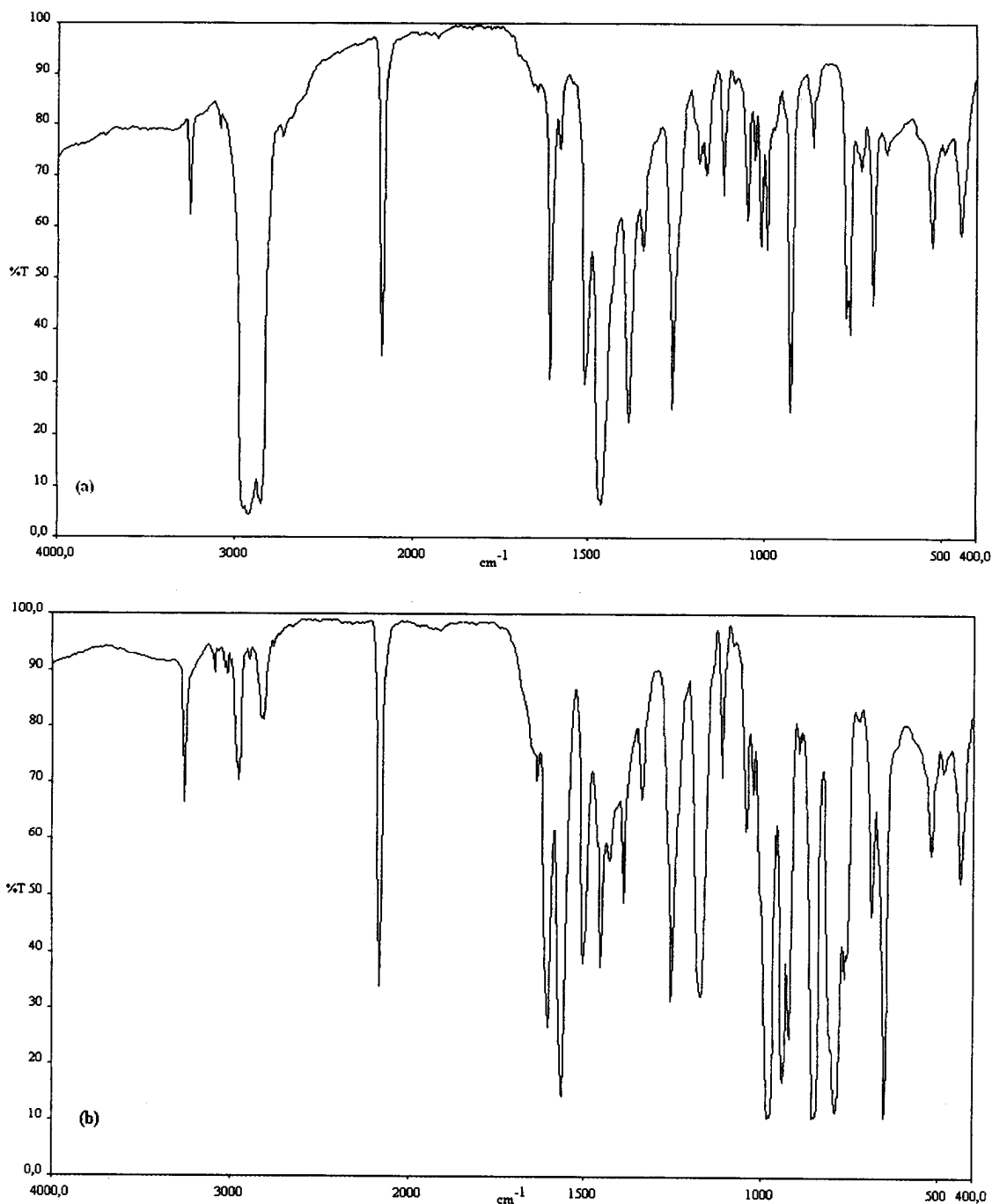


Fig. 1: The MIR spectra of the Ni-pp-Cd complex in nujol (a) and hexachloro-1,3-butadiene (b).

