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Experimental and Theoretical Vibrational Spectroscopic Study of Zinc (II) Halide Complexes of 4-Acetylpyridine

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Abstract

In the present work, we present a detailed experimental and theoretical study of the zinc (II) halide complexes of 4-acetylpyridine (abbreviated as 4-Ap) (Zn $(L)_2$ X_2, [where L: C_7OH_7N; X: Cl, Br and I]). The infrared and Raman spectra of the zinc (II) halide complexes of 4-Ap have been recorded between 400-4000 cm^{-1} and 5-3500 cm^{-1} regions, respectively. The analysis of the FT-IR and FT-Raman spectra indicates that some structure-spectra correlations. For a given series of isomorphous complexes, the sum of the differences between the values of the vibrational modes of uncoordinated 4-Ap was found to increase in order of second ionization potentials of metal. The molecular geometry and vibrational frequencies of the zinc (II) halide complexes of 4-Ap in the ground state have been calculated by using the Density Functional Method (B3LYP) with LANL2DZ and SDD as basis sets. A complete assignment of the fundamentals was proposed based on the total energy distribution (TED) calculation.

1. INTRODUCTION

Pyridine ring system occurs in the structures of wide variety of natural products, biological and industrial compounds. It also has been used very frequently as a proton acceptor in studies involving hydrogen bonded complexes. Its derivatives are used as non-linear materials and photochemicals [1]. Therefore, the vibrational spectra of substituted pyridine have been the subject of several investigations because of its biological and industrial usefulness.

Medhi et al. [2] reported the first detailed vibrational assignment of 2, 3 and 4-Acetylpyridine. In that study, they reported the experimental frequencies of the title molecules. Medhi et al. [2] recorded and analyzed the infrared absorption spectra and the laser Raman spectra in both pure and liquid state of 2, 3, 4-Acetylpyridine. They determined empirically assigned IR and Raman bands in that work. Sett and coworkers assigned again these bands using empirical force field approximation based on acetyl and pyridine group [3].

Güllüoğlu et al. was investigated transition metal (II) halide 4-Ap complexes. In that study, the vibrational spectra of metal (II) halide of the 4-Ap complexes (M X_2(4-Ap)$_2$ (M:Ni, Cd and Zn, X:Cl, and M:Cd; X:I)) was reported [4]. The only structural infrared work had been that of Cabral et all [5] on the Co(4-Ap)$_2$Cl$_2$ complexes, yet in this study only a few values of the 4-Ap frequencies were given. Yurdakul et al. was reported the vibrational spectra of metal (II) tetracyanonickelate complexes of 4-Ap [6].

The lack of theoretical and experimental study of Zinc metal complexes of 4AP and its industrial importance triggered this work and the present investigation has been aimed to carry out a complete

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vibrational analysis of the title compound. To the best our knowledge, any theoretical study which is carried out by using density functional methods has not been reported for the vibrational spectra of the metal complexes of 4-Ap. In the present study, we have reported the IR and Raman spectra of metal complexes of 4-Ap [Zn $(NC_7H_7O)_2$ X_2; X: Cl, Br and I]. Using the density functional calculation the B3LYP with SDD and LANL2DZ basis sets to determine experimentally the vibrational modes of the Zn complexes of 4-Ap.

2. COMPUTATIONAL DETAIL

Gaussian 09W [7] software package was used for the theoretical calculations. The quantum chemical calculations were performed applying the DFT (B3LYP) with SDD and LANL2DZ basis sets. The geometry optimizations were followed by wavenumber calculations using same basis sets. The calculated frequencies were scaled with scaling factors [8]. The Total Energy Distribution (TED) of vibrational modes was calculated by using the Scaled Quantum Mechanics (SQM) program [9].

3. EXPERIMENTAL

All chemicals were reagent grade and were used without further purification. Metal chloride, bromide or iodide was dissolved in absolute ethanol (10 ml). To this, 1 mmol of the 4-Ap solution in ethanol was added. The mixture was stirred magnetically at room temperature. The precipitated complexes were filtered, washed with ether and dried. The freshly prepared compounds were analyzed for C, H and N by LECO-932 model analyzer in Table 1 [10 ,11].

Table 1. *Analytic data for compounds prepared.*

Compounds	C (% found, %calculated)	N (% found, %calculated)	H (% found, %calculated)
Zn(4-Ap)Cl_2	44.421/45.600	7.326/7.401	3.371/3.727
Zn(4-Ap)Br_2	35.785/35.971	5.896/5.992	3.757/3.018
Zn(4-Ap)I_2	29.715/29.950	5.021/4.989	2.641/2.513

The samples of the Zinc (II) halide complexes of the 4-Ap is in powder forms at room temperature. Infrared spectra of the samples were recorded between for the 400-4000 cm^{-1} on a Mattson 1000 FTIR spectrometer which was calibrated using polystyrene bands. The samples were prepared as a KBr disc. FT-Raman spectra of the sample were recorded between 5-3500 cm^{-1} region on a Bruker FRA 106/S FT-Raman instrument using 1064 nm excitation from an Nd:YAG laser. The detector is a liquid nitrogen cooled Ge detector.

