



Heterocyclic Azo Dyes Derived from Adenine: Synthesis, Spectral Characterization, a wool Dying

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Abstract

The novel (La-PAA) of the ligand 8-[3-(pyrazoyl)azo]Adenine (PAA) was synthesized with the molar ratio (1:3), which was appointed by using the mole ratio method. The C.H.N.S elemental analysis, magnetic measurement, thermal analysis, and spectral methods (UV-Vis, FTIR, and HNMR) were employed to support the mode of binding and geometrical structure for ligand (PAA) and (La-PAA) complex. The FTIR and ¹H N.M.R. spectral results showed that the (PAA) acts as neutral N, N-bidentate with La (III), as well as the absorption results in specific octahedral structures for (La-PAA) complex. The thermal decomposition of the (PAA) ligand and its (La-PAA) complex performed many steps, and the (La-PAA) complex is more thermal stable than the free ligand. The dyeing performance of the free ligand and (La-PAA) complex was tested, and they have straightforward and bright colors. The photostability of the free ligand (PAA) and [La(PAA)₃]Cl₃.3H₂O complex in ethanol at a concentration of (10-4M) and subjecting them to ultraviolet (U.V.) radiation for two hours at room temperature. Finally, this research aimed to synthesize and characterize the ligand (PAA) and its complex, as well as test the ability of the ligand (PAA) and its complex on wool fiber.

Keywords: Azo, dyeing, adenine, spectral study, ligand, complex.

1. Introduction

There are two separate kinds of azo compounds, depending on whether the R1 and R2 are alkyl or aryl groups. The word "azo" is derived from the word "azote," a French word for nitrogen [1,2]. The azo dye era began with the development of Bismarck brown and aniline yellow in the 1860s. [3]. Numerous studies on the synthesis, spectral analysis, physical characteristics, and elemental analysis of various azo dye types and their complexes with lanthanide elements, the lanthanide metal complexes, have been published. In azo dye-containing synthesis in both industrial and inorganic chemistry, ligands constitute a crucial topic of study [4]. Since azo dyes' metal complexes have been extensively researched for use in industrial and spectral analytical applications, there has been a significant interest in azo dyes as chelating ligands and their metal complexes in coordination chemistry [5].



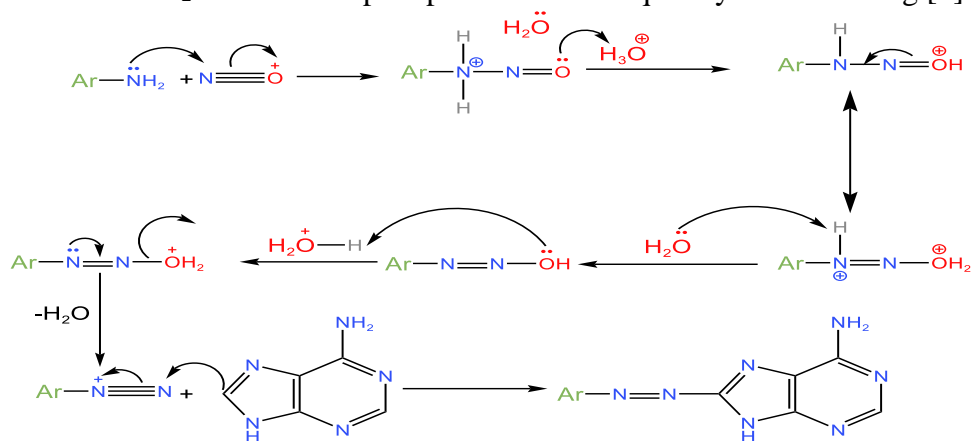
As 60–80% of all organic colorants, azo colorants are the most important category of synthetic dyes. They are widely employed in substrates such as plastic, waxes, textile fibers, mineral oils, papers, food products, cosmetic, and molecular memory storage [6]. Assembling a new ligand (PAA) and applying [La (III)] in this investigation. Dyeing performance for wool was investigated for the ligand (PAA) and La-complex.

2. Materials and Methods

In each instance, the best materials and solvents that were available were used. Analyses of the ligand's elements, metal content, and (La-PAA) complex are evaluated utilizing the (C.H.N.S) (Eure EA 3000 Elemental Analyzer). Infrared Fourier Transform of the series spectrophotometry includes (FT-IR) spectrophotometry, which employs this technique. CsI was utilized to record infrared spectra in the $(250-4000) \text{ cm}^{-1}$ range using the spectrophotometer SHIMADZU 8400s. In order to record UV-Vis spectra for the ligand and (La-PAA) complex under investigation in the range of $(200-1100) \text{ nm}$, a (SHIMADZU 1800 UV-Vis spectrophotometer) was utilized. On a BRUKER AV 400 Avance-III, the $^1\text{H-NMR}$ spectra were measured (400 MHz and 100 MHz). The use of thermal analysis (TGA) is to ascertain the amount of metal present in the synthesized ligands and (La-PAA) complex (SDT Q600 V20.9 Build). The melting points of each chemical were calculated using the Gallenkamps melting point instrument. The molar conductance of metal ion complexes in deionized distilled water (10^{-3} M). A Sherwood scientific auto-magnetic susceptibility balance model was used to test the complex magnetic susceptibility at room temperature.

2.1 Synthesis of azo dyes ligands

At first, the diazonium salt was prepared from 3-aminopyrazol (0.83 g; 0.01), which was dissolved in a mixture of 10 mL of distilled water and 10 ml of conc. CH_3COOH and diazotized at 5°C with a 10% solution of NaNO_2 . The solution was then put in an ice bath for 20–30 minutes with stirring. After that, diazonium salt solution was gradually added to (1.351 g; 0.01 mole) of an alkaline alcoholic solution [10%, 12 mL, NaOH in ethanol] adenine. The resultant mixture was neutralized at pH 5–6, as in **Scheme 1**, and the solution was left to precipitate overnight. This residue was filtrated and washed a number of times with a mixture (1:1) of ethanol and H_2O . The color precipitate was subsequently left for during [7].



Where Ar= 3-aminopyrazole

Scheme 1. Mechanisms of of PAA ligand synthesis.

2.2 Synthesis of La- PAA complex

The $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex was synthesized in a mole ratio of (M:L) (1:3) by adding (0.693 g; 0.003 mole) of the (PAA) ligand in absolute ethyl alcohol to an aqueous solution of metal ion salt $[\text{La}(\text{III})]$ (0.245; 0.001 mole). After 3 hours of refluxing using ethanol: acetone (3:1) as the solvent, the combined solution's outcome was modified using thin layer chromatography (TLC). The colorful precipitate produced was filtered, repeatedly washed with water and ethanol (1:1), and then allowed to dry.

3. Results

3.1 Physicochemical feature

The novel is a yellow-colored azo ligand (PAA) with an adenine core, which was sketched in **Scheme 1**. $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex is dark yellow, solid, amorphous in nature, non-hygroscopic, and stable at room temperature, as well as soluble in water, ethanol, methanol, DMSO, etc. The analytical and physical results are displayed in **Table 1**. The elemental analysis data was found to be in good agreement with the calculated data, and the metal-to-ligand ratio (M:L) is (1:3) stoichiometry. The molar conductance measurement was proposed for the (1:3) electrolytic nature of the complexes in (10^{-3} M) water, as in **Table 1**.

Table 1. Physicochemical advantage of the synthesized compounds.

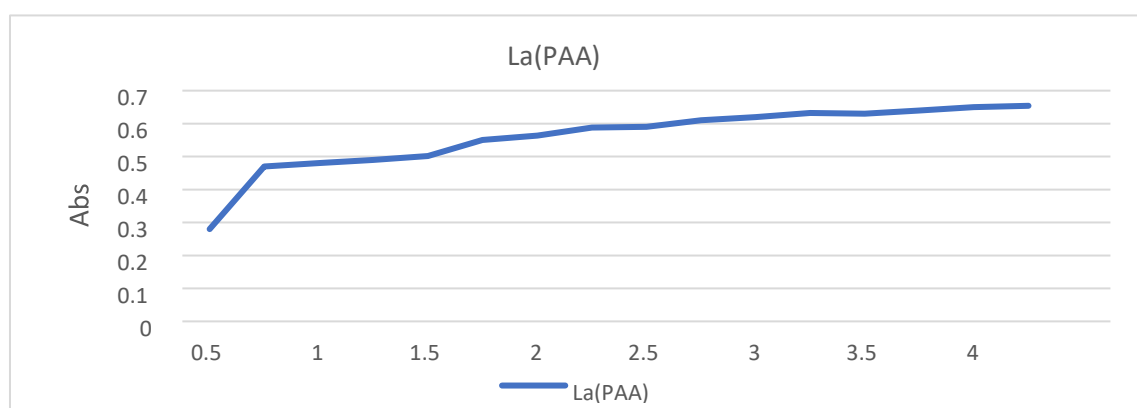
Comp. (M.wt) (gm/mol)	M:L	Color λ (nm)	% Experimental					M.P (C°)	Λ_m (S.mol ⁻¹ .cm ²)
			C	H	N	M	Cl		
PAA(C ₈ H ₉ N ₉) (231.22)	-	Brown 322	41.51 (41.87)	3.89 (3.82)	54.49 (54.88)	-	-	110	-
$[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ (991.57)	1:3	Yellow 334	29.04 (28.45)	3.32 (3.89)	38.12 (37.54)	17.88 18.23	10.45 10.08	360	118.33

3.2 Nature of (La-PAA)

The most often used technique for identifying the kind of complexes formed in a solution that requires separation is the mole ratio approach [8], which was utilized to examine the stoichiometric reaction between the ligand (PAA) and the $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$. The absorbance versus molar ratio of the sample was measured using this method (M: L) when the ligand concentration is adjusted to 0.25 mL while the metal ion concentration remains same, this type of figure permits a significant break. This is because the complex was created, and there is no reliable dissociation. Currently, this shows the composition of complexes. The outcomes are shown in **Figure 1** along with the link between absorbance and (M: L) ratio **Table 2** shows the results for $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ are (1:3) (M:L).

Table 2. Absorbance versus mole ratio for (PAA) and (La-PAA) complex solutions at (λ max).

M:L	Absorbance at λ max (nm)
	La (PAA) (402)
1:0.25	0.28
1:0.5	0.47
1:0.75	0.48
1:1	0.49
1:1.25	0.502
1:1.5	0.55
1:1.75	0.564
1:2	0.588
1:2.25	0.59
1:2.5	0.61
1:2.75	0.62
1:3	0.632
1:3.25	0.63
1:3.5	0.64
1:3.75	0.65
1:4	0.654

**Figure 1.** Molar ratio curves for PAA-La ion solutions at λ max and $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$

3.3 Thermogravimetric analysis (TGA)

The ligand thermal degradation (PAA) and $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex were discussed by TGA in the range (25-800) °C with argon gas. The suggested formula was verified using thermal analysis, which was also used to examine the thermal stability of the synthesized ligand (PAA) with the $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex. The results seem to agree with the formula suggested by the analytical data [9]. **Figures 2 , 3** and **Table 3** explained that the ligand (PAA) was decomposed in three steps, but $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complexes decomposed in four steps.

There is no mass loss up to 270 °C in the case of the ligand, an indication of a lack of moisture, while in the case of $[\text{La}(\text{PAA})_3] \text{Cl}_3 \cdot 3\text{H}_2\text{O}$, the decomposition was up to 25–90.5 °C due to lattice water. The residues of (PAA) and $[\text{La}(\text{PAA})_3] \text{Cl}_3 \cdot 3\text{H}_2\text{O}$ were (26.9%) and (34.17%), respectively, which is an indication that the (La-PAA) is more stable than the ligand.

Table 3. TGA of ligand (PAA) and $[\text{La}(\text{PAA})_3] \text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex.

Comp.	Molecular formula (molecular weight) g/mole	Step	TG. Range of the decompositi on on (0 C°)	Suggested assignment	Calculate %	Found %
PAA	$\text{C}_8\text{H}_9\text{N}_9$ (231.22)	1	25-270	$\text{C}_4\text{H}_9\text{N}_{2.75}$	41.3	42.21
		2	270-360	C_2	10.37	10.23
		3	360-800	$\text{C}_2\text{N}_{1.75}$	20.97	20.66
		Residue	<800 C°	$\text{N}_{4.5}$	27.24	26.9
$[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$	$\text{LaC}_{24}\text{H}_{33}\text{N}_{27}\text{Cl}_3\text{O}_3$ (991.57)	1	(25-90.5) C°	H_{33}O_3	8.06	8.04
		2	90.5- 196.71	$\text{C}_8\text{N}_3\text{Cl}_3$	23.80	23.88
		3	196.71- 543.95	C_8N_8	20.67	20.41
		4	543.95- 800	C_8N_2	12.30	13.08
		Residue	< 800 C°	LaN_{14}	34.17	34.58

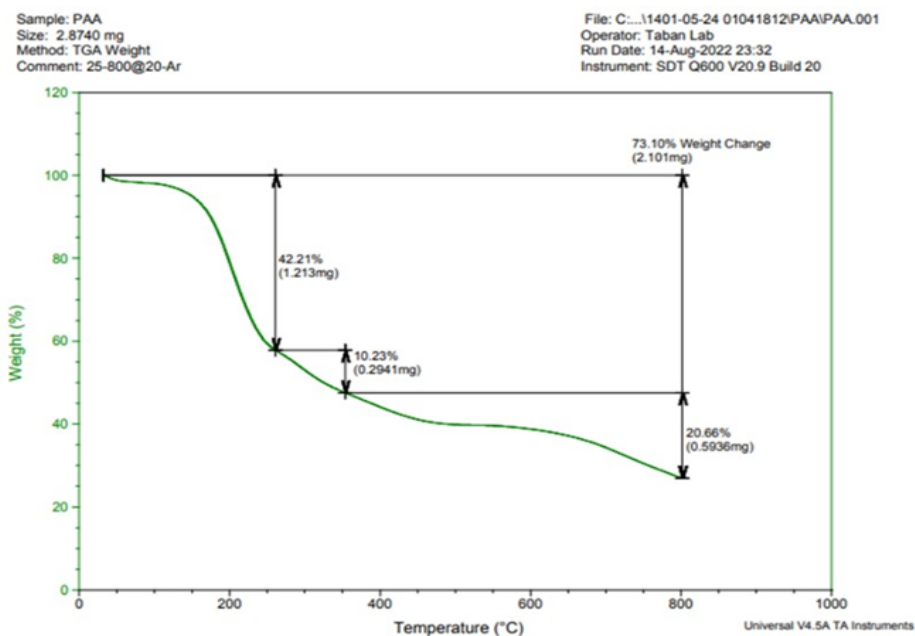


Figure 2. Thermogram of PAA ligand.

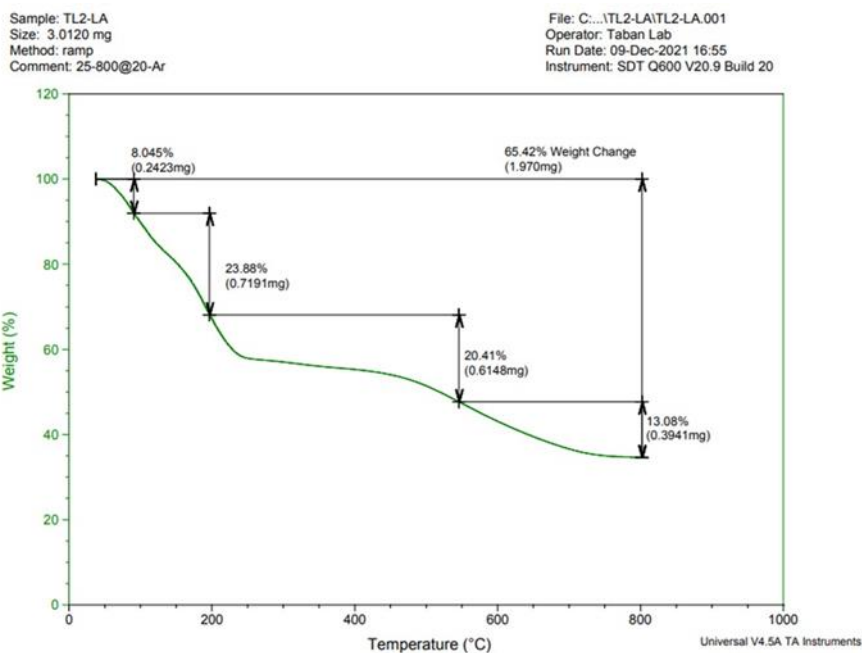


Figure 3. Thermogram of the $[La(PAA)_3]Cl_3 \cdot 3H_2O$ complex

3.4 The 1H NMR Spectra of the ligand PAA

The HNMR investigation for the free ligand PAA was displayed in **Figure 4** (DMSO-d₆). A singlet signal is attributed to the δ (NH, H) of the pyrazole moiety at (11.86) ppm and the δ (CH) of the pyrimidine moiety at (3.3 ppm) ppm [10]. The signals at (8.09 and 8.25 ppm) were indicative of δ (-NH₂, 2H) in adenine [11], whereas the chemical shift at (8.45 ppm) was traced back to δ (-NH) in the imidazole moiety [12]. The several signals that were seen between (7.00 and 7.9) ppm belonged to the proton of the naphthalene ring [13].

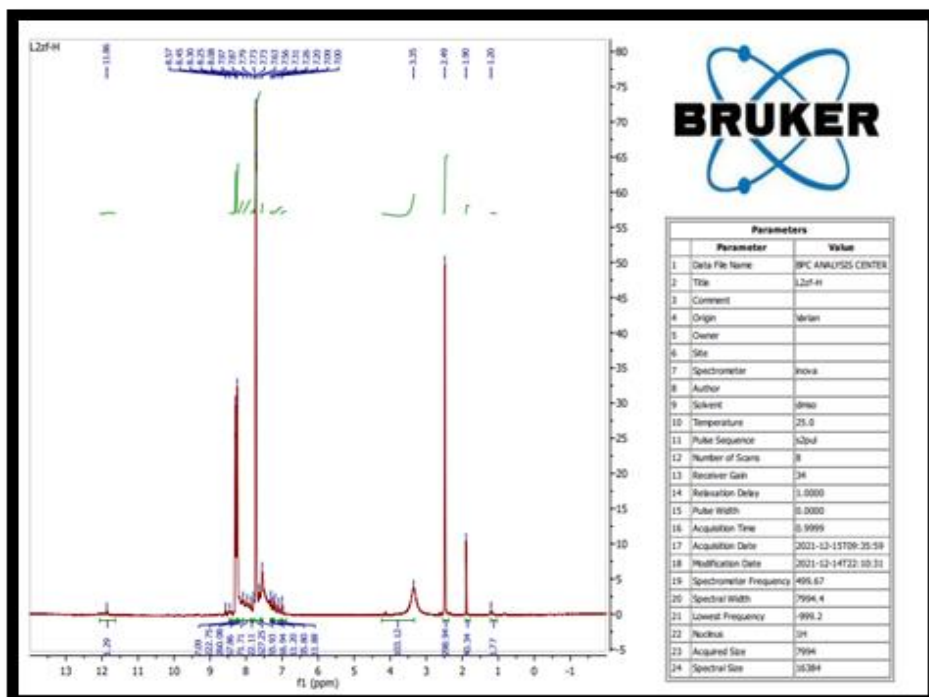


Figure 4. 1H NMR Spectrum for the PAA ligand

3.5 Electronic spectra and magnetic properties

The UV-Vis spectra of the free ligand (PAA) in the solvent ethanol [10^{-4}] with extend (200-1100) nm show two bands at 274 nm, 36496.35 cm^{-1} and 322 nm, 31152.65 cm^{-1} , which were attributed to the ($\pi \rightarrow \pi^*$) transition for intramolecular charge transfer taking place via the azo moiety, as in **Figure 5** [14]. **Figure 6** shows the electronic spectra of the $[\text{La}(\text{PAA})_3] \text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex, while the data obtained are included in **Table 4**. Chelating to the lanthanide ion causes both chromic shifts in the absorption band. Due to the partially filled 4f- orbital, most lanthanide ions absorb electromagnetic energy, particularly in the visible region of the spectrum, which excites the ions from their ground state to a higher electronic state. Electric radiation and magnetic dipoles can both excite f-f transitions. Transitions of the electric dipole are prohibited by parity (Laporte-forbidden) and much weaker than the magnetic dipole transitions, which are often parity-allowed and not visible. These transitions were, therefore, absent from the spectra of the $[\text{La}(\text{PAA})_3] \text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex because they were fragile and obliterated by the severe band absorption (PAA) [15]. The magnetic properties of the $[\text{La}(\text{PAA})_3] \text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex are paramagnetic.

Table 4. Electronic spectra for the ligand (PAA) and $[\text{La}(\text{PAA})_3] \text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex.

Compound	λ_{max} (nm)	Absorption band (cm^{-1})	Transition	Geometry
PAA	274	36496.35	($\pi \rightarrow \pi^*$)	-
	321	31152.65	($\pi \rightarrow \pi^*$)	-
$[\text{La}(\text{PAA})_3] \text{Cl}_3 \cdot 3\text{H}_2\text{O}$	402	24875.62	C.T	O.h

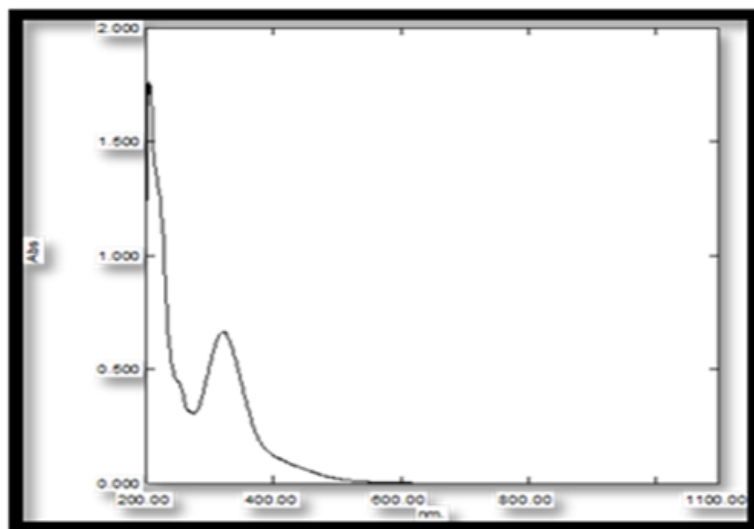


Figure 5. The PAA ligand.

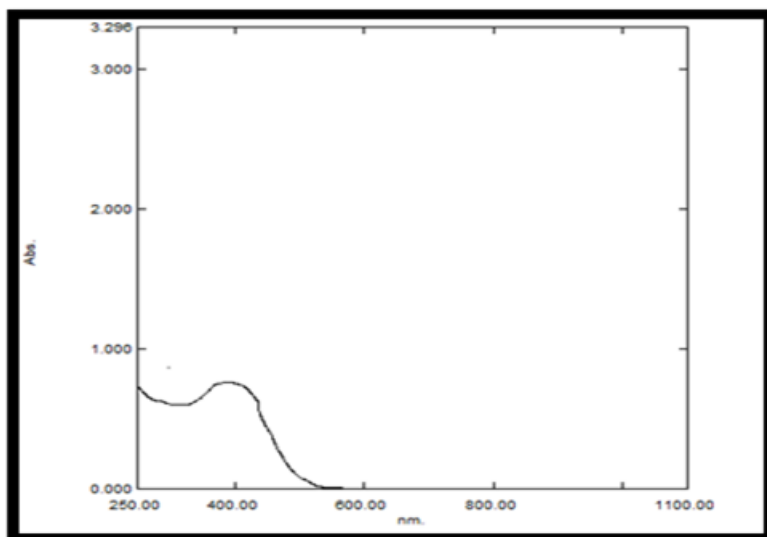


Figure 6. The $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$.

3.6 FT-IR spectra of PAA ligand and $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex

Azo dye ligands (PAA) and the $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex were characterized by FTIR spectra with samples produced as KBr discs. The influential FT-IR vibration bands of the (PAA) ligand and $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex are shown in Table 5, which may be used to investigate the coordination between the ligand and $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex. Their spectra were captured between (250 and 4000 cm^{-1}), through **Figures 7 and 8**.

1) The most important band for the azo compound is the azo moiety in the spectrum of the free ligand, which appeared at (1413) cm^{-1} , which was displaced to a higher wavelength at ν (1542) cm^{-1} in the spectra of the $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex, showing that the pair of electrons on the nitrogen atom for the azo moiety is in a state of coordination with the metal ion [16]. So, the intensity of this band was reduced with a doublet shape in the spectrum of the $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex when compared to the spectrum of a free ligand (PAA) [16].

2) The FT-IR spectrum of the free ligand (PAA) was allocated to the band with the symbol (N-H), but the spectrum of the complex's symmetric (NH_2) moiety remained unchanged in **Table 5**. The little shift in position or form, which is frequently ascribed to a decrease or rise in resonance as a result of chelating, suggests that this moiety did not chelate [17].

3) The imine moiety ($\text{C}=\text{N}$) for the imidazole ring in adenine was referenced by the ligand (PAA) in a band at (1701-1687) cm^{-1} . As compared to the spectra of the ligand, this band was pushed to its most excellent wavelength in the region of (1745) cm^{-1} in the $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex because of the coordination with the metal ion [18].

4) The bands were attributed to ν ($\text{C}=\text{N}$) pyr. and ν ($\text{C}=\text{N}$) prm has little effect on complexation [19] **Table 5** and **Figures 7, 8**.

5) The spectra of $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex were recorded new bands in the (420457) cm^{-1} and (615-661) cm^{-1} , respectively, which belong to ν (Ln-Nazo) and (Ln-Nimd.) [17].

6) According to the information above, the ligand (PAA) functions as a neutral N, N-bidentate through the nitrogen atoms in the azo and imidazole moiety of adenine.

Table 5. Vibration bands of the (PAA) ligand and [La(PAA)₃]Cl₃.3H₂O complex.

Assessment center	ν (N-H)	ν (C=N)pyr.	ν (C=N)imd	ν (C=N)pyrm	ν (N=N)azo	ν (M-N)azo	ν (M-N)imd.
PAA	3355 st. 3431 b,st	1639 sh,m	1701 d,m 1687 d,m	1558 st.	1413 st,sh	-	-
[La(PAA) ₃]Cl ₃ .3H ₂ O	3404 b,st 3423b , st.	1623sh, m	1745	1554 st.	1542 m.	420 w 457 w.	615 w. 661 w.

s=strong, m=medium, w=weak, sh=sharp, prm.=Pyrimidine , imd.=Imidazole pyr=Pyrazole.

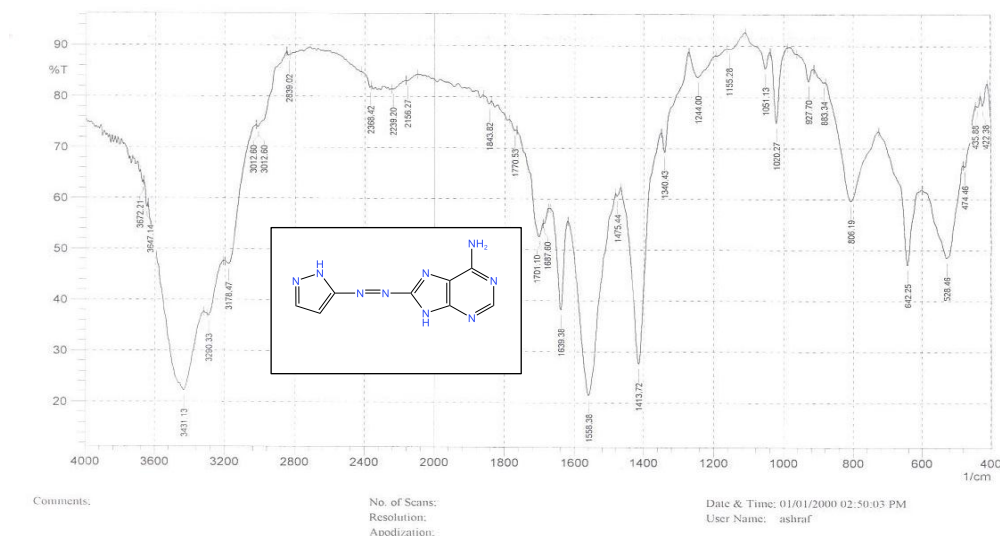


Figure 7. The FTIR spectrum of (PAA) ligand.

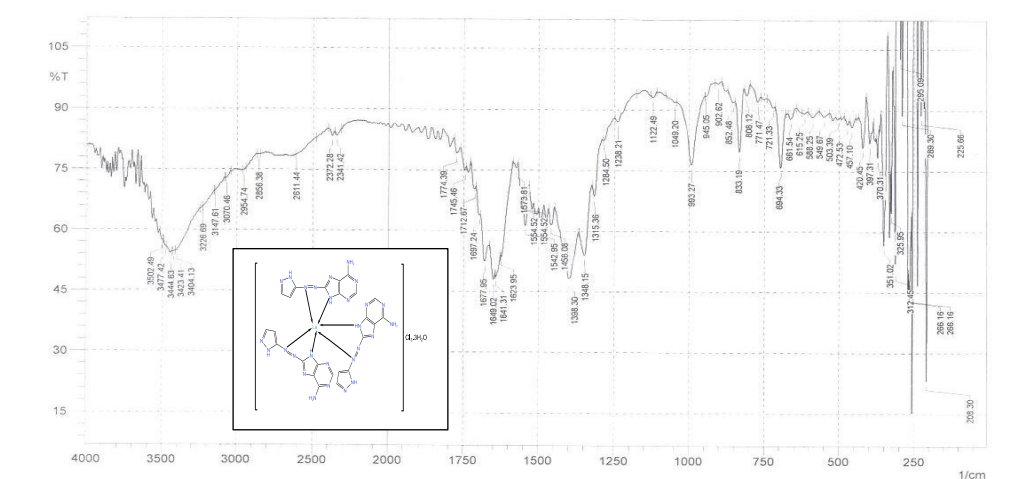


Figure 8. The FTIR spectrum of [La(PAA)₃]Cl₃.3H₂O complex.

3.7 Wool dyeing

The free ligand (PAA) and [La(PAA)₃]Cl₃.3H₂O complex were tested on wool fiber. Wool fiber is a complicated structure that contains protein filaments, the majority of which are keratin amino groups and carboxyl groups [20]. Numerous polar groups, including -OH, -NH, and -SH groups, are present in wool fiber. In polyamide fiber, there may be an amino group at the end

of the chain as well as a sizable number of -NH groups [21]. The kind of metal and its valence state, washing time (60 min), solution concentration, solution length, pH, temperature (40 Co), and other factors all affect how quickly and how much metal is absorbed. Particularly at alkaline pHs, the nitrogen atoms of amino and amide groups are capable of forming coordination bonds. The hue of the wool textile was in the range of yellow to brown after being dyed with the ligand (PAA) and $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex **Figure 9**.



Figure 9. The wool textile dyeing of ligand (PAA) with its metal complexes wash fastness.

When soap with a 2% concentration was used to test the textile color fastness for washing, the outcomes were excellent **Table 6**. According to the Iraqi Standard No. 3610 for wool textiles, the findings were converted to a grayscale, as shown in **Table 6**. The results of dyeing and different fastness characteristics of the $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex and azo ligand (PAA) on wool textile.

Table 6. Results of dyeing and various fastness feature of azo ligand (PAA) and $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex on wool textile.

compound	color fastness	Staining
PAA	4	4
$[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$.	4	4

Grading:5-4 (good), 3(moderate), 1-2(not good)

3.8 Photo stability

By soaking the ligand (PAA) and $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ complex in ethanol at a concentration of (10^{-4}M) and subjecting them to ultraviolet (UV) radiation for two hours at room temperature, their photostability was examined, as in **Table 7**. The photostability % was calculated [22] using the difference between the initial absorbance (i.e., before irradiation and the final absorbance, to the beginning absorbance). The following findings were obtained from the photostability test: (PAA) > $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$.

Table 7. Photo degradation details of ligands and $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ under irradiation ($\lambda = 256 \text{ nm}$).

Compound	Time (min)	Abs (nm)	Photo stability percentage
PAA	0	1.955	6.08%
	10	1.845	
	20	1.934	
	30	1.994	
	40	1.91	
	50	1.973	
	60	1.977	
	75	1.934	
	90	1.922	
	105	1.925	
	120	1.836	
	$[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$	0	
10		1.985	
20		1.942	
30		1.933	
40		1.955	
50		1.99	
60		1.962	
75		1.944	
90		1.952	
105		1.988	
120		1.962	

5. Conclusion

Following spectral and analytical physicochemical studies on the ligand (PAA) and $[\text{La}(\text{PAA})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$, certain conclusions have been drawn that establish the following points: The ligand (PAA), which acted as a neutral N, N-bidentate chelating ligand that bonded to La (III), produced an octahedral chelating complex through the nitrogen atoms of imidazole in adenine and with a nitrogen atom in the azo moiety.

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Conflict of Interest

The authors declare that they have no conflicts of interest.

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References

1. Sharma, A.; Kasem, M.; Ali, E.; Moustafa, M. Synthesis and Characterization of Some New Azo Compounds Based on 2, 4-Dihydroxy Benzoic Acid. *Journal of Basic and Environmental Sciences*. 2014, 1, 76-85. <https://jbesci.org/uploads/1.3.1.pdf>.

2. Al-Majidi, S.M.H.; Al-Khuzai., M.G.A. Synthesis and Characterization of New Azo Compounds Linked to 1, 8-Naphthalimide and Studying Their Ability as Acid-Base Indicators. *Iraqi Journal of Science* **2019**, *60(11)*, 2341-2352. <https://doi.org/10.24996/ijs.2019.60.11.4>.
3. Kadhim, S.M.; Mahdi, S.M. Preparation and Characterization of New (Halogenated Azo-Schiff) Ligands with Some of their Transition Metal Ions Complexes. *Iraqi Journal of Science* **2022**, *63(8)*, 3283-3299. <https://doi.org/10.24996/ijs.2022.63.8.4>.
4. Abdallah, M.; Alfakeer, M.; Hasan, N.; Alharbi, A.M.; Mabrouk, E. Polarographic Performance of Some Azo Derivatives Derived from 2-Amino-4-Hydroxy Pyridine and Its Inhibitory Effect on C-steel Corrosion in Hydrochloric Acid. *Oriental Journal of Chemistry* **2019**, *35(1)*, 98-109. <http://dx.doi.org/10.13005/ojc/350111>.
5. Gavin, J.; Ruiz, JF.; Kedziora, K.; Windle, H.; Kelleher, DP.; Gilmer, JF. Structure Requirements for Anaerobe Processing of Azo Compounds: Implications for Prodrug Design. *Bioorganic & Medicinal Chemistry Letters* **2012**, *22(24)*, 7647-7652. <https://doi.org/10.1016/j.bmcl.2012.10.014>.
6. Hussein, N.A; Abbas, A.K. Synthesis, Spectroscopic Characterization and Thermal Study Of Some Transition Metal Complexes Derived from Caffeine Azo Ligand with Some of Their Applications. *Eurasian Chem Commun* **2021**, *4(1)*, 67-93. <https://doi.org/10.22034/ecc.2022.307545.1245>.
7. Smith, M.B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms and Structure*. 6th editio John Wiley & Sons, **2007**. <https://onlinelibrary.wiley.com/doi/book/10.1002/0470084960>
8. Abbas, Khider, A.; Kadhim, R.S. Metal Complexes of Proline-Azo Dyes, Synthesis, Characterization, Dying Performance and Antibacterial Activity Studies. *Orient J Chem* **2017**, *33(1)*, 402-417. <http://dx.doi.org/10.13005/ojc/330148>
9. Issa, Y.; El-Hawary, W.; Youssef, A.; Senosy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. **2010**, *75*, 1297-1303.
10. Karçı, F.; Demirçalı, A.; Şener, İ.; Tilki, T. Synthesis of 4-Amino-1H-Benzo [4, 5] Imidazo [1, 2-A] Pyrimidin-2-one and Its Disperse Azo Dyes. Part 1: Phenylazo Derivatives. *Dyes and Pigments*. **2006**, *71(2)*, 90-96. <https://doi.org/10.1016/j.dyepig.2005.06.006>.
11. Huo, Y.; Lu, J.; Hu S.; Zhang, L.; Zhao, F.; Huang, H.;Huang, B.; Zhang, L. Photoluminescence Properties of New Zn (II) Complexes with 8- Hydroxyquinoline Ligands: Dependence on Volume And Electronic Effect of Substituents. *Journal of Molecular Structure*. **2015**, *1083(14)*, 144-151. <https://doi.org/10.1016/j.molstruc.2014.11.029>.
12. Mubark, H.M.H.; Witwit, I.N.; Ali, A.A.M. Synthesis of New Azo Imidazole Ligand and Fabricating It's Chelate Complexes with Some Metallic Ions. *Journal of Physics: Conference Series*. **2020**, *1660*, 012031. <https://doi.org/10.1088/1742-6596/1660/1/012031>.
13. Matsushita, Y.; Jang, I-C.; Imai, T.; Fukushima, K.; Lee, S-C. Naphthalene Derivatives from Diospyros Kaki. *The Japan Wood Research Society*. **2010**, *56(5)*, 418-421. <https://doi.org/10.32604/jrm.2021.014286>.
14. Dinçalp, H.; Toker, F.; Durucasu, İ.; Avcıbaşı, N.; Icli, S. New Thiophene-Based Azo Ligands Containing Azomethine Group in the Main Chain for the Determination of Copper (II) Ions. *Dyes and Pigments*. **2007**, *75(1)*, 11-24. <https://doi.org/10.1016/j.dyepig.2006.05.015>.
15. Abbas, A.K. Lanthanide Ions Complexes of 2-(4-amino antipyrine)-L-Tryptophane (AAT): Preparation, Identification and Antimicrobial Assay. *Iraqi Journal of Science*. **2015**, *56(4C)*, 3297-3309.
16. Mallikarjuna, N.M.; Keshavayya, J.; Maliyappa, M.R.; Ali, R.S.; Venkatesh, T. Synthesis, Characterization, Thermal And Biological Evaluation Of Cu (II), Co (II) And Ni (II) Complexes of Azo Dye Ligand Containing Sulfamethaxazole Moiety. *Journal of Molecular Structure*. **2018**, *1165(5)*, 28-36. <https://doi.org/10.1016/j.molstruc.2018.03.094>.

17. Mallikarjuna, N.M.; Keshavayya, J. Synthesis, Spectroscopic Characterization and Pharmacological Studies on Novel Sulfamethaxazole Based Azo Dyes. *Journal of King Saud University-Science*. **2020**, 32(1), 251-259. <https://doi.org/10.1016/j.jksus.2018.04.033>.
18. Silverstein, R.M.; Webster, F.X.; Kiemle, DJ. Spectrometric Identification of Organic Compounds, 7th editio"John Wiley & Sons. **2005**. <https://doi.org/10.1021/ed039p546>.
19. Essam, M.S.; Nagwa, M.M. H. Synthesis and Antimicrobial Evaluation of Some Pyrazole Derivatives. *Molecules*. **2012**, 17(5), 4962-4971. <https://doi.org/10.3390/molecules17054962>
20. Kant, R. Textile dyeing industry an environmental hazard **2011**. <https://doi.org/10.4236/ns.2012.41004>.
21. Jasim, D.J.; Abbas, A.K. Divalent Metal Complexes Of Azosulfamethaxazole: Synthesis And Characterization With Study Some Of Their Applications. *NVEO-NATURAL VOLATILES & ESSENTIAL OILS Journal| NVEO*. **2021**, 8(4), 8272-8300.
22. Dabish, R.A.; Abbas. A.K. Synthesis and Spectral Studies of Some New Complexes Containing Azo Ligand with Anticancer, Antibacterial and Dyeing Performance. *Annals of the Romanian Society for Cell Biology* **2021**, 25(4), 7968-8006.