



Spectral Study of Pt (II), Cr (II) Polymeric Complexes of the Ligand N- Crotonyl -2- Hydroxy-Phenylazomethine

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Abstract

The polymeric complexes were obtained from the reaction of polymeric Schiff base. N-crotonyl-2-hydroxyphenylazomethine (HL), with divalent metals Pt (II), Cr (II). The modes of bonding and overall geometry of the complexes were determined through spectroscopic methods and compared with that reported from analogous monomeric ligand. This study revealed square planar geometry around the metal center for [Pt(L)Cl] and distorted octahedral geometry for Cr complex [Cr(L)Cl(H₂O)₂].

Keywords: Schiff Base, Polymeric Complexes, Spectroscopic Methods, Divalent Metals.

1. Introduction

Polymer-metal complexes are composed of polymeric ligand and metal ions. They show unique characteristics in absorption spectrum, coordination structure, stability, redox reaction, catalytic activities, electrochemical reactions, and other areas, compared with those of corresponding low-molecular-weight metal complexes.

Complexation of polymeric ligand with metal ions as well as the ligand substitution reaction of polymer-metal complexes is utilized to separate metal ions and/or small molecules^[1]. Coordination polymers are usually known for their thermal stability^[2]. However, some other equally good application has been reported such as being used as converters of

Solar energy and removal of SO_x and NO_x from the environment^[18]. While (X= the number of Oxygen atom).

Recently, an important new focus for environmental inorganic chemistry has been the selective removal of metal ions from aqueous solution, including waste treatment, with polymer supported chelate system^[3].

2. Experimental

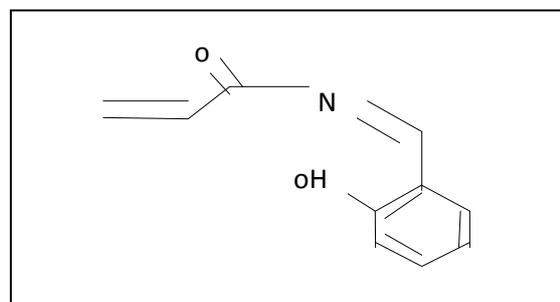
All reagents were obtained commercially (Aldrich Company, UK) and used without purification. Ethyl methyl ketone peroxide (EMKP) or 2, 2'-azobisisobutyronitrile (AIBN) were used as initiator to prepare the ligand. IR spectra recorded as KBr or CsI discs using Shimadzu 8300FTIR spectrophotometer in the range 4000-250cm⁻¹. Electronic spectra were measured in the region 200-900 nm using 10⁻³M solutions in DMF at 25°C using Shimadzu 160 spectrophotometer. Conductivity measurements were made in DMF using a Jenway 4071 digital conductivity meter.

3. Preparation of the Complexes

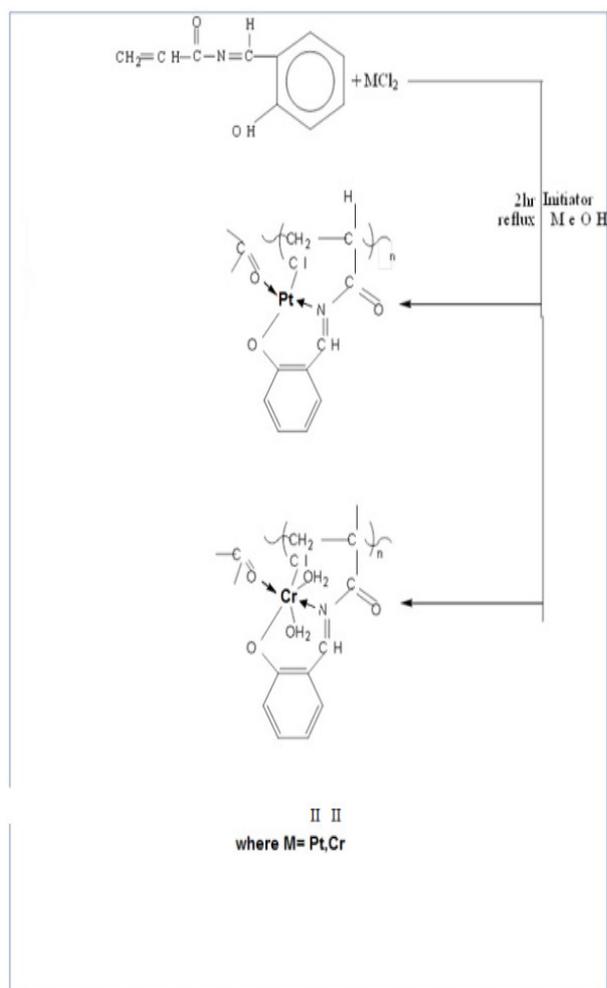
A mixture of the ligand HL (1mmol) in methanol (15ml) containing a few drops of HCl was added to a stirred solution of metal salt (1.1mmol) over 15 min using K₂PtCl₄ for Pt complex, and CrCl₃.6H₂O for Cr complex in hot methanol (15ml) with 32% EMKP (1ml) in

methanol (30ml) as the initiator. As shown in scheme (1).

The resulting mixture was refluxed under N_2 atmosphere for 3h, resulting in the formation of colored solution. The solution was concentrated by slow evaporation of the methanol at room temperature. The solid product formed was collected by filtration and washed with Ethanol (10ml) and finally with diethyl ether (15ml). The above procedure was used to give a dark brown solid for Pt^{2+} complex and yellowish green for Cr^{2+} complex.



Scheme (2) Schiff Base HL.



Scheme (1) Preparation of Cr, Pt Complexes.

4. Result and Discussion

The reaction of salicylaldehyde with acrylamide afforded the new Schiff base N-crotonyl-2-hydroxy phenylazomethine HL in good yield. (scheme2)

The IR spectrum for the ligand fig (1-A) shows a distinct band at 1666 cm^{-1} due to $\nu(C=O)$. The spectrum also shows characteristic bands related to the, $\nu(C=N)$, $\nu(C=C)$ and $\nu(O-H)$ functional groups (Table 1) [4,5]. The U.V-Vis spectrum of HL fig (1-B) exhibits an intense absorption peak at 260 and 277 nm, which assigned to $\pi \rightarrow \pi^*$, and an absorption peak at 325 nm assigned to $n \rightarrow \pi^*$ [Table 2]. The polymeric complexes were synthesized by heating 1mmole of Schiff base with 1.1 mmole of the metal chloride, in methanol using MEKP or AIBN as initiator and a few drops of concentrated HCL [17]. The two complexes $[Cr(L)Cl(H_2O)_2]$ and $[Pt(L)Cl]$ were obtained. The important infrared bands for the complexes together with their assignments are listed in [table 1]. The IR spectra of the complexes Figures (2, 3) exhibited HL bands with appropriate shifts due to complex formation [Table 1].

The two complexes show a strong band at $(1628.9-1631.7)\text{ cm}^{-1}$, assigned to a $\nu(C=N)$ stretch of reduced bond order [6]. This can be attributed to delocalization of metal electron density (t_2g) to the π system of the ligand. The $\nu(C=O)$ stretching band at 1666 cm^{-1} in the free ligand is shifted to lower frequency and observed around $(1668.3-1653)\text{ cm}^{-1}$ for the complexes, indicating coordination of the oxygen of the $\nu(C=O)$ group to the metal [7]. In the IR spectrum of the $pt(II)$ complex, the $\nu(C=O)$ small shift of 2.3 cm^{-1} on complexation could be attributed to the weak linkage between the oxygen atom and metal Centre. At lower frequency the complexes exhibit bands around $(590 - 540)$ and $(430-450)\text{ cm}^{-1}$ which are assigned to $\nu(M-O)$ and $\nu(M-N)$, respectively [15]. An additional band observed around 3398.3 cm^{-1} in $[Cr(L)Cl(H_2O)_2]$ is assigned to coordinated aqua (H_2O) ligands [14]. The molar conductivity measurement for the complexes between 15 and $20\text{ s.cm}^2\text{mole}^{-1}$ indicating their non-electrolytic behavior [8] and

enhance that the chlor atom is inside the coordination ball ^[13]. The unit of conductivity is siemens=ohm⁻¹ and the unit of molar conductivity is s.cm²mole⁻¹.

The IR spectra of the complexes exhibit far- IR active bands around (340-335) cm⁻¹ which are assigned to the ν (M-CL) vibration. These vibrations are characteristic of terminally coordinated chloride ^[10-11]. The spectra of Pt (II)

complex Fig (4) shows two bands (271-301) nm related to the ligand field ^[12] and a peak at 407 nm can be attributed to the $^1A_{1g} \rightarrow ^1B_{1g}$ transition suggesting square planer structure ^[17].

The electronic spectra of the Cr(II) , complex Fig (5) exhibit a high intensity peak around 214 nm related to the charge transfer transition ,and 224 nm assigned to $^1A_{1g} \rightarrow ^1B_{1g}$ transition suggesting distorted Octahedral structure ^[12].

Table 1,
Infrared Spectral Data (wave number ν) cm^{-1} for Ligand and its Complexes.

compound	$\nu(c-H)$ aliph	$\nu(c=N)$	$\nu(c=O)$	$\nu(Nc=O)$	$\nu(M-N)$	$\nu(c=O-M)$	$\nu(M-O)$	$\nu(M-Cl)$
Ligand HL	2750	1625	1666	700	-	-	-	-
[Pt(L)Cl]	2390	1628.9	1668.3	746.4	430	682.8	590	340
[Cr(L)Cl] [(H ₂ O) ₂]	2335	1631.7	1653	750	450	592	540	355

Table 2,
Electronic Data of Ligand and its Metal Complexes.

compound	λnm	$\bar{\nu}$ wave number cm^{-1}	ϵ_{max} molar $^{-1}cm^{-1}$	Assignment
Ligand HL	260	38461	1500	$\pi \rightarrow \pi^*$
	277	36101	2039	$\pi \rightarrow \pi^*$
	325	30769	72	$n \rightarrow \pi^*$
[Cr(L)Cl(H ₂ O) ₂]	214	46728	414	Charge transfere
	224	44642	336	$^1A_{1g} \rightarrow B_{1g}$
[Pt(L)Cl]	271	36900	1940	Ligand field
	301	33222	1431	Ligand field
	407	24570	611	$^1A_{1g} \rightarrow B_{1g}$

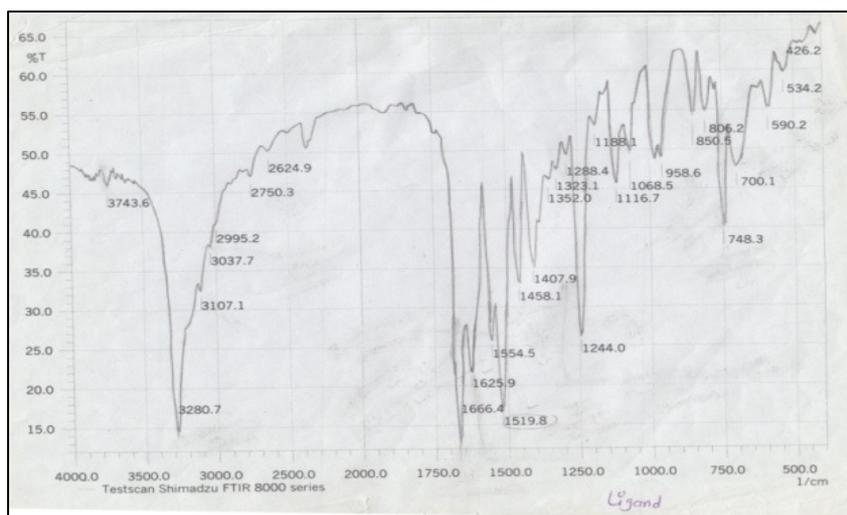


Fig. 1-A. Infrared Spectrum of the Ligand (HL).

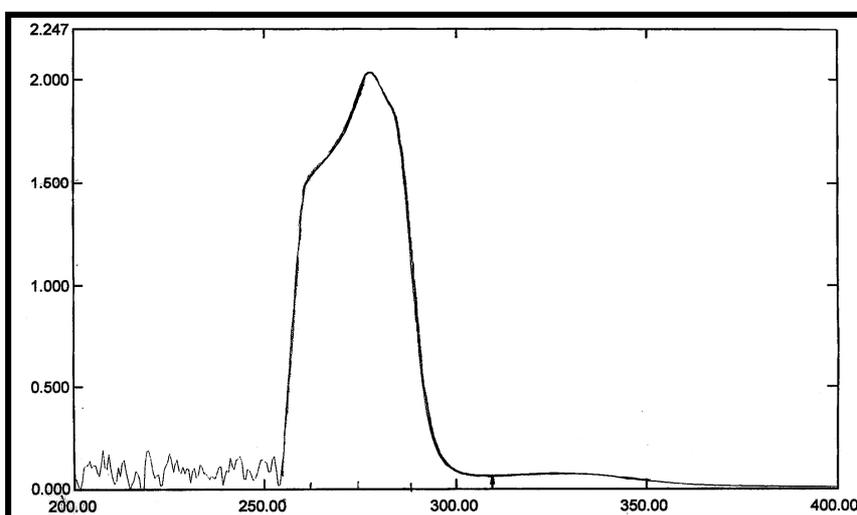


Fig. 1-B. Electronic Spectrum of the Ligand (HL).

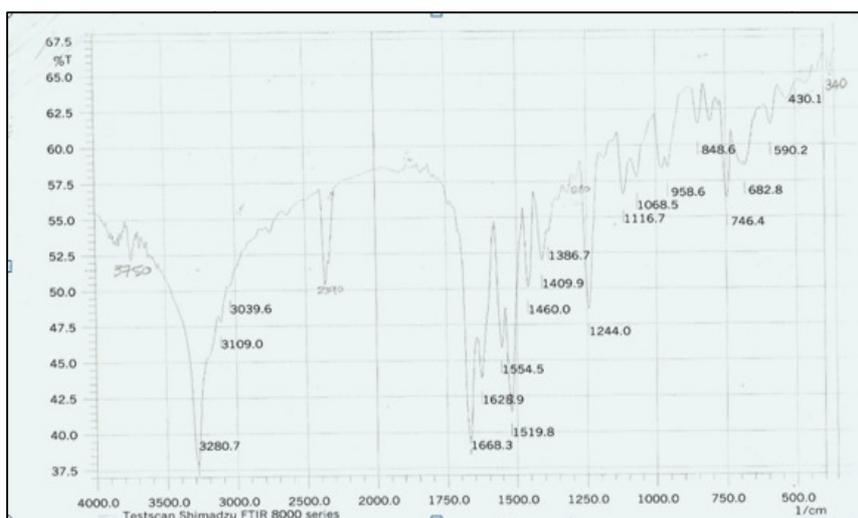


Fig. 2. Infrared Spectrum of [Pt(L)Cl] Complex.

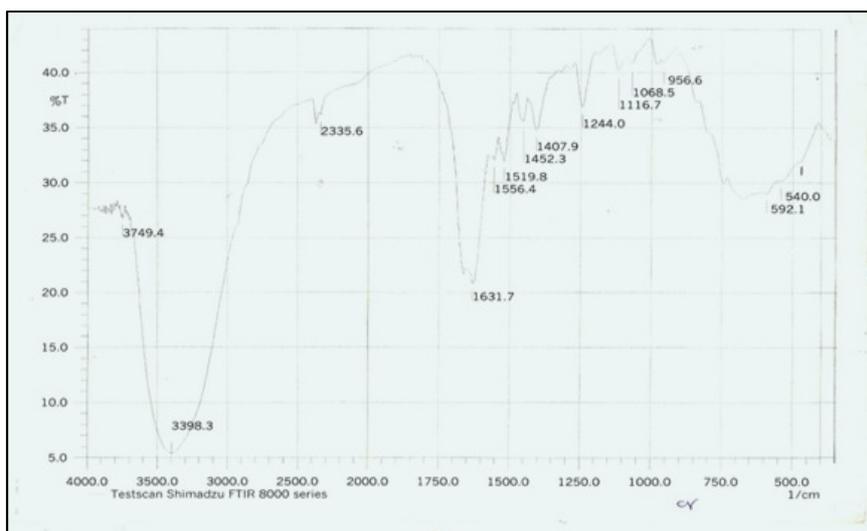


Fig. 3. Infrared Spectrum of $[Cr(L)Cl(H_2O)_2]$ Complex.

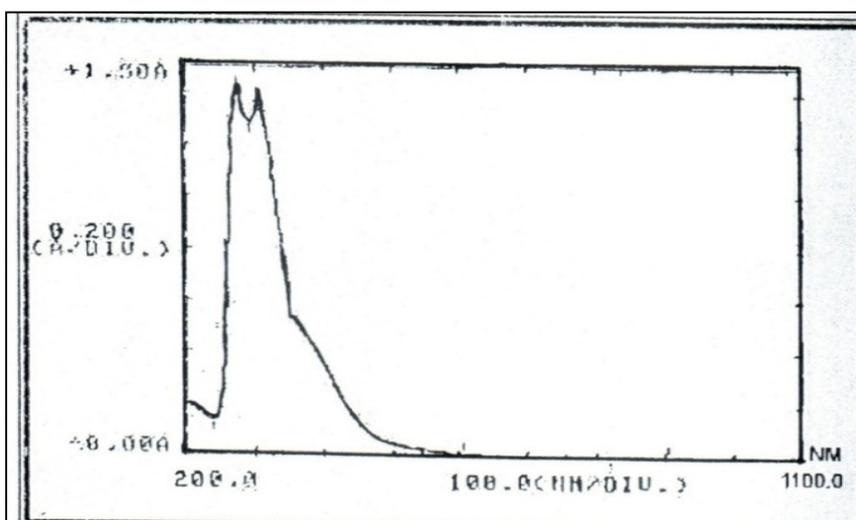


Fig. 4. Electronic Spectrum of $[Pt(L)Cl]$ Complex.

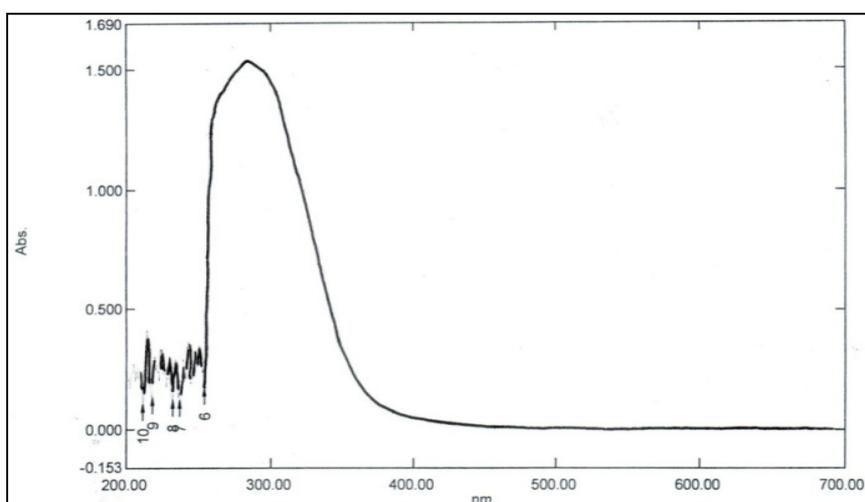


Fig. 5. Electronic Spectrum of $[Cr(L)Cl(H_2O)_2]$ Complex.

5. Conclusion

In the present work the synthesis and spectral study of coordination complexes from polymer of the Schiff base HL have been explored. In these complexes, the metal center is still able to adjust its preferred geometry which involves (C=O) coordination via its oxygen atom. Depending on spectral study of UV and IR spectrum and conductivity measurement, the proposed structure of the complexes were expected as follow: square planer for [Pt(L)Cl] and distorted octahedral for [Cr(L)Cl(H₂O)₂].

6. References

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الدراسة الطيفية للمعقدات البوليميرية لكل من Cr (II) , Pt (II) للليكند N- Crotonyl -2- Hydroxy-phenylazomethine

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الخلاصة

يمكن الحصول على المعقدات البوليميرية عن طريق تفاعل (قاعدة شيف) للليكند المتبلر N- Crotonyl -2- Hydroxy-phenylazomethin مع عناصر ثنائية التكافؤ. نوع التآصر والشكل الهندسي الكلي للمعقدات يمكن الحصول عليه عن طريق الدراسات الطيفية ومقارنتها بالنسبة للمعقد [HL]. هذه الدراسات أظهرت ان الشكل الفراغي لمركز العنصر بالنسبة لمعقد البلاتين [Pt(L)Cl] هو مربع مستوي. واما بالنسبة لمعقد الكروم [Cr(L)Cl(H₂O)₂] فقد كان ثماني السطوح مشوه.