4. RESULTS AND DISCUSSIONS

4.1. Molecular Structure

The dichlorobis (pyridine) Zn(II) complexes were made structural investigation by Steffen et al. In that study, the molecular geometry of the Zn $(pyridine)_2$ Cl_2 complexes were given by X-ray diffraction technique [12]. The Zn(II) atoms was coordinated by two nitrogen atoms from two pyridine ligands and two chlorine atoms, and coordination geometry of the Zn(II) atom was distorted tetrahedral configuration.

The complexes of $Zn(nicotinamide)_2$ X_2 (X: Cl and Br) [13, 14], $Zn(isonicotinamide)_2$ X_2 (X:Cl and Br) [15, 16] and the $Zn(L)_2X_2$ (L: 4-Methylpiperidine, 4-cyanopyridine, 4-carbinylpyridine, 4-pyridinecarboxamide and 4-carbomethoxypyridine; X:Cl and Br) [17] are distorted tetrahedral configuration. Moreover, these are reported that the complexes of the Zn $(4\text{-}Ap)_2$ X_2 (X: Cl and Br) was distorted tetrahedral configuration [15]. Accordingly, we were considered that the zinc complexes of the 4-Ap is distorted tetrahedral configuration. The Zinc atoms are coordinated by two nitrogen atoms from two 4-Ap ligands and two chlorine atoms. The molecular geometry of the complexes was given in Fig.1.

Bond lengths and bond angles form the geometry optimizations using B3LYP calculation were listed in Table 2. The optimized structure of the Zinc (II) halide complexes of 4-Ap was given in Fig.1. The optimized geometric parameters of the zinc complexes of 4-Ap were compared with those of X-ray diffraction data of 4-acetylpyridinium chloride [18].

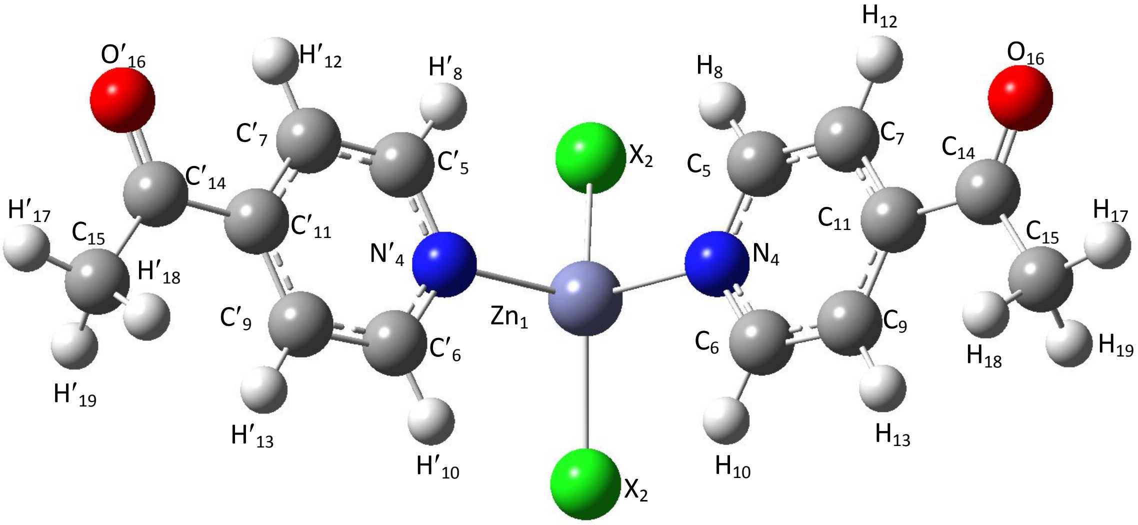

Figure 1. *The Zinc metal complexes of 4-Ap structure and atoms numbering (Zn* $(C_7OH_7N)_2 X_2$ *X: Cl, Brand I).*

The Zn-N distances of the zinc chloride complex of the pyridine molecule was determined at 2.049 Å by using X-ray data [12]. We calculated at 2.142 Å(for Zn(4-Ap)$_2$Cl$_2$), at 2.491 Å (for Zn(4-Ap)$_2$Br$_2$) and at 2.686 Å (for Zn(4-Ap)$_2$I$_2$) by B3LYP/LANL2DZ calculations for Zinc (II) halide complexes of the 4-Ap. It is noted that the M-N bond length values depend on the halogen for a given metal complexes decrease in the order I>Br>Cl.

The two Zn-X bond lengths in each compound were found to be slightly different. The Zn-Cl bond length are at 2.327 Å and at 2.319 Å, but Zn-Br bond length is at 2.152 Å and Zn-I bond length is at 2.165 Å. Theoretical computed geometric parameters were found to be slightly different for SDD and LANL2DZ basis sets.

