COORDINATION COMPOUNDS =

Synthesis and Characterization of Hg(II) and Zn(II) Complexes Based on 3–[(4–Chlorophenylamido)]propenoic Acid¹

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Abstract—3-[(4-Chlorophenylamido)]propenoic acid has been synthesized by reaction of maleic anhydride and 4-chloroaniline in 1:1 molar ratio in glacial acetic acid and its metal complexes have been synthesized by the reaction of 3-[(4-chlorophenylamido)] propenoic acid with HgCl₂ and [Zn(CH₃COO)₂] \cdot 2H₂O in 2 : 1 molar ratio, respectively. All the synthesized compounds have been characterized by the elemental analysis, IR, UV/Vis and NMR (¹H, ¹³C) spectroscopy. Conductance for the reported compounds has been recorded in ethanol and suggests the non-electro lytic nature of complexes. IR data of metal complexes shows that the ligand is bound to the metal via both carboxylate oxygen atoms and complexes exhibits 4-coordinated geometry in solid state. NMR (¹H, ¹³C) study confirms the structure of the 3-[(4-chlorophenylamido)]propenoic acid and the reported complexes.

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INTRODUCTION

Transition metals form complexes with carboxylate anions. A versatile carboxylate anion can adopt a wide range of bonding modes, including monodentate, symmetric and asymmetric chelating, and bidentate and monodentate bridging [1, 2]. Transition metal complexes have attracted great interest for their application in industrial and synthetic processes, such as catalysis, photochemistry, and biological applications [3]. The self-assembly of organic ligands coordinated to metal ions or organometallic substances has been extensively studied [4]. The increasing interest in this field is mainly due to the potential relevance of such complexes to catalysis [5]. Coordination complexes of transition metal had been widely studied for their antimicrobial and [6, 7] anticancer properties. One of the most potent and [8, 9] effective antitumour agents was discovered in the last century serendipitously by Rosenberg [10]. Various tumor cell lines are now growing resistance to cisplatin e.g., acquired cisplatin resistance in some preclinical tumor models [11]. In the present study, Zn(II) and Hg(II) complexes of 3– [(4-chlorophenylamido)]propenoic acid were synthesized and characterized.

EXPERIMENTAL

Materials and Instrumentation

Maleic anhydride, 4-chloro aniline, glacial acetic acid, zinc acetate and mercuric chloride were purchased from E. Merck, Germany. Acetone, methanol, ethanol, chloroform, dichloromethane, ether, toluene, *n*-hexane, DMSO and benzene were purchased from Riedel-de Haen and were used without any further purification. Melting points were determined by using capillary tube on an electrothermal melting point apparatus, model Stuart (SMP3) and are uncorrected. FT-IR Spectra were recorded as KBr discs on Perkin-Elmer-1000 spectrophotometer in the range of 4000-250 cm⁻¹. Elemental analysis was done on a CHN analyzer 932 Leco, USA. Conductance of the complexes was noted from 712 conductometer of Metrohm. Ultraviolet-visible spectra in 800–200 nm range were recorded on a Schimadzu TCC-240 A spectrophotometer (AvH, Germany). ¹H and ¹³C NMR spectra were recorded on Bruker-AM 300 MHz-FT-NMR spectrometer using CDCl₃ as internal reference.

Synthesis of 3-[(4-Chlorophenylamido)] Propenoic Acid HL

Maleic anhydride (1 gm, 10.19 mmol) was dissolved in glacial acetic acid (10 mL) in (500 mL) beaker, while 4-chloroaniline (1.3 gm, 10.19 mmol) was also dissolved in glacial acetic acid (10 mL) in (500 mL) beaker. Then mix both solutions dropwise with constant stirring. Continue the stirring for 3–4 hours. Light vellow precipitates formed were filtered off and washed with distilled water and dried in air. The product was crystallized in acetone : *n*-hexane (1 : 1).

¹ The article is published in the original.

