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دراسة طيفية لتأثير معقدات فلزية جديدة على استقرار متعدد كلوريد الفايثيل

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قسم الكيمياء، كلية العلوم، الجامعة المستنصرية، بغداد، العراق

المخلص:

هذه الدراسة تتعلق بتحضير ليكاند رباعي جديد $[H_2L]$ من نوع N_2O_2 وتحضير معقداته الفلزية مع الكروم (III)، الحديد (III)، النحاس (II) والزنك (II)، وكما تم تشخيص المعقدات بطرائق الرنين النووي المغناطيسي H^1 و C^{13} ، وأطياف الأشعة تحت الحمراء، والأطياف الإلكترونية، والتحليل الدقيق للعناصر CHN، والعزم المغناطيسي والتوصيلية المولارية في محاليل ثنائي مثيل فورم أميد. اعتمادا على النتائج العملية التي تم الحصول عليها، فإن الأشكال الهندسية المقترحة هي: ثماني التماثل لمعقدات الكروم والحديد، بينما المربع المستوي ورباعي التماثل لمعقدات النحاس والزنك على التوالي.

كما تمت دراسة تأثير هذه المعقدات الصلبة الجديدة على التفكك الضوئي لرقائق متعدد كلوريد الفايثيل والمضافة بنسبة وزنيه بين 2 - 2.5 % . إن التغيير في معدل الوزن الجزيئي لمتعدد كلوريد الفايثيل مع وقت التشعيع تم تتبعه لتحديد درجة النشاط لهذه المعقدات الصلبة من ناحية التفكك الضوئي وذلك بتقدير معاملات الكربونيل، الكربوكسيل والبولين. أظهرت النتائج أن معقدات الكروم والحديد الثلاثية تزيد من معدل كسر أصرة كربون-كربون ومن التفكك نتيجة الضوء فوق بنفسجي في حين أظهر معقد الزنك الثنائي أنه أكثر استقرارا عند الضوء فوق بنفسجي.



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ORIGINAL ARTICLE

Spectroscopic study of the effect of a new metal chelate on the stability of PVC

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Abstract This work deals with the preparation of a new tetradentate ligand [H₂L] of the N₂O₂ type, N{2[3(1-carboxyiminoethyl)-1-phenyl]butylidene-2-amino propionic acid}, and its metal complexes with Cr(III), Fe(III), Cu(II) and Zn(II) and fully characterized by H¹ NMR, C¹³ NMR, FT-IR, UV–Vis, CHN elemental analysis, magnetic moment and molar conductance in DMF solutions. Based on the experimental results obtained, octahedral geometries of Cr(III) and Fe(III) have been suggested, while Cu(II) and Zn(II) had square planar and tetrahedral symmetries, respectively.

The effect of this new metal complex on the photo degradation of poly(vinyl chloride) PVC films blended with a concentration range of 2–2.5% by weight of this new complex was investigated. The changes in the average molecular weight of PVC with irradiation time were tracked to determine the order of activities of each metal complex toward the photodegradation of PVC, and the photodegradation of PVC films was determined by measuring carbonyl, hydroxyl and polyene indices. The results showed that Cr(III) and Fe(III) complexes increase the rate of C–C cleavage and behave as UV photo degradation substances, while the Zn(II) complex behaves as a UV stabilizer.

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1. Introduction

Environmental impact of polymeric materials is largely determined by the low molecular mass compounds released from the materials. Qualitative and quantitative determination of these compounds is especially important in the safety assess-

ment of plastic materials to be used in medical applications and food packaging.

Synthesis of a polymer-bound chelating ligand and the selective chelating of specific metal ions is a field of active research (Pittmann, 1980). A number of heterocyclic compounds including polydentate amines, crown ethers, bipyridines, naphthyridines, 2-aminobenzothiazol and 2-mercaptobenzothiazole have been bound with mainly polystyrene divinylbenzene copolymers or linked with poly(vinyl chloride) (PVC) (Gardette et al. 1993; Emad and Ayad, 2010). The Schiff base ligand H₂L and its complexes with Ti(III), Cr(III), Fe(III), Mn(III), Zr(IV) and UO₂(VI) have been synthesized and characterized by elemental analysis, FTIR, solid state reflectance spectra, magnetic susceptibility measurements and thermal analysis (Poonam et al., 2010). Improving PVC properties like

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thermal stability and photo stabilization has been of interest in recent years due to large-scale applications of PVC (Andrady and Searle, 1989; Aliwi et al., 2006). Photodegradation of 1:1 w/w blend of polycaprolactone and poly(vinyl chloride) has been studied by following CO₂ emission during UV exposure. It was found that the blend gave lower CO₂ emission than either of the two homopolymers indicating that the interaction of the two components in the blend provided a beneficial reduction of photodegradation (Christensen et al., 2008). Unstabilized PVC and its mixtures with two sulfur-free and two sulfur-containing organotin stabilizers were exposed at 35°C to a radiation of 300–420 nm wavelength with dominant $\lambda = 345$ nm. The significant increase in the chloro allyl group content during irradiation affects the rate of thermal dehydrochlorination (Ymazal and Vymazalova, 1991). The kinetics of photodegradation of poly (vinyl chloride) has been studied in the presence and in the absence of oxygen. The value of quantum yield of hydrogen chloride evolved indicates that only one in every 100 photons absorbed induces dehydrochlorination of PVC with formation of polyenes. The independence of ϕ_{HCl} on the irradiation time and on the initial amounts of unsaturation in the polymer argues in favor of the alkene-photosensitized degradation process (Decker and Blandier, 1982).

