Synthesis, Characterization, Theoretical studies and Photostability of Mefenamic acid Derivative with some divalent metal ions

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ABSTRACT: A new Mefenamic acid derivative [(4-amino-5-(2-(2,3- dimethylphenyl)aminophenyl)-1,2,4-triazole-3-thion)[L], was synthesized and characterized by (FT-IR), UV-Vis and ¹H,¹³C-NMR Spectroscopy as well as elemental analysis (C.H.N).[L] has been used as a chelating ligand to prepare some complexes of (Co(II), Ni(II), Cu(II), Zn(II)and Cd(II)) ions. The prepared complexes were identified and their geometrical were suggested in solid state by using (FT-IR) and (UV-Vis) spectroscopy ,elemental analysis(C.H.N), Flame atomic absorption technique, in addition to magnetic susceptibility and conductivity measurements. The work also include a theoretical treatment of the formed complexes in the gas phase, this was done using the (hyperchem-8) program for the molecular mechanics and semi-empirical calculations. The heat of formation (ΔH°) and binding energy (ΔE_b) for ligand and their complexes were calculated by (PM3) method at 298 K. It was found that the ligand [L] and its metal complexes were stable, which agreed well with the experimental studies in solid state. Furthermore the electrostatic potential of the free ligand [L] was calculated to investigate the reactive sites of the molecules. PM3 were used to evaluate the bond length and vibrational spectra for the ligand [L] and their metal complexes then comparing with the experimental values.

The work, which also included the induce Photostabilization of (PVC) film in air was investigated in the absence and presence of [L] and its complexes with transition metals (Co(II), Ni(II), Cu(II), Zn(II)and Cd(II)) by accelerated weathering tester. Polymer has been mixed with these complexes in solvent which containing of complex 0.5 % by weight. The photostabilization activity of these compounds was determined by monitoring the carbonyl (I_C=O),polyene(Ipo) and hydroxyl (I_OH) indexes, weight loss method with irradiation time. It was found that the (I_C=O) (Ipo) and (I_OH) indexes values increased with irradiation time and this increase depend on the type of additives.

KEYWORDS: Triazole, Photochemistry, Metal complexes, PVS, UV light, Theoretical treatment, photostability.

1 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 (Jones et al., 1965; Goswami et al., 1984; Holla et al., 1987; Abdon et al., 1990; Mishra et al., 1991; Street et al.,1995). There are known drugs containing the 1,2,4-triazole group e.g. Triazolam( Brucato et al., 1978), Alprazolam (Raslan et al.,2003), Etilzolam, and Furaclylin(Singha et al.,2012). N4-amino and 3-thione of 1,2,4-triazoles with substitution at 5-position have been studies as anti-inflammatory and antimicrobial agents (Awad et al., 2008). 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, isothiocyanates and thiosemicarbazides or involved in heterocyclic ring, e.g. mercapto derivatives of triazoles, oxadizoles and thiodiazoles (Guveli and Ulkuseven, 2011; Alagöz et al.,2009; Jaiswal,2012). In this work, we report the preparation of the new (4-amino-5-(2-(2,3-dimethylphenyl)aminophenyl) -1,2,4-triazole-3-thion )as a ligand(L), in an attempt to introduce the Mefenamic acid substituted at 5-position in the structure of 4-amino-3-thione-1,2,4-triazole
Synthesis, Characterization, Theoretical studies and Photostability of Mefenamic acid Derivative with some divalent metal ions

ring, to investigation of the coordination behavior of the prepared new ligand(L) compound towards[Co(II), Ni(II), Cu(II), Zn(II) and Cd(III)] metal ions. Theoretical study in the gas phase by using semi-empirical method in order to show the most stable conformation and to compare this results with the experimental data. Also the prepared complexes of (4-amino-5-(2-(2,3-dimethylphenyl) aminophenyl) -1,2,4-triazole-3-thion ) were used to enhance the photostabilization Polymer(PVC),by mixing with these complexes in solvent which containing 0.5 % by weight of complex, which produced by the casting method from THF solvent. The photostabilization of polymer films were studied at room temperature under irradiation of light λ=313 nm wave lengt with intensity 6.02*10^5Ein Dm^{-2} S^{-1}. The photostabilization activity of these compounds was determined by monitoring the carbonyl (ν_c=1650 cm^{-1}), polyene (ν_π=8300 cm^{-1}) and hydroxyl (ν_ω=3432 cm^{-1}) indexes, weight loss method with irradiation time. It was found that the (ν_c), (ν_π) and (ν_ω) indexes values increased with irradiation time and this increase depend on the type of additives. (Andrady et al., 1988; Grassie and Scott, 1985).

2 MATERIALS AND METHODS

2.1 INSTRUMENTATION

Melting points were recorded on a Gallenkamp MF B600 010F melting point apparatus .Elemental analyses (C.H.N.S) were obtained using EA-034.mth. for ligand and their metal complexes. Bruker Spectrophotometer model ultra-shield at 300 MHz(H-NMR and ^{13}C).Metal contents of complexes were estimated spectrophotometrically using Flame atomic absorption Shimadzu-670 AA Spectrophotometer. Infrared spectra were recorded using FT-IR-8300 Shimadzu in the range of (4000-400) cm^{-1}. 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-1-1Mark V by using platinum electrode (EDC 304) with cell constant (1cm^{-1}), concentration (10^{-3} M) in dimethylformamide as a solvent at room temperature. Electronic spectra were obtained using UV-1650PC-Shimadzu Spectrophotometer at room temperature, the measurement were recorded using a concentration of (10^{-5}M) of the (L) ligand and their metal complexes in dimethylformamide as a solvent.

2.2 SYNTHESIS OF LIGAND (L)

The (L) was prepared starting from Mefenamic acid (MFA) according to the general steps (Beat et al.,1975; Mahajan et al.,2011; Mandal et al.,2011), scheme(1).

2.2.1 PREPARATION OF (2-(2,3-DIMETHYL PHENYL)AMINO ETHYL BENZOATE (G_1))

Sulphuric acid (8 ml) was added dropwise with continuous stirring to a solution of carboxylic acid (Mefenamic acid) (0.1 mol) in 200ml ethanol. The mixture was heated under reflux for 10 hours. On cooling, the mixture was poured on to crushed ice , the precipitated crystalline solid was filtered, washed with water, followed by 10% sodium hydrogen carbonate solution and finally with water then the crude product was recrystallized from ethanol, to give (84%) yield of compound (G_1), off white crystal with melting point (108-110)°C.

2.2.2 PREPARATION OF (2-(2,3-DIMETHYL PHENYL)AMINO ETHYL BENZOHYDRAZIDE (G_2))

Ester of (G_1) (0.1 mol) was dissolved in absolute ethanol (50ml). To the above solution was added hydrazine hydrate 80% (0.1mol). The resulting reaction mixture was refluxed on a steam bath for 10-12 hours. On cooling, cold water (150 ml) was added to the mixture and the separated white crystalline solid was filtered, washed with cold water, dried and crystallized from ethanol, to give (82%) yield of compound (G_2), white colors with melting point (156-158)°C.

2.2.3 PREPARATION OF (2-(2,3-DIMETHYL PHENYL)AMINO ETHYL BENZOYLHYDRAZINE CARBODITHIOATE (G_3))

Compounds (G_2) (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 (G_3) was filtered, washed with cold methanol and dried.
2.2.4 Preparation of Ligand (4-amino-5-(2-(2,3-dimethylphenyl)aminophenyl)-1,2,4-triazole-3-thion) (L)

A mixture of compound \( G_3 \) (0.05 mol) and 80% hydrazine hydrate (10 ml) was heated under reflux till the evolution of hydrogen sulphide completely down (about 6 hour). On cooling, water (200 ml) was added and the mixture was neutralized with 10% hydrochloric acid and allowed to stand for three hours. The separated crude product was filtered, washed with water, dried and crystallized from ethanol, to give (80%) yield of compound (L), white powder with melting point \( (215-217) \) C.

<table>
<thead>
<tr>
<th>Scheme 1</th>
<th>Synthesis of Ligand (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image.png" alt="Reaction Scheme" /></td>
<td></td>
</tr>
</tbody>
</table>

2.2.5 Preparation of Metal Complexes of (L) \([A_1 – A_5]\)

The salts of \([\text{Co(CH}_3\text{COO})_2.4\text{H}_2\text{O, Ni(CH}_3\text{COO})_2.4\text{H}_2\text{O,Cu(CH}_3\text{COO})_2.\text{H}_2\text{O, }\text{Zn (CH}_3\text{COO})_2.2\text{H}_2\text{O and Cd(CH}_3\text{COO})_2.2\text{H}_2\text{O}]\) were dissolved in ethanol and added to an ethanolic solution of (L) in (1:2) (metal : ligand) mole ratio respectively with stirring. The reaction mixture was heated under reflux for (4) hours, 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 (C.H.N), flame atomic absorption, FT-IR and Uv-Vis spectrophotometers, magnetic and conductivity measurements.

3 Programs Used in Theoretical Calculation

3.1 Hyperchem-8

It is a sophisticated molecular modeler editor and powerful computational package, that is known for its quality, flexibility and ease of use, uniting 3D visualization and animation with quantum chemical calculations, mechanic and dynamic (Stewart et al, 1996; Cook, 1998).

3.2 Types of Calculation

a) Single point, b) Geometry optimization, c) Vibrational frequency, d) Bond length

3.3 Computational Methods

Hyperchem offers ten semi-empirical molecular orbital methods, with options for organic and main group compounds for transition metal complexes and spectral simulation (Choinacki and Pruchnik, 2001; Nahari, 2007). Choose 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.
4 PHOTOSTABILIZATION OF POLYMER

EXPERIMENTAL TECHNIQUES

4.1 FILMS PREPARATION

Commercial PVC supplied by Petkim Company (Turkey) was re-precipitated from THF solution by times and finally dried under vacuum at room temperature for 24 hours. Fixed concentrations of poly vinyl chloride solution (5 g/100 ml) 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 hours (Yousif et al., 2009). To remove the possible residual THF solvent, film samples were further dried at room temperature for three hours under reduced pressure. The films were fixed on stands specially used for irradiation. The stand is provided with an aluminum plate (0.6 mm in thickness) supplied by Q-panel company.

4.2 IRRADIATION EXPERIMENTS

Accelerated testing technique 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 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.

4.3 PHOTODEGRADATION MEASURING METHODS

A. MEASURING THE PHOTODEGRADATION RATE OF POLYMER FILMS USING INFRARED SPECTROPHOTOMETRY

The degree of photodegradation of polymer film samples was followed by monitoring FTIR spectra in the range 4000–400 cm\(^{-1}\) using FTIR 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 equation (1)

\[
I_s = \frac{A_s}{A_r}
\]

where

As = Absorbance of peak under study, Ar = Absorbance of reference peak, Is = Index of group under study

Actual absorbance, the difference between the absorbance of top peak and base line (ATop Peak – A Base Line) is calculated using the Base Linemethod.

B. DETERMINATION OF AVERAGE MOLECULAR WEIGHT MV USING VISCOMETRY METHOD.

The viscosity property was used to determine the average molecular weight of polymer, equation (2), using the Mark-Houwink relation.

\[
[\eta] = K M^\alpha
\]

where:

[\eta] = The intrinsic viscosity, K, \(\alpha\) 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) and the flow times of polymer solution and pure solvent are \(t\) and \(t_0\) respectively. Specific viscosity (\(\eta_{sp}\)) was calculated as follows, equation (3):
\[ \eta_{re} = \frac{h}{c} (3) \]

Where: \( \eta_{re} \) = Relative viscosity.

\[ \eta_{sp} = \eta_{re} - 1 (4) \]

The single-point measurements were converted to intrinsic viscosities by the equation (5):

\[ [\eta] = \left(\frac{\eta_{sp}}{C} - \ln \eta_{re}\right)^{\frac{1}{2}} (5) \]

Where: \( C \) = Concentration of polymer solution (g/100 ml)

By applying equation (5), the molecular weight of degraded and undergirded polymer can be calculated. Molecular weights of PVC with and without additives were calculated from intrinsic viscosities measured in THF solution using the following equation (6):

\[ [\eta] = 4.17 \times 10^{-4} M^{0.6} (6) \]

5 RESULTS AND DISCUSSION:

PART (I) STUDY COMPLEXES IN SOLID STAT

A-ELEMENTAL ANALYSES

The physical and analytical data of the (L) ligand and \([A_1- A_5]\) metal complexes are given in Table (1). The results obtained from elemental analysis are in satisfactory agreement with the calculated value. The suggested molecular formula was also supported by spectral measurement as well as magnetic moment. The new (L) ligand was soluble in common organic solvents such as (ethanol, acetone and methanol), whereas \([A_1 - A_5]\) of new complexes colored crystalline solid complexes were soluble in (CHCl\(_3\), DMF and DMSO).

\[ \begin{array}{|c|c|c|c|c|c|c|c|c|}
\hline
\text{Comp NO.} & \text{Color} & \text{Melting point} & \text{Yield} & \text{Metal analysis found} & \text{Calc.} & \text{Suggested formula} \\
\hline
L & White & 213-217 & 80 & 61.73 & 5.47 & 22.51 & 10.29 & - & (C\(_{16}\)H\(_{17}\)N\(_5\)S) \\
[A_1] & Brown & 234d & 90 & 54.07 & 5.01 & 17.52 & 8.01 & 7.37 & [Co(C\(_{32}\)H\(_{34}\)N\(_{10}\)S\(_2\))(CH\(_3\)COO)\(_2\)] \\
[A_2] & Yellowish green & 260d & 78 & 54.09 & 5.01 & 17.53 & 8.01 & 7.35 & [Ni(C\(_{32}\)H\(_{34}\)N\(_{10}\)S\(_2\))(CH\(_3\)COO)\(_2\)] \\
[A_3] & Dark green & 250d & 88 & 53.76 & 4.98 & 17.42 & 7.97 & 7.90 & [Cu(C\(_{32}\)H\(_{34}\)N\(_{10}\)S\(_2\))(CH\(_3\)COO)\(_2\)] \\
[A_4] & Off white & 200d & 90 & 53.64 & 4.97 & 17.38 & 7.95 & 8.12 & [Zn(C\(_{32}\)H\(_{34}\)N\(_{10}\)S\(_2\))(CH\(_3\)COO)\(_2\)] \\
[A_5] & Off white & 270d & 85 & 50.62 & 4.69 & 16.40 & 7.49 & 13.17 & [Cd(C\(_{32}\)H\(_{34}\)N\(_{10}\)S\(_2\))(CH\(_3\)COO)\(_2\)] \\
\hline
\end{array} \]

B-NUCLEAR MAGNETIC RESONANCE SPECTRA

(1) PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF (L)

The nuclear magnetic resonance spectra of the newly synthesized ligand (L) gave satisfactory spectra data and the molecular structure was assigned on the basis of \(^1\)H.N.M.R chemical shifts. The spectra were determined in d\(_6\)DMSO solution as an internal reference. According to the results obtained from the chemical shifts spectra, the molecular structure of the
ligand can be illustrated: \( \delta H_{(1,2)} = 2.095-2.281 \text{ppm} \) (6H, s, CH\(_3\)), \( \delta H_{(3)} = 5.3 \text{ppm} \) (2H, s, NH\(_2\)), \( \delta H_{(4)} = 9.47 \text{ppm} \) (1H, s, NH), \( \delta H_{(5)} = 12.41 \text{ppm} \) (1H, s, NH), \( \delta Ph = 6.706-7.89 \text{ppm} \) (7H). Figure (1).

\( \delta H_{(1,2)} = 2.095-2.281 \text{ppm} \) (6H, s, CH\(_3\)), \( \delta H_{(3)} = 5.3 \text{ppm} \) (2H, s, NH\(_2\)), \( \delta H_{(4)} = 9.47 \text{ppm} \) (1H, s, NH), \( \delta H_{(5)} = 12.41 \text{ppm} \) (1H, s, NH), \( \delta Ph = 6.706-7.89 \text{ppm} \) (7H). Figure (1).

(2) \( ^{13}\text{C} \) NUCLEAR MAGNETIC RESONANCE SPECTRA OF (L)

The data of \( ^{13}\text{C} \)-NMR 1,2,4-triazole displayed good solubility in DMSO. The data gave additional support for the composition of the complexes. The observed changes are evidences of complexation had happened because the chemical shift of a compound is heavily depended on its electronic environment, Fig(2) 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.

C- INFRARED SPECTROSCOPIC STUDY

The characteristic stretching vibration modes concerning (L) and its metal complexes [A\(_{1}-A_{5}\)] are described in Table (2). (L) exhibited band at(3439),(3209,3269),(1643),(1041),(1591),(1380),(976,956) and (804) cm\(^{-1}\), these can be assigned to \( \nu(NH) \), (\( \nu_{s}NH_{2} \) and \( \nu_{as}NH_{2} \)), \( \nuC=N \), \( \nuC=S \), \( \delta NH, \nuC=N \), Thioamid(I)), \( \nu(N\cdots C\cdots S) \), Thioamid (III)) and \( \nu(C-S) \), Thioamid (IV)) respectively[20]. In all complexes [A\(_{1}-A_{5}\)], the ligand (L) behave as a bidentate coordinating with metal through sulfur of thiocarbonyl and nitrogen of amino group, therefor the bands due to \( \nu(C=S) \), (\( \nu_{s} \) and \( \nu_{as} \) of NH\(_2\)) and four (I-IV) thioamide bands were shifted to a lower frequency as in Table (2). As well as a new bands for complexes (A\(_{1}\) and A\(_{2}\)) in the region (1521,1537) cm\(^{-1}\) which may be assigned to the asymmetric vibration of coordinated carboxylate groups (\( \nu_{as}coo^{-} \)) and the bands in the region (1302-1305) cm\(^{-1}\) may be attributed to the symmetric vibration of carboxylate group (\( \nu_{s}coo^{-} \))[Silvertein and Bassler,1980; Silverstein et al.,2005]. The large differences between the frequencies of (\( \nu_{as}coo^{-} \)) and (\( \nu_{s}coo^{-} \)),(\( \Delta v>200\text{cm}^{-1} \)) in [A\(_{1}\) and A\(_{2}\)] complexes are indicative of the involvement of the coordination of the carboxylate groups to the metal ion in a monodentate fashion (Silvertein and Bassler,1980; Nakamoto,1997).On Comperision with [A\(_{1}\)] and [A\(_{2}\)] complexes, the newly synthesized copper, zinc and cadmium complexes[A\(_{3}\),A\(_{4}\) and A\(_{5}\)] show appearance of new bands in the region (1655-1665cm\(^{-1}\)) which may be assigned to the vibration of un coordinated carboxylate groups. Other low intensity bands observed in the region (445-460),(518-520) and (523-544) cm\(^{-1}\) are attributed to \( \nu(M-S) \) and \( \nu(M-N) \) respectively in the all complexes except (A\(_{1}\) and A\(_{2}\)) and \( \nu(M-O) \) in the case of (A\(_{1}\) and A\(_{2}\)) complexes modes respectively (Qurban,2011; Nakamoto,1997)
Table 2 stretching vibrational frequencies (cm⁻¹) located in the FT-IR spectra of (L) and their metal complexes

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>ν_C=S</th>
<th>ν_C=N</th>
<th>ν NH₂ (as,s)</th>
<th>ν NH</th>
<th>ν_COO (as,s)(Coord.)</th>
<th>ν_COO uncoord.</th>
<th>M-N</th>
<th>M-S</th>
<th>M-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1041</td>
<td>1643</td>
<td>(3269,3209)</td>
<td>3439</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[A₁]</td>
<td>1020</td>
<td>1640</td>
<td>(3252,3212)</td>
<td>3441</td>
<td>(1537,1305)</td>
<td>-</td>
<td>530</td>
<td>459</td>
<td>523</td>
</tr>
<tr>
<td>[A₂]</td>
<td>1030</td>
<td>1643</td>
<td>(3263,3211)</td>
<td>3440</td>
<td>1512,1302(1)</td>
<td>-</td>
<td>532</td>
<td>457</td>
<td>540</td>
</tr>
<tr>
<td>[A₃]</td>
<td>1030</td>
<td>1640</td>
<td>(3252,3200)</td>
<td>3439</td>
<td>-</td>
<td>1665</td>
<td>529</td>
<td>460</td>
<td>-</td>
</tr>
<tr>
<td>[A₄]</td>
<td>1022</td>
<td>1640</td>
<td>(3252,3194)</td>
<td>3440</td>
<td>-</td>
<td>1655</td>
<td>530</td>
<td>455</td>
<td>-</td>
</tr>
<tr>
<td>[A₅]</td>
<td>1030</td>
<td>1645</td>
<td>(3240,3155)</td>
<td>3442</td>
<td>-</td>
<td>1660</td>
<td>533</td>
<td>454</td>
<td>-</td>
</tr>
</tbody>
</table>

D-Electronic Spectra, Magnetic susceptibility and conductivity measurements. (Figgis, 2000; Hassan et al., 2008; Ibraheem et al., 2010; Thakar et al., 2010).

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 π→π* and another at 31545, 29411 cm⁻¹ due to n→π*.

A₁: The measured magnetic moment was (4.2 B.M) this show the cobalt ion it,s brown complex typical of d⁷ system with three unpaired electrons indicating a quartet state and suggest high spin octahedral geometry. The electronic spectrum of the brown (A₁) complex in chloroform exhibited two bands at 15384 and 18691 cm⁻¹, assignable to ¹g→¹g (as) and ¹g→¹g (as) transitions respectively for an octahedral geometry of Co(II). The value of various ligand field parameters (ν₁, B₁, B₂ 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 was non electrolyte, Table (3).

A₂: The light green (A₂) complex in chloroform exhibited bands at 15267 and 25974 cm⁻¹ assigned to ³A₂g→¹T₁g (ν₂) and ³A₂g→¹T₁g (ν₃) transitions respectively, Table (2), which indicate octahedral geometry of Ni(II). The absence of any band below 10,000 cm⁻¹ eliminates the possibility of tetrahedral environment in this complex. The different ligand field parameters (B, B' and Dq) have been calculated using the same diagram and found to be (611, 0.54 and 1099.224) respectively (M-L) (Ni-L) bond is covalent. Magnetic moment (3.09 B.M) of solid complex, Table (2), showed a higher orbital contribution. Conductivity measurement in DMF showed that the complex was nonionic, Table (3).

A₃: The measured magnetic moment was (1.92 B.M) this show the Cu(II) ion it,s dark green complex typical of d⁶ system. Electronic spectrum in chloroform, shows one broad band at 14084 cm⁻¹ which corresponds to ¹B₂g→¹A₁g transition, and a shoulder band at 25773 cm⁻¹ which assigned to ³B₂g→¹B₂g 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, Table (3).

The two complexes [A₄] and [A₅] were colourless in chloroform solution, so that no (d-d) transition can be expected in the visible region, as well as were diamagnetic as expected for d¹⁰ ions. The conductivity measurements indicate ionic behavior of the complexes, Table (3).
Table 3  Electronic spectra (CHCl₃), Magnetic moment (B.M) and Conductance in (DMF) for metal complexes

| Symb. | Maximum absorption
<table>
<thead>
<tr>
<th>υₘₐₓ</th>
<th>(cm⁻¹)</th>
<th>Band assignment</th>
<th>10Dq</th>
<th>Molar Cond. S.cm².mol⁻¹</th>
<th>μeff. B.M</th>
<th>Suggested geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A₁]</td>
<td>7039.9 (Cal.) 1538.4 1869.1</td>
<td>²T₁g→²T₂g(F)</td>
<td>⁴T₁g→²A₁g(F)</td>
<td>⁴T₁g→²T₂g(F)</td>
<td>9337.6</td>
<td>15.65</td>
</tr>
<tr>
<td>[A₂]</td>
<td>10992.24 (Cal.) 15267 25974 33112</td>
<td>³A₁g→²T₂g(F)</td>
<td>⁴A₁g→³T₁g(F)</td>
<td>³A₁g→²T₁g(F)</td>
<td>10976</td>
<td>18.09</td>
</tr>
<tr>
<td>[A₃]</td>
<td>14084 25773</td>
<td>⁷B₁g→²A₁g</td>
<td>⁷B₁g→²B₂g+²Eg</td>
<td>C.T</td>
<td>-</td>
<td>168.22</td>
</tr>
<tr>
<td>[A₄]</td>
<td>32258 38167 47619</td>
<td>ILCT</td>
<td>-</td>
<td>166.86</td>
<td>0.0</td>
<td>T.h</td>
</tr>
<tr>
<td>[A₅]</td>
<td>31055 34482 47169</td>
<td>ILCT</td>
<td>-</td>
<td>170.9</td>
<td>0.0</td>
<td>T.h</td>
</tr>
</tbody>
</table>

General Proposed Stereo Chemistry Structure of Complexes [A₁-A₅]:

According to the results obtained from the elemental analysis, spectral studies, magnetic and conductivity measurements, the general structure of the above mentioned complexes [A₁-A₅] can be illustrated as follows:
Part (2) Study Complexes in Gas phase

Theoretical studies of (L) ligand and their metal complexes [A₁-A₅]

a- Electrostatic Potentials

The electrostatic potential (E.P) describes the interaction of energy of the molecular system with a positive point charge. (E.P) 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 (E.P) of the free ligands (L) were calculated and plotted as 3D and 2D contour to investigate the reactive sites of the molecules, Figure (3). The results of calculations show that the LUMO of transition metal ions prefer to react with the HOMO of sulfure and nitrogen atoms of free ligands (L).

b- Optimized energies

The conformations of the free ligands and their complexes obtained from the semi-empirical and molecular mechanics for calculations were fully re-optimized to estimate the heat of formation (ΔHº) and binding energy (ΔEᵃ) by using the (PM3) method for free ligand (L) and their metal complexes is shown in Table (4).

Table 4 Conformation energetic (in KJ.mol⁻¹) for ligands and their metal complexes

<table>
<thead>
<tr>
<th>Comp.</th>
<th>PM3</th>
<th>ΔHº</th>
<th>ΔEᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td></td>
<td>532.958</td>
<td>-17237.78</td>
</tr>
<tr>
<td>[A₁]</td>
<td></td>
<td>-82634.277</td>
<td>-241013.37</td>
</tr>
<tr>
<td>[A₂]</td>
<td></td>
<td>-781.116</td>
<td>-41912.129</td>
</tr>
<tr>
<td>[A₃]</td>
<td></td>
<td>211.67</td>
<td>-35667.124</td>
</tr>
<tr>
<td>[A₄]</td>
<td></td>
<td>855.52</td>
<td>-34816.181</td>
</tr>
<tr>
<td>[A₅]</td>
<td></td>
<td>1005.164</td>
<td>-34647.978</td>
</tr>
</tbody>
</table>
c- Optimized vibrational spectra for ligand (L) and their metal complexes

The vibrational spectra of the free ligand [L] and their metal complexes have been calculated, Tables (5) Figure 5. The theoretically calculated wave numbers for this ligands showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations (Azhary, 1998). The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligands (L) and their metal complexes which included in Table(5) and their respective experimental vibrational modes are shown in the same table, Figure (4).

![Vibrational Spectra](image)

**Figure 4 The Calculated Vibrational frequencies of (L)**

<table>
<thead>
<tr>
<th>Table 5 Comparison of Experimental and Theoretical vibrational Frequencies for the Ligand and their metal complexes(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp.</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>L</td>
</tr>
<tr>
<td>1021**</td>
</tr>
<tr>
<td>1.92***</td>
</tr>
<tr>
<td>[A₁]</td>
</tr>
<tr>
<td>910**</td>
</tr>
<tr>
<td>10.78***</td>
</tr>
<tr>
<td>[A₂]</td>
</tr>
<tr>
<td>1037**</td>
</tr>
<tr>
<td>0.67***</td>
</tr>
<tr>
<td>[A₃]</td>
</tr>
<tr>
<td>945**</td>
</tr>
<tr>
<td>8.25***</td>
</tr>
<tr>
<td>[A₄]</td>
</tr>
<tr>
<td>999**</td>
</tr>
<tr>
<td>-2.25***</td>
</tr>
<tr>
<td>[A₅]</td>
</tr>
<tr>
<td>998**</td>
</tr>
<tr>
<td>-3.10***</td>
</tr>
</tbody>
</table>

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d- Bond length measurements for the (L) and their metal complexes

The Gaussian suite of software was employed throughout this study optimizations were carried out for the model systems represented in Figure (5). The initial state for structure didn’t 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 ligands and its metal complexes by using the semi-empirical (PM3) method at geometry optimization (0.001 Kcal/mol), to give excellent agreement with the experimental data (Kunkeler et al., 1996; Keypour et al., 2004), as it shown in Table (6), Figure (5).

![Figure 5](image_url)
Table 6  Selected bond lengths (Å) for ligands (L ) and their metal complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>C=S</th>
<th>N-NH₂</th>
<th>M-S</th>
<th>M-N</th>
<th>M-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1.634</td>
<td>1.430</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[A₁]</td>
<td>1.758</td>
<td>1.821</td>
<td>2.277</td>
<td>1.873</td>
<td>1.373</td>
</tr>
<tr>
<td>[A₂]</td>
<td>1.762</td>
<td>1.488</td>
<td>2.284</td>
<td>1.882</td>
<td>1.282</td>
</tr>
<tr>
<td>[A₃]</td>
<td>1.732</td>
<td>1.870</td>
<td>2.468</td>
<td>2.132</td>
<td>-</td>
</tr>
<tr>
<td>[A₄]</td>
<td>1.771</td>
<td>2.754</td>
<td>2.137</td>
<td>.8457</td>
<td>-</td>
</tr>
<tr>
<td>[A₅]</td>
<td>1.751</td>
<td>3.345</td>
<td>2.270</td>
<td>1.956</td>
<td>-</td>
</tr>
</tbody>
</table>

**PART (3) PHOTOSTABILIZATION STUDY**

The (4-amino-5-(2-(2,3-dimethylphenyl)aminophenyl)-1,2,4-triazole-3-thion) complexes with Co(II), Cd(II), Ni(II), Zn(II) and Cu(II) 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.

**a). Photochemical Study of(L) complexes with PVC films by infrared spectroscopy**

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 was 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 (Yousif et al., 2009). 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}). It is reasonable to assume that the growth of carbonyl index is a measure to the extent of degradation. However, in Figure (6), the I_{CO} of A₃ > A₄ > A₂ > A₁ > A₅ showed lower growth rate with irradiation time with respect to the PVC control film without additives. Because the growth of carbonyl index with irradiation time is lower than PVC control, as seen in Figure (6), it is suitable 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 (A₃), (A₄), (A₅), and (L) which is the least active. Just like carbonyl, hydroxyl and polyene compounds are also produced during photodegradation of PVC. Therefore, hydroxyl index (I_{OH}) and polyene index(I_{PO}) could also be monitored with irradiation time in the presence and absence of these additives. Results are shown in Figure (7 and 8).

![Figure 6](image-url)

*Figure 6 Relationship between the (I_{CO}) and irradiation time of PVC films (40μm) thickness containing 0.5% additives*
b) Determination of the Stabilizing Efficiency by Weight Loss Method For L and their metals complexes

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 absence and in 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 (Yousif et al., 2009). The results of the weight loss as a function of the irradiation time is shown and 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 degradated product) of photodegraded PVC stabilized by L complexes in comparison with the weight loss of photodegraded unstabilized PVC. The stabilizing efficiency of the investigated photostabilizers was found to follow the order:

\[\text{PVC} > \text{L}_1 > \text{A}_3 > \text{A}_1\]
Synthesis, Characterization, Theoretical studies and Photostability of Mefenamic acid Derivative with some divalent metal ions

Figure 9 Variation of the weight loss of PVC films (40μm) thickness containing 0.5% additives with the irradiation time

c) Variation of PVC molecular weight during photolysis in the presence of (4-amino-5-(2-(2,3-dimethylphenyl)aminophenyl)-1,2,4-triazole-3-thion) complexes

The analysis of relative changes in viscosity–average molecular weight (Mv) has been shown to provide a versatile test for random chain scission. Figure (10) shows the plot of (Mv) versus irradiation time for PVC film with and without 0.5% (wt/wt) of the selected additives, with absorbed light intensity of 1.052*10^-8 ein dm^-3 s^-1. (Mv) is measured using eq. (3) with THF as a solvent at 25°C. It is worth mentioning that traces of the films with additives are not soluble in THF, Figure (10), indicating that cross linking or branching in the PVC chain does occur during the course of photolysis. (Gugumus, 1990; Yousif et al., 2009). For better support of this view, the number of average chain scission (S; average number cut per single chain) was calculated using the following relation:

\[ S = \frac{M_v,o}{M_v,t} - 1 \]

where \( M_v,o \) and \( M_v,t \) are viscosity–average molecular weight at initial (o) 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 cross linking occurrence. It is observed that insoluble material was formed during irradiation, which provided additional evidence to the idea that cross linking does occur.

Figure 10 Variation of the viscosity average molecular weight with irradiation time of PVC films (40 μm) control and with 0.5 wt% of additives
Changes in the main chain scission ($S$) during irradiation of PVC films (40 μm) control and with 0.5 wt% of additives

For randomly distributed weak bond links, which rapidly break in the initial stages of photodegradation, the degree of deterioration $\alpha$ is given as follows:

$$\alpha = \frac{m_s}{M_0}$$

where $m$ is the initial molecular weight. The plot of $\alpha$ as a function of irradiation time is shown in Figure (12). The values of $\alpha$ 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 $\alpha$ increase rapidly with time; these indicators indicate a random breaking of bonds in the polymer chain.

c). Suggested mechanisms of photostabilization of PVC by (4-amino-5-(2-(2,3-dimethylphenyl)aminophenyl)-1,2,4-triazole-3-thion) complexes

Depending on the overall results obtained, the efficiency of 4-amino-5-(2-(2,3-dimethylphenyl)aminophenyl)-1,2,4-triazole-3-thion complexes as stabilizer for PVC films can be arranged according to the change in the carbonyl and hydroxyl concentration as a reference for comparison, $A_1 > A_2 > A_3 > A_4 > A_5 > L$. Metal chelate are generally known as photostabilizers for PVC through both peroxidede composer and excited-state quencher. Therefore, its expected that these complexes act as peroxidede composer through the proposed mechanism Scheme (2). (Yousif et al., 2010). 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 benzothiazoldissipates the UV energy to harmless heat energy Scheme (3). This mechanism is in agreement with that reported (Adil et al., 2011)
Synthesis, Characterization, Theoretical studies and Photostability of Mefenamic acid Derivative with some divalent metal ions

Scheme (2) Suggested mechanism of photostabilization of complexes as peroxide decomposer

Scheme (3) Suggested mechanism of photostabilization of triazole as UV. Absorber

REFERENCES