Compound No.	Molecular formula	Molecular mass	% Yield	mp (°C)
HL	C ₁₀ H ₈ O ₃ NCl	225.5	92	204-207
(1)	$\mathrm{C_{20}H_{14}O_6N_2Cl_2Hg}$	649.5	80	180-183
(2)	$C_{20}H_{18}O_8N_2Cl_2Zn$	550.28	83	155-158

 Table 1. Physical data of 3-[(4-chlorophenylamido)]propenoic acid and its complexes



Synthesis of Compound (1)

3-[(4-chlorophenylamido)]propenoic acid (2 mmol) was dissolved on heating at $40-50^{\circ}$ C in (35-40 mL) acetone in round-bottom flask (250 mL) with constant stirring. Then the solution of HgCl₂ (1 mmol) dissolved in (20-25 mL) acetone was added drop wise to the reaction mixture and stirred it for 3 hours. Precipitates formed were filtered and dried in air. Purity of the product was checked by TLC.



Synthesis of Compound (2)

3-[(4-chlorophenylamido)]propenoic acid (2 mmol) was dissolved on heating at 40–50°C in (35–40 mL) mathanol in round-bottom flask (250 mL) with constant stirring. Then the solution of zinc acetate $[Zn(CH_3COO)_2] \cdot 2H_2O$ (1 mmol) dissolved in (20–25 mL) methanol was added drop wise to the reaction solution and stirred it for three hours. Precipitates formed were filtered and dried in air.



RESULTS AND DISCUSSION

3-[(4-chlorophenylamido)]propenoic acid and its complexes were synthesized in crystalline solid state. They have sharp melting points and are soluble in common organic solvents. Physical data are summarized in Table 1.

Elemental analysis (CHN)

Elemental analysis was done to compare the observed values of percentage of the carbon, hydrogen and nitrogen in the synthesized compounds with those of calculated and predicted values. The observed values are in very good agreement with the calculated values. Elemental data are given in the Table 2.

Infrared Spectroscopy

Infrared spectra of the HL and compounds (1)–(2) were recorded in the range 250–4000 cm⁻¹. The complexation of ligand with metal is confirmed by disappearance of –OH band, which appears at 3370 cm⁻¹ in the ligand. This is characteristic of carboxylic acid. Replacement of carboxylic group hydrogen by the metal, brought about characteristic changes in IR spectra of complexes in comparison with the spectra of ligand. The difference (Δv) between $v_{asym}(COO^-)$ and $v_{sym}(COO^-)$ is a parameter that identifies the type of bonding metal-ligand. The values of Δv are 167 and 172 cm⁻¹ for compounds (1) and (2), respectively, while $\Delta v = 235$ cm⁻¹ for ligand [12]. In addition, the ligand and compounds (1) and (2), exhibit bands in

Compound No.	%	С	Н	Ν
HL	Calculated	53.20	3.54	6.20
	Found	53.16	3.59	6.16
(1)	Calculated	36.95	2.15	4.31
	Found	36.99	2.11	4.35
(2)	Calculated	43.61	3.27	5.08
	Found	43.59	3.31	5.03

 Table 2. CHN analysis of 3-[(4-chlorophenylamido)]propenoic acid and its complexes

Table 3. IR data (cm^{-1}) of 3-[(4-chlorophenylamido)]propenoic acid and its complexes

Comp. No.	νОН	vH ₂ O	vNH	vC=0	vCOO asym	vCOO sym	Δν	νМ-С	νМ-О
HL	3370	_	3273	1702	1628	1393	235	_	—
(1)	_	_	3276	1701	1485	1318	167	508	442
(2)	_	3480	3274	1706	1489	1317	172	504	440

 Table 4. Conductance of 3-[(4-chlorophenylamido)]propenoic acid and its complexes

Comp. No.	Conductance µs/cm	
HL	0.40	
(1)	16.14	
(2)	36.46	

 Table 5.
 UV/Vis data of 3-[(4-chlorophenylamido)]propenoic acid and its complexes

Comp. No.	$\nu(cm^{-1})$	Assigned transition
HL	38214	$n \longrightarrow \pi^*$ transition
(1)	41896	Charge transfer band
(2)	44642	Charge transfer band

the range of 3273-3276 cm⁻¹ due to the v(NH) group. The amide group in all the complexes is not affected and remains unchanged, strongly indicating non-involvement in complex formation. The appearance of bands at 440–442 cm⁻¹ (M–O) confirms the bonding of oxygen atoms of ligand to the metal atom [13]. IR spectral data is given in Table 3.

Conductance

The molar conductance values of the synthesized complexes (1)-(2) determined in ethanol (concentration = 0.001 M) at room temperature, suggests the

non-electrolytic nature of complexes. Data is given in Table 4.

UV-Visible Spectroscopy

The UV-visible spectral data of 3-[(4-chlorophenyIamido)]propenoic acid and its complexes recorded in methanol are given in Table 5. Absorption of the 3-[(4-chlorophenylamido)]propenoic acid in the region 38214 cm⁻¹ is due to the $n \rightarrow \pi^*$ transition. The absorption spectra of complexes (1) and (2) are transparent in the visible part of the spectrum, because both these metal ions have completely filled *d* orbitals and have no bands due to *d*-*d* transitions. However, the presence of high-intensity bands at 41896 and 44642 cm⁻¹ in the spectra of the complexes (1) and (2) is indicative of the presence of the ligand and thus the formation of the complexes.

NMR Spectroscopy ¹H NMR

Three distinct informations are generally obtained from this technique. The chemical shift of peak gives information about the environment of proton involved, the intensity of each peak corresponds to number of protons and multiplicity tells about the number of neighbouring protons.

The signals in ¹H NMR spectra are sharp and wellresolved. From the ¹H NMR spectra of HL it showed the broad multiplet in the range 7.33–7.68 ppm for the C_6H_4 protons [14]. The resonance signal at the range 6.30– 6.51 ppm represents the unsaturated group with the *"J*(¹H, ¹H) coupling 8.0 Hz, and a singlet at 13.13 ppm

Proton No.	HL	(1)	(2)	
CI	7.33–7.68 m	7.36–7.77	7.31–7.72 m	
-NH	10.51 s	10.51 s	10.51 s	
-CH=CH-	6.30–6.34 d,d (8.0)	6.32–6.37 d,d (8.0)	6.49–6.55 d,d (8.0)	
	6.47–6.51 d,d (8.0)	6.30–6.34 d,d (8.0)	6.45–6.57 d,d (8.0)	
-OH	13.13 s	-	_	

Table 6.	¹ H NMR data	(ppm) of 3-	[(4-chlorophe	nylamido)]propenoic a	cid ^a and its complexes
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Note: ^a—Multiplicity is given as s; singlet, d,d; doublet of doublet, m; multiplet.

confirms the carboxylic proton resonance, while the disappearance of OH signal in complexes (1) and (2) confirms the complex formation. The ¹H NMR data is presented in Table 6.

¹³C NMR

¹³C NMR spectroscopy gives direct information about its carbon skeleton because its spectrum displays signals arising from all the carbon atoms present in the molecule. The ¹³C NMR spectrum of compound **HL** shows a signal at 163.87 ppm for the C=O carbon. The signals at 137.93, 132.19, 130.81 and 129.13 ppm are for the aromatic carbons. The number of the signals found corresponds with the presence of magnetically non-equivalent carbon atom, which was assigned by comparison with literature values [14]. The signals in the range 121.51–128.01 ppm, revealing the presence of

 Table 7. ¹³C NMR data (ppm) of 3-[(4-chlorophenyla-mido)]propenoic acid^a and its complexes

¹³ C No.	HL	(1)	(2)		
1	137.93	137.90	137.91		
2,2'	132.19	132.16	132.18		
3,3'	130.81	130.82	130.84		
4	129.13	129.13	129.13		
5	163.87	163.80	163.84		
6	128.01	128.01	128.02		
7	121.50	121.54	121.57		
8	167.34	170.12	170.44		
2' 2' 0 11 2					



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olefinic carbon atom and the signal at 167.34 ppm confirms the carboxylic carbon atom. The carboxylic carbon shows downfield shift in the range of 170.12-170.44 in the complexes (1) and (2) thus confirming the complexation. The ¹³C NMR data is given in Table 7.

CONCLUSIONS

3-[(4-chlorophenylamido)]propenoic acid and its metal complexes have been synthesized in quantitative yield, under stirring condition. The ligand HL and the synthesized compounds have been characterized by the elemental analysis, IR and NMR (¹H, ¹³C) spectroscopy. Elemental analysis data shows the good agreement between calculated and found values of carbon, hydrogen and nitrogen. IR data of the complexes shows that ligand act as bidentate and complexes (1)-(2) exhibits 4-coordinated geometry in solid state and conductance data suggests the nonelectrolytic nature of complexes. UV/Vis spectral data shows the transitions above 4000 cm^{-1} , which can be assigned as charge transfer band. (¹H, ¹³C) data of HL and complexes (1)-(2) confirms the structure of 3-[(4-chlorophenylamido)]propenoic acid and complexes.

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