The aim of this study was concerned with the synthesis and characterization of new metal complexes of Cr(III), Fe(III), Cu(II) and Zn(II) with Schiff base ligand derived from alanine and benzoyl acetone and also with their photo degradation effects on PVC films toward UV light at 254 nm.

2. Materials and methods

2.1. Chemicals

PVC was a commercial polymer produced by Fluka company with an average molecular weight of $M_w = 75300 \text{ g mol}^{-1}$ and was used after dissolving in dry Tetra Hydro Furan (THF) and precipitation in absolute ethanol. All reagents and solvents were obtained from commercial sources and no further purification was need and used as received.

2.2. Apparatus

Micro elemental analysis CHN, of solid new complexes was determined using Carlo-Earba elemental analyzer model EA-1108. Flame Atomic Absorption measurements were carried out using Shimadzu AA-670 spectrophotometer for determination of Cr, Fe, Cu and Zn in metal chelates. FT-IR spectra were recorded as KBr disks in the range of 4000–200 cm^{-1} using FT-IR Shimadzu model A760 spectrometer. UV–Vis

spectra were recorded in THF using Shimadzu UV–Vis 8400 spectrophotometer with 1 cm quartz cell. Molar conductivity measurements were made with dimethyl formamide(DMF) solutions (10^{-3} M) using Jenway 4071 digital conductivity meter. ¹H NMR spectra were recorded using a Varian Mercury 300 NMR spectrometer operating at 300 MHz. ¹³C NMR spectra were recorded on the same instrument with an operating frequency of 75 MHz. Data were processed using Mest ReNova (version 6.2.0) desktop NMR data processing software. Magnetic moments of Cr(III), Fe(III) Zn(II) and Cu(II) solid complexes were measured with a magnetic susceptibility balance (Jonson, Matthey catalytic system Division) in chemistry department laboratories at Al-Nahrain university, Baghdad.

2.3. Synthesis

2.3.1. Preparation of H₂L ligand, *N*{2[3(1-carboxyiminoethyl)-1-phenyl]butylidene-2-amino propionic acid}

To a 20 ml of warm ethanol solution, 1.62 g (0.01 mol) of benzoyl acetone and 1.76 g (0.02 mol) of alanine in 15 ml of de-ionized water were added at which a clear yellow solution was produced which was refluxed for 4–6 h on a hot water bath. The resulting solution was allowed to cool, whereupon a pale yellow crystalline needle separated. The product was filtered and recrystallized from hot methanol, m.p. 188–190 °C, and yield: 70%, Scheme 1: (see Scheme 2).

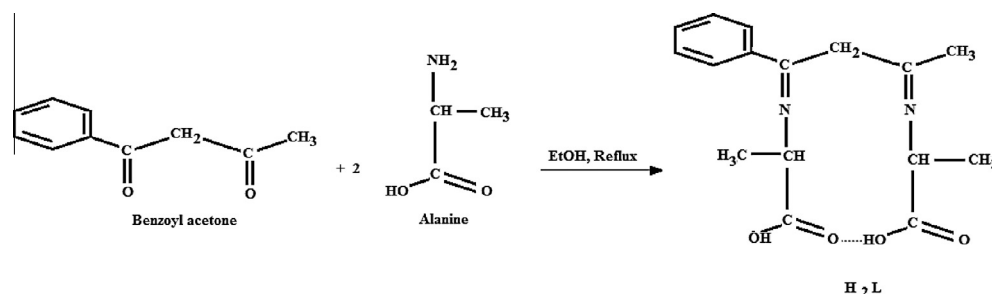
2.3.2. Preparation of Cr(III), Fe(III), Cu(II) and Zn(II) complexes

Cr(III), Fe(III), Cu(II) and Zn(III) complexes were prepared by refluxing the respective hydrate metal chloride, 1 mmol in 15 mL of ethanol, with 1 mmol (0.304 g) H₂L ligand for 3–4 h. The colored complexes obtained were filtered off, washed with ethanol and dried in desiccators over CaCl₂ pellets.

