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Synthesis, density functional theory calculations and luminescence of lanthanide complexes with 2,6-bis [(3-methoxybenzylidene)hydrazinocarbonyl] pyridine Schiff base ligand

Ziyad A. Taha¹ | Taher S. Ababneh² | Ahmed K. Hijazi¹ | Qutaiba Abu-Salem³ | Abdulaziz M. Ajlouni¹ | Shroq Ebwany¹

¹Department of Applied Chemical Sciences, Faculty of Arts and Sciences, Jordan University of Science and Technology, Irbid, Jordan

²Department of Chemistry, Tafila Technical University, Al-Tafila, Jordan

³Department of Chemistry, Faculty of Science, University of Al al-Bayt, Al-Mafraq, Jordan

Correspondence

Ziyad A. Taha, Department of Applied Chemical Sciences, Faculty of Arts and Sciences, Jordan University of Science and Technology, Irbid 22110, Jordan. Email: tahaz33@just.edu.jo

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Abstract

A pyridine-diacylhydrazone Schiff base ligand, L = 2,6-bis[(3-methoxy benzylidene) hydrazinocarbonyl]pyridine was prepared and characterized by single crystal X-ray diffraction. Lanthanide complexes, Ln–L, {[LnL(NO₃)₂]NO₃.xH₂O (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Er)} were prepared and characterized by elemental analysis, molar conductance, thermal analysis (TGA/DTGA), mass spectrometry (MS), Fourier transform infra-red (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy. Ln–L complexes are isostructural with four binding sites provided by two nitro groups along with four coordination sites for L. Density functional theory (DFT) calculations on L and its cationic [LnL(NO₃)₂]⁺ complexes were carried out at the B3LYP/ 6-31G(d) level of theory. The FT-IR vibrational wavenumbers were computed and compared with the experimentally values. The luminescence investigations of L and Ln–L indicated that Tb–L and Eu–L complexes showed the characteristic luminescence of Tb(III) and Eu(III) ions. Ln–L complexes show higher antioxidant activity than the parent L ligand.

KEYWORDS

DFT, lanthanide complexes, luminescence, Schiff Base, X-ray

1 | INTRODUCTION

Considering the photophysical and magnetic significance of lanthanide ions, there is overriding interest in the development of their complexes.^[1] Lanthanide complexes exhibit potential applications in biomedical diagnostics, catalysis, tunable photonic devices, magnetic resonance imaging, luminescence, metalloorganic chemical vapor deposition and sol-gel technology, organometallic and medicinal chemistry.^[2-5]

Acylhydrazones are an important class of Schiff base compounds with a keto-type structure (O = C-N-N = CH-). In the recent past, pyridine-diacylhydrazones ligands possessing a central pyridine ring and two alkoxybenzaldehyde moieties on each side connected by a carbohydrazide linkage have attracted much attention not only for their aesthetically fascinating structures but also for their broad range of biological activities such as antioxidant, antimicrobial, anticancer, antiinflammatory, analgesic, hypotensive, agonistic, and hallucinogenic.^[6-11] Furthermore, pyridine-diacylhydrazones are important multidentate ligands for the construction of coordination complexes with metal centers.^[12-16] Their metal complexes have attracted intense interest in many areas such as multimetallic enzymes, homogeneous and heterogeneous catalysis.^[16-18]

Following our recently published work towards the complexation of lanthanide(III) nitrate salts with dimethyl pyridine-2,6dicarboxylate, we were interested in the synthesis of a 2,6-bis[(3methoxybenzylidene)hydrazine carbonyl]pyridine L ligand derived from dimethyl pyridine-2,6-dicarboxylate ligand.^[19] In comparison with dimethyl pyridine-2,6-dicarboxylate ligand, the L ligand possesses more coordination sites that can bind and stabilize different

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Abbreviations used: DFT, density functional theory; DMF, dimethylformamide; DMSO, dimethylsulphoxide; DTGA, differential thermogravimetric analysis; HAT, hydrogen atom transfer; IR, infra-red; NMR, nuclear magnetic resonance; TCSPC, time-correlated single photon counting; TMS, tetramethylsilane; UV, ultraviolet.

