

Vibrational analysis of Nickel (II) and Zinc (II) complexes of Diethyl (2-oxo-1-phenyl) ethyl phosphonate

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Abstract The FT-IR and FT-Raman spectra of $[(CH_3CH_2O)_2P(O)CC_6H_4=CH-O]_2Ni \cdot 2H_2O$ and $[(CH_3CH_2O)_2P(O)CC_6H_4=CH-O]_2Zn \cdot 1\frac{1}{2}H_2O$ are recorded and analysed on the basis of vibrations of benzene ring, ethoxy and ethene group, P = O bond and P-O-C bond. It is confirmed that the zinc complex is a mixture of (Z) and (E) isomer while the nickel complex is (Z)-isomer alone. A strong hydrogen bonding is identified between the oxygen atom in P = O and the Hydrogen atom in the ethene group in the (E)-isomer of the zinc complex.

Keywords FT-IR and FT-Raman spectrum, hydrogen bonding

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Synthesis and characterization of complexes of alkyl phosphonates are of considerable interest in recent years because of the variety of structural coordination modes present in them. Spectroscopic (IR, electronic and EPR) and magnetochemical studies on cobalt (II), nickel (II), copper (II) and zinc (II) complexes of diethyl (2-oxo-1-phenyl) ethyl phosphonate synthesized using the corresponding metal acetates and halides are reported in the literature [1,2]. Similar studies reveal that the lithium salt of diethyl (1-methyl-2-oxoethyl) phosphonate exists as a mixture of (Z) and (E) forms, while lithium salt and zinc complex of diethyl (2-oxo-1-phenylethyl) phosphonate have (Z)-chelate structure [3,4]. The Fe(III) and Cr(III) complexes also exist in (Z)-chelate and (E)-enolate forms [5]. In the present work, we report the analysis of the FT-IR and FT-Raman spectra of two newly synthesized phosphonates-namely Bis(2-diethoxyphosphonyl-2-phenyl-ethenolate) nickel (II) Dihydrate, $[(CH_3CH_2O)_2P(O)CC_6H_4=CH-O]_2Ni \cdot 2H_2O$

$=\text{CH-O})_2\text{Ni}\cdot 2\text{H}_2\text{O}$, hereafter abbreviated as PN and Bis(2-diethoxyphosphonyl-2-phenyl – ethenolate) zinc (II). $1\frac{1}{2}$ Hydrate, $[(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{CC}_6\text{H}_5=\text{CH-O})_2\text{Zn}\cdot 1\frac{1}{2}\text{H}_2\text{O}$, hereafter abbreviated as PZ.

The nickel (II) and zinc (II) complexes were obtained from the corresponding metal halides ($\text{NiBr}_2\cdot 3\text{H}_2\text{O}$ and ZnCl_2) and diethyl (2-oxo-1-phenyl) ethyl phosphonate in the presence of potassium hydroxide. The reaction was carried out at room temperature in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution. The PN and PZ complexes are obtained as green and white powders, respectively. The FT-IR and FT-Raman spectra of both the samples are recorded using a Bruker IFS 66V FT-IR/FT-Raman Spectrometer. The FT-Raman spectra, over the range $50\text{--}3000\text{ cm}^{-1}$ are recorded using an Nd-YAG laser of wavelength 1064 nm and power 200 mW. The FT-IR spectra are obtained over the range $400\text{--}4000\text{ cm}^{-1}$ with the samples as KBr pellets using globar source.

The structural studies of these complexes [2] reveal that PN is octahedrally coordinated by the bidentate phosphonyl ligand, two of the coordination sites being occupied by water molecules. The ^1H , ^{13}C and ^{31}P NMR data for the zinc complex prove that the product is a mixture of (Z) and (E)-isomers, with the (Z)-isomer being predominant.