Table 2*. Bond lengths and bond angles for Zn (4-Ap)*$_2$*X*$_2$ *(X: Cl, Br and I) compounds.*

	Zn(4-Ap)$_2$Cl$_2$		Zn(4-Ap)$_2$Br$_2$		Zn(4-Ap)$_2$I$_2$		
Bond Lengths (Å)	LANL2DZ	SDD	LANL2DZ	SDD	LANL2DZ	SDD	X-Ray [12]
M$_1$-X$_2$	2.327	2.273	2.152	2.113	2.165	2.128	
M$_1$-X$_3$	2.319	2.266	2.152	2.113	2.165	2.127	
M$_1$-N$_4$	2.142	2.106	2.491	2.400	2.686	2.603	
N$_4$-C$_5$	1.363	1.362	1.363	1.363	1.364	1.363	1.326
N$_4$-C$_6$	1.359	1.359	1.360	1.359	1.360	1.359	1.324
C$_5$-C$_7$	1.400	1.400	1.399	1.399	1.399	1.399	1.361
C$_6$-C$_9$	1.403	1.403	1.403	1.403	1.403	1.403	1.368
C$_7$-C$_{11}$	1.412	1.412	1.412	1.412	1.411	1.412	1.385
C$_9$-C$_{11}$	1.410	1.410	1.410	1.410	1.409	1.410	1.386
C$_{11}$-C$_{14}$	1.513	1.513	1.513	1.513	1.513	1.514	1.506
C$_{14}$-C$_{15}$	1.517	1.517	1.517	1.517	1.517	1.517	1.482
C$_{14}$-O$_{16}$	1.250	1.250	1.250	1.250	1.250	1.250	1.214
Bond Angles (°)							

X_2-M_1-X_3	139.5	136.1	104.5	103.9	101.2	100.6	
X_2-M_1-N_4	101.5	102.7	103.1	104.6	104.9	106.1	
X_3-M_1-N_4	101.8	102.8	103.1	104.6	104.9	106.1	
N_4-M_1-N'_4	108.0	107.1	136.1	131.4	131.7	128.0	
M_1-N_4-C_5	120.3	120.2	120.2	120.3	120.4	120.2	
M_1-N_4-C_6	120.2	120.3	120.4	120.5	120.5	120.7	
C_5-N_4-C_6	119.4	119.3	119.1	119.1	118.9	118.9	121.9
N_4-C_5-C_7	121.7	121.7	121.8	121.9	121.9	122.0	120.6
N_4-C_6-C_9	121.8	121.8	121.9	121.9	122.0	122.0	119.8
C_5-C_7-C_{11}	119.3	119.3	119.4	119.4	119.4	119.4	119.2
C_6-C_9-C_{11}	119.2	119.3	119.3	119.3	119.3	119.3	119.9
C_7-C_{11}-C_9	118.3	118.2	118.2	118.2	118.2	118.1	118.6
C_7-C_{11}-C_{14}	118.8	118.9	118.8	118.9	118.9	118.9	118.7
C_9-C_{11}-C_{14}	122.7	122.8	122.8	122.8	122.8	122.9	122.7
C_{11}-C_{14}-C_{15}	119.0	119.0	119.0	119.1	119.0	119.1	119.8
C_{11}-C_{14}-O_{16}	119.4	119.4	119.3	119.3	119.3	119.3	118.2
C_{15}-C_{14}-O_{16}	121.5	121.4	121.5	121.5	121.5	121.5	122.0

4.2. Assignment of Fundamentals

A detailed IR and Raman spectroscopic study on the Zinc (II) halide of the 4-Ap has been reported. The zinc halide complexes of 4-Ap belongs to C_1 symmetry. The zinc halide of 4-Ap molecule has 35 atoms, which has 99 normal modes. All the vibrations are active in both IR and Raman spectra. The IR and Raman spectra of the zinc halide complexes of 4-Ap are given in Figs. 2-3. The calculated infrared and Raman frequencies together with the experimental data of the ligand are presented in Tables 3 and 4.