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lanthanide metal ions with high coordination numbers. Moreover it has flexible groups that can accommodate and protect lanthanide metal atoms from solvent molecules, which avoid non-radiative deactivation processes.^[20] Moreover, L is efficient in the displacement of water molecules present in the coordination sphere of lanthanide ions that quenches the luminescence by absorption of the emitted radiation in the vibrational excitation processes via the vibrational levels of the O-H of water molecules.^[21]

This work reports the synthesis of the L ligand by a condensation reaction between 2-methoxybenzaldehyde and 2,6bis(hydrazinocarbonyl)pyridine in ethanol and describes its crystal structure. Additionally the coordinating behavior of L with lanthanide metals (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Er) has been investigated by elemental analysis, conductivity measurements, spectral analysis (IR, NMR, UV-Vis and mass) and thermal studies. The antioxidant activity and photoluminescence properties of L and Ln-L have been investigated.

2 | EXPERIMENTAL

2.1 | Materials

All materials used were purchased from commercial suppliers as AR grade and used without further purification. 2,6-Bis(hydrazinocarbonyl)pyridine was synthesized following a previously reported procedure.^[22]

2.2 | Measurements

Elemental analyzes were measured on a Euro EA elemental CHN analyzer 3000. The Ln-L complexes were analyzed for their lanthanide contents by complexometric titration with EDTA using xylenol orange as an indicator after decomposition with HCl.^[23] Mass spectra were measured using an API-3200 mass spectrometer equipped with an ESI (electrospray ionization) source and the detection was performed on positive mode ionization. The infrared spectra were recorded as KBr pellets on a JASCO FT-IR model 470 spectrophotometer in the region 4000-400 cm⁻¹. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance spectrophotometer (400 MHz) in D₆-DMSO using tetramethylsilane (TMS) as an internal standard reference. Conductance measurements were recorded at room temperature in dimethylformamide (DMF) $(1.0 \times 10^{-3} \text{ M})$ using a WTW LF 318 conductivity meter with cell type WTW Tetracon 325 and cell constant 0.97. TGA thermograms were collected in the temperature range 300-1200 K using a Con PCT-2A thermobalance analyzer with a heating rate of 10 K min⁻¹. Electronic absorption spectra were measured on a UV-2401PC UV-Visible spectrophotometer (Schimadzu Corporation) in the range 200-700 nm in dimethylformamide (DMF) solutions at room temperature. Emission spectra were recorded in DMF $(1.0 \times 10^{-6} \text{ M})$ at constant room temperature on an Edinburgh instrument model FS900SDT spectrophotometer equipped with 1.0 cm quartz cuvettes in wavelength range 200 to 700 nm with a spectral resolution of 2.0 nm. In addition, its light source and detectors were a 450 W Xe lamp and an R955 photomultiplier tube, respectively. Luminescence decay curves were measured using a time-correlated

single photon counting technique (TCSPC) using an Edinburgh Instruments unit model 199. Photoluminescence quantum yields (Φ) of the complexes were obtained using sulfuric acid solution (0. 1 M) of quinine sulfate (0.1 µg ml⁻¹) as a standard reference at 25°C. Single crystal X-ray diffraction data of the L were collected on a Bruker APEX 2 DUO diffractometer at 100 K with monochromatic Cu K α radiation $(\lambda = 1.54178 \text{ Å})$ and crystal size $0.20 \times 0.10 \times 0.10 \text{ mm}^3$. The data were integrated, scaled and corrected for absorption with SADABS using multi-scan method.^[24] The structure was solved by direct methods SHELXS-97 and refined with SHELXL-2013.^[25,26] H atoms were refined at idealized positions riding on the parent C or N atoms with isotropic displacement parameters Uiso (H) = 1.2 Ueq (C/N) or 1.5 Ueg (-CH₃) and C-H 0.95-0.98 Å and N-H 0.88 Å. The antioxidant activity of the different compounds was estimated by the DPPH[•] (diphenyl picryl hydrazyl) radical scavenging method reported previously.^[19]