The characteristic frequencies observed in the FT-IR and FT-Raman spectra recorded for both the complexes are listed in Table 1. The interpretation of the spectra is done on the basis of characteristic vibrations of phenyl (Ph) and Ethoxy (EtO) groups. Vibrations of $\text{P}=\text{O}$, P-O-C , CH of the ethene group, *etc* are also identified. The EtO group provides 18 normal vibrations, of which 15 are attributed to ethyl and the remaining 3 are attributed to the C–O

Table 1. Spectral data (cm^{-1}) and band assignments of $[(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{CC}_6\text{H}_5=\text{CH-O})_2\text{Ni}\cdot 2\text{H}_2\text{O}$ and $[(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{C}_6\text{H}_5=\text{CH-O})_2\text{Zn}\cdot 1\frac{1}{2}\text{H}_2\text{O}$

$[(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{CC}_6\text{H}_5=\text{CH-O})_2\text{Ni}\cdot 2\text{H}_2\text{O}$		$[(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{C}_6\text{H}_5=\text{CH-O})_2\text{Zn}\cdot 1\frac{1}{2}\text{H}_2\text{O}$		Assignments		
Raman	IR	Raman	IR	Phenyl group	Ethoxy/Ethene group	Miscellaneous
	3431mbr		3456 wbr			$\nu\text{H}_2\text{O}$
	3085vw		3085 vw	12 a		
3059s	3056vw	3039s	3056vw	1		
	3017vw		3017vw	15b	νCH	
2979m	2981m	2973m	2982m		$\nu_4\text{CH}_3$	
2943m	2929w	2930s	2928m		$\nu_2\text{CH}_2$	
2906w	2905w	2897m	2905sh		$\nu_1\text{CH}_3$	
2888vw	2866 vw	2870w	2854w		$\nu_5\text{CH}_2$	
		2765vw				$\delta\text{CH}_2 + \omega\text{CH}_2$
		2724vw				A Band
		1955vwbr				B Band
2129m						17b + 19a
2109m						$\omega\text{CH}_2 + \rho\text{CH}_2$
2033m			1741vw			16v + 18a
						C Band

Table 1 (Cont'd)

1594vs	1603sh	1596vvs	1603sh	16a		$\delta\text{H}_2\text{O}$
1556m	1551vvs	1555sh	1548vvs	16b	$\nu\text{C} = \text{C}$	
1498vw	1493w	1493vw	1493w	13a	$\delta\text{O} - \text{CH}_2$	
1473vvw	1478vw	1476vvw	1476sh		$\delta_s \text{CH}_3$	
1433m	1444w	1445w	1444w	13b	δCH_2	
	1393sh		1394sh		$\omega\text{O} - \text{CH}_2$	
1350w	1359s	1341w	1365s		$\delta_s \text{CH}_3$	
	1332sh		1335m	9		
	1320m	1321w	1318m		ωCH_2	
	1300w	1302w	1296m	3		
1284w					τCH_2	
1266m	1254m	1267s	1257m	15a		
1244s					$\nu\text{C}-\text{O}$	
1187vw		1184w		17a	ρCH_3	
	1173m		1167m			$\nu\text{P} = \text{O}$
1158vw		1156w		17b		
1082wbr	1102w	1099w	1098w		$\nu\text{C}-\text{O}/\nu\text{C}-\text{C}$	
	1053s		1052s			$\nu_s \text{P}-\text{O}-\text{C}$
1038m	1025vs	1305w	1023vs			
1000vs		1001vs		6		
970w	963s	955vw	965s	19a		
837vw	821sh		819sh		δCH	
791vw	794m	790vw	796m		ρCH_2	
770vw	759m	761vw	761m	4		$\nu_s \text{P}-\text{O}-\text{C}$
697m	700m	693w	700m	8		
	671m		668m			H_2O libration
627vwbr	623vw	621w	620vw	18b		
554w	551m	551vw	549m	20b		
513w	512w		507w			H_2O libration
483w	487vw		476vw	18a		} Metal-Oxygen Vibrations
			465w			
			442vw			
			426vw			
414w		409vw		20a	$\delta \text{O}-\text{C}-\text{C}$	
397w		340vw		14b		
278m						} External Modes
252w						
133m						
112s						
84vvs		97vs				