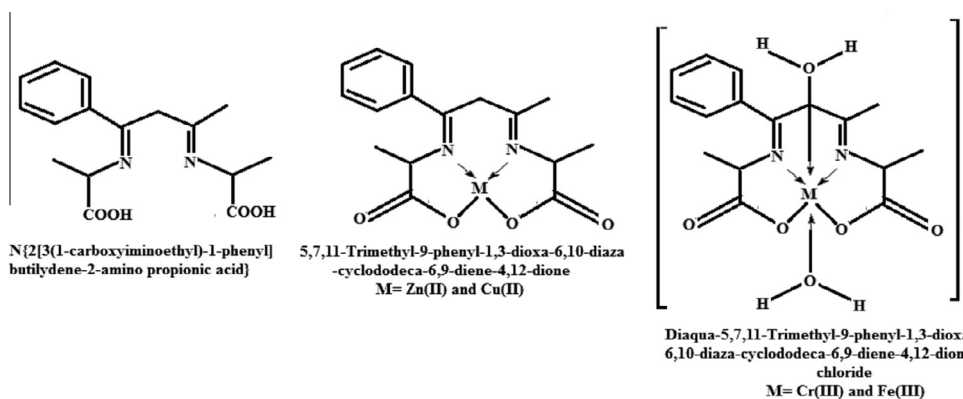
PVC films have been prepared by dissolving 0.01 g of purified PVC (control) in 10 ml of dry THF to make films of even thickness of 60 μm , then drying in air at 35 °C for 24 h to remove the solvent, whereas the preparatin of PVC films incorporated with Cr(III), Fe(III), Cu(II) or Zn(II) chelates has been carried out by casting 0.2–0.25 g in 10 ml of dry THF to the solution of PVC at the same concentration above.

2.4. Determination of average molecular weight (M_w)

Viscosity property was used to determine the average molecular weight of PVC polymer using the Mark–Houwink relation. PVC films with and without additives were calculated from intrinsic viscosities measured in the THF solution at 25 °C



Scheme 1 Preparation of H₂L ligand.



Scheme 2 Suggested geometrics and names of prepared complexes.

with an Ostwald U tube viscometer. Eqs. (1) and (2) were used to deduce the molecular weight (Emad et al., 2009):

$$[\eta] = K\overline{M}_w^\alpha \quad (1)$$

$$[\eta] = (\sqrt{2}/C)(\eta_{sp} - \ln \eta_{rel})^{1/2} \quad (2)$$

η is the intrinsic viscosity, α and K are the constants that depend upon the polymer–solvent system at a particle temperature, and C is the concentration of the polymer solution. Solutions were made by dissolving the polymer in a THF solvent, g/100 ml; the flow times of the polymer solution and pure solvent are t and t_0 respectively. Specific viscosity η_{sp} was calculated as follows (Eqs. (3) and (4)):

$$\eta_{rel} = t/t_0 \quad (3)$$

where η_{rel} is the relative viscosity

$$\eta_{sp} = \eta_{rel} - 1 \quad (4)$$

The quantum yield of the main chain scission ϕ_{cs} (Emad et al., 2009) was calculated from viscosity measurements using the following relation (Eq. (5)):

$$\phi_{cs} = (CA/\overline{M}_{w,0}) \left[([\eta_0]/[\eta])^{1/\alpha-1} \right] / I_0 t \quad (5)$$

where C is the concentration; A is the Avogadro number; M_w is the initial average molecular weight; $[\eta_0]$ is the intrinsic viscosity of the PVC polymer before irradiation; $[\eta]$ is the intrinsic viscosity of PVC polymer after irradiation; I_0 is the incident intensity and t the irradiation time in seconds.

2.5. Determination of carbonyl index (I_{co})

Changes in the FT-IR spectra of the PVC samples due to the carbonyl group were analyzed and the effects of Cr(III), Fe(III) and Zn(II) chelates estimated. Actual absorbance, the difference between the absorbance of top peak and base line ($A_{\text{Top peak}} - A_{\text{Base line}}$) is calculated using the base line method (Terence and Robin, 2006; Harris and Kratochvil, 1981). Carbonyl index was calculated by comparison of the FT-IR absorption peak at 1720 cm^{-1} with the reference peak at 1890 cm^{-1} . This method is called the band index method (Rabic and Ranby, 1975)

$$I_s = A_{S(1720)} / A_{r(1890)} \quad (6)$$

A_s is the absorbance of the peak under study, A_r is the absorbance of the reference peak, and I_s is the index of the group under study.

2.6. Photo degradation

Accelerated weatherometer QUV tester (Q-panel company, USA) was used for irradiation of PVC films. Samples are fixed vertically and parallel to the lamps to make sure that the ultra-violet incident radiation is perpendicular to the samples, the temperature of the tester chamber was kept constant at 50°C for all samples. The quantum yield ϕ_{cs} values of the polymer chain scission were determined using Eq. (7):

$$\frac{1}{P_{n,t}} - \frac{1}{P_{n,o}} = \frac{M_{mvc}}{WA} \phi_{cs} I_a t \quad (7)$$

where W is the weight of the irradiated polymer film sample, M_{mvc} is the molecular weight of monomer vinyl chloride, A is the Avogadro number ($6.023 \times 10^{23} \text{ mol}^{-1}$), I_a is the light absorbed by the polymer sample, and $P_{n,o}$, $P_{n,t}$ are the average degree number of polymerization initially and at any exposure time t during degradation. The electronic spectra of the irradiated PVC films were determined in the THF solution. The FT-IR spectra of the PVC films blended with Cr(III), Fe(III), Cu(II) or Zn(II) complexes were determined and recorded as KBr disks in the range of $4000\text{--}200 \text{ cm}^{-1}$.

3. Results and discussion

3.1. Characterization of metal chelate

Analytical data (Table 1) agree well with the suggested formula. Conductivity measurements of the Cr(III) complex in DMF (10–3 M) lie in the range of $80\text{--}95 \text{ S cm}^2 \text{ mol}^{-1}$ indicating its electrolytic behavior in a 1:1 ratio, in contrast Zn(II) and Cu(II) complex solutions are neutral. The Ostwald dilution of molar conductance in DMF solutions for Cr(III) and Fe(III) complexes, confirms the stability of such complexes in solutions via estimation of K_a or K_f values, which were 1.09×10^3 and $4.25 \times 10^3 \text{ mol}^{-1} \text{ L}$, respectively (Gehad et al., 2006; Majid et al., 2011). The ^1H NMR spectrum of the free Schiff base H_2L ligand in DMSO-d_6 solvent shows peaks at 2.5, 4.5, 7–8 and 10 ppm assigned to $\text{HC}=\text{N}$, OH (enolic), COOH , aliphatic CH_3 and methylenic $-\text{CH}_2$ group (Zahid et al., 2006). All the protons were found as to be in their expected region. In the spectra of the diamagnetic Zn(II) complex, coordination of the ligand via azomethine-N and carboxylate-O was established by down field shifting of these signals in the Zn(II) complex due to increased conjugation

Table 1 Physical properties, elemental analysis and molar conductance of prepared complexes.

Comp.	Color	m.p (°C)	% Calculated (found)				Λ_m^a	$K_f \text{ mol}^{-1} \text{ L}$
			C	H	N	M		
H ₂ L	Yellow	188–190	63.15(62.88)	6.57(6.41)	9.2(9.51)	–	–	–
[CrL(H ₂ O) ₂]Cl	Dirty green	295–297	45.01(44.18)	5.15(4.66)	6.56(7.00)	12.42(11.99)	79	1.09×10^3
[FeL(H ₂ O) ₂]Cl	Dark red	305 ^d	44.70(43.85)	5.12(4.32)	6.51(6.99)	13.03(12.47)	82	4.52×10^3
[CuL]	Brown	320 ^d	52.53(52.03)	4.92(5.01)	7.66(8.29)	17.37(16.77)	20	–
[ZnL]	Pale yellow	330 ^d	53.03(52.62)	4.97(5.11)	7.73(8.14)	16.57(15.63)	18	–

^a $\text{S cm}^2 \text{ mol}^{-1}$ (10^{-3}M) solution of DMF.

^d Decomposed.

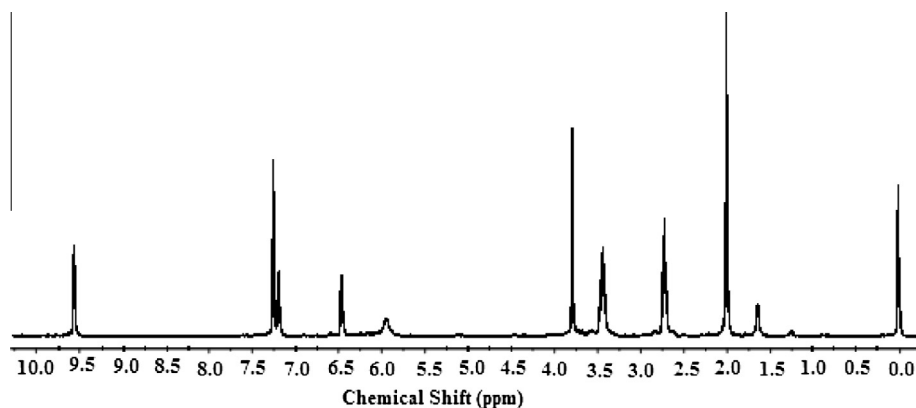


Figure 1 ^1H NMR spectrum of H₂L in d⁶-DMSO.

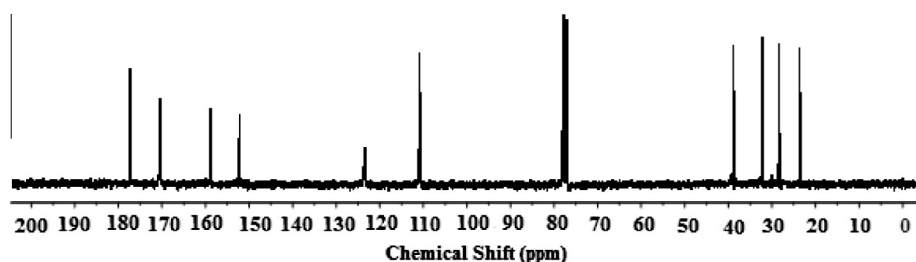


Figure 2 ^{13}C NMR spectrum of H₂L in d⁶-DMSO.

and coordination. Also the disappearance of the peak at 11.95 ppm revealed the deprotonation of the COOH group and coordination to the Zn(II) ion (John, 2003; Stejskal and Memory, 1994). Complexes are sparingly soluble in acetonitrile, 1,2-dichloroether and dry THF, but highly soluble in DMF and DMSO. The molar conductance value in 10^{-3}M DMF indicates that the chloride ions are outside of the coordination sphere for complexes, Cr(III) and Fe(III).

3.2. Proton NMR spectra

The spectral information from ^1H NMR and ^{13}C NMR of the ligand N{2[3(1-carboxyiminoethyl)-1-phenyl]butylidene-2-amino propionic acid} and its Zn(II) chelate complex with respect to TM references is shown in Figs. 1–4. Multiple peaks around $\delta 7$ –8 ppm show the presence of the benzylidene H group. The peak at 10 ppm that appears as a singlet investigates the proton of the carboxylic group COOH. However the other two peaks in the high field 3–5 ppm refers to protons

of CH₂, CH and CH₃ groups (Sathisha et al., 2007; Kalsi, 1999). Upon complication, deprotonation of COOH, via disappearance of the signal of carboxylic groups reveals the coordination of the oxygen atom to the zinc ion (John, 2003; Khandar et al., 2002), and the other shifts of the Zn(II) complex support the complication through nitrogen atoms of two isomethine C=N groups, Figs. 1 and 3 (Zahid et al., 2006; Stejskal and Memory, 1994). ^1H NMR (ppm) for H₂L ligand: 7.51 (5H, Ar), 11.51(2H, COOH), 3.71(6H, 2CH₃), 3.21(3H, CH₃), 2.85(2H, CH₂), and ^{13}C NMR (ppm) for H₂L in d⁶-DMSO: 170(COOH), 145–150 (C=N) and 120–140 (C₆H₅).

Also ^{13}C NMR of H₂L and Zn(II) chelates in d⁶-DMSO, Figs. 2 and 4 shows corresponding peaks of COOH at 170 ppm and 158 ppm for isomethine groups, which undergo down shift in the Zn(II) chelate and confirm the coordination and formation of the tetradentate ligand N₂O₂ and Zn(II) chelate (John, 2003; Khandar et al., 2002). ^1H NMR (ppm) for Zn^(II)L complex: 7.86(5H, Ar), 3.51(6H, 2CH₃), 3.11(3H, CH₃), 2.44 (2H, CH₂) and ^{13}C NMR (ppm) for Zn^(II)L in

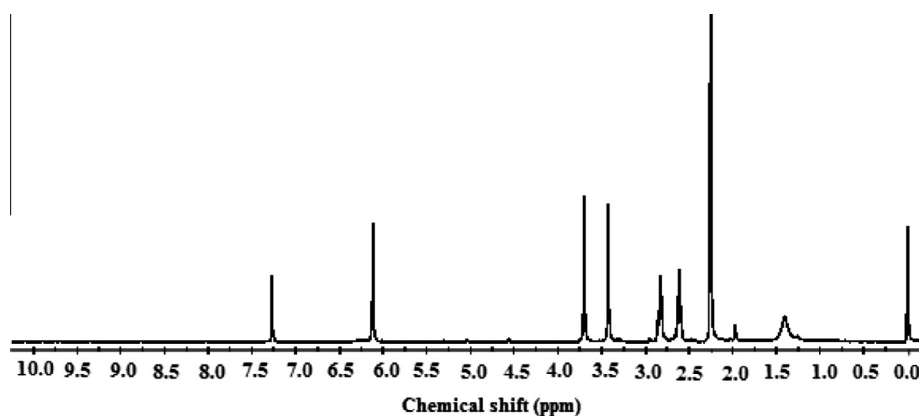


Figure 3 ^1H NMR spectrum of Zn(II) complex in d^6 -DMSO.

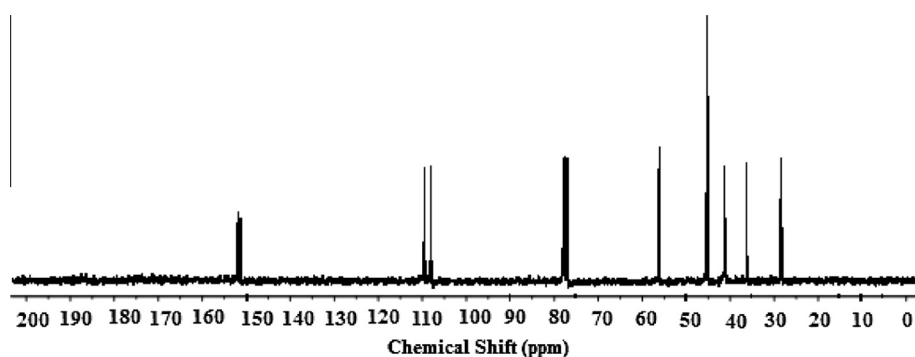


Figure 4 ^{13}C NMR spectrum of Zn(II) complex in d^6 -DMSO.

Table 2 FT-IR spectra ($\nu \text{ cm}^{-1}$), electronic spectra (λ_{max} nm) and magnetic properties of the metal complexes.

Comp.	FTIR $\bar{\nu}$ (cm^{-1})	Assignment	UV-Vis, λ_{max} nm	μ_{eff} B.M
H_2L	1685(s), 3400–2800	(COOH)	274 (36496)	
	1637(s)	C=N	333 C.T.(30030)	
	722(w)	$\delta \text{ CH}_2$	252 (39682)	
$\text{Cr}^{\text{III}}\text{L}$	1664(s)	C=O	388 ^a (25773)	3.41
	1624(s)	C=N	450 ^a (22220)	
	500–550	Cr–O	670 ^a (14925)	
	490	Cr–N		
	390	Cr–Cl		
$\text{Fe}^{\text{III}}\text{L}$	3323–3600(s) ^a	O–H(H_2O)		4.95
	1662(s)	C=O		
	1620(s)	C=N		
	400–530(m)	Fe–O, Fe–N	376 C.T. (26595)	
	3400–3550(s) ^a	O–H(H_2O)	325 (30769)	
$\text{Cu}^{\text{II}}\text{L}$	830–840(m) ^b	O–H		1.05
	1640(s)	C=O	430 (23256)	
	1608(s)	C=N	350 C.T. (28571)	
$\text{Zn}^{\text{II}}\text{L}$	1587–1554			Diamagnetic
	490–515(m)	Cu–O, Cu–N		
	1648(s)	C=O	240 (41400)	
	1575(s)	C=N	350 C.T. (28571)	
	505(m)	Zn–O		
415(m)	Zn–N			

C.T. = charge transfer, w = weak, s = strong, b = broad, m = medium.

^a Vibration modes of O–H coordinated water.

^b Rocking of water molecules in Cr(III) and Fe(III) complexes.

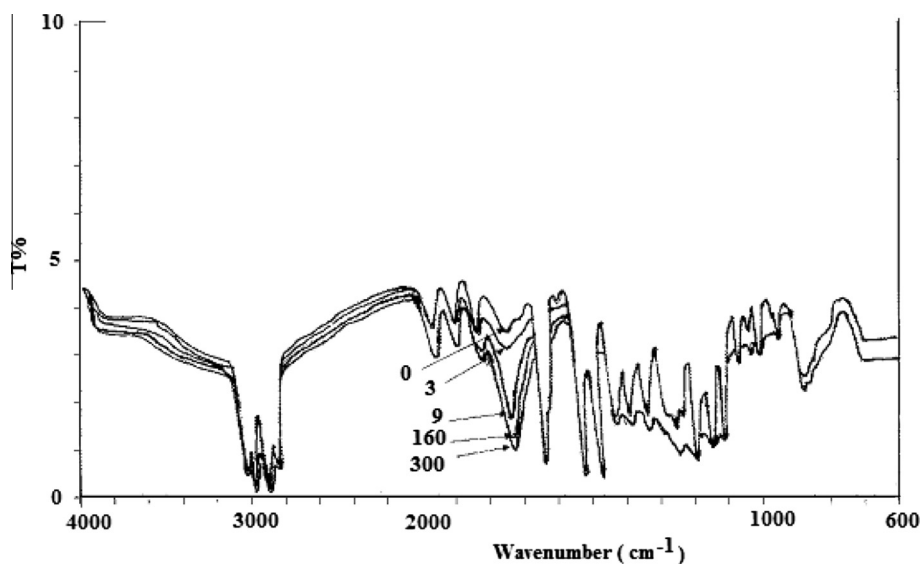


Figure 5 Changes in FT-IR spectrum of PVC films blended with Fe(III) complex with irradiated time at 254 nm.

d^6 -DMSO: 158 (2 C=N), 115 (C_6H_5), 82(CH_2), 56(2 CH_3) and 40–50 ($CH-CH_3$).

3.3. Electronic spectra and magnetic properties

The distinguishable absorption bands of UV-Vis. Spectra of the H_2L ligand and its metal complex solutions were recorded in absolute ethanol and DMF over the 800–200 nm range listed in Table 2. The ligand solution shows three peaks at 252 nm (39682 cm^{-1}), 274 nm (36496 cm^{-1}) and 330 nm (30030 cm^{-1}) which may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ intra-ligand charge transfer (Chandra and Pundir, 2008; Lever, 1984). The electronic spectrum of the Cr(III) complex displayed three absorption bands at 388 nm (25773 cm^{-1}), 450 nm (22222 cm^{-1}) and 670 nm (14925 cm^{-1}) assignable to $A_2g^4 \rightarrow T_2g^4$, $A_2g^4 \rightarrow T_1g^4(f)$ and $A_2g^4 \rightarrow T_1g^4(p)$, respectively. The magnetic moment of the solid Cr(III) complex is

3.41 B.M., which confirms the high spin octahedral geometry around the Cr(III) ion.

The UV-Vis spectrum of the brown solution of the Fe(III) complex in DMF exhibits two peaks at 376 nm (26595 cm^{-1}) and 325 nm (30769 cm^{-1}) assigned to the d-d transition type $A_1g^6 \rightarrow T_2g^4$ and $A_1g^6 \rightarrow T_1g^4$, respectively suggesting an octahedral symmetry around the Fe(III) ion (Chandra and Pundir, 2008). The red solution of the Cu(II) complex exhibits two absorption bands at 430 nm (23256 cm^{-1}) and 350 nm (28571 cm^{-1}) pertaining to $A_1g^2 \rightarrow B_2g^2$ and $A_1g^2 \rightarrow B_1g^2$, respectively confirming the square planar geometry around the Cu(II) ion. The comparatively low magnetic moment of Cu(II), 1.05 B.M. indicates the presence of orbital contribution of ligand electron with the odd electron of the Cu(II) ion. The pale yellow solution of the Zn(II) complex exhibits high intensity peaks at 240 nm (41400) and 350 nm (28571 cm^{-1}) corresponding to the L-M charge transfer of the tetrahedral Zn(II) complex (Sathisha et al., 2007; Lever, 1984).

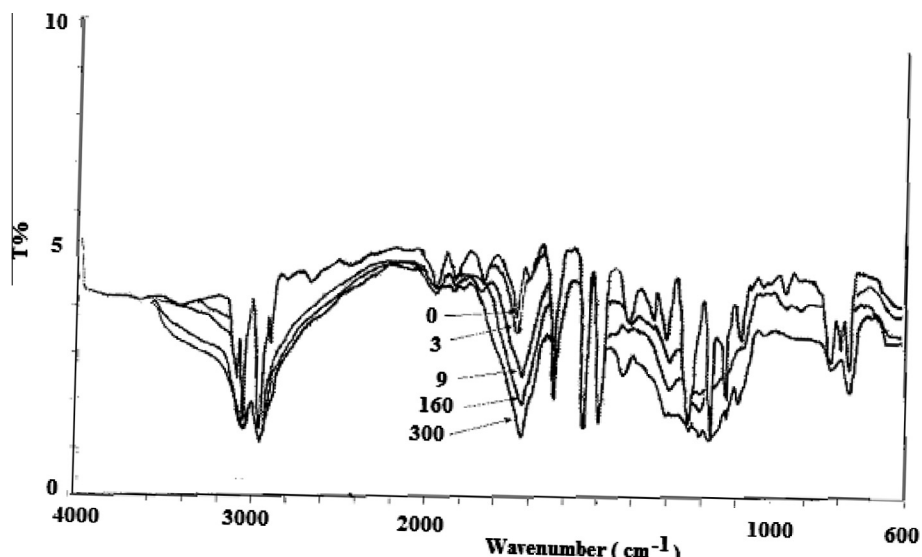


Figure 6 Changes in FT-IR spectrum of PVC films blended with Cr(III) complex with irradiated time at 254 nm.

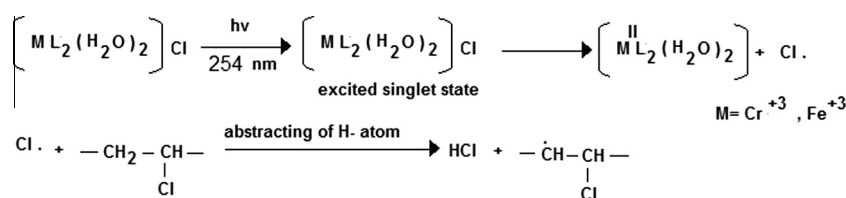
3.4. FT-IR spectra

Characteristic vibration frequencies have been identified and it is inferred that the spectrum of the free ligand (Table 2) exhibits a broad band around 3600–2800 cm^{-1} due to intramolecular hydrogen bonding of the OH–carboxylic group (Nakamoto, 1997). In the spectra of all the complexes this band has disappeared indicating the coordination of COO–oxygen to the metal ion via de-protonation (Table 2). The ligand spectrum however displays a sharp ν (C=O), absorption band at 1700 cm^{-1} confirming that the condensation takes place on the side chain of the $-\text{NH}_2$ group of alanine with the carbonyl group of benzoyl acetone. The other bands at 1620 cm^{-1} and 1630 cm^{-1} are assignable to ν (C=C) and ν (C=N) stretching vibrations, respectively, whereas the FT-IR spectra of metal chelates show medium bands in the range of 520–535 cm^{-1} and 490–505 cm^{-1} which are assigned to M–N and M–O modes, respectively. A strong broad band in the 3320–3600 cm^{-1} region in the spectra of Cr(III) and Fe(III) complexes indicates the presence of coordinated water in these complexes. The presence of coordinated water was further confirmed by the appearance of non-ligand band in the 835–845 cm^{-1} region assignable to the rocking mode of water (Stejskal and Memory, 1994; Mishra and Kumar, 2009; Panchal and Patel, 2004).

According to the results obtained from ^1H NMR, ^{13}C NMR, FT-IR, UV–Vis and magnetic moments measurements, we have concluded the suggested geometries of the prepared complexes as below.

3.5. Variation of PVC molecular weight during photolysis

It is found that the additives of Cr(III) and Fe(III) complexes to PVC film abate the depression in Mw which supports the photodegradation of PVC films due to the formation of the Cl^\cdot free radical resulting from the counter ion in the structure of the complex as shown:



In contrast the Zn(II) chelate additive to PVC films acts as photostabilizer, due to slow depression in the average molecular weight Mw. Photo degradation with the Zn(II) chelate becomes slower and bond scission may be random.

The quantum yield for the chain scission was calculated for PVC films with and without 2–2.5% wt/wt of the metal chelate additive. The ϕ_{cs} values of PVC films in the presence of the Zn(II) chelate additive are less than those of Cr(III) and Fe(III) chelates additives. High values of ϕ_{cs} are due to the counter ion Cl in Cr(III) and Fe(III) chelates (4.2×10^{-7} and 4.95×10^{-7} respectively). However the low value of ϕ_{cs} for PVC films blended with the Zn(II) chelate (2.99×10^{-7}), is due to the absorption of UV energy at one site and the distribution of electronic excitation over many bonds so that the

probability of a single bond breaking is small, or the absorbed energy is dissipated by non selective processes (Terence and Robin, 2006).

3.6. Photo degradation and photo stabilization of PVC blended with metal chelates

Accelerated degradation of PVC and how degradation occurs with irradiation light of wavelength 254 nm have been studied, if accelerated photo degradation can take place under accelerational sunlight, this method will become an excellent one for the degradation of waste plastics, which is mainly required for green chemistry.

The changes in Mw, I_{CO} , I_{OH} , I_{Poly} of PVCs blended with Cr(III) and Fe(III) are much more higher than those in PVC casted with the Zn(II) complex, which confirms that the Zn(II) complex acts as primary photo stabilizer (Simon and Valko, 1992; Fisch and Bucaloglu, 1998), while Cr(III) and Fe(III) complexes increased the photodegradation of PVC via enhancing the cleavage at C–Cl and C–C bonds with the possibility of photo oxidation of Cr(III)–Cr(IV), Cr(V) and Cr(VI) states, and reduction of Fe(III)–Fe(II) state.

Irradiation of PVC films leads to a clear change in their FT-IR spectrum as shown in Figs. 5 and 6. Appearance of bands at 1750 cm^{-1} and 1720 cm^{-1} attributed to the formation of carbonyl groups, the first is related to chloroketone and the second one is due to aliphatic ketone, together with the formation of band at 1615 cm^{-1} related to alcohol functions (Yang et al., 2002). The absorptions of (C=C)_n, –OH and C=O are used to follow the extend of polymer degradation during irradiation. This absorption was calculated as carbonyl index (I_{CO}), polene index (I_{Poly}) and hydroxyl index (I_{OH}). The increase of I_{CO} , I_{Poly} and I_{OH} of PVC films blended with Cr(III) and Fe(III) chelates suggests the increase of photodegradation of the C–C bond, in contrast the Zn(II) chelate acts as photo stabilizer (Chen et al., 2008). From these experimental results, it is clear that new chromophores are introduced in pre-

irradiated PVC. Since these samples have absorption maxima at longer wavelengths including the region of terrestrial sunlight photo degradation in terrestrial sunlight can be expected.

4. Conclusion

In this paper, we have explored the synthesis and coordination chemistry of Cr(III), Fe(III), Cu(II) and Zn(II) complexes derived from the bidentate Schiff base H_2L . The ligand behaves as a dibasic bidentate species upon complication with the nitrogen atom of the C=N group and the oxygen atom of the carboxylate group. The effect of 0.2% W/W of Cr(III), Fe(III) and Zn(II) complexes on the photo degradation of

PVC films has been studied. It has been found that Cr(III) and Fe(III) chelates enhanced the ratio of C–C cleavage via depression in the average molecular weight M_w of the studied PVC films. However the Zn(II) chelate increased the photostabilization of the polymer via lowering of the quantum yield ϕ_{cs} of the scissions and indices of carbonyls, hydroxyls and polyenes. From these results we foresee an excellent future for degradation and removal of waste plastics by adding low concentrations, 2–2.5% w/w of a new metal complex which is an important factor in green analytical chemistry.

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