2.3 | Synthesis of the ligand L

To a hot suspension of 2,6-bis(hydrazinocarbonyl)pyridine (0.195 g, 1 mmol) in 20 ml of absolute ethanol, a solution of 2methoxybenzaldehyde (0.272 g, 2.0 mmol) in 40 ml of ethanol was added with stirring and refluxed for 3 h. The white precipitate obtained was collected by filtration, washed with ethanol and air dried. The product was further re-crystallized from ethanol and the filtrate was kept at room temperature. After about 2 weeks, a colorless needle single crystal suitable for X-ray diffraction was obtained and separated by filtration. Yield: 91%; M. Pt. = 274.7-275.5°C; ¹H NMR (400 MHz, DMSO-d₆, ppm) δ: 3.93 (6H, s, -OCH₃), 7.05-7.07 (2H, m, Ar), 7.16-7.18 (2H, d, Ar), 7.45-7.47 (2H, m, Ar), 7.94-7.96 (2H, d, Ar), 8.27-8.29 (1H, m, py), 8.34-8.36 (2H, dd, py), 9.09 (2H, s, -N = CH), 12.35 (2H, s, -NH). ¹³C NMR (100 MHz, DMSO-d₆, ppm) δ: 162.1, 160.7, 151.07, 147.9, 142.6, 134.7, 128.4, 128.2, 124.8, 123.6, 114.7, 58.5. IR (KBR, cm⁻¹) 3170, 1677, 1659, 1600, 1572, 1248, 1159, 1080. Anal. Calcd. for C₂₃H₂₁N₅O₄: C, 64.03; H, 4.91; N, 16.23. Found; C, 64.17; H, 4.85; N, 16.07. ESI-MS (positive mode, m/z) calculated for $C_{23}H_{21}N_5O_4 [L + H]^+ = 431.2$, found 432.2.

2.4 | Synthesis of the complexes, Ln-L

All complexes were obtained following the same general procedure. To a solution of the L ligand (1.0 mmol, 0.432 g) dissolved in 10 ml chloroform, 1.0 mmol of lanthanide nitrate {Ln(NO₃)₃.xH₂O, x = 6 for Ln = La, Pr, Nd, Sm, Gd, Tb, Dy; x = 5 for Ln = Eu and Er) dissolved in 10 ml ethylacetate was slowly added at room temperature. The mixture was stirred at room temperature for 3 h. The precipitate formed was filtered off, washed several times with 1:1 V:V ratio of ethyl acetate: chloroform mixture and dried under vacuum. All attempts to grow a single crystal suitable for single X-ray diffraction were unsuccessful.

[LaL(NO₃)₂]₂(NO₃)₂.4H₂O: Yield: 67%; ¹H NMR (400 MHz, DMSO- d_{6} , ppm) δ: 3.94 (6H, s, -OCH₃), 3.85 (6H, s, -OCH₃), 7.05–8.35 (22H, Ar), 9.04 (2H, s, -N = CH), 8.96 (2H, s, -N = CH), 12.46 (2H, s, -NH), 12.28 (2H, s, -NH).. ¹³C NMR (100 MHz, DMSO- d_{6} , ppm) δ: 159.44, 158.95, 148.34, 147.8, 142.9, 134.7, 128.1, 128.2, 124.6, 123.7, 114.9, 56.3.

2.5 | Computational method

All DFT calculations were performed with the Spartan 16 software package at the B3LYP/6-31G(d) level of theory which uses Becke's three-parameter hybrid function $B3^{[27,28]}$ with the non-local correlation of Lee-Yang-Parr LYP^[29] and the polarized 6-31G(d)^[30,31] basis set in the gas phase. Geometry of the L ligand and the cationic lanthanide complexes [LnL(NO₃)₂]¹⁺ were fully optimized without any specific geometrical constraints. The absence of imaginary frequencies in the vibrational analysis indicated a minimal energy structure.^[27-31]

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the L ligand

The L ligand was synthesized in high yield (91%) by a simple condensation reaction of 2-methoxybenzaldehyde with 2,6-bis(hydrazinocarbonyl)pyridine in ethanol (Scheme 1).