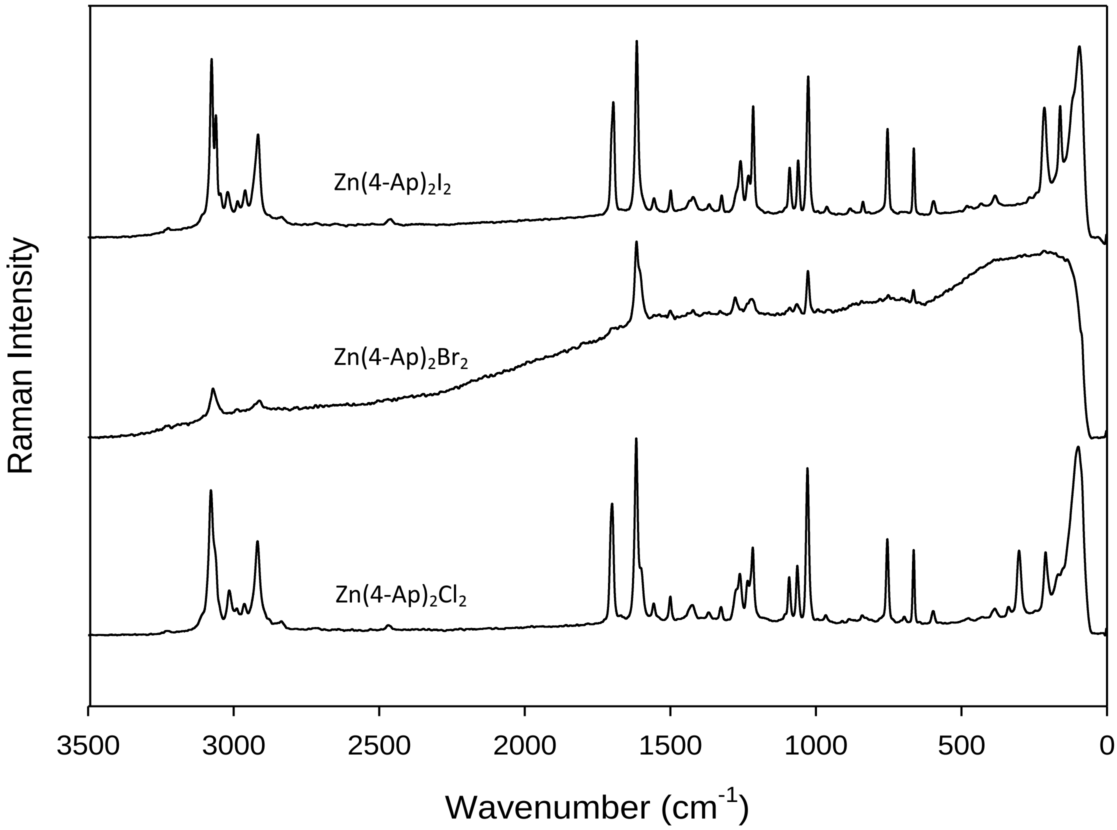

Figure 2. *FT-Raman spectra of Zn (4-Ap)$_2$ X$_2$ (X: Cl, Br and I) compounds.*

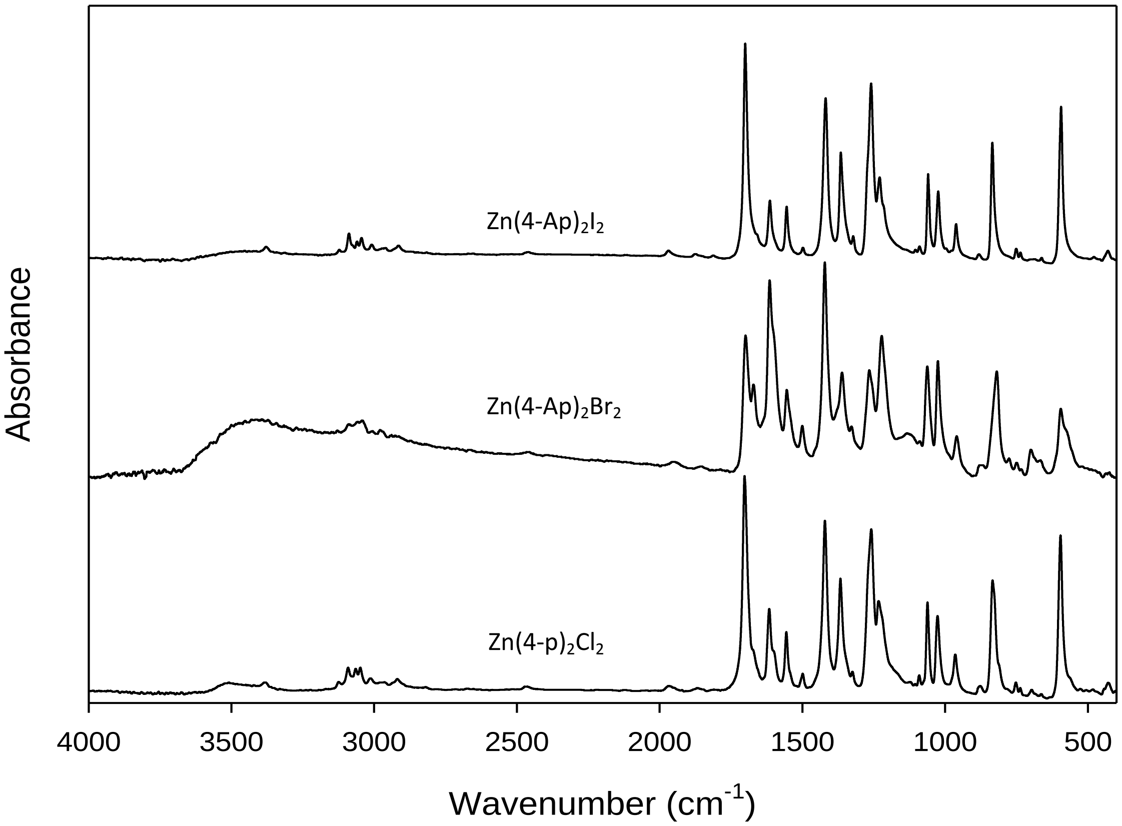

Figure 3. *FT-IR spectra of Zn (4-Ap)$_2$ X$_2$ (X: Cl, Br and I) compounds.*

4.2.1. Pyridine group vibrations

The hetero-aromatic structure shows the presence of the C-H stretching vibrations in the region 3200-3000 cm^{-1}, which is characteristic region for the ready identification of the C-H stretching vibrations. Nine C-H stretching modes were predicted in the 3060-3130 cm^{-1} region. The C-H ring stretching modes were observed at 3048 cm^{-1}, 3065 cm^{-1} and 3091 cm^{-1} in the FT-IR spectra and 3077 cm^{-1} in the FT-Raman spectra for Zn(4-Ap)$_2$Cl$_2$. Medhi et al. [2] observed at 3082 cm^{-1}, 3066 cm^{-1} and 3047 cm^{-1} for free 4-Ap molecule in the FT-IR spectra. These modes were observed at 3079 cm^{-1}, 3064 cm^{-1} and 3048 cm^{-1} for free 4-Ap molecule in the FT-IR spectra.

The CC stretching vibration of pyridyl group observed at 1598 cm^{-1} in the FT-IR spectra was observed at 1597 cm^{-1} by Medhi et al. [2]. The FT-IR spectra show up at about 1615 cm^{-1} when 4-Ap is coordinated to the metal ion. The ring stretching vibrations observed at 1617 cm^{-1} (for Cl$_2$), 1615 cm^{-1} (for Br$_2$) and 1614 cm^{-1} (for I$_2$) in the infrared spectra of the zinc complexes.

***Table 3**. Comparison of the observed and calculated vibrational spectra of Zn (4-Ap)$_2$X$_2$(X: Cl, Br and I) compounds.*

	Zn(4-Ap)$_2$Cl$_2$				Zn(4-Ap)$_2$Br$_2$				Zn(4-Ap)$_2$I$_2$				
Assignment	Exp. IR	Exp. RA.	SDD Freq	LANL2DZ Freq	Exp. IR	Exp. RA.	SDD Freq	LANL2DZ Freq	Exp. IR	Exp. RA.	SDD Freq	LANL2DZ Freq	TED (%)≥10
NMX Bend		97	107	105			89	85		94	83	79	$\delta_{XMN}(39)+\Gamma_{CNMX}(38)$
Ring Torsion		165	170	176			165	171		161	158	164	$\Gamma_{CCCC}(21)+\Gamma_{CNCC}(15)+\Gamma_{CCNM}(10)$
MN Str		213	198	199		211	191	179		209	167	165	$\upsilon_{MN}(64)$
MX Str		302	341	326			268	261		305	248	243	$\upsilon_{MX}(99)$
ρ(C-CH$_3$)*		337	364	365			363	364		330	362	363	$\delta_{CCO}(25)+\delta_{CCC}(26)(Ap)+\upsilon_{CC}(19)(Py-Ap)$
Ring Torsion		383	393	393			393	392		381	392	391	$\Gamma_{CCCN}(42)$
δ(C=O)	436	425	438	438	435		438	439	430	429	438	438	$\Gamma_{CCCC}(23)+\Gamma_{OCCC}(10)(Ap)$
CCC Bend	484	474	457	458			457	458	480	479	457	457	$\delta_{CCC}(36)+\delta_{CCO}(16)(Ap)+\upsilon_{CC}(10)(Py-Ap)$
-C=O Bending	595	595	600	601	595		601	601	593	593	600	600	$\Gamma_{OCCC}(12)+\Gamma_{CCCH}(11)(Ap)$
