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# Synthesis, Spectroscopy of New Lanthanide Complexes with Schiff Base Derived From (4-Antipyrinecarboxaldehyde with Ethylene Di-Amine) and Study the Bioactivity

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# **Abstract:**

The study involved preparing a new compound by combining Schiff bases generated from compounds for antipyrine, including lanthanide ions (lanthanum, neodymium, erbium, gadolinium, and dysprosium). The preparation of the ligand from condensation reactions (4-antipyrinecarboxaldehyde with ethylene di-amine) at room temperature, and was characterization using spectroscopic and analytical studies ( FT-IR, UV-visible spectra, <sup>1</sup>H-NMR, mass spectrometry, (C.H.N.O), thermogravimetric analysis (TGA), in addition to the magnetic susceptibility and conductivity measurement of the synthesis complexes, among the results we obtained from the tests, we showed that the ligand behaves with the (triple Valence) lanthanide ions, the multidentate behavior through two oxygen atoms of the carbonyl group and two nitrogen atoms of the azomethine group with all the prepared complexes in a molar ratio (1:1). The participation of six groups of bidentate nitrate in the coordination and indicating that their complexes have values of magnetic moment and paramagnetic character and, based on the results of those measurements, the geometrical shape of the complexes was proposed. The biological activity of the prepared complexes was studied using the antibacterial activity, as the results of its effectiveness showed the direction of the bacteria used (Staphylococcus aureus, Bacillus subtilis, Escherichia coli, and Klebsiella pneumoniae) at the concentration of  $1 \times 10^{-3} M$ 

Keywords: 4-antipyrinecarboxaldhyed, Biological Activity, Metal complexes (lanthanide), Schiff's bases, Thermogravimetric Analysis.

# **Introduction**:

The Schiff base is named after its 1864 Hugo Schiff discoverer and is an organic compound containing an aryl or alkyl group (C=N), in which the atom of nitrogen is linked to the atom of carbon by a double bond, and the atom of nitrogen is linked to an aryl or alkyl group and the general formula is  $-CH=N- \text{ or } > C=N-, (R^1R^2-C=NR^3)^{1-3}.$ 

Schiff bases (Azomethine) are one of the most important ligands in coordination chemistry because they participate in the preparation of many complexes with ions of internal transition elements (lanthanides) and transition elements in particular, due to their ability to coordinate and form using diverse coordination complexes applications 4, 5. The stability property of Schiff bases depends on the carbonyl compounds and

amines that will be used in their preparation, whether they are Aliphatic or aromatic, with amines with the partial withdrawal of water 6, 7. The biological activity of Schiff base metal complexes is one of the key areas of investigation, with the objective of generating safe and effective therapeutic drugs for the treatment of bacterial infections and cancer 8. Several Schiff base metal complexes have a diverse set of biological and pharmacological features. Internal transition metal complexes of Schiff base ligands, which have donor atoms are particularly "O" and "N" donor atoms, are particularly important due to their biological properties, which include antibacterial <sup>9</sup>, antifungal, anti-inflammatory 10, analgesic, anticonvulsant, antioxidant 11, and anthelmintic properties 12.

Lanthanide Schiff base complexes have also been used as biological models to explore the structure of biomolecules and biological processes <sup>13, 14</sup>.

The sequence of 15 metallic elements, from lanthanum to lutetium, is called lanthanides 15-17. Lanthanides are sometimes called elements of rare earth. These elements include 4f-orbitals in the differentiating electron. The name lanthanides come from the lanthanum (La) prototype element of lanthanides <sup>18</sup>. Lanthanide chemistry significantly from that of the main group and transition metal elements due to the presence of four f orbitals that are spatially 'buried' inside the atom and are thus protected from the ligand field. As a result, the size of Lanthanide ions has a significant impact on their chemistry. Because the 4 f electrons are spatially buried, there is no mixing of ligand and metal orbitals, and the connection between the ligands and the Ln<sup>+3</sup> ions is solely electrostatic. Because of their high charge density, Ln<sup>+3</sup> ions are usually hard Lewis acids that like to connect to hard base atoms such as oxygen. The absence of any directed bonding feature results in a high coordination number (> 6 and up to 12) 19. The largeness of the lanthanide ions increases the coordination number (CN) easily above six. In lanthanide complexes, the coordinated number is usually 8 and 9<sup>20</sup>. Lanthanide contraction refers to the gradual shrinking of the atomic elements La atomic number 57 and Lu atomic number 71 <sup>21</sup>. The atomic numbers of rare earth elements have a constant decline. Because – New electrons reach the 4f orbital that, because of their different form, has a particularly bad shielding effect as a result of nuclear attraction and electron shell contraction <sup>22</sup>, Because they prefer to create complexes with a higher coordination number because of the huge size of ions and their proclivity to form ionic bonds rather than covalent interactions that result in coordination complexes <sup>23, 24</sup> of electronic forms (4 f), The high ionic radius of these metal ions, as well as the atomic number or oxidation number of the lanthanides, cause structural variation <sup>25</sup>.

The biological features of antipyrine and its derivatives are intriguing. As a potential oxygen donor bond, it can form stable complexes with lanthanide element ions of structural importance <sup>26</sup>. Antipyrine and its derivatives have piqued the interest of many researchers due to the various possibilities for coordinating antipyrine derivatives with lanthanide ions and hence their complexelastic behavior, being possible oxygen donor bonds capable of creating stable complexes with metal ions <sup>27</sup>. Furthermore, antipyrine and its derivatives exhibit intriguing pharmacological properties and are being used for multiple therapeutic purposes

they are antibacterial as well as anti-inflammatory <sup>28</sup>. The research aims to prepare and characterize the new ligand and their complexes from the lanthanide nitrate salt [M (NO<sub>3</sub>)<sub>3</sub>].6H<sub>2</sub>O, M = La<sup>+3</sup>, Nd<sup>+3</sup>, Er<sup>+3</sup>, Gd<sup>+3</sup>, and Dy<sup>+3</sup> using the available spectroscopic methods and the study of biological efficacy <sup>29-31</sup>.

# Materials and Methods: Materials:

The following chemicals were used in this study: 4-Antipyrine Carboxaldehyde (sigma Aldrich 97%), ethylene di-amine (sigma Aldrich 99%), absolute ethanol (B.DH 99%), and lanthanide nitrate [M (NO<sub>3</sub>)<sub>3</sub>].6H<sub>2</sub>O (Sigma Aldrich),  $M = La^{+3}$ ,  $Nd^{+3}$ ,  $Er^{+3}$ ,  $Gd^{+3}$ , and  $Dy^{+3}$ .

# **Instrumentation:**

The microanalysis element of the studied ligand and complexes was carried out with a Thermo Finnegan flash device Energy Center in Syria. Infrared spectroscopy of ligand and its complexes were recorded within the range (4000 -250 cm<sup>-1</sup>) using a device of the type (Shimadzu FTIR-spectrometer) and using a disk (KBr) for ligands and (CsI) for complexes at Baghdad University \ College of Science \ Department of Chemistry. Also, the <sup>1</sup>H-NMR magnetic spectra of the prepared ligands were recorded by using a Bruker 400 MHz AVANCE spectrometer after dissolving it with (DMSO-d<sup>6</sup>) solvent and using Si(CH<sub>3</sub>)<sub>4</sub> as a reference for measurement at room temperature in Ankara / Turkey, and the mass spectra of the prepared compounds were recorded by a Network Mass Selective device at the University of Ankara \ Turkey, Melting point (M.p) of the prepared ligand and their complexes using a device from the English company Stuart with a temperature range of 300 degrees Celsius at the College of Science for Women \ Department of Chemistry.

# **Methods:**

# Preparations of Schiff's Bases of Ligand:

Preparing a Schiff's base L was prepared by mixing in the flask round bottom 100 ml of 1.2g of 4-Antipyrinecarboxaldehyde (2mol) 0.1667g (1 mol) ethylene di-amine and adding 3-5 drops of glacial acetic acid, in presence of 20 ml of ethanol absolute 99.9 %. The mixture was placed on reflux a stirring at room temperature (4-6 hours), the precipitation of the yellowish-white was completed was then collected by filtration, washed with ethanol absolute dried for 24 hours, and then recrystallized from hot absolute ethanol. The yellowish-white powder was collected by filtration and then dried for hours. Yield 75 % and melting point (M.p) 211 - 213 °C. The ligand was characterized by several techniques <sup>32</sup>. Show the scheme .1 Synthesis and Prepare of Schiff base ligand.

4-antipyrine carboxaldhyed

ethylene diamine

ligand

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Scheme .1 Synthesis of ligand

# **Preparations of Lanthanide Complexes:**

In a 25 ml round bottom flask, 0.1 g of ligand was dissolved in 5 ml of methanol, then gradually with stirring dissolving add 0.0948 g of salts [M (NO<sub>3</sub>)<sub>3</sub>].6H<sub>2</sub>O;  $M^{+3}$  = La, Nd, Er, Gd, and Dy was added in 5 ml of methanol absolute to make the complexes. The mixture was reflux stirred for 4-7 hours, and then left to precipitate, and then the precipitate was collected and purified with water and ether and let dry to obtain a pure precipitate

# **Results and Discussion:**

Microanalysis of elements and some of their physical properties is one of the results. As shown in Table.1, other methods were used to identify the ligand and Schiff base complexes, including the infrared spectrum, a mass spectrum, and the proton NMR spectrum.

Table 1. The CHNO analysis and some physical characteristics of ligand L and lanthanide complexes

| Table 1: The CIT to analysis and some physical characteristics of figure 2 and fantamate complexes |        |                           |            |                       |        |         |         |         |
|--|--------|---------------------------|------------|-----------------------|--------|---------|---------|---------|
| Ligand / complexes   | Yield% | M.p.                      | color      | Analysis (calculated) |        |         |         |         |
|  |        | $^{\mathrm{o}}\mathrm{C}$ |            | C%                    | Н%     | N%      | Ο%      | M.wt    |
| $L/[C_{26}H_{28}O_2N_6]$   | 75%    | 211-213                   | yellowish- | 69.07                 | 6.10   | 17.96   | 6.84    | 456.96  |
|  |        |                           | white      | (68.40)               | (6.18) | (18.41) | (7.01)  |         |
| $[La_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$   | 65%    | 290 Dec                   | White      | 37.45                 | 4.12   | 14.97   | 26.84   | 1671.02 |
|  |        |                           | smoke      | (37.38)               | (4.10) | (15.09) | (26.81) |         |
| $[Nd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$   | 70%    | 260 Dec                   | khaki      | 37.18                 | 4.11   | 14.95   | 26.60   | 1681.70 |
|  |        |                           |            | (37.14)               | (4.08) | (14.99) | (26.64) |         |
| $[Er_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$   | 65%    | 270 Dec                   | Pale gold  | 36.17                 | 4.04   | 14.52   | 25.87   | 1727.73 |
|  |        |                           | erode      | (36.15)               | (3.97) | (14.59) | (25.93) |         |
| $[Gd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$   | 68%    | 270 Dec                   | ivory      | 36.59                 | 4.02   | 14.72   | 26.25   | 1707.71 |
|  |        |                           |            | (36.57)               | (4.01) | (14.76) | (26.23) |         |
| $[Dy_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$   | 65%    | 260 Dec                   | Pale       | 36.38                 | 4.01   | 14.69   | 25.98   | 1718.21 |
|  |        |                           | orange     | (36.35)               | (3.99) | (14.67) | (26.07) |         |

# FT-IR Spectroscopy of the Ligand:

The compound  $[C_{26}H_{28}O_2N_6]$  was discovered using an FT-IR spectrum, which revealed bands (3441, 3043, 2908, 1645, and 1591) cm<sup>-1</sup> that are attributed to (O-H) moisture <sup>33</sup>, C-H (Ar), C-H (Aliph), C=O <sup>34</sup>and C=N <sup>35</sup>. Show the Fig .1

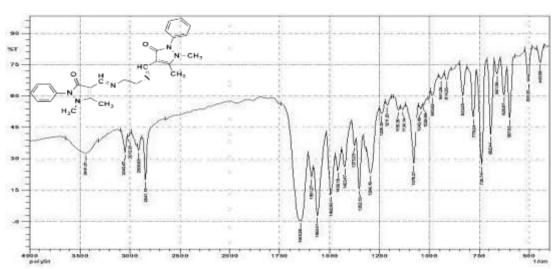
# <sup>1</sup>H-NMR Spectroscopy for the Ligand:

Figure .2 Shows the peaks of the <sup>1</sup>H-NMR ligand spectrum: (d<sup>6</sup>-DMSO — 400 MHz) ligand has a single peak in 2.56 ppm CH<sub>3</sub>, one peak in 3.20

and 3.67 ppm  $CH_2$  and  $CH_3$ , 7.30 ppm multiple chemical shifts back in CH, 7.51 ppm multiple chemical shifts back in the 4-aminoantipyrin ring in the  $CH_2$  ring. Azomethine proton peak (CH = N) has been linked to signals of 8.04 ppm  $^{36}$ .

# **Mass Spectrometry of Ligand:**

LC-mass spectrum is as shown in fig.3, the mass spectra of the  $[C_{26}H_{28}O_2N_6]$  shown molecular ion peaks at (456.96) g mol<sup>-1</sup>, this agreed extremely well with the estimated values (456.55) g mol<sup>-1</sup> <sup>37</sup>.



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Figure 1. FT-IR of Ligand /  $[C_{26}H_{28}O_2N_6]$ 

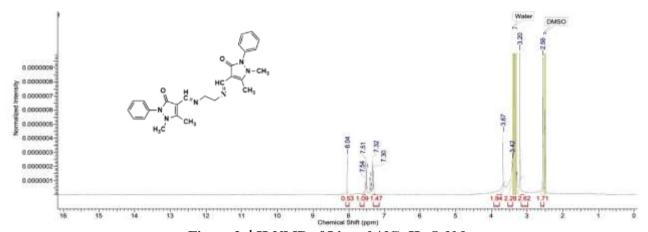


Figure 2.  $^{1}$  H-NMR of Ligand /  $[C_{26}H_{28}O_{2}N_{6}]$ 

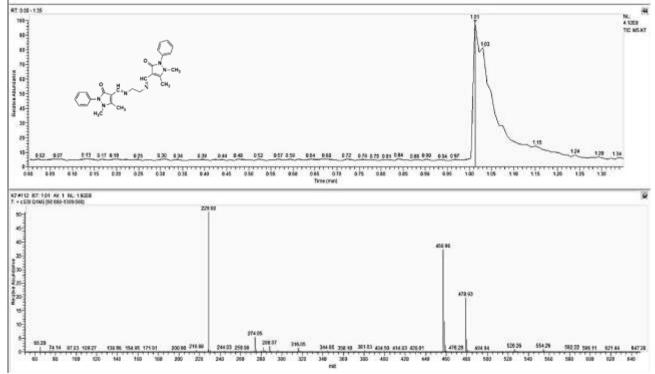


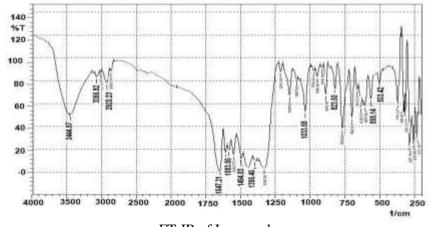
Figure 3. LC- Mass of Ligand /  $[C_{26}H_{28}O_2N_6]$ 

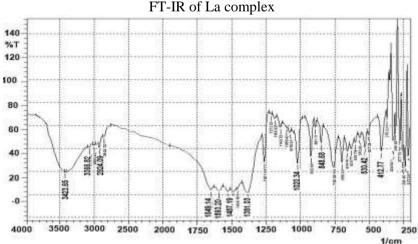
# Fourier-Transform Infrared Spectroscopy (FTIR) of lanthanide Complexes:

The Fourier-transform infrared Spectroscopy (FT-IR) of the prepared ligand, the appearance of a beam at the site (1591) Cm<sup>-1</sup>, which refers to the absorption band v(C=N) of the ligand, and a strong sharp beam at the site (1645) Cm<sup>-1</sup>, which belongs to the bundle v(C=0), and upon comparison, the infrared spectra of the Schiff's bases and their complexes appear to have a displacement towards higher frequencies of the beam the compact absorption v(C=N) of the complexes  $([La_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O,$  $[Nd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O, [Er_2(C_{26}H_{28}O_2N_6)_2]$  $(NO_3)_6$ ].6H<sub>2</sub>O,  $[Gd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ ,  $[Dy_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O)$  at the sites (1583-1593-1581-1577, and 1578) Cm<sup>-1</sup>, respectively, and a shift towards higher frequencies of the bundle absorption beam v(C=O) of the complexes at the sites (1647 - 1649 - 1649 - 1647, and 1647) Cm<sup>-1</sup> respectively, All of this confirms the presence of coordination between the two nitrogen atoms of the azomethine and ketone oxygen groups in 4antipyrinecarboxaldehyde. There is a scarcity of such assignments in the literature, while it appears

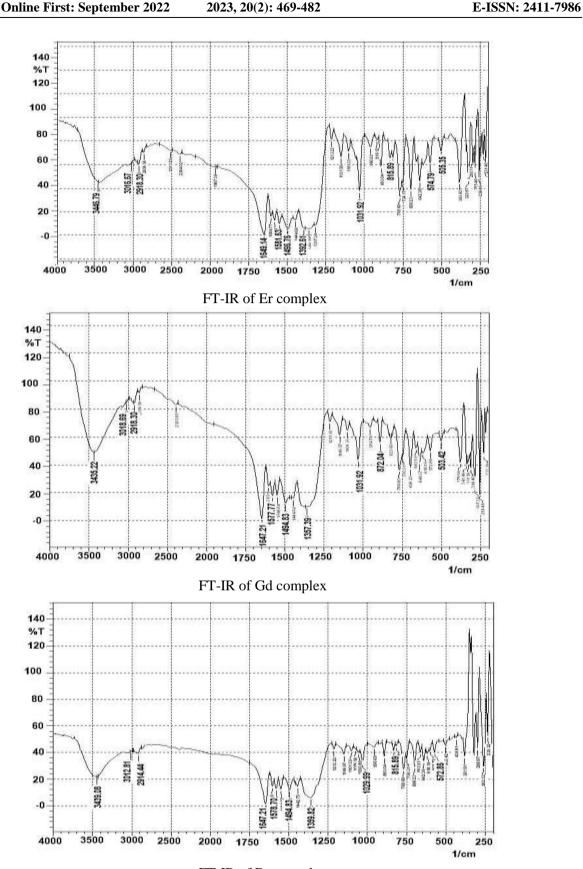
that (M-O) and (M-N) may be expected in the complexes' 400-600 cm<sup>-1</sup> range, showed an absorption beam that belongs to the bundle of (M-N) compounds ( $[La_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ ,  $[Nd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O, [Er_2(C_{26}H_{28}O_2N_6)_2].6H_2O, [Er_2(C_{26}H_{28}O_$  $(NO_3)_6].6H_2O,[Gd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$  $[Dv_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ ) at the sites (503, 412, 505, 503,435)Cm<sup>-1</sup>, respectively, and an absorption beam that returns to the bundle (M-O) of the compounds  $([La_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$  $[Nd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O, [Er_2(C_{26}H_{28}O_2N_6)_6].6H_2O, [Er_2(C_{26}H_{28}O_$  $)_2(NO_3)_6].6H_2O, [Gd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O,$  $[Dy_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O)$  at the sites (565 – 530 - 574 - 572, and 572) Cm<sup>-1</sup>, respectively <sup>38, 39</sup>. Wide absorption packs due to not coordinating water molecule appear with the lanthanide ions (outside the coordination sphere) in general at the range (3300 cm<sup>-1</sup> - 3500 cm<sup>-1</sup>). It was noticed that the prepared complexes gave absorption packs in the range (3439 cm<sup>-1</sup>- 3439 cm<sup>-1</sup>), and this supports the presence of incoordination water molecules (outside the coordination sphere). It is worth noting that the prepared ligand possesses water molecules due to moisture at the (3441 cm<sup>-1</sup>) <sup>40</sup>. As shown in Table .2 and Fig.4

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FT-IR of Dy complex
Figure 4. FT-IR spectra Ligand and Lanthanide complexes

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Table 2. FT-IR spectrum of the prepared ligand and lanthanide complexes

| I abic 2  | • 1 1 11 5  | pecu un                          | i or the                            | Pr cpar                    | cu ngan                    | u ana i                                 | umumam                                  | uc comp                                 | JICACS                                  |                            |                            |
|---|---|----------------------------------|-------------------------------------|----------------------------|----------------------------|---|---|---|---|----------------------------|----------------------------|
| Ligand / complexes  | v(H-O)<br>Cm <sup>-1</sup><br>water<br>molecule<br>due to<br>moisture | v(C-H)<br>Cm <sup>-1</sup><br>Ar | v(C-H)<br>Cm <sup>-1</sup><br>aliph | v(C=O)<br>Cm <sup>-1</sup> | v(C=N)<br>Cm <sup>-1</sup> | v(NO <sub>3</sub> )<br>Cm <sup>-1</sup> | v(M-O)<br>Cm <sup>-1</sup> | v(M-N)<br>Cm <sup>-1</sup> |
| L/C <sub>26</sub> H <sub>28</sub> O <sub>2</sub> N <sub>6</sub> | 3441  | 3043                             | 2908                                | 1645                       | 1591                       | 1560                                    |   |   |   |                            |                            |
| $[La_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$                    | 3444  | 3066                             | 2920                                | 1647                       | 1583                       | 1494                                    | 1396                                    | 1033                                    | 823                                     | 565                        | 503                        |
| $[Nd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$                    | 3423  | 3066                             | 2924                                | 1649                       | 1593                       | 1487                                    | 1381                                    | 1020                                    | 848                                     | 530                        | 412                        |
| $[Er_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$                    | 3446  | 3016                             | 2918                                | 1649                       | 1581                       | 1496                                    | 1392                                    | 1031                                    | 815                                     | 574                        | 505                        |
| $[Gd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$                    | 3435  | 3018                             | 2918                                | 1647                       | 1577                       | 1494                                    | 1357                                    | 1031                                    | 823                                     | 572                        | 503                        |
| $[Dy_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$                    | 3439  | 3012                             | 2914                                | 1647                       | 1578                       | 1494                                    | 1359                                    | 1029                                    | 815                                     | 572                        | 435                        |

# Electron transfers in lanthanides, Magnetic sensitivity and Molar Conductance of lanthanide Complexes:

In Table .3, we present the electronic spectra of the ligand and its complexes. The ligand spectra data displayed three bands at 242 nm, 267 nm, and 303 nm which resulted from intra-ligand charge transfer due to the  $\pi \rightarrow \pi^*$  transition of the aromatic rings bonds and  $n\rightarrow\pi^*$  transition of the (C=O) and (C=N) bonds 41. The Ln+3 complexes showed three types of transitions resulting from the 4f electrons of lanthanides: (i) internal 4f-4f transitions resulting in sharp, narrow transitions in Laporte bands of relatively weak intensity. (ii) Allowed to are 4f <sup>n</sup> - 4f <sup>n-1</sup> (n - 1) d, which are relatively broad and available widely. (iii) Also important are the strong electron transfer bands in ultraviolet region 42, three absorption frequencies at 582 - 891- 918 nm, 489 - 521- 652, 802 nm, and 757 - 806 - 909 nm,  $[{}^{4}\mathbf{I}_{9/2} \rightarrow {}^{4}\mathbf{G}_{7/2}, {}^{4}\mathbf{I}_{9/2} \rightarrow$  $^2D_{7/2}, \quad ^4I_{9/2} \rightarrow \quad ^2P_{1/2}], \quad [^3H_4 \rightarrow ^4I_{15/2}, \quad ^4I_{15/2} \rightarrow ^4G_{11/2}], \\ [^8S_{7/2} \rightarrow ^6I_{7/2}], \quad [^5I_{11} \rightarrow ^6H_{5/2}, \quad ^6H_{15/2} \rightarrow ^6P_{5/2}] \quad \text{respectively to}$ complexes Nd, Er, Gd and Dy. The exception is the (La<sup>+3</sup>) ion, absorbed in the visible and nearultraviolet regions due to the absence of electrons in the (4f) orbitals of the ion (La<sup>+3</sup>). The colors of these ions' compounds are due to the electronic transition of the  $(f \rightarrow f)$  type, and the bands of this spectrum appear in the form of sharp absorption bands, Because 4f is not an outer orbit electron, it is not impacted by the ligand or solvent, hence it is

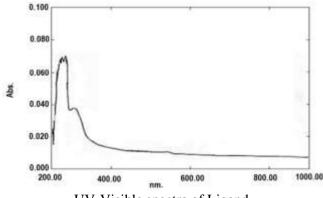
sharp and clear, and this phenomenon is the inverse of what is seen in the electronic spectrum of transition elements The transitions have been assigned to metal to ligand charge transfer (MLCT)or ligand to metal charge transfer (LMCT) <sup>43</sup>. The absorption spectra of all examined Ln<sup>+3</sup> (lanthanide) complexes differ from the free Schiff base ligand in both intensity and pattern, showing that the Schiff base ligand is coordinated to Ln<sup>+3</sup> ions. Show the Fig. 5

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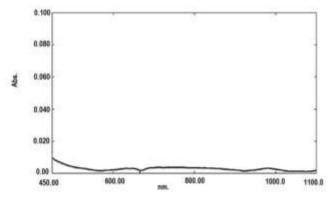
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# Magnetic sensitivity:

It is challenging to assess the magnetic susceptibility of f-block constituents. Their (µ) values are computed by taking spin and orbital components into account, because 4f-electrons are inside the (5s and 5p) electrons and behave in a core-like manner 44. The magnetic moment values of the lanthanide Ln<sup>+3</sup> complexes demonstrate that the lanthanum La<sup>+3</sup> complexes are diamagnetic, whereas the others are paramagnetic, as seen in Tables 3. The magnetic moments of all the complexes tested are quite close to the theoretical values computed for free lanthanide Ln<sup>+3</sup> ions. These findings differed slightly from the Van Vleck values, indicating that the 4f electrons had a good role in the bonding 45. Molar conductivity as shown in Table 3, that all the lanthanide complexes is nonconductive in solvent DMF in concentration  $1 \times 10^{-3}$ M.



UV-Visible spectra of Ligand



UV-Visible spectra of La complex

0.050

0.040

0.030

0.020

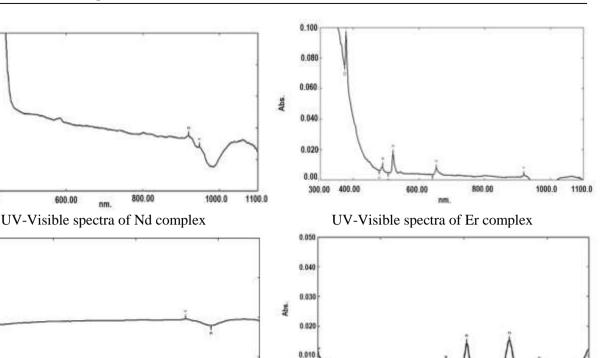
0.010

0.00

0.050

0.000

-0.050



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1100.00

UV-Visible spectra of Gd complex

Figure 5. The UV-Visible spectroscopy of ligand and lanthanide complexes

0.00

Table 3. Electronic spectra and physical properties of ligand and lanthanide complexes their prepared complexes in DMF solvent

| Compound   | Conductivity- DMF/   | Absorption bonds | Assigned   | Magnetic        |
|--|--|------------------|--|-----------------|
|  | (Cm <sup>2</sup> . ohm <sup>-1</sup> . mol <sup>-1</sup> ) | nm               | transition   | sensitivity B.M |
| L /[ C <sub>26</sub> H <sub>28</sub> O <sub>2</sub> N <sub>6</sub> ]   |  | 242, 267, 303    | $n \rightarrow \pi^*, n \rightarrow \pi^*,$            |                 |
|  |  |                  | $\pi \rightarrow \pi^*$                                |                 |
| $[La_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$   | 20   |                  | ${}^{1}S_{0}$  | Dia             |
| $[Nd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$   | 14   | 582 - 891- 918   | $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{7/2}$        | 4.56            |
|  |  |                  | $^4I_{9/2} \rightarrow ^2D_{7/2}$                      |                 |
|  |  |                  | $^{4}\text{I}_{9/2} \rightarrow ^{2}\text{P}_{1/2}$    |                 |
| [Er <sub>2</sub> (C <sub>26</sub> H <sub>28</sub> O <sub>2</sub> N <sub>6</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> ].6H <sub>2</sub> O | 23   | 489 - 521- 652   | ${}^{3}\text{H}_{4} \rightarrow {}^{4}\text{I}_{15/2}$ | 2.92            |
| , , , , ,  |  |                  | ${}^{4}I_{15/2} \rightarrow {}^{4}G_{11/2}$            |                 |
| $[Gd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$   | 29   | 802              | ${}^{8}S_{7/2} \rightarrow {}^{6}I_{7/2}$              | 3.70            |
| $[Dy_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$   | 40   | 757 - 806 - 909  | ${}^{5}I_{11} \rightarrow {}^{6}H_{5/2}$               | 3.55            |
|  |  |                  | $^{6}\text{H}_{15/2} \rightarrow ^{6}\text{P}_{5/2}$   |                 |

# **Thermogravimetric Analysis:**

As shown in Table 4, the results of the ligand and its lanthanide complexes are thermal results decomposed are recorded From the TGA curve of the ligand in Fig. 6, it was noticed that it displayed three stages of decomposition. In the range 75 - 290 °C, the estimated mass loss of 44.5% (calculation 43.8%) due to the decomposition of the  $C_{12}H_{12}N_2O$  molecule in the first step, The range 290 – 394 °C, the estimated mass loss of 13.2% (calculation 12.2%) due to the decomposition of  $C_2H_4N_2$  molecule, In the final stage, from 394 – 530 °C, the estimated mass loss of 25.8% (calculation 26.9%), due to loss of a  $C_6H_7N_2O$  molecule with complete decomposition  $^{46}$ . The TG curves of  $M = La^{+3}$ ,  $Nd^{+3}$ ,  $Er^{+3}$ ,  $Gd^{+3}$ , and  $Dy^{+3}$ , showed four decomposition

steps shown in Table .4 and Figs. 7, 8, 9, 10, and 11. Thermal analyzes of the lanthanide complexes showed that the process of disintegration or loss passes through several stages and the process occurs through 4 steps, as in the scheme .2, and this is evidence of good thermal stability, where the loss in the first a step is water 25-100 °C, this means that water is outside the coordination range, in each stage losing a part of their weight and liberating a certain compound from the compounds that were prepared. They differed among themselves in the temperature ranges, which they disintegrated as a result of the different nature of the ion forming the complex. The remaining material after the dissociation process is completed may belong to the Lanthanide oxide that makes up the complex

M<sup>+3</sup>=La, Nd, Er,Gd and Dy

$$[M_{2}(C_{26}H_{28}N_{5}O_{2})_{2}(NO_{3})_{6}].6H_{2}O \xrightarrow{-6H_{2}O} [M_{2}(C_{26}H_{28}N_{5}O_{2})_{2}(NO_{3})_{6}] \xrightarrow{-6NO_{3}} M_{2}(C_{26}H_{28}N_{5}O_{2})_{2} \xrightarrow{-C_{48}H_{48}N_{8}O_{4}} C_{4}H_{8}M_{2}N_{4} \xrightarrow{\circ} C \xrightarrow{-C_{4}H_{8}N_{2}O_{4}} C_{4}H_{8}M_{2}N_{4} \xrightarrow{\circ} C \xrightarrow{-C_{4}H_{8}N_{2}O_{4}} C_{4}H_{8}N_{2}N_{4} \xrightarrow{-C_{4}H_{8}N_{2}O_{4}} C_{4}H_{8}N_{2}O_{4}$$

Scheme .2 TGA-analyses of lanthanide complexes

Table 4. Thermogravimetric Analysis data of (L) ligand and lanthanide complexes

| Sample) (step)      | Temperature .range °C | TG Weig | ght mass loss |                      |
|---------------------|-----------------------|---------|---------------|----------------------|
|                     |                       | Calc%   | found%        | Reaction             |
| $L_{(1)}$           | 75 - 290              | 43.8    | 44.5          | $C_{12}H_{12}N_2O$   |
| $L_{(2)}$           | 290 - 394             | 12.2    | 13.2          | $C_2H_4N_2$          |
| $L_{(3)}$           | 394 - 530             | 26.9    | 25.8          | $C_6H_7N_2O$         |
|                     | al residual           | 18.5    | 16.5          | $C_6H_5$             |
| $La_{(1)}$          | 35 - 80               | 6.4     | 6.6           | $6(H_2O)$            |
| $La_{(2)}$          | 80 - 215              | 22.2    | 23.0          | $6(NO_3)$            |
| $La_{(3)}$          | 215 - 445             | 47.9    | 48.1          | $C_{48}H_{48}N_8O_4$ |
| $La_{(4)}$          | 445 - 555             | 6.7     | 5.5           | $C_4H_8N_4$          |
| Fin                 | al residual           | 19.4    | 16.8          | $La_2O_3$            |
| $Nd_{(1)}$          | 25 - 78               | 6.4     | 5.8           | 6(H <sub>2</sub> O)  |
| $Nd_{(2)}$          | 87 - 200              | 22.1    | 21.7          | $6(NO_3)$            |
| $Nd_{(3)}$          | 200 - 445             | 47.6    | 46.5          | $C_{48}H_{48}N_8O_4$ |
| $Nd_{(4)}$          | 445 - 540             | 6.6     | 7.1           | $C_4H_8N_4$          |
| Fin                 | al residual           | 20.0    | 18.9          | $Nd_2O_3$            |
| $\mathrm{Er}_{(1)}$ | 30 - 85               | 6.2     | 5.9           | $6(H_2O)$            |
| $\mathrm{Er}_{(2)}$ | 85 - 215              | 21.5    | 20.5          | $6(NO_3)$            |
| $\mathrm{Er}_{(3)}$ | 215 - 450             | 46.3    | 47.3          | $C_{48}H_{48}N_8O_4$ |
| $\mathrm{Er}_{(4)}$ | 450 - 573             | 6.4     | 6.7           | $C_4H_8N_4$          |
| Fin                 | al residual           | 22.3    | 19.6          | $Er_2O_3$            |
| $Gd_{(1)}$          | 27 - 85               | 6.3     | 6.9           | $6(H_2O)$            |
| $Gd_{(2)}$          | 85 - 225              | 21.7    | 22.0          | $6(NO_3)$            |
| $Gd_{(3)}$          | 225 - 435             | 46.8    | 45.9          | $C_{48}H_{48}N_8O_4$ |
| $Gd_{(4)}$          | 435 - 550             | 6.5     | 7.2           | $C_4H_8N_4$          |
| Fin                 | al residual           | 21.2    | 18.7          | $Gd_2O_3$            |
| $Dy_{(1)}$          | 25 - 70               | 6.2     | 5.8           | 6(H <sub>2</sub> O)  |
| $\mathrm{Dy}_{(2)}$ | 70 - 220              | 21.6    | 20.8          | $6(NO_3)$            |
| $Dy_{(3)}$          | 220 - 435             | 46.5    | 47.2          | $C_{48}H_{48}N_8O_4$ |
| $\mathrm{Dy}_{(4)}$ | 435 - 540             | 6.2     | 6.4           | $C_4H_8N_4$          |
| Final residual      |                       | 21.7    | 19.5          | $Dy_2O_3$            |

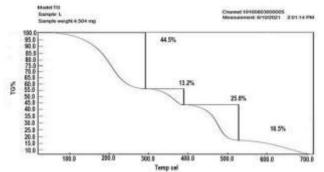
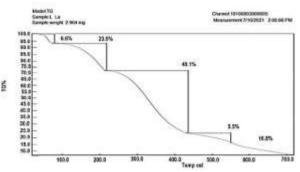
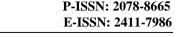


Figure 6. TC-analysis of ligand



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Figure 7. TG- analysis of La complex



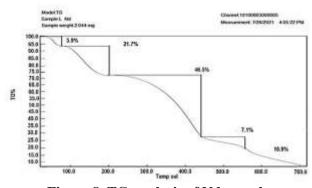


Figure 8. TG-analysis of Nd complex

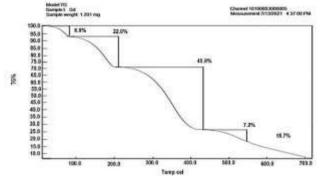


Figure 10. TG-analysis of Gd complex

# Model TD Transpiled ST Transpi

Figure 9. TG-analysis of Er complex

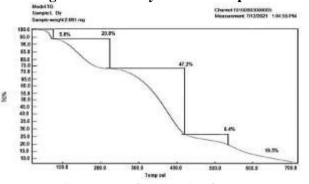


Figure 11. TG-analysis of Dy complex

# **Biological Activity:**

The biological activity of the prepared compounds by diffusion method was studied. Four types of bacteria were used in this study, two types of Gram-positive and two types of Gram-negative:

- 1- *Staphylococcus aureus* and Bacillus subtilis (Gram-positive bacteria)
- 2- Escherichia coli and Klebsiella pneumoniae (Gram-negative bacteria)

These types were tested because of their importance in the medical field, as they cause many diseases. The method used is to calculate the inhibitory effect of chemical compounds (agar well diffusion method) and it is done as follows: 38 mg of agar is dissolved in 1L of distilled water and mixed well in a glass conical flask, then heated until the agar melts, then put the culture medium in a sterile device for 15 minutes, then pour the culture medium into sterile plastic dishes and leave it to solidify. Then the bacteria are grown in a sterile liquid food nutrient medium, where they are left for 24 hours in an incubator and at a temperature of 37°C. A certain concentration of these chemical compounds is prepared and dissolved in a solvent DMSO with  $1 \times 10^{-3}$  M concentrations, then a hole

is made in each dish using a pure cork piercing with a diameter of 1 ml after that, 0.1 ml of the solutions is placed in the holes of the aquariums planted with bacteria. Then the area of the inhibition zone diameters resulting from the effect of the prepared compounds was measured using a ruler, and a table was drawn up showing the biological activity of the prepared compounds against bacteria <sup>47</sup>.

In Figure .12, note that ligand L variable activity and complexes as antibacterial are more active, with the ligand showing greater activity against (Gram-positive) Staphylococcus aureus than against other bacteria. The variable activity was also found in the complexes as some complexes showed greater activity against positive bacteria and some against negative bacteria, as shown in Table 5. Showing that  $[Dy_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ complexes are the most effective against all types of bacteria, followed by  $[Gd_2(C_{26}H_{28}O_2N_6)_2 (NO_3)_6]$ .6H<sub>2</sub>O. and  $[Er_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ , while  $[La_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ ,  $(C_{26}H_{28}O_2N_6)_2$   $(NO_3)_6$ ].6H<sub>2</sub>O it only had an inhibitory effect on Gram-positive bacteria and had no effect on Gram-negative bacteria 48.

Table .5 The Biological activity effects of the ligand and its lanthanide complexes dissolved in DMSO at Concentration 1×10<sup>-3</sup>M on four types of pathogenic bacteria

| Sample                                       | Staphylococcus<br>aureus | Bacillus<br>subtilis                    | Escherichia coli | Klebsiella<br>penumoniae |  |  |  |
|--|--------------------------|---|------------------|--------------------------|--|--|--|
| C H CN(I)                                    |                          | 2 |                  | F                        |  |  |  |
| $C_{26}H_{28}O_2N_6(L)$                      | ++                       | +                                       | +                | +                        |  |  |  |
| $[La_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ | ++++                     | ++                                      | -                | -                        |  |  |  |
| $[Nd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ | ++                       | ++                                      | +                | -                        |  |  |  |
| $[Er_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ | +++                      | +++                                     | -                | ++                       |  |  |  |
| $[Gd_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ | ++++                     | ++                                      | +                | +                        |  |  |  |
| $[Dy_2(C_{26}H_{28}O_2N_6)_2(NO_3)_6].6H_2O$ | +++                      | ++                                      | ++               | ++                       |  |  |  |

[(-) indicates (18-20) mm, (+) indicates (21-24) mm, (++) indicates (24-28) mm, (+++) indicates (28-32) mm, (++++) indicates (32-35) mm]

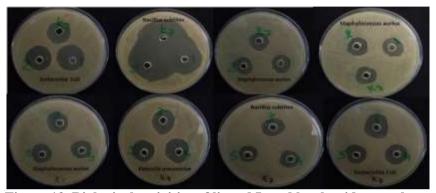


Figure 12. Biological activities of ligand L and lanthanide complexes

# **Conclusion:**

In this study, lanthanide complexes were synthesis and characterization for (La<sup>+3</sup>, Nd<sup>+3</sup>, Er<sup>+3</sup>, Gd<sup>+3</sup>, and Dy<sup>+3</sup>). Schiff's bases are produced by the condensation reaction of (2mol) antipyrinecarboxaldehyde with (1mol) ethylene diamine. The synthesis of Schiff bases ligand and lanthanide complexes by using various analytical and spectroscopic techniques. The complexes were found to be stable at room temperature. Based on the spectroscopic data, it was concluded that lanthanides Ln<sup>+3</sup> coordinates to 16 oxygen atoms (12 from nitrate and four from antipyrine ligand) four nitrogen azomethine (C=N), multidentate ligand, and their binuclear complexes with lanthanides. We conclude that the complexes are more biologically effective than the ligand, is more bioactivity complexes bacteria Staphylococcus aureus and Bacillus subtilis.

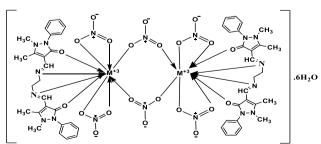


Figure 13. Suggesting the structure of lanthanide complexes

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# **Authors' declaration:**

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for republication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

# **Authors' contributions statement:**

N. Sh. conceived this idea, based on the expressions of K. A. H. and Sh. M. N. Sh. supervised the project. K. A. H. and Sh. M. carried out the experiment, wrote the manuscript, and performed the analysis. All authors discussed the results and contributed to the final manuscript.

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# التشخيص وتحضير لمعقدات اللانثانيدات الجديدة مع قاعدة شف المشتقة من (4-أنتيبيرين كربوكسالدهيد مع إيثيلين داى أمين) ودراسة النشاط البيولوجي

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# الخلاصة:

تضمنت الدراسة تحضير معقدات جديد من خلال الجمع بين قواعد شف الناتجة من مركبات اللانتيبايرين ، بما في ذلك أيونات اللانثانيدات (اللانثانوم، والنيوديميوم، والإربيوم، والجادولينيوم، والديسبروسيوم). حضر الليكاند من تفاعلات التكثيف (٤٠ - انتيبيرين كاربوكسالدهيد مع ايتلين داي امين) في درجة حرارة الغرفة، وتم تشخيصها باستخدام الدراسات الطيفية والتحليلية (أطياف الأشعة تحت الحمراء، الأطيافُ الإلكترونيةُ (طيفُ الآشعة فوق البنفسجية-المرئيةُ)، طيف الرنين النووي المغناطيسي، طيف الكتلي، تُحليل الدقيق للعناصر (الكاربون. الهيدروجين النتروجين . الاوكسجين)، التحلل الحراري الوزني (TGA) ، بالإضافة إلى الحساسية المغناطيسية وقياس الموصلية المولارية للمعقدات، من بين النتائج التي حصلنا عليها من القياسات لاحضنا أن الليكاند يسلك مع أيونات اللانثانيدات (تنائية النوى) السلوك رباعي المخلب من خلال ذرتين من الأكسجين مجموعة الكاربونيل وذرتان نيتروجين مجموعة الأزوميثين مع جميع المعقدات المحضرة و بنسبة مولية (1:1). تم التحقق من تناسق من خلال مشاركة ست مجاميع من نترات ثنائية المخلب في التنسيق، وتشير إلى أن مجمعاتها تحتوي على قيم للعزم المغناطيسية ذات الصفة البارامغناطيسي، وبناءً على نتائج تلك القياسات، تم اقتراح الشكل الهندسي للمعقدات. تمت دراسة الفعالية البيولوجية لليكاند والمعقدات المحضرة باستخدام النشاط المضاد للبكتيريا، حيث أظهرت نتائج فعاليتها اتجاه البكتيريا المستخدمة (المكورات العنقودية الذهبية، العصوية الرقيقة، الإشريكية القولونية أو العصيات القولونية و الكَلِبْسية الرئوية) بتركيز (1×10-3 مول)

الكلمات المفتاحية: ٤ - انتيبيرين كربوكسالدهيد ، النشاط البيولوجي ، المعقدات المعدنية (اللانثانيدات) ، قواعد شف, تحلل الحراري