The CHN analysis is in agreement with the formula of the L ligand. The L ligand was soluble in DMSO, DMF and chloroform. The IR spectrum of L displayed in Figure 1 shows several bands at 3170, 1677, 1659, 1600, 1572, 1248, 1159 and 1080 cm⁻¹ assigned to N–H, C = O, C = N (azomethine), C = C, C = N (pyridine), C–O (phenolic), C–N and N–N groups, respectively, Figure 1(i, a). In addition, a group of medium and weak absorption bands in the region 3100–2800 cm⁻¹ due to C–H stretching vibrations of aromatic and methoxy groups are



seen together with a broad absorption band extending from 3700 to 3000 cm^{-1} , Figure 1(ii, inset), due to the intermolecular hydrogen bonding [N-H-··O] and [C-H-··O] interactions.^[13] The ¹H NMR spectrum of L shows two singlets at 9.09 and 12.35 ppm corresponding to the resonances of HC = N and NH protons. The pyridine and aromatic protons are resonated in the regions of 8.27-8.36 (integrating for three protons) and 7.05-7.96 ppm (integrating for eight protons), respectively. A sharp singlet at 3.85 ppm is attributed to six protons of methoxy groups. ¹³C NMR spectrum has shown four signals for the C = O, Ar-O, HC = N and OCH₃ carbons at 162.14, 160.65, 151.07 and 58.45 ppm respectively. The δ (ppm) at 147.90, 142.59, 134.69, 128.38, 128.15, 124.83, 123.59 and 114.71 are due the carbon atoms of pyridine and aromatic rings.

3.2 | X-ray structure of L ligand

The molecular structure of L is shown in Figure 2, crystal data are presented in Table 1, and selected bond lengths and angles are listed in Table 2. L has C15/C19/N20/N21, C13/C12/N11/N10, C1/C9/ N10/N11 and C23/C22/N21/N20 torsion angles of 175.4(2)°, 174.2(2)°, 177.3(2)° and 178.0(2)°, respectively. The dihedral angles of the pyridine ring plane with the aromatic planes II [O30, C24, C23, C28, C27, C26 and C25] as well as III [O7, C2, C1, C6, C5, C4 and C3] are 51.5(2)° and 38.3(2)°, respectively. Planes II and III (aromatic rings) are almost orthogonal with a dihedral angle 84.8(2)°. The C = N bond distance [1.283(2) Å] is in good agreement with that reported



FIGURE 1 Infrared spectra for (a) I and (b) eu-I complex in the range of: 1800-1000 (i) and 1000-400 (inset 4000-2500) (ii)

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FIGURE 2 Molecular structure of L with anisotropic displacement ellipsoids drawn at the 50% probability level

 TABLE 1
 Crystallographic data for the L ligand

| Empirical formula | $C_{23}H_{21}N_5O_4$ |
|---|------------------------------------|
| Formula mass | 431.45 |
| Temperature (K) | 100(2) |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimension (Å, °) | |
| а | 7.9385 (1) |
| b | 11.5587 (2) |
| c | 12.5666 (2) |
| α | 90.532 (1) |
| β | 95.347 (1) |
| γ | 107.948 (1) |
| Volume, Å ³ , Z | 1091.33 (3), 2 |
| Calculated density, (mg/ m ³) | 1.313 |
| μ (mm ⁻¹) | 0.76 |
| F(000) | 452 |
| Crystal size (mm ³) | 0.20 × 0.10 × 0.10 |
| Range for data collection (°) | 3.5-66.1 |
| Index ranges (h, k, l) | -9/9, -13/13, -14/14 |
| Reflections collected | 24225 |
| Independent reflections | 3665 ($R_{int} = 0.069$) |
| Absorption correction | Multi-scan |
| Refinement method | Full-matrix least-squares on F^2 |
| Data/ restraints/ parameters | 3665/0/291 |
| Goodness-of-fit on F ² | 1.06 |
| Final R indices $[l > 2\sigma (l)]$ | $R_1 = 0.043, wR_2 = 0.112$ |
| Final R (all data) | $R_1 = 0.044, wR_2 = 0.110$ |
| $\Delta ho_{max/min}$ (e·Å ⁻³) | 0.45/-0.45 |

in the literature.^[32] Also the carbonyl C19–O29 and C12–O18 reveals one-dimensional network. The building unit of this network composed of supramolecular dimer structures assembles through short hydrogen bonding interactions between the amide H and the carbonyl oxygens