stretching frequencies attributed to piperazine molecule within the pp ligand should decrease and increase due to the consecutive inductive effects, respectively (on coordination, NH and NC bonds should become weaker and CH bonds should become stronger) [13]. It is clearly observed in Table-1 and

Figs. 1, 2 that these requirements are fulfilled for pp in our compounds. The observed shifts of the vibrational frequencies are consistent with the Hofmann- T_d -type complexes and clathrates of piperazine molecule as reported in [14]. These shifts in frequencies have been explained in terms of

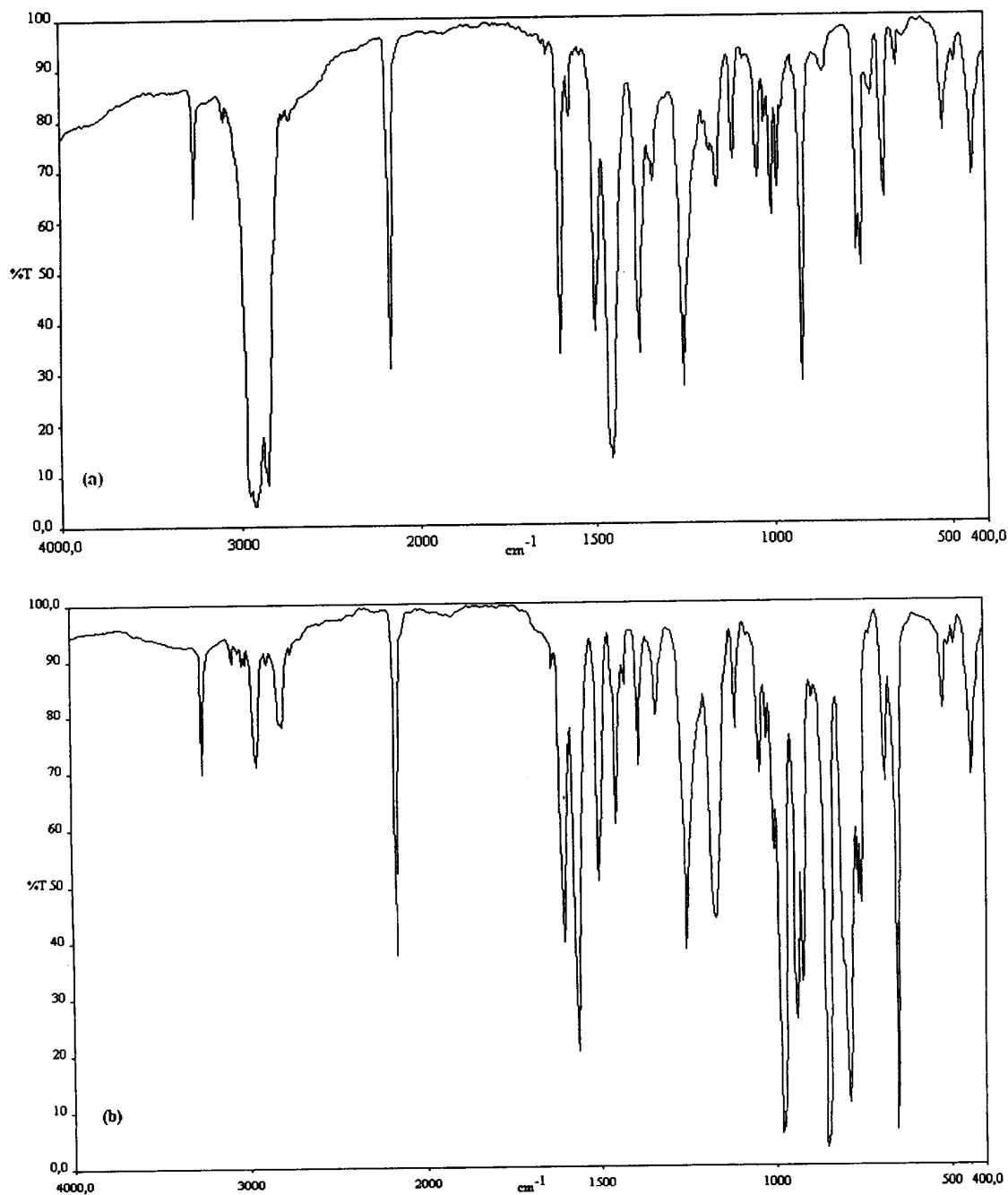


Fig. 2: The MIR spectra of the Ni-pp-Hg complex in nujol (a) and hexachloro-1,3-butadiene (b).

coupling of the internal vibration modes of pp ligand molecule with M-N vibrations [5-7, 14-15]. However the strong CN stretching frequency attributed to phenyl attached to one of the nitrogens of piperazine showed no shift in these compounds. Regarding the phenyl molecule within the pp ligand, the vibrational

bands of the molecule possess small shifts. These shifts are due to the environmental changes on complexation.

From the comparison of the spectral data presented in Table-1, we have concluded that the pp

Table-1: The vibrational wavenumbers (cm^{-1}) of pp in the Ni-pp-M (M = Cd or Hg) compounds.

* Mode	* Assignment	* pp	Ni-pp-Cd	Ni-pp-Hg
V ₁	v(NH)	3278 sb	3256 s	3256 s
V ₅	v(CH)	3091 m	3090 m	3091 m
V ₇	v(CH)	3059 m	3069 w ^b	3062 w ^b
V ₈	v(CH)	3036 m	3035 w ^b	3034 w ^b
V ₉	v(CH)	3023 m	3020 w ^b	3020 w ^b
V ₁₁	v(CH ₂)	2944 s	2953 s ^b	2958 s ^b
V ₁₃	v(CH ₂)	2881 w	2894 w ^b	2896 w ^b
V ₁₄	v(CH ₂)	2824 vs	2827 s ^b	2825 s ^b
V ₁₅	(NH) _{def.}	1670 w	1639 w	1636 w
V ₁₇	v(CC)	1600 vs	1603 vs	1603 vs
V ₁₈	v _{ring}	1579 m	1575 m	1575 m
V ₂₁	v _{ring}	1498 vs	1504 vs	1504 vs
V ₂₂	$\delta_s(\text{CH}_2)$	1452 s	1452 s ^b	1452 s ^b
V ₂₄	w(CH ₂)	1407 sh	1424 w ^b	1423 w ^b
V ₂₆	v(CN)	1380 s	1380 s ^b	1380 s ^b
V ₂₉	v _{ring} +t(CH ₂)	1325 s	1338 m	1338 m
V ₃₂	$\delta(\text{CH})+t(\text{CH}_2)$	1235 vs	1254 vs	1254 vs
V ₃₃	$\delta(\text{CH})$	1190 m	1178 m	1179 w
V ₃₆	$\delta(\text{CH})+v_{16}(\text{a}_u)$	1146 s	1159 m	1158 m
V ₃₈	$\delta(\text{CH})+\rho_r(\text{CH}_2)$	1081 m	1082 w	1083 w
			1110 s	1112 s
V ₃₉	v _{ring}	1059 s	1044 s	1045 s
V ₄₁	v _{ring}	1032 s	1024 m	1024 m
V ₄₃	ring breathing	992 s	1006 s	1006 s
			989 s	990 s
V ₄₆	w(CH ₂)	937 s	923 vs	923 vs
V ₅₀	$\gamma(\text{CH})+v_{\text{ring}}$	881 s	860 s	865 m
V ₅₄	(CH) _{def.}	758 vs	759 vs	757 vs
			767 vs	767 vs
V ₅₅	$\gamma(\text{CH})$	735 sh	723 m	723 m
V ₅₇	γ_{ring}	693 vs	689 vs	688 vs
V ₅₉	$\delta_{\text{ring}}+\text{ring band}$	625 s	649 m	652 m
V ₆₀	δ_{ring}	517 vs	521 s	521 s
V ₆₃	$\rho_r(\text{NH})$	485 w	487 w	488 w
V ₆₄	δ_{ring}	437 m	438 s	440 s

* Taken from Ref. [12]. ^b In hexachloro-1,3-butadiene. vs: very strong, s: strong, m: medium, w: weak, b: broad, sh: shoulder.

Table-2: The vibrational wavenumbers (cm^{-1}) of the $\text{M}(\text{CN})_4$ group in the Ni-pp-M (M = Cd or Hg) compounds.

* Assignment	* K ₂ Cd(CN) ₄	* K ₂ Hg(CN) ₄	Ni-pp-Cd	Ni-pp-Hg
v ₁ (CN)A ₁	(2149)	(2149)	(2177) vs	(2178) vs
v ₂ (CN)F ₂	2145	2146	2163 vs	2166 vs
v ₄ [v(MC)+ $\delta(\text{NCM})$]F ₂	316	330	353 s	352 s
v ₅ [v(MC)+ $\delta(\text{NCM})$]F ₂	250	235	266 s	270 s

* Taken from Ref. [16]. vs: very strong, s: strong. The values in the parenthesis are the Raman value.

molecules in our compounds have been coordinated as a unidentate ligand coordinating only through the NH nitrogen. Unidentate coordination of the pp ligand has also been supported by the shifts in the position of the NH deformation mode from the free ligand value of 1670 cm^{-1} to 1600 cm^{-1} and no shift in the position of the CN stretching [9].

$\text{M}(\text{CN})_4$ (M = Cd or Hg) group vibrations

Assignments of the bands for the $\text{M}(\text{CN})_4$ (M = Cd or Hg) ions in the spectra of the present compounds have been carried out by means of the vibrational data of the $\text{K}_2\text{M}(\text{CN})_4$ (M = Cd or Hg) salts in the solid phase reported by Jones [16] who assigned the vibrational data on the basis of T_d -symmetry. The studies on these salts have shown that the K-CN distances are 2.9 \AA in $\text{K}_2\text{Cd}(\text{CN})_4$ [17], $\text{K}_2\text{Hg}(\text{CN})_4$ [18] while the Cd-NC distances are 2.3 \AA in the T_d -symmetry. Therefore, we have used them as references to account for the vibrational changes when the stiffer M-NC bonding takes place. The

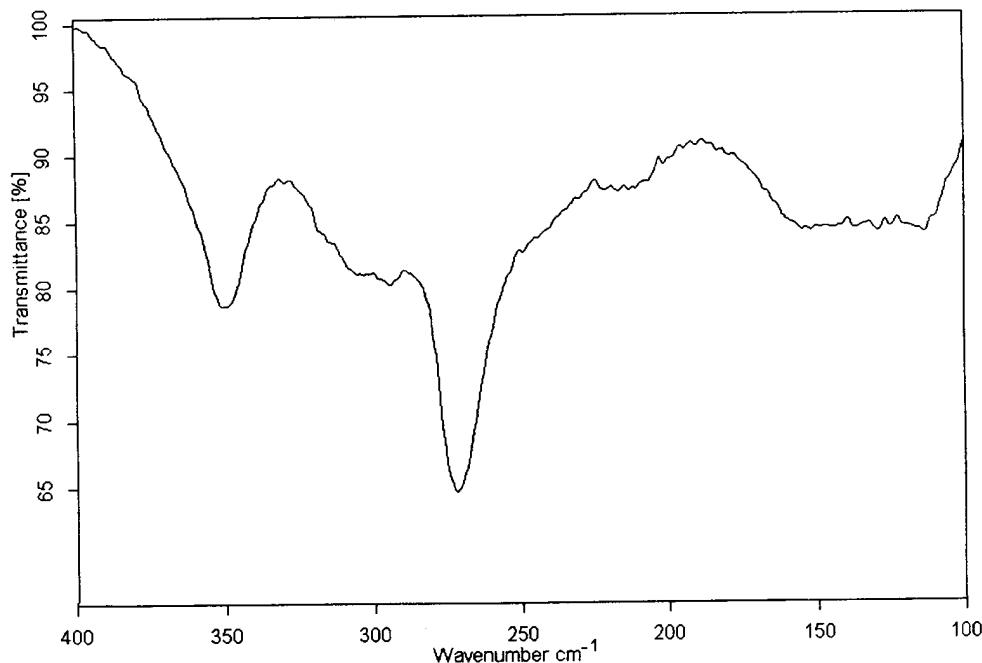


Fig. 3: The FIR spectrum of the Ni-pp-Hg complex.

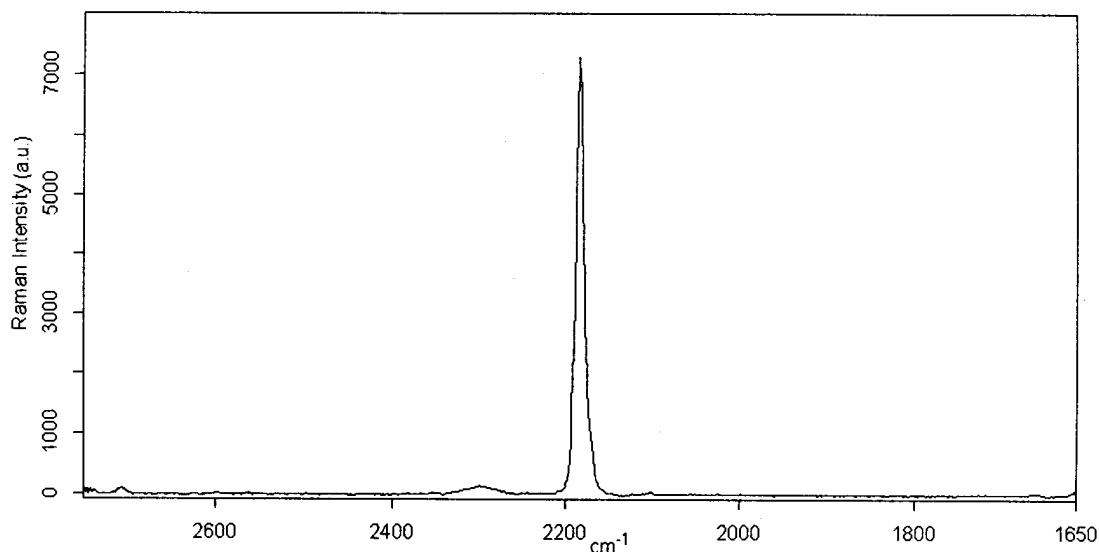


Fig. 4: The Raman spectrum of the Ni-pp-Cd complex.

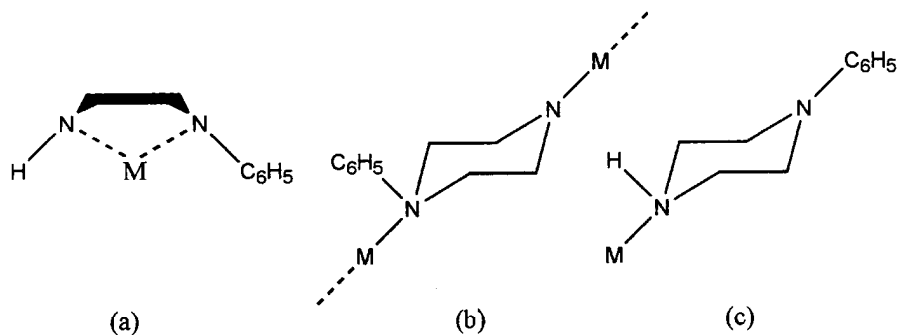


Fig. 5: Various forms of coordinated pp ligand molecule.

vibrational data for $M(CN)_4$ groups in our complexes are given in Table-2 along with Jones's data.

The vibrational frequencies of the $M(CN)_4$ group in the complexes appear to be much higher than those for the $M(CN)_4$ groups in $K_2M(CN)_4$ ($M = Cd$ or Hg). Such frequency shifts have been observed for other Hofmann- T_d type complexes [5-7, 14] and also clathrates [14-15], and have been explained that the shifts arise from the mechanical coupling of the internal modes of $M(CN)_4$ ($M = Cd$ or Hg) with metals as both ends of the CN group are bonded to the transition metals. Accordingly the shifts observed in the compounds can be attributed to the mechanical coupling of the internal modes of $M(CN)_4$ with metal.

As a result, the similarities obtained for the spectral features of the present compounds with the Hofmann- T_d type structures, let us to conclude, that

the compounds presented in this study are also examples of the Hofmann- T_d type complexes.

Experimental

All the chemicals used were of reagent grade (Aldrich) and they were used without further purification. The compounds were prepared as follows: at first step 1 mmol of $K_2M(CN)_4$ ($M = Cd$ or Hg) was dissolved in distilled water, then slightly more than 2 mmol of the liquid pp were added to this solution under stirring. After a short time, 1 mmol of $NiCl_2$ dissolved in distilled water was added drop wise to the prepared mixture, again under stirring. The final mixture was left for stirring for a week at room temperature. The obtained product was filtered and washed with water, ethanol and ether successively and dried in a desiccator using P_2O_5 as desiccant.

The infrared spectra of the complexes were recorded in the region of (4000-100) cm^{-1} with Perkin-Elmer FT-IR 2000 and Bruker IFS 66v/S vacuum FT-IR spectrometers at a resolution of 4 cm^{-1} . In order to provide better identifications for the vibrational bands of the compounds prepared in this study two different mulls (nujol and hexachloro-1,3-butadiene) were used. In the MIR region of spectrum, bands of nujol were reported at 1377 cm^{-1} , 1461 cm^{-1} , 2858 cm^{-1} , 2925 cm^{-1} and of hexachloro-1,3-butadiene at 655 cm^{-1} , 793 cm^{-1} , 852 cm^{-1} , 941 cm^{-1} , 981 cm^{-1} , 1170 cm^{-1} , 1564 cm^{-1} , 1610 cm^{-1} , respectively. The Raman spectra of the compounds were recorded in the region of (2800-1650) cm^{-1} with Bruker Senterra Dispersive Raman Microscope using the 532 nm line of a 3B diode laser.

The compounds were analyzed for metals Ni, Cd and Hg metals with a Perkin Elmer 4300 ICP-OES and for C, H and N via a Fisons EA-1108 elemental analyser. Ni, Cd and Hg metals were investigated at 231.604 nm, 228.802 nm and 253.652 nm, respectively. The results are as following; (found % / calculated %) $\text{Ni}(\text{C}_{10}\text{H}_{14}\text{N}_2)_2\text{Cd}(\text{CN})_4$ ($M_r=599.64$): C(47.78/48.07), H(4.59/4.71), N(18.32/18.69), Ni(9.57/9.79), Cd(18.53/18.74) and $\text{Ni}(\text{C}_{10}\text{H}_{14}\text{N}_2)_2\text{Hg}(\text{CN})_4$ ($M_r=687.82$): C(41.64/41.91), H(3.92/4.1), N(15.91/16.29), Ni(8.31/8.54), Hg(28.36/29.16).

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