SYNTHESIS, CHARACTERIZATION, THEORETICAL STUDIES AND PHOTOSTABILIZATION OF MEFENAMIC ACID DERIVATIVE WITH SOME DIVALENT METAL IONS

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A new mefenamic acid derivative, (4-amino-5-(2-(2,3-dimethylphenyl)aminophenyl)-1,2,4-triazole-3-thion (**L**), has been synthesized and characterized by spectroscopic and elemental analysis. The ligand (**L**) has been used as a chelating agent to prepare complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions. The structure of the complexes, in solid state, has been suggested. The theoretical treatment of the complexes, in the gas phase, has been studied using the Hyperchem-8 program for the molecular mechanics and semi-empirical calculations. The heat of formation ($\Delta H_f°$) and binding energy (ΔE_b) for the ligand and their complexes were calculated by PM3 method. The electrostatic potential of the ligand (**L**) has been calculated to investigate the reactive sites of the molecule. Photostabilization of PVC film in air was investigated in the absence and presence of the ligand **L** and theirs complexes by accelerated weathering tester. It was found that various indices values increased with irradiation time and this increase depend on the type of additives.

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Introduction

1,2,4-Triazole constitute an interesting group of heterocyclic compounds containing three N atoms in a 5-membered ring and its derivatives represent some of the most biologically active classes of compounds possessing a wide spectrum of biological and pharmacological properties.[1-6] There are known drugs containing the 1,2,4-triazole group e.g. Triazolam,[7] Alprazolam,[8] Etizolam and Furacylin.[9] N4-amino and 3-thione of 1,2,4-triazoles with substitution at 5-position have been studies as anti-inflammatory and antimicrobial agents.[10] An important and versatile class of well-established biologically active compounds are those with the –N-C=S moiety (" soft" sulfur atom besides the "hard" nitrogen). This group is found in many basic structures of drugs either to be part of an open chain, e.g. thiocarbamates, isothiocynates and thiosemicarbazides or involved in heterocyclic ring, e.g. mercapto derivatives of triazoles, oxadizoles and thiodiazoles.[11-13]

In this work, we report the preparation of 4-amino-5-(2-(2,3-dimethylphenyl) aminophnyl-1,2,4-triazole-3-thion (**L**) as a ligand, in an attempt to prepare a new ligand with a 4-amino-3-thione-1,2,4-triazole ring , substituted at 5-position with mefenamic acid residue, and to investigate the coordination behaviour of the prepared new ligand towards Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions. Theoretical study, in the gas phase, by using semi-empirical method has been performed in order to show the most stable conformation and to compare these results with the experimental data. Also the prepared complexes of (**L**) were used to enhance the photostabilization of polymer polyvinyl chloride (PVC). The photostabilization activity of these compounds was determined by monitoring the carbonyl (I_{CO}), polyene (I_{PO}) and hydroxyl (I_{OH}) indices, weight loss method with irradiation time. It was found that the (I_{CO}), (I_{PO}) and (I_{OH}) indices values increased with irradiation time and this increase depend on the type of additives.[14,15]

Experimental

Instrumentation

Melting points were recorded on a Gallenkamp MF B600 010F melting point apparatus Elemental analyses were obtained using EA-034 for the ligand and their metal complexes. Metal contents of complexes were estimated spectrophotometrically using Flame atomic absorption Shimadzu-670 AA Spectrophotometer. Bruker Spectrophotometer model ultra-shield was used at 300 MHz for `H- and ^{13}C- NMR. IR spectra were recorded using FT-IR-8300 Shimadzu in the range of 4000-400 cm^{-1}. Electronic spectra were obtained using UV-1650PC-Shimadzu spectrophotometer at room temperature, the measurement were recorded using a solution of 10^{-3}M concentration of (**L**) ligand and its metal complexes in DMF as a solvent.

Magnetic susceptibilities of samples in the solid state were measured by using a Bruker BM6 magnetic balance. The molar conductivity was measured by using Electrolytic Conductivity Measuring set Model MC-1-Mark V by using platinum electrode (EDC 304) with cell constant (1 cm^{-1}), concentration (10^{-3} M) in DMF as solvent at room temperature.

Synthesis of ligand (L)

The ligand (**L**) was prepared starting from mefenamic acid (MFA) according to the following general steps can be seen on Scheme 1.[16-18]

Preparation of (2-(2,3-dimethyl phenyl)amino ethyl benzoate (G1)

Sulphuric acid (8 mL) was added dropwise with continuous stirring to a solution of MFA (0.1 mol) in 200 mL ethanol. The mixture was heated under reflux for 10 h. After cooling, the mixture was poured on to crushed ice, the precipitated crystalline solid was filtered, washed successively with water, 10% NaHCO$_3$ solution and water. The crude product was recrystallized from ethanol, to give compound **G1** as off white crystals, in 84 % yield, m. p. = 108-110 $^{\circ}$C.
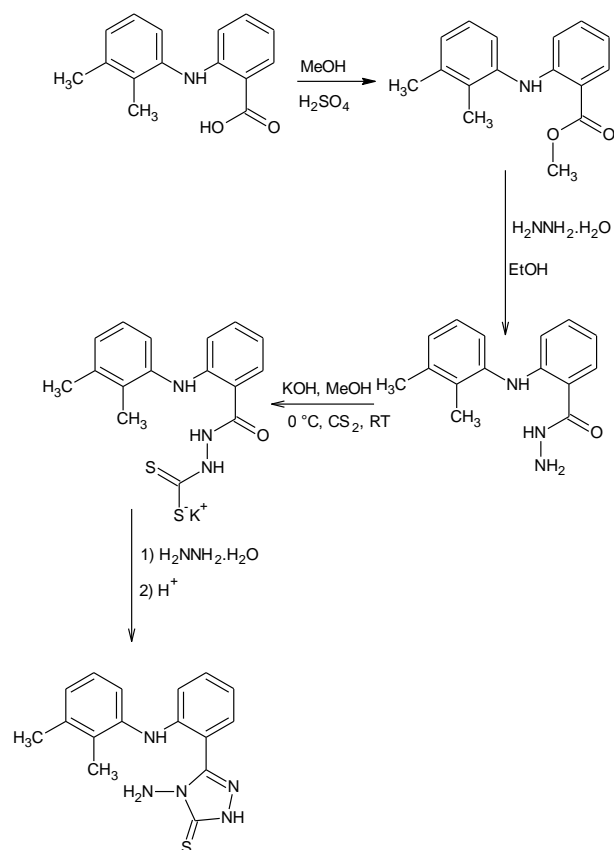
Scheme 1. Synthesis of the ligand **L**.

Preparation of(2-(2,3-dimethyl phenyl)amino ethyl benzohydrazide (G2)

Ester of **G1** (0.1 mol) was dissolved in absolute ethanol (50 mL). To the above solution was added 80 % hydrazine hydrate (0.1 mol). The resulting reaction mixture was refluxed on a steam bath for 10-12 h. After cooling, cold water (150 mL) was added to the mixture and the separated white crystalline solid was filtered, washed with cold water, dried and recrystallized from ethanol to give 82 % yield of **G2**, white colour, m p. 156-158 $^{\circ}$C.

Preparation of (2-(2,3-dimethyl phenyl)amino ethyl benzoyl)hydrazine carbodithioate (G3)

Compound **G2** (0.05 mol) was treated with a solution of potassium hydroxide (0.0643 mol) in ethanol (70 mL) at 0°C with stirring, then 7 mL of carbon disulfide was added

dropwise and the reaction mixture was stirred overnight at room temperature. The solid product (**G3**) was filtered, washed with cold methanol and dried.

Preparation of 4-amino-5-(2-(2,3-dimethylphenyl)aminophenyl)-1,2,4-triazole-3-thion (L)

A mixture of compound **G3** (0.05 mol) and 80 % hydrazine hydrate (10 mL) was heated under reflux till the evolution of hydrogen sulphide completely ceases (about 6 h). After cooling, water (200 mL) was added and the mixture was neutralized with 10 % HCl and allowed to stand for three h. The separated crude product was filtered, washed with water, dried and recrystallized from ethanol to give 80 %)yield of compound **L**, as white powder with melting point 215-217 $^{\circ}$C.

Preparation of metal complexes (A1–A5)

Suitable amounts of Co(CH$_3$COO)$_2$.4H$_2$O, Ni(CH$_3$COO)$_2$.4H$_2$O, Cu(CH$_3$COO)$_2$.H$_2$O, Zn(CH$_3$COO)$_2$.2H$_2$O and Cd(CH$_3$COO)$_2$.2H$_2$O were dissolved in ethanol and added to an ethanolic solution of **L** in 1:2 mole ratio of metal : ligand with stirring. The reaction mixture was heated under reflux for 4 h, during this time a precipitate was formed. The product was filtered off, washed with hot ethanol, followed by cold water and then dried under vacuum. All complexes were identified by elemental analysis, flame atomic absorption, FT-IR and UV-VIS spectroscopy, magnetic and conductivity measurements.

Computational methods

Four types of calculations, viz., single point, geometry optimization, vibrational frequency and bond length, were carried out, using Hyperchem-8, a sophisticated molecular modeler editor and powerful computational package. This program known for its quality, flexibility and ease of use, uniting 3D visualization and animation with quantum chemical calculations, mechanic and dynamic.[19,20] Hyperchem offers ten semi-empirical molecular orbital methods, with options for organic and main group compounds for transition metal complexes and spectral simulation.[21,22] We chose parameterization model version 3 (PM3) which including transition metals. PM3 were used for the calculation of heat of formation, binding energy, total energy and bond length for all metal complexes.

Photostabilization of polymer

Commercial PVC supplied by Petkim Company(Turkey) was re-precipitated from THF solution and finally dried under vacuum at room temperature for 24 h. Fixed concentrations of PVC solution (5 g 100 mL^{-1}) in THF were used to prepare polymer films with 40 μm thickness (measured by a micrometer type 2610 A, Germany). The films were prepared by evaporation technique at room temperature for 24 h.[6,23] To remove the possible residual THF solvent, film samples were further dried at room temperature for three h under reduced pressure. The films were fixed on stands specially used for irradiation. The stand is provided with an aluminium plate (0.6 mm in thickness) supplied by Q-panel company.

Irradiation experiments

Accelerated weatherometer Q.U.V. tester (Q. panel, company, USA), was used for irradiation of PVC films. The accelerated weathering tester contains stainless steel plate, which has two holes in the front side and a third one behind. Each side contains a lamp (type Fluorescent Ultraviolet Lights) 40 Watt each. These lamps are of the type UV-B 313 giving spectrum range between 290–360 nm with a maximum wavelength at 313 nm. The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation is perpendicular to the samples. The irradiated samples were rotated from time to time to ensure that the intensity of light incident on all samples is the same.

The degree of photodegradation of polymer film samples was followed by monitoring FT-IR spectra in the range 4000–400 cm^{-1} using FT-IR 8300 Shimadzu Spectrophotometer. The position of carbonyl absorption is specified at 1720 cm^{-1}, the hydroxyl group at 3450 cm^{-1} and 1604 cm^{-1} is due to polyene group. The progress of photodegradation during different irradiation times was followed by observing the changes in carbonyl and hydroxyl peaks. Then carbonyl and hydroxyl indices were calculated by comparison of the FTIR absorption peak at 1720, 3450 and 1604 cm^{-1} with reference peak at 1450 cm^{-1}, respectively. This method is called band index method which includes as shown in eqn. (1).

$$I_s = \frac{A_s}{A_r} \qquad (1)$$

where

A_s = Absorbance of peak under study,

A_r = Absorbance of reference peak,

I_s = Index of group under study.

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.

Determination of average molecular weight using viscometry method

The viscosity property was used to determine the average molecular weight (M_{av}) of the polymer, using the Mark-Houwink relation (eqn. 2).

$$[\eta] = KM^\alpha \qquad (2)$$

where

$[\eta]$ is the intrinsic viscosity,

K and α are constants depending upon the polymer-solvent.

The intrinsic viscosity of a polymer solution was measured with an Ostwald U-tube viscometer. Solutions were made by dissolving the polymer in a solvent (g 100 mL^{-1}) and the flow times of polymer solution and pure solvent are designated as t and t_0 respectively. Specific viscosity (η_{sp}) was calculated by eqns. (3) and (4).

$$\eta_{re} = \frac{t}{t_0} \qquad (3)$$

where η_{re} = relative viscosity.

$$\eta_{sp} = \eta_{re} - 1 \qquad (4)$$

The single-point measurements were converted to intrinsic viscosities by the eqn. (5).

$$[\eta] = (\sqrt{2/c})(\eta_{sp} - \ln \eta_{re})^{1/2} \qquad (5)$$

where c = concentration of polymer solution in g 100 mL^{-1}).

By applying eqn. (5), the molecular weight of degraded and un-degraded polymer can be calculated. Molecular weights of PVC with and without additives were calculated from intrinsic viscosities measured in THF solutions using eqn. (6).

$$[\eta] = 4.17 \times 10^{-4} M_{av}^{0.6} \qquad (6)$$

Results and discussion

Study of the complexes in solid state

The physical and analytical data of the ligand (**L**) and its metal complexes are given in Table 1. The results obtained from elemental analysis are in satisfactory agreement with the calculated values. The suggested molecular formula was also supported by spectral measurement as well as magnetic moment. The ligand **L** is soluble in common organic solvents such as (ethanol, acetone and methanol), whereas the new complexes are coloured crystalline solids, soluble in chloroform, DMF and DMSO.

The nuclear magnetic resonance spectra of **L** gave satisfactory spectra data and the molecular structure was assigned on the basis of ^{1}H-NHR spectrum. The spectra were obtained in DMSO-d_6 solution as an internal reference. According to the results obtained from the spectrum (Figure 1), the molecular structure of the ligand can be illustrated $\delta H_{(1,2)}$ = 2.095-2.281 ppm (6H, s, CH$_3$), $\delta H_{(3)}$ = 5.3 ppm (2H, s, NH$_2$), $\delta H_{(4)}$ = 9.47 ppm (1H, s, NH), $\delta H_{(5)}$ = 12.41 ppm (1H, s, NH), δPh = 6.706-7.89 ppm (7H).

Table 1. Physical data for Ligand (**L**) and its metal complexes (**A1-A5**).

Comp. No.	Color	M. P.	Yield %	Analysis found/calculated					Suggested formula
				C%	H%	N%	S%	M%	
L	White	215-	80	61.73	5.47	22.51	10.29	-	$(C_{16}H_{17}N_5S)$
A1	Brown	234d	90	54.07	5.01	17.52	8.01	7.37	$[Co(C_{32}H_{34}N_{10}S_2)(CH_3COO)_2]$
A2	Yellowish	260d	78	54.09	5.01	17.53	8.01	7.35	$[Ni(C_{32}H_{34}N_{10}S_2)(CH_3COO)_2]$
A3	Dark green	250d	88	53.	4.98	17.42	7.97	7.90	$[Cu(C_{32}H_{34}N_{10}S_2)](CH_3COO)_2$
A4	Off white	200d	90	53.64	4.97	17.38	7.95	8.12	$[Zn(C_{32}H_{34}N_{10}S_2)](CH_3COO)_2$
A5	Off white	270d	85	50.62	4.69	16.40	7.49	13.17	$[Cd(C_{32}H_{34}N_{10}S_2)](CH_3COO)_2$

Table 2. Stretching vibrational frequencies (cm^{-1}) located in the FT-IR spectra of (**L**) and their metal complexes.

Comp. No.	$v_{C=S}$	$v_{C=N}$	vNH_2 (as,s)	v_{NH}	v_{COO^-} (as,s)(coord.)	v_{COO^-} uncoord.	M-N	M-S	M-O
L	1041	1643	3269,3209	3439	-	-	-	-	-
A1	1020	1640	3252,3212	3441	1537, 1305	-	530	459	523
A2	1030	1643	3263,3211	3440	1512, 1302	-	532	457	540
A3	1030	1640	3252,3200	3439	-	1665	529	460	-
A4	1022	1640	3252,3194	3440	-	1655	530	455	-
A5	1030	1645	3240,3155	3442	-	1660	533	454	-

The ^{13}C-NMR spectrum for **L** showed the following peaks. $C_{(1)} = 169.615$, $C_{(2)} = 161$, $C_{(3)} = 148$, $C_{(4)} = 138$, $C_{(5)} = 137$, $C_{(6)} = 134$, $C_{(7)} = 131.64$, $C_{(8)} = 131.17$, $C_{(9)} = 126.18$, $C_{(10)} = 125.94$, $C_{(11)} = 122.13$, $C_{(12)} = 116.55$, $C_{(13)} = 113.02$, $C_{(14)} = 111.29$, $C_{(15)} = 20.16$, $C_{(16)} = 14.37$ (Figure 2).

The characteristic stretching vibration modes concerning **L** and its metal complexes (**A1 – A5**) are presented in Table 2. In all complexes (A1-A5), the ligand (L) behave as a bidentate coordinating with metal through sulfur of thiocarbonyl and nitrogen of amino group, therefore the bands due to $v_{(C=S)}$, (v_s and v_{as} of NH_2) and four (I-IV) thioamide bands were shifted to a lower frequency as it can be seen in Table, as well as the new bands for complexes (A₁ and A₂) in the region of 1521, 1537 cm⁻¹, which may be assigned to the asymmetric vibration of coordinated carboxylate groups ($v_{as}coo^-$) and the bands in the region of 1302-1305v cm⁻¹ may be attributed to the symmetric vibration of carboxylate group (v_scoo^-).[24, 25]

The large differences between the frequencies of [$v_{as}(coo^-)$] and [$v_s(coo^-)$], ($\Delta v > 200cm^{-1}$) in (**A1**) and (**A2**) complexes are indicative of the involvement of the coordination of the carboxylate groups to the metal ion in a monodentate fashion.[24,26] In contrast to (**A1**) and (**A2**) complexes, the complexes (**A3**), (**A4**) and (**A5**) show appearance of new bands in the region of 1655-1665 cm⁻¹ which may be assigned to the vibration of uncoordinated carboxylate groups. Other low intensity bands observed in the region of 445-460, 518-520 and 523-544 cm⁻¹ may be attributed to v_{M-S} and v_{M-N} respectively, in the all complexes and v_{M-O} in the case of (**A1**) and (**A2**) complexes, respectively.[26,27]

The electronic spectra of the free ligands (**L**) and their complexes (**A1– A5**) were recorded in chloroform solution. The spectrum of **L** shows a strong band at 42194 cm⁻¹, which is attributed to $\pi \rightarrow \pi^*$ and others at 31545, 29411 cm⁻¹, due to $n \rightarrow \pi^*$.

The measured magnetic moment of A1 is 4.2 B.M, this indicated that the cobalt ion in the complex is typical of d⁷ system with three unpaired electrons indicating a quartet state and suggest high spin octahedral geometry. The electronic spectrum of **A1** in chloroform exhibited two bands at 15384 and 18691 cm⁻¹, assignable to $^4T_1g \rightarrow {}^4A_2g_{(F)}$ and $^4T_1g \rightarrow {}^4T_1g_{(P)}$ transitions respectively for an octahedral geometry of Co(II). The value of various ligand filed parameters v_1, B⁻, β and Dq have been calculated using Tanabe-Sugano diagram for d⁷ system and found to be 7039.9, 623,0.642 and 934.5 respectively. The molar conductivity measurement in DMF showed that the complex is non electrolyte (Table 3).

The light green **A2** complex in chloroform exhibited bands at 15267 and 25974 cm⁻¹ assigned to $^3A_2g \rightarrow {}^3T_1g_{(F)}$ (v_2) and $^3A_2g \rightarrow {}^3T_1g_{(P)}$ (v_3) transitions respectively, which indicate octahedral geometry of Ni(II). The absence of any band below 10000 cm⁻¹ eliminates the possibility of tetrahedral environment in this complex. The different ligand field parameters B⁻, β and Dq have been calculated using the same diagram and found to be 611, 0.54 and 1099.224 respectively indicating that Ni-**L** bond is covalent. Magnetic moment, 3.09 B.M, of the solid complex showed a higher orbital contribution. Conductivity measurement in DMF showed that the complex was nonionic.

Table 3. Electronic spectra, magnetic moment and conductance in for the metal complexes

Symb.	λ_{max} cm^{-1}	Band assignment	10Dq	Molar Cond. S.cm^2.mol^{-1}	µeff. B.M	Suggested geometry
A1	7039.9 (Cal.)	$^4T_1g{\rightarrow}^4T_2g_{(F)}$	9337.6	15.65	4.2	OC-6
	1538.4	$^4T_1g{\rightarrow}^4A_2g_{(F)}$				
	1869.1	$^4T_1g{\rightarrow}^4T_1g_{(P)}$				
A2	10992.24 (Cal.)	$^3A_2g{\rightarrow}^3T_2g_{(F)}$	10976	18.09	3.09	OC-6
	15267	$^3A_2g{\rightarrow}^3T_1g_{(F)}$				
	25974	$^3A_2g{\rightarrow}^3T_1g_{(P)}$				
	33112	C.T				
A3	14084	$^2B_1g{\rightarrow}^2A_1g$	-	168.22	1.92	SP-4
	25773	$^2B_1g{\rightarrow}^2B_2g+{}^2Eg$				
A4	32258	ILCT	-	166.86	0.0	T-4
	38167					
	47619					
A5	31055	ILCT	-	170.9	0.0	T-4
	34482					
	47169					

The measured magnetic moment of **A3** is 1.92 B.M showing that the Cu(II) ion in the dark green complex is a d^9 system. Electronic spectrum in chloroform, shows one broad band at 14084cm^{-1} which corresponds to $^2B_1g{\rightarrow}^2A_1g$ transition, and a shoulder band at 25773cm^{-1} which is assigned to $^2B_1g{\rightarrow}^2B_2g+{}^2Eg$ transition. The position of these bands is in a good agreement with that reported for highly distorted octahedral geometry. Conductivity measurement in DMF showed that the complex was highly ionic.

The two complexes (**A4**) and (**A5**) are colourless in chloroform solution, so there is no d-d transition in the visible region, The complexes are diamagnetic as is expected for d^{10} ions. The conductivity measurements indicate ionic behaviour of the complexes.

Stereochemical structure of the complexes

According to the results obtained from the elemental analysis, spectral studies, magnetic and conductivity measurements, the suggested general structure of the complexes (**A1–A2**) can be illustrated as Figure 3. The Complexes **A3** and **A4** has tetrahedral and **A5** square-planar structure with the same coordination sites of the ligand **L**.

Theoretical studies of the ligand and their metal complexes

The electrostatic potential (EP) describes the interaction of energy of the molecular system with a positive point charge. EP is useful for finding sites of reaction in a molecule. Positively charged species tend to attack a molecule where the electro static potential is strongly negative (electrophonic attack). The EP of the free ligand was calculated and plotted as 3D and 2D contour to investigate the reactive sites of the molecules (Figure 4). The results of calculations show that the LUMO of transition metal ions prefer to react with the HOMO of sulfur and nitrogen atoms of the free ligand.

The conformations of the free ligand and its complexes obtained from the semi-empirical and molecular mechanics calculations that were fully re-optimized to estimate the heat of formation (ΔH_f^o) and binding energy (ΔE_b) by using the PM3 method for free ligand (**L**) and its metal complexes (Table 4).

The vibrational spectra of (**L**) and its metal complexes have been calculated (Supplementary Material). The theoretically calculated wave numbers showed that some deviations from the experimental values but these deviations are within the generally acceptable limits in theoretical calculations.[28]

The Gaussian suite of software was employed throughout this study for bond length measurements. Optimizations were carried out for the model systems represented in the Supplementary Material. The initial state for structure did not give bond lengths naturally so that the geometry optimization was used for correct bond lengths. Calculation parameters were optimized of bond lengths for the free ligand and its metal complexes by using the semi-empirical PM3 method, at geometry optimization of 0.001 kcal mol^{-1}, to give excellent agreement with the experimental data,[29] as it shown in Table 5.

Photostabilization study

The complexes of Co(II), Cd(II), Ni(II), Zn(II) and Cu(II) with (**L**) were used as additives for the photostabilization of PVC films. To study the photochemical activity of these additives for the photostabilization of PVC films, the carbonyl, hydroxyl and polyene indices were monitored with irradiation time using IR spectrophotometry.

The irradiation of PVC films with UV light of wavelength λ=313 nm led to a clear change in the FT-IR spectrum. The appearance of bands in 1720 cm^{-1} has been attributed to the formation of carbonyl groups related to aliphatic ketone. The hydroxyl band that appeared at 3450 cm^{-1} was annotated to the hydroxyl group and 1604 cm^{-1} is due to polyene group.[30] The absorption of the carbonyl, hydroxyl and polyene groups was used to follow the extent of polymer degradation during irradiation. This absorption was calculated as carbonyl index (I_{co}), hydroxyl index (I_{OH}) and polyene index (I_{PO}).

M=Co,Ni ,   R=C$_{14}$H$_{14}$N
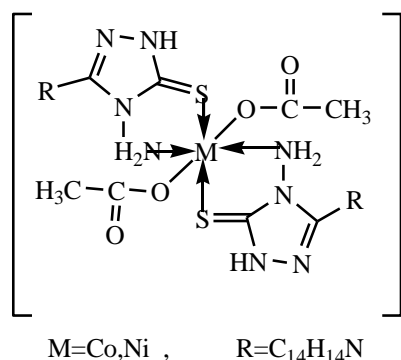
Figure 3. Suggested structure of the complexes A1 and A2.
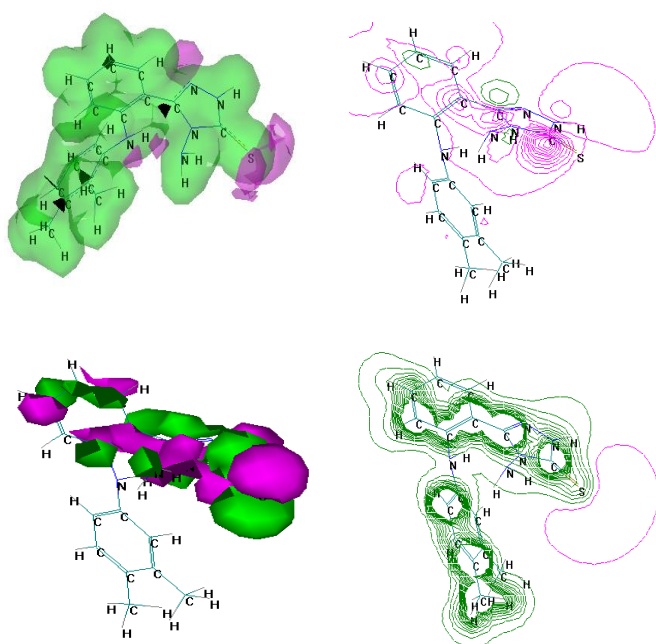
Figure 4. HOMO and LUMO 3D (a) and 2D (b) and electrostatic potential 3D (c) and 2D (d) contours for **L**.

**Table 4.** Conformation energetic (in kJ mol^{-1}) for the ligand and its metal complexes.

Compound	PM3	
	ΔH^o_f	ΔE_b
L	532.958	-17237.78
A1	-82634.277	-241013.37
A2	-781.116	-41912.129
A3	211.67	-35667.124
A4	855.52	-34816.181
A5	1005.164	-34647.978

It is reasonable to assume that the growth of carbonyl index is a measure to the extent of degradation. However, in Figure 6, the Ico of **L>A3>A4>A5>A1>A2** showed lower growth rate with irradiation time with respect to the PVC control film without additives.

**Table 5.** Selected bond lengths (A^0) for ligand (**L**) and its metal complexes.

Compounds	C=S	N-NH$_2$	M-S	M-N	M-O
L	1.634	1.430	-	-	-
A1	1.758	1.821	2.277	1.873	1.373
A2	1.762	1.488	2.284	1.882	1.282
A3	1.732	1.870	2.468	2.132	-
A4	1.771	2.754	2.137	1.8457	-
A5	1.751	3.345	2.270	1.956	-

Because the growth of carbonyl index with irradiation time is lower than PVC control, as seen in figure 7, it is reasonable to conclude that these additives might be considered as photostabilizers of PVC polymer. Efficient photostabilizer shows a longer induction period. Therefore, the **A2** is the most active photostabilizer, followed by **A1**, **A5**, **A4**, **A3**, and **L** which is the least active. Just like carbonyl, hydroxyl and polyene compounds are also produced during photodegradation of PVC. Therefore, I$_{OH}$ and I$_{PO}$ could also be monitored with irradiation time in the presence and absence of these additives. Results are shown in Figures 7 and 8.
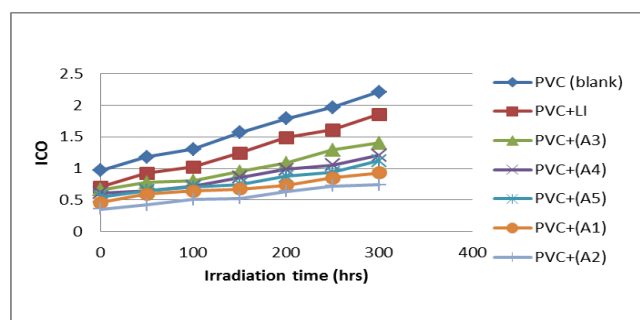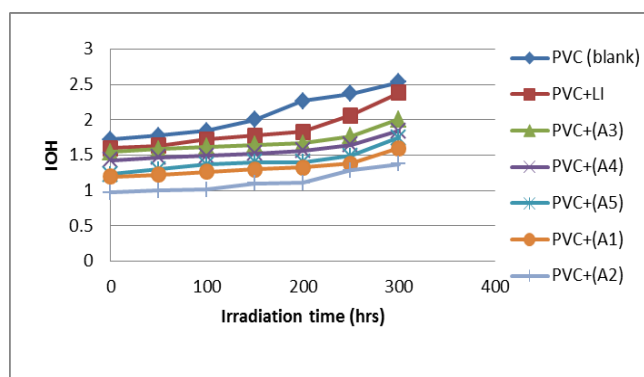

**Figure 6.** Relationship between the I_{CO} and irradiation time of PVC films of 40 μm thickness.

The photodegradation of PVC is commonly known to be accompanied by a dehydrochlorination process (the evolution of HCl gas) consequently, weight loss occurs, which increases with increasing irradiation time. The stabilizing efficiency was determined by measuring the % weight loss of photodegraded PVC films in the absence and in the presence of additives. The weight loss percentage as a function of the irradiation time can be used as a good measure of the degree of degradation and consequently can measure the stabilizing potency of the stabilizer and how long that stabilizer would protect the polymer.[31] The results of the weight loss as a function of the irradiation time is shown in Figure 9. The results clearly showed the low extent of weight loss (i.e., the low extent of dehydrochlorination as evolved HCl is the main degradative product) of photodegraded PVC stabilized by the complexes of (**L**) in comparison with the weight loss of photodegraded unstabilized PVC. The stabilizing efficiency of the investigated photostabilizers was found to follow the order: PVC >**L>A3>A4>A5>A1>A2**.
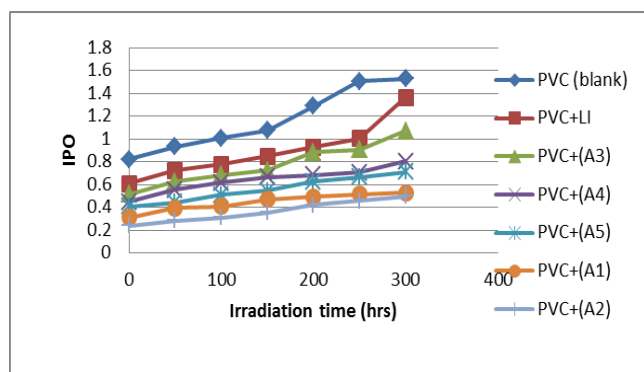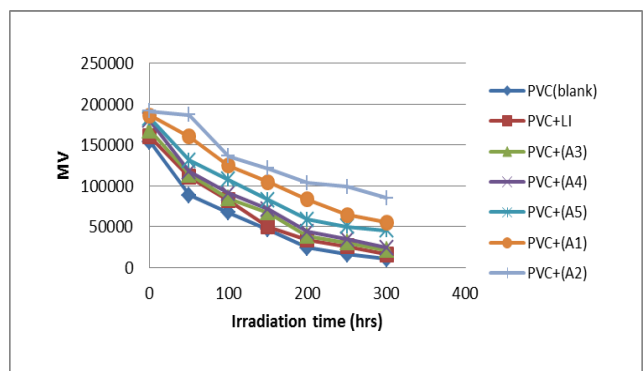
Figure 7. Relationship between the I_{po} and irradiation time of PVC films (40 μm) thickness containing 0.5 % additives.

Figure 8. Relationship between the I_{OH} and irradiation time for PVC films of 40 μm thickness.
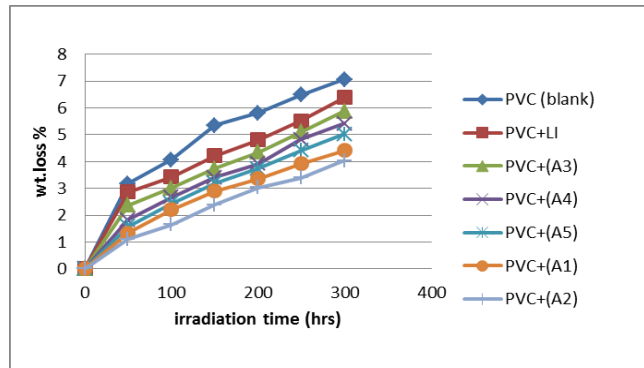
Figure 9. Variation of the weight loss of PVC films of 40 μm thickness with the irradiation time.


Figure 10. Variation of the viscosity average molecular weight with irradiation time of PVC films of 40 μm thickness.

The analysis of relative changes in viscosity–average molecular weight (Mav) has been shown to provide a versatile test for random chain scission. Figure 10 shows the plot of (Mav) versus irradiation time, with absorbed light intensity of 1.052×10^{-8} ein dm^{-3} s^{-1}, for PVC film with and without 0.5% (wt/wt) of the selected additives. Mav is measured using eqn. (3) with THF as a solvent at 25 ^{0}C. It is worth mentioning that traces of the films with additives are not soluble in THF, indicating that crosslinking or branching in the PVC chain does occur during the course of photolysis.[30,32] For better support of this view, the number of average chainscission (S; average number cut per single chain) was calculated using eqn. (7).

$$S = \frac{M_{av,0}}{M_{av,t}} - 1 \qquad (7)$$

where $M_{av,o}$ and $M_{av,t}$ are viscosity–average molecular weights at initial (zero) and at irradiation time (t), respectively. The plot of S versus time is shown in Figure 11. The curve indicates an increase in the degree of branching such as that might arise from crosslinking occurrence. It is observed that insoluble material was formed during irradiation, which provided an additional evidence to the idea that crosslinking does occur.
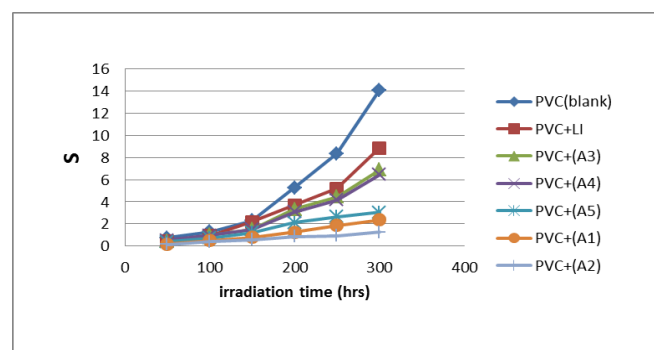

Figure 11. Changes in the main chain scission (S) during irradiation of PVC films of 40 μm thickness.

For randomly distributed weak bond links, which rapidly break in the initial stages of photodegradation, the degree of deterioration α is given by eqn.(8).

$$\alpha = \frac{mS}{M_{av}} \qquad (8)$$

where m is the initial molecular weight.

The plot of α as a function of irradiation time is shown in Figure 12. The values of α of the irradiated samples are higher when additives are absent and lower in the presence of additives when compared with the corresponding values of the additive-free PVC. In the initial stages of photodegradation of PVC, the value of α increase rapidly with time; these indicators indicate a random breaking of bonds in the polymer chain.
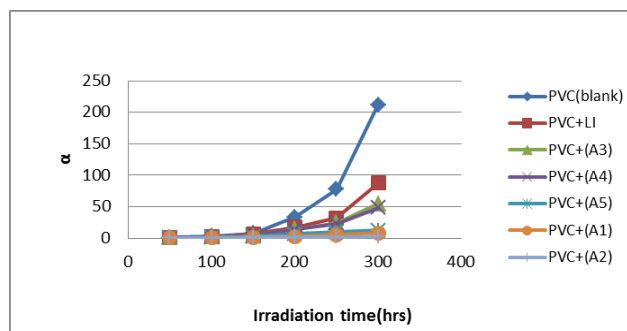
Figure 13. Changes in the degree of deterioration (α) during irradiation of PVC films of 40 μm thickness.

Mechanism of the photostabilization

Depending on the overall results obtained, the efficiency of the complexes as stabilizer for PVC films can be arranged according to the changes in the carbonyl and hydroxyl concentration as a reference for comparison and the efficiency is **A2>A1>A5>A4>A3>L**. Metal chelate are generally known as photostabilizers for PVC through both peroxide decomposer and excited-state quencher. Therefore, it is expected that these complexes act as peroxide decomposer (Scheme 2).[30,32] The ring of benzothiazol in this compound plays an important role in the mechanism of stabilizing process by acting as UV absorber. The UV light absorption by these additives containing benzothiazol dissipates the UV energy to harmless heat energy (Scheme 3). This mechanism is in agreement with that reported ones.[32,33]
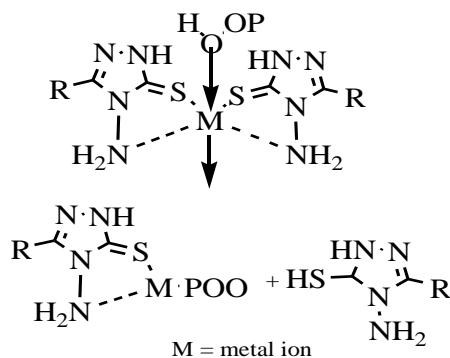
Scheme 2. Suggested mechanism of photostabilization of complexes as peroxide decomposer.
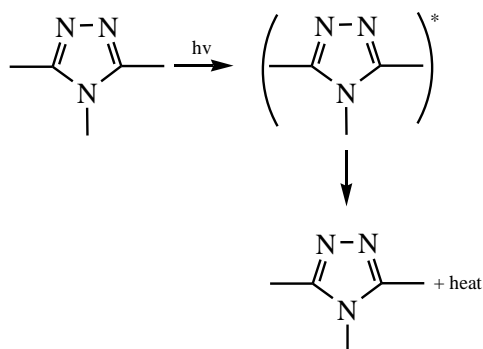
Scheme 3. Suggested mechanism of photostabilization of triazole as UV-absorber.

References

[1]Jones,D. H., Slack, R. S.,Woolridge, K. R. H., *J. Med. Chem.*, **1965**, *8*, 676.

[2]Goswami, B. N., Katiki, J. C. S., Baruah, J. N., *J. Heterocyclic Chem.*, **1984**, *2*, 225.

[3]Holla, B. S., Kallurya, B., Sridhar, K. R., *Current Sci.*, **1987**, *56*, 236.

[4]Abdon, N. A., Amin, F. M., Mansura. A, J., *Pharm. Sci.*, **1990**, *6*, 25.

[5]Mishra, R. K., Tiwari, R. K., Srivastava, S. K., Bahel, S. C.*, J. Indian Chem. Soc.*, **1991**, *68*, 110.

[6]Street, L. J., Baker, R., Baker, W. B., Davey, W. B., Guibin, A. R., Jelley, R. A., *J. Med. Chem.*, **1995**, 38, 1799

[7]Brucato, A. , Coppola, A. , Gianguzza, S., Provenzano, P. , *Boll. Soc. Ital. Biol. Sper.*, **1978**, *54*, 1051-1057.

[8]Raslan, M. A., Khalil, M. A., *J. Heteroatom Chem.*, **2003**, *14*, 114-120.

[9]Singha, T., Singh, J., Naskar, A., Ghosh, T., Mondal, A., Kundu, M., Harwansh, R. K., Maity, T. K., *Indian J. Pharm. Educ. Res.*, **2012**, *46 (4),* 346-351.

[10]Awad, I., Abdel-Rahman, A., Bakite, E., *J. Chem. Technol. Biotechnol.*, **2008**, *51*, 483–486.

[11]Guveli, S., Ulkuseven, B., *Polyhedron*, **2011**, *30 (8),* 1385-1388.

[12]Alagöz, C. D., Brauer, J., Mohr F., *J. Organomet. Chem.*, **2009**, *694*, 1283-1288.

[13]Jaiswal, N., Singh, A. K., Singh, D., Ahmad, T, Int. Res. J. Pharm., **2012***, 3(3),* 83–89

[14]Grassie, N., Scott, G., *Polymer Degradation and Stabilization*, Cambridge University Press, London, UK, **1985.**

[15]Andrady, A. L., Hamid, S. H., Hu, X., Torikai, A., *J. Photochem. Photobiol.B*., **1988**, *46*. 96–103.

[16]Boehner, B., Dawes, D., Meyer, W., Sturm, E., DE2500485, 1975.

[*17*]Mahajan, D. P., Bendre, R. S., *J. Drug Design Discov,*, **2011**, *2(2),* 464.

[18]Mandal, V., Sen, S. K., Mandal, N.*, Indian J. Microbiol.*, **2011**, *51*, 22-29

[19]Stewart, J. J., Lipkowitz, K. B., Boyd, D. B., (eds.), *Reviews in Computational Chemistry*, John Wiley & Sons, **1996**, 72-80.

[20]Cook, D. B., *Handbook of Computational Quantum Chemistry*, Oxford University Press, Oxford, **1998**, 149.

[21]Choinacki, H., Pruchnik, F., *Int. J. Mol. Sci*., **2001**, *2(44)*, 11-17.

[22]Nahari, T. T.,   ISESCO Sci. Tech. Vision, **2007**, *3(3)*, 32-40.

[23]Rabek, J. F, *Photostabilization of Polymers:Principles and Application*, Elsevier, England, 19990.

[24]Silvertein, R., Bassler, G., *Spectrometric identification of organic compounds*, 5th Edition, John Wiley & Sons, New York, **1980**.

[25]Sliverstein, R., Bassler, G., Morrill, T., *Spectrometric Identification of Organic Compounds*, 7th Edition, John Wiley & Sons, New York, **2005**.

[26]Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 6th Edition, JohnWiley & sons, New York, **1997**.

[27]Qurban, S., *J. Pure Sci*., **2011**, *7 (2)*, 94–104.

[28]Thakar, A. S., Simgh, K .K., Joshi*, K. T., Eur. J. Chem.*, **2010**, *1*, 1396-1406.

[29]Atlas, M. R., Alfres, E., Alfres, B., Lawrence, C. P., *Laboratory manual. Experimental Microbiology*, Mosby- Year Book, Inc., **1995**.

[30]Yousif, E. A., Aliwi, S. M., Ameer, A. A., Ukal, J.R., *Turk. J. Chem*., **2009**, *33*, 39–410.

[31]Yousif, E., Salimon, J., Salih, N.,. *Arabian J. Chem*., **2014**, *7*, 306-311.

[32]Gugumus, F., *Mechanism of Polymer Degradation and Stabilization*, Elsevier, Amsterdam, **1990**.

[33]Adil, H., Yousif, E., Salimon, J., *New Stabilizers for PVC Based on Benzothiazole Complexes*, LAMBERT Academic Publishing, Germany, **2011**.