TABLE 2 Selected bond lengths (Å) and angles (°) for the L

| Bond angles | | |
|-------------|---|--|
| 1.227 (2) | O18-C12-C13 | 121.01 (12) |
| 1.225 (2) | O29-C19-C15 | 120.68 (12) |
| 1.283 (2) | O18-C12-N11 | 124.88 (12) |
| 1.283 (2) | O29-C19-N20 | 124.68 (12) |
| 1.381 (2) | C9-N10-N11 | 114.31 (11) |
| 1.380 (2) | C22-N21-N20 | 115.95 (11) |
| 1.351 (2) | | |
| 1.353 (2) | | |
| | Bond angles 1.227 (2) 1.225 (2) 1.283 (2) 1.283 (2) 1.381 (2) 1.380 (2) 1.351 (2) 1.353 (2) | Bond angles 1.227 (2) O18-C12-C13 1.225 (2) O29-C19-C15 1.283 (2) O18-C12-N11 1.283 (2) O29-C19-N20 1.381 (2) C9-N10-N11 1.380 (2) C22-N21-N20 1.351 (2) Image: Comparison of the state |

TABLE 3 Hydrogen bond geometry (Å, °)

| D-H···A | D-H | Н…А | D····A | D-H…A |
|---------------------------|------|------|-----------|-------|
| N11-H11-029 ⁱ | 0.88 | 2.07 | 2.895 (1) | 154.6 |
| N20-H20-018 ⁱⁱ | 0.88 | 2.00 | 2.855 (1) | 164.4 |
| C9-H9-029 ⁱ | 0.95 | 2.32 | 3.141 (2) | 144.9 |
| C22-H22-O18 ⁱⁱ | 0.95 | 2.55 | 3.324 (2) | 139.3 |

[a] Symmetry codes: (i) - x, -y + 1, -z + 1; (ii) - x + 1, -y + 1, -z + 1

as well between C9/C22–H and oxygen atoms (Table 3). The supramolecular dimer structures are connected via two types of intermolecular N–H···O and C–H···O [N20–H20···O18 2.00 Å; N20–H20–O18 164.4°, C22–H22···O18 2.55 Å; C22–H22–O18 139.3°] hydrogen bonding interactions. The dimeric supramolecules are then connected to the next one through the carbonyl oxygen O29 atom via also N– H···O and C–H···O hydrogen bonding interactions [N11–H11···O29 2.07 Å; N11–H11–O29 154.6°, C9–H9···O9 2.32 Å; C9–H9–O9 144.9°]. These hydrogen bonding interactions result in supramolecular arrays of endless chains of dimeric units running along the *a*-axis (Figure 3).

O hydrogen bonding interactions running along the *a*-axis. Hydrogen bonds are shown as dashed red lines with some labeled atoms (other C–H atoms were omitted for clarity).

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FIGURE 3 Partial crystal packing diagram, viewed down the *b* crystallographic axis, showing $N-H\bullet\bullet\bullet$ and $CH\bullet\bullet\bullet$

3.3 | Properties of the complexes

Direct mixing of L with the nitrates of Ln(III) ions at room temperature in a molar ratio 1:1, formed complexes with the general formula LnL(NO₃)_{3·x}H₂O as is evident from the elemental analysis. The complexes were stable, non-hygroscopic and yellow in color (except for La, which was white). They were soluble in DMF and DMSO, insoluble in H₂O, CHCl₃, THF, CH₃CN and C₆H₆. In DMF, Ln-L molar conductivity (Λ_m) values lie in the range of 69.7–79.8 Ω^{-1} cm⁻¹ mol⁻¹ and are consistent with that reported for 1:1 electrolytes.^[33] The mass spectrum of the Sm-L complex showed peaks at 707.24, 645.44 and 586.52 m/z that are attributed to Sm mono-ligand species [SmL(NO₃)₂]⁺, [SmL(NO₃)]⁺² and [SmL]⁺³, respectively. In addition, several atomic ions were presented in the low mass range of the spectrum, including Sm (m/z = 151.3) and NO₃⁻ (m/z = 62.47). Mass spectra of other Ln-L complexes showed fragmentation patterns qualitatively similar to each other and similar to the Sm-L complex, exhibiting a mono-nuclear peak [LnL(NO₃)₂]⁺ (Table 4).