Ring Bending	665	664	655	655	667	664	655	655	662	663	655	655	$\delta_{CCN}(30)+\delta_{CCC}(28)$
Ring Bending	737		730	732	738		730	732	738		730	732	$\upsilon_{CC}(32)+\upsilon_{CC}(15)(Ap)+\delta_{CNC}(16)$
Ring Torsion	754	753	743	744	750	751	742	744	751	753	742	743	$\Gamma_{CCNC}(18)+\Gamma_{CCCN}(18)+\Gamma_{CCCC}(16)$
Ring Torsion	835	838	849	849	820		848	848	835	836	847	846	$\Gamma_{HCCC}(38)+\Gamma_{HCCN}(13)$
Ring Torsion	879	882	897	898	883		896	896	883	880	895	894	$\Gamma_{HCCC}(50)+\Gamma_{HCCN}(19)+\Gamma_{HCNM}(10)$
CH$_3$ Rock.	966	961	944	944	959	951	944	945	962	960	944	944	$\upsilon_{CC}(33)+\delta_{CCH}(32)(Ap)$
CH$_3$ Rock.	1027	1029	1029	1029	1025	1027	1030	1029	1024	1025	1029	1029	$\delta_{CCH}(51)+\Gamma_{OCCH}(15)(Ap)$
CH Bend	1062	1064	1043	1043	1062	1063	1043	1043	1059	1064	1042	1042	$\upsilon_{CN}(23)+\delta_{CCH}(23)+\delta_{CCC}(14)+\delta_{CCN}(15)$
CH Bend	1092	1091	1088	1088	1088	1088	1089	1089	1089	1089	1090	1089	$\delta_{CCH}(33)+\upsilon_{CC}(29)$
CH Bend	1107		1090	1090			1092	1092	1106		1092	1092	$\delta_{CCH}(33)+\upsilon_{CC}(29)$
CH Bend		1216	1210	1210		1217	1211	1212		1216	1211	1212	$\delta_{CCH}(44)+\delta_{NCH}(22)+\upsilon_{CN}(17)$
C- CH$_3$ Str	1234	1233	1244	1244	1232		1244	1245	1230	1230	1244	1245	$\upsilon_{CC}(49)(Ap)$
Ring Str.	1259	1260	1255	1258	1266		1254	1257	1260	1258	1254	1257	$\upsilon_{CC}(40)+\upsilon_{CN}(53)$
CH Bend	1326	1324	1317	1318	1328	1327	1318	1319	1321	1322	1319	1319	$\delta_{CCH}(67)$
CH$_3$ Wagg.	1367	1366	1371	1372	1363		1372	1372	1365	1363	1372	1372	$\delta_{HCH}(45)+\delta_{CCH}(41)$ (Ap)
CH$_3$ Scis.	1421	1422	1436	1436	1422	1420	1436	1437	1419	1419	1436	1436	$\delta_{HCH}(55)+\Gamma_{HCCC}(10)+\Gamma_{HCCO}(10)(Ap)$
Ring Str.	1500	1500	1527	1528	1501	1499	1527	1528	1498	1498	1527	1528	υ_{CC} (36)+υ_{CN} (36)
Ring Str.	1557	1555	1529	1530	1555		1529	1530	1555	1555	1528	1530	υ_{CC} (36)+υ_{CN} (36)
C-C Str	1617	1617	1587	1589	1615	1615	1588	1589	1614	1615	1587	1589	υ_{CC} (50)
C=O Str	1702	1700	1609	1608	1699		1609	1608	1700	1694	1609	1609	υ_{C0} (74)
Symm. CH$_3$ Str	2919	2917	2931	2931	2913	2911	2931	2931	2915	2915	2931	2931	υ_{CH2} (100) (Ap)
Asymm. CH$_3$ Str	2990	2986	3005	3006	2979	2986	3005	3006	2974	2984	3005	3006	υ_{CH3} (100) (Ap)
Asymm. CH$_3$ Str	3014	3013	3062	3063	3010		3062	3063	3010	3019	3063	3064	υ_{CH3} (100) (Ap)
CH Str	3048		3100	3100	3043		3101	3098	3044	3044	3097	3094	υ_{CH} (96)
CH Str	3065	-	3123	3124	3059		3124	3124	3060	3060	3123	3124	υ_{CH} (97)
CH Str	3091	3077	3129	3129	3090	3071	3129	3128	3088	3075	3128	3128	υ_{CH} (96)

0.961 scale factor used for B3LYP/SDD and LANL2DZ basis sets; υ: stretching; δ: bending; Γ:torsion; asymm: asymmetric; symm: symmetric; str: stretching; scis: scissoring; wagg: wagging; bend: bending; rock: rocking; py: pyridine group; Ap: acetyl group.

***Table 4**. The IR and Raman wavenumbers (cm^{-1}) of the $Zn(4\text{-}Ap)X_2$ (X: Cl, Br and I) complexes.*

Assignment	$Zn(4\text{-}Ap)_2Cl_2$		$Zn(4\text{-}Ap)_2Br_2$		$Zn(4\text{-}Ap)_2I_2$		Free 4-Ap		
	IR.	RA.	IR.	RA.	IR.	RA.	IR.*	RA.*	Exp. IR.
CH Str	3091	3077	3090	3071	3088	3075	3082		3079
CH Str	3065		3059		3060	3060	3066	3066	3064
CH Str	3048		3043		3044	3044	3047	3050	3048
Asymm. CH_3 Str	3014	3013	3010		3010	3019	3009	3010	3012
Asymm. CH_3 Str	2990	2986	2979	2986	2974	2984	2972		
Symm. CH_3 Str	2919	2917	2914	2911	2915	2915	2923	2922	2921
C=O Str	1702	1700	1699		1700	1694	1696	1694	1695
C-C Str	1617	1617	1615	1615	1614	1615	1597	1596	1598
Ring Str.	1557	1555	1555		1555	1555	1557	1556	1558
Ring Str.	1500	1500	1501	1499	1498	1498	1494	1492	1492
CH_3 Scis.	1421	1422	1422	1420	1419	1419	1410		1409
CH_3 Wagg.	1367	1366	1363		1365	1363	1362		1363
CH Bend	1326	1324	1328	1327	1321	1322	1324	1324	1324
Ring Str.	1259	1260	1266		1260	1258	1267	1267	1268
C- CH_3 Str	1234	1233	1232		1230	1230	1220	1214	1224
CH Bend	1107		-		1106		1115	-	1118
CH Bend	1092	1091	1088	1088	1089	1089	1083	1084	1083
CH Bend	1062	1064	1062	1063	1059	1064	1063	1064	1064
CH_3 Rock.	1027	1029	1025	1027	1024	1025	1021		1022
CH_3 Rock.	966	961	959	951	962	960	-	962	964
Ring Torsion	879	882	883		883	880	875		879
Ring Torsion	835	838	820		835	836	817		815
Ring Torsion	754	753	750	751	751	753			
Ring Bending	737		738		738		736	739	738
Ring Bending	665	664	667	664	662	663	664	666	665
-C=O Bending	595	595	595		593	593	590	589	588
CCC Bend	484	474			480	479	465		468
δ(C=O)	436	425	435	435	430	429	417		422
Ring Torsion		383				381			
$\rho(C\text{-}CH_3)$*		337				330			
MX Str		302				305			
MN Str		213		211		209			
Ring Torsion		165				161	158	160	
NMX Bend		97				94			
Total Shifts	125		79		63				

* Taken from Ref. [2]. υ: stretching; δ: bending; Γ:torsion; asymm:asymmetric; symm:symmetric; str:stretching; scis:scissoring; wagg:wagging; bend:bending; rock:rocking; py:pyridine group; Ap:acetyl group.

4.2.2. Acetyl group vibrations

Vibrations of the acetyl group in 4-Ap can be described by 15 normal modes. The CH_3 fundamental modes are two asymmetric CH_3 stretching, one symmetric CH_3 stretching, two asymmetric CH_3 bending, one symmetric CH_3 bending, two CH_3 rocking and one CH_3 torsion vibrations. C=O fundamentals modes are one C=O stretching and two C=O bending vibrational. The C-CH_3 fundamental modes are one C-CH_3 stretch and two C-CH_3 bending vibrations. The calculated and observed wave numbers of respective bands were listed in Table 5. We expected to observe three bands at about 3020 – 2920 cm^{-1} region for the CH_3. Five CH_3 stretching modes were predicted in this region. The stretching vibration of the CH_3 were observed at 3012 cm^{-1} (Asymm.), at 2921 cm^{-1} (Symm) for free 4-Ap molecule in the FT-IR spectra. Medhi et al. [2] observed at 3009 cm^{-1} (Asymm.), 2972cm^{-1} (Asymm.) and 2923 cm^{-1} (Symm.) for free 4-Ap molecule in the FT-IR spectra. We observed at 3014 cm^{-1} (Asymm.), 2990 cm^{-1} (Asymm.) and 2919 cm^{-1} (Symm.) for $Zn(4\text{-}Ap)_2 Cl_2$ in the FT-IR spectra. The Asymmetric CH_3 vibrations in the Zinc (II) halide compounds was shift to higher wavenumber region than those in the free 4-Ap, while the symmetric CH_3 vibrations was shift to lower wavenumber region than those in the free 4-Ap molecules. The asymmetric CH_3 bending bands usually occur 1430-1470 cm^{-1} in region. In this region, the asymmetric CH_3 bending modes were predicted in the region from 1436 -1448 cm^{-1}. We observed at 1421 cm^{-1} (for $Zn(4\text{-}Ap)_2 Cl_2$), 1422 cm^{-1} (for $Zn(4\text{-}Ap)_2Br_2$), 1419 cm^{-1} (for $Zn(4\text{-}Ap)_2I_2$) and 1409 cm^{-1} (for free 4-Ap) in the FT-IR spectra. Moreover, the symmetric CH_3 bending vibration appears in the 1360-1400 cm^{-1} region. The symmetric CH_3 bending vibration observed at 1367 cm^{-1} (for $Zn(4\text{-}Ap)_2Cl_2$), 1363 cm^{-1} (for Zn $(4\text{-}Ap)_2 Br_2$) , 1365 cm^{-1} (for Zn $(4\text{-}Ap)_2 I_2$) and 1363 cm^{-1} (for free 4-Ap) in the FT-IR spectra. [19]

The C=O stretching vibration of the acetyl group was observed at 1696 cm^{-1}in the free 4-Ap molecule [2]. We observed at 1695 cm^{-1} in the FT-IR spectra for free 4-Ap molecule. This vibration observed at 1702 cm^{-1} (for Zn $(4\text{-}Ap)_2 Cl_2$), 1699 cm^{-1}($Zn(4\text{-}Ap)_2 Br_2$) and 1700 cm^{-1} (for Zn $(4\text{-}Ap)_2 I_2$) in the FT-IR spectra.

The vibrations of the C-CH_3 was observed at 1253 cm^{-1}, 355 cm^{-1} and 219 cm^{-1} (respectively C-CH_3 stretching, in plane and out of plane bending vibrations) for free 4-Ap molecule [2]. In plane C-CH_3 bending vibration observed at 337 cm^{-1} for Zn $(4\text{-}Ap)_2 Cl_2$ in the FT-Raman spectra. The stretching and out of plane vibrations of the C-CH_3 could not be observed in the FT-Raman spectra.

***Table 5**. Vibrations of the acetyl group in the free and zinc (II) halide complexes.*

		$Zn(4\text{-}Ap)_2Cl_2$	$Zn(4\text{-}Ap)_2I_2$	$Zn(4\text{-}Ap)_2Br_2$	4-Ap	
Vibrations	Mode No	Observed/Calculated	Observed/Calculated	Observed/Calculated	New IR	Exp. IR[a]
$\upsilon_{as}(CH_3)$	ν_{90}	3014/3063	3010/3063	3010/3064	3012	3009
$\upsilon_{as}(CH_3)$	ν_{89}	2990/3006	2979/3090	2974/3006	-	2972
$\upsilon_{s}(CH_3)$	ν_{87}	2919/2931	2913/2931	2915/2931	2921	2923
$\upsilon(C{=}O)$	ν_{85}	1702/1608	1699/1608	1700/1609	1695	1696
$\delta_{as}(CH_3)$	ν_{74}	1421/1436	1422/1437	1419/1436	1409	1410
$\delta_{s}(CH_3)$	ν_{71}	1367/1372	1363/1372	1365/1372	1363	1362
$\upsilon(C\text{-}CH_3)$	ν_{65}	/1247	/1248	/1248	-	1253
$\rho(CH_3)$	ν_{54}	1027/1029	1025/1029	1024/1029	1022	1021
$\rho(CH_3)$	ν_{46}	966/944	959/945	962/944	964	962*
$\delta(C{=}O)$	ν_{35}	595/601	595/601	593/600	588	599
$\delta(C{=}O)$	ν_{28}	436/438	435/439	430/438	422	417
$\rho(C\text{-}CH_3)$*	ν_{25}	337/365	/364	330/363	-	355
$\delta(C\text{-}CH_3)$	ν_{20}	/229	/211	/201	-	219

- This peak observed in the FT-Raman spectra. [a] Taken from Ref [6]

4.2.3. M-N vibrations

The M-N stretching modes are assigned between 300-200 cm^{-1} in regions. We expect that the υ(M-N) mode will shift to lower frequencies with increasing of M-N bond lengths in Tables 3 and 4. The calculated M-N bond lengths decrease in the order I>Br>Cl when the M-N stretching wavenumbers increase in the complexes studied. This mode was observed experimentally at 213 cm^{-1} (for Cl_2), 211 cm^{-1} (for Br_2) and 209 cm^{-1} (for I_2) in the Raman spectra of Zinc compounds.

The total shifts were given at the bottom of Table 4. It should thus be possible to compare the shift values of isomorphous complexes as well as observing for a given metal the effect of changing the stoichiometry of the complex and of changing the counter ligand from Cl, Br and I. The shifts were observed in the vibrational spectra of pyridine and pyridine derivative halide complexes and vibrations with M-N (ligand) vibrational modes [20-23]. Therefore, we infer that the M-N (4-Ap) bond strength and thus the Zn-N (4-Ap) stretching mode wavenumber increase in the same order. It is also noted that for isomorphous complexes the shift values depend on the halogen for a given metal it decreases in the order Cl>Br>I.

4.2.4. M-X vibrations

In the infrared spectra of the Zinc chloride complex of the pyridine molecule, the M-X vibrations were observed at 324 cm^{-1} and 292 cm^{-1} [17]. These vibrations were observed at 336 cm^{-1} and at 298 cm^{-1} for Zinc chloride of the 4-Ap [17]. We were calculated at 326 cm^{-1} and at 261 cm^{-1} in the Zinc chloride complex of the 4-Ap for B3LYP/LANL2DZ calculation. We experimentally observed at 302 cm^{-1} in the FT-Raman spectra. In the Zinc bromide and iodine complexes, this peaks calculated at 228 cm^{-1} ($Zn(4\text{-}Ap)_2Br_2$) and 226 cm^{-1} ($Zn(4\text{-}Ap)_2I_2$) for B3LYP/LANL2DZ calculations and 261 cm^{-1} ($Zn(4\text{-}Ap)_2Br_2$) and 243 cm^{-1} ($Zn(4\text{-}Ap)_2I_2$) for B3LYP/SDD calculations. It is reported that for zinc(II) metal halide complexes the shift values depend on the halogen for a given metal it decreases in the order Cl>Br>I.

5. CONCLUSIONS

The analysis of the IR and Raman spectra of metal halide complexes of 4-Ap indicates that there are some structure spectra correlations. The new complexes obtained were characterized by using elemental analysis, FT-IR and FT-Raman measurements The IR spectroscopic study of three new halide complexes has shown that they have similar structures with the 4-Ap molecule bound directly to metal (Zn). It is noted that for isomorphous complexes the shift values depend on halogen for given metal it decreases in order Cl>Br>I. Analogous shifts on coordination are observed in the vibrational spectra of pyridine derivatives, and explained as the coupling of the internal modes of the aromatic molecule with the M-N (ligand) vibrations. The DFT (B3LYP) calculations on the structure and vibrational spectra have been carried out Calculated and experimental data were found to be in good agreement.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors

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