Abbreviations :

w - weak

m - medium

s - strong

v - very

br - broad

sh - shoulder

 τ - twisting

v - stretching

 ω - wagging

 δ - bending

 ρ - rocking

Subscript a - asymmetric

Subscript s - symmetric

stretching vibration, C–O deformation and EtO torsion. In monosubstituted benzenes, 6 of the 30 number of normal vibrations are substituent sensitive [6]. The numbering of these modes are done according to Herzberg's convention [7,8]. However, in the present study, since some of the modes have the same frequency range an unambiguous assignment of certain normal vibrations is not possible.

The CH stretching vibrations of the benzene ring usually absorb weakly to moderately between 3120 and 3000 cm^{-1} [6]. The three weak IR bands at 3085 , 3056 and 3017 cm^{-1} in the case of both nickel and zinc compounds may be assigned to the 12a, 1 and 15b modes. The CH stretching frequency which corresponds to mode 1 is observed with strong intensity at 3059 cm^{-1} in the Raman spectra of both the compounds. The CH stretching vibration (CH) of the ethene group also appear in this region [9]. The methyl and methylene stretching vibrations namely $\nu_a\text{CH}_3$, $\nu_a\text{CH}_2$, $\nu_s\text{CH}_3$ and $\nu_s\text{CH}_2$ are observed in the region between 2982 and 2854 cm^{-1} [6,10]. These frequencies are such that $\nu_a\text{CH}_3 > \nu_a\text{CH}_2 > \nu_s\text{CH}_3 > \nu_s\text{CH}_2$.

The ring stretching vibrations 16a, 16b, 13a and 13b are good group vibrations. When the Benzene ring is substituted by C = C, the 16a and 16b are expected at $1620 - 1585\text{ cm}^{-1}$ and $1590 - 1565\text{ cm}^{-1}$ respectively [6, 11]. The very intense Raman band at 1594 and 1596 cm^{-1} in PN and PZ, respectively are assigned to the 16a mode. The corresponding IR band is observed as shoulder at 1603 cm^{-1} in both the compounds. The bands of 16b mode are observed as very intense IR bands at 1551 and 1548 cm^{-1} and as medium intense Raman bands at 1556 and 1555 cm^{-1} (shoulder) for PN and PZ, respectively. However, the IR bands of 16b mode is usually weaker than the 16a mode [6, 11]. The intensity reversal of these modes of vibration and the shifting of the 16b mode to the lower frequency side may be due to the strong coupling between this mode and the $\nu\text{C} = \text{C}$ vibration of the alkene group which occurs in the same region [9]. The bending mode of water also appears in this region.

The asymmetric deformation $\delta_a\text{CH}_3$ is observed at 1478 cm^{-1} in PN and 1476 cm^{-1} in PZ and the symmetric deformation $\delta_s\text{CH}_3$ is observed around 1350 cm^{-1} . The methyl rock (ρCH^3) is assigned to the absorption lines at 1187 and 1184 cm^{-1} in PN and PZ respectively. An ethoxy group on a phosphorous atom absorbs near 1485 ($\delta\text{O-CH}_2$) and 1395 cm^{-1} ($\omega\text{O-CH}_2$) [11]. In the present study, $\delta\text{O-CH}_2$ mode appears as weak bands at 1493 cm^{-1} in both the compounds and $\omega\text{O-CH}_2$ as shoulders at 1393 cm^{-1} (PN) and 1394 cm^{-1} (PZ).

The P-O-C stretching is characterized by a very strong band in the region $1050-970\text{ cm}^{-1}$ [11-13]. In most ethoxy phosphorous compounds, this band is a doublet [11]. Both the compounds under investigation shows very strong doublets in this region. These are probably due to the asymmetric P-O-C stretching vibration. The medium intense IR bands at 751 cm^{-1} (PN) and 761 cm^{-1} (PZ) may be due to the symmetric stretching of P-O-C. Very weak Raman bands are observed in this region. The stretching of the P = O bond gives rise to a strong band at $1300 - 1140\text{ cm}^{-1}$ [11, 14]. Zdravkova et al [2] has assigned the P = O stretching band at 1170 and 1175 cm^{-1} for the nickel and zinc complexes. In the present investigation, this band is observed as medium intense band at 1173 and 1167 cm^{-1} , respectively, for PN and PZ.

A very strong Raman band at $1000 \pm 10\text{ cm}^{-1}$ is a good group frequency characteristic of monosubstituted benzenes [8]. This band is due to the in plane trigonal ring deformation (mode 6) in which successive carbon atoms move toward and away from the centre of the hexagon. In the IR, it is usually weak. In the present study, the very intense Raman band at 1000 and 1001 cm^{-1} for PN and PZ respectively, are assigned to the mode 6. No IR band is observed for this mode.

The CH out of plane deformation near 770 cm^{-1} (mode 4) and the out-of-plane ring deformation absorbing near 690 cm^{-1} (mode 8) form a pair of strong bands characteristic of monosubstituted benzene derivatives [6]. Both these modes appear as medium intense bands in the IR and as weak bands in the Raman. The ring breathing mode 2 of monosubstituted benzenes usually contribute a strong Raman band, whose position is highly substituent sensitive [8, 15]. Its frequency moves in the range $1100\text{-}620\text{ cm}^{-1}$ depending on the mass of the substituent. In the present study, no strong Raman band other than the band around 1000 cm^{-1} is observed in this region. This may be because of the overlapping of this mode with the in-plane ring deformation mode 6.

The substituent sensitive modes 20b, 18a and 14b are assigned around 551 , 483 and 360 cm^{-1} , respectively [16, 17]. The weak Raman bands around 625 (mode 18b) and 410 cm^{-1} (mode 20a) are characteristic bands of monosubstituted benzene ring [11]. The metal – oxygen vibrations shows very weak bands in the region $487\text{-}426\text{ cm}^{-1}$ [18]. In the case of zinc complex, four bands are observed in this region which may be due to the presence of metal-oxygen bonds of varying strength. This observation supports the presence of both (Z) and (E)-isomers in the compound as suggested in the structural report [2]. The nickel compound shows only one band in this region, indicating that only one structure, namely the (Z)-isomer alone is present in the compound.

The broad absorption band at 3431 and 3456 cm^{-1} for PN and PZ respectively, are due to the stretching vibrations of the water molecules. Librations of water molecules are observed as medium intense bands around 670 cm^{-1} and as weak bands around 510 cm^{-1} . Combination bands are observed in the range of $2765\text{-}2033\text{ cm}^{-1}$.

Strong hydrogen bonded systems are characterised by the appearance of a trio of very weak broad bands in the region $2800\text{-}2400$, $2350\text{-}1900$ and $1720\text{-}1600\text{ cm}^{-1}$ [19]. In the present investigation, the weak and broad bands at 2724 , 1955 and 1741 cm^{-1} in the spectra of PZ suggest the presence of a strong hydrogen bonding in the compound. In the (E)-isomer of the PZ compound, the hydrogen atom in the ethene group come closer to the oxygen atom of the $\text{P}=\text{O}$ bond. Hence, a strong hydrogen bond ($\text{O}\cdots\text{H}-\text{C}$) may be expected between the two [20]. This type of bond formation has a tendency to reduce the energy of $\text{P}=\text{O}$. The red shift of 6 cm^{-1} in the frequency of the stretching vibrations of $\text{P}=\text{O}$ bond in PZ when compared to that in PN confirms the lowering of the $\text{P}=\text{O}$ bond energy, which is a clear indication of its participation in a strong hydrogen bonding.

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