Thermograms of the free L revealed a remarkable single-step mass loss centered at 624 K and corresponding to complete degradation of L (Figure 4). Thermograms of the Ln–L complexes were approximately similar, indicating isostructural complexes. As general examples, Sm–L and Eu–L thermograms are shown in Figure 4. It is

evident that H₂O is present in the structure of these complexes. The TGA thermograms showed a gradual weight loss step starting from 300 K to 401 K with a major loss at 342 K for Sm-L and from 303 K to 371 K with a major loss at 342 K for Eu-L. The observed losses of 4.78% (calcd. 4.47%) and 2.28% (calcd. 2.03%) may be attributable to the giving away of two and one uncoordinated H₂O molecules from Sm-L and Eu-L complexes, respectively. Further weight losses were observed in the range of 401-580 K and 371-574 K with peak temperatures at 539 K and 537 K for Sm-L and Eu-L complexes, respectively. These can be apparently associated with the release of three nitrates groups from Sm (weight loss 22.4%, calcd 23.1%) and Eu (weight loss 25.65%, calcd. 24.61%) structures. Furthermore, the thermograms showed a loss starting from 580 K to 873 K with a couple of major losses at 614 K (11.43%,) and 745 K (20.31%,) for Sm-L and from 574 K to 861 K with major losses at 605 K (10.58%,) and 727 K (20.88%,) for Eu-L. The latter stage seems to be the final step of thermolysis and may be due to the collapse of the L ligand. Thereafter, weight decreased gradually with a rate of about 5% per 100 K and reduced at 1100 K to 20.1% (calc. 21.61) and 22.89% (calcd. 22.35%) of the initial values for Sm-L and Eu-L complexes, respectively. The residual weight of the complexes basically agrees with the calculated values and may correspond to the formation of Sm₂O₃ and Eu₂O₃.^[34]

TABLE 4 Yield, elemental analytical and molar conductance (Λ_m) data of the L ligand and its complexes

| | | | Found (calculated | | | | |
|---|--------------|-----------|-------------------|-------------|---------------|-------------|----------------------------------|
| Complex | Abbreviation | Yield (%) | С | Н | N | Ln | Λ _{ma} (Ω-1 cm-1 mol-1) |
| $C_{23}H_{21}N_5O_4$ | L | 91 | 64.17 (64.03) | 4.85 (4.91) | 16.07 (16.23) | - | 0.89 |
| [LaL(NO ₃) ₂]NO ₃ .2H ₂ O | La-L | 67 | 35.28 (34.86) | 3.20 (3.18) | 13.79 (14.14) | 17.0 (17.5) | 72.3 |
| [PrL(NO ₃) ₂]NO ₃ .2H ₂ O | Pr-L | 87 | 35.23 (34.77) | 3.13 (3.17) | 14.15 (14.11) | 19.1 (18.7) | 69.7 |
| [NdL(NO ₃) ₂]NO ₃ .H ₂ O | Nd-L | 95 | 35.76 (35.43) | 2.79 (2.97) | 14.62 (14.37) | 18.0 (18.5) | 76.7 |
| [SmL(NO ₃) ₂]NO ₃ .2H ₂ O | Sm-L | 83 | 34.12 (34.37) | 3.15 (3.13) | 13.48 (13.94) | 18.2 (18.7) | 74.0 |
| [EuL(NO ₃) ₂]NO ₃ .H ₂ O | Eu-L | 92 | 34.68 (35.08) | 3.30 (2.94) | 14.48 (14.23) | 19.3 (19.3) | 77.8 |
| [GdL(NO ₃) ₂]NO ₃ .H ₂ O | Gd-L | 89 | 34.73 (34.85) | 2.71 (2.92) | 14.41 (14.14) | 19.7 (19.8) | 76.0 |
| [TbL(NO ₃) ₂]NO ₃ .2H ₂ O | Tb-L | 94 | 33.73 (34.00) | 3.55 (3.16) | 13.37 (13.79) | 19.8 (19.6) | 79.8 |
| [DyL(NO ₃) ₂]NO ₃ .2H ₂ O | Dy-L | 85 | 33.63 (33.85) | 3.43 (3.09) | 13.29 (13.73) | 19.6 (19.9) | 74.8 |
| [ErL(NO ₃) ₂]NO ₃ .H ₂ O | Er-L | 91 | 34.29 (34.41) | 3.58 (2.89) | 13.70 (13.96) | 20.6 (20.8) | 73.4 |

[a] 1.0×10^{-3} M at 25°C in DMF.



FIGURE 4 Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) of: L, Eu–L and Sm–L complexes

Complexation affects the NMR spectrum by making the HC = N, O-CH₃ and NH proton resonances non-equivalent. This effect shows up most clearly in the ¹H NMR spectrum of the La-L complex in which the resonances appear as pairs, within about 0.2 ppm of one another.^[13] The chemical shift for the N = CH proton is observed as a pair at δ 9.04 and 8.96 ppm. The signals at δ 12.46 and 12.28 ppm corresponded to NH protons. The signals in the δ 7.05–8.35 ppm region integrating for 11 protons were assigned to the protons of the aromatic and pyridine rings. The two singlets at δ 3.85 and 3.94 ppm integrating for 6 H correspond to the protons of the –CH₃OH groups. The ¹³C NMR spectrum of La–L exhibits 12 resonances as in the free L ligand. The four signals at δ 159.44, 158.95, 148.34 and 56.3 ppm were due to C atoms of C = O, C–O, CH = N and OCH₃ groups, respectively. The eight resonances located between δ 145.00–112.02 ppm were attributable to the aromatic and pyridine carbon atoms.

The FT-IR spectral data of L and its Ln–L complexes are listed in Table 5. The data of Ln–L complexes were almost similar, reflecting the similarity in the coordination environment around Ln ions in the complexes. Comparing the IR spectrum of Eu–L complex with the free L ligand, we observed the presence of an absorption band attributable to v(N-H) at 3176 cm⁻¹ and a shift of the v(C = O) band to a lower frequency of 1645 cm⁻¹ (Figure 1i). This may indicate that the coordination to Eu(III) ion occurs through the C = O oxygen atoms in keto form. Tamboura et *al.* report a similar observation for La and Er complexes with polyhydrazone Schiff base ligands derived from 2,6-

diformyl-4-chlorophenol and hydrazides.^[35] The coordination in the keto form has been further supported by the appearance of the C-N and N-N bands at 1164 and 1079 cm⁻¹ nearly in the same positions as in the free L ligand.^[36] The observed large shift in the azomethine v(C = N) at 1545 cm⁻¹ is again in agreement with Tamboura et al. report and is evidence of C = N nitrogen atom coordination with Eu(III) ion, Figure 1(i).^[35] Conversely, the u(C = N) mode of the pyridine ring at 1572 cm⁻¹ and its other two vibrations at 1465 and 1487 cm⁻¹ are nearly in the same positions as in the free L. Figure 1(i).^[14] This result confirmed that the pyridine N atom is not involved in the coordination. Further evidence for the coordination through both N and O atoms comes from the appearance of two new non-ligand bands at 430 and 477 cm⁻¹, which were tentatively assigned to v(Eu-O) and v(Eu-N), respectively, Figure 1(ii).^[37] Moreover, the presence of a broad band extending from 3700 to 3250 cm⁻¹ with two maxima at 3420 and 3265 cm⁻¹ could mean that uncoordinated water molecules are present in the complex, as is evident from the TGA study. The water molecules may be hydrogen bonded with each other or with the oxygen of the nitrates.^[17,35] The Eu-L spectrum also exhibited nitrate absorption bands at 1495, 1322, 1295, 1021 and 818 cm⁻¹ (Figure 1). The separation between the 1495 and 1295 cm⁻¹ bands, which were assigned to v_5 and v_2 stretching modes of the coordinated nitrate groups ($C_{2\nu}$), is 200 cm⁻¹ and consistent with the general trend observed for nitrate ions coordinated bi-dentately to metals in complexes.^[38] The absorp-

As all attempts performed to get a single crystal suitable for X-ray diffraction were unsuccessful for any one of the isolated Ln–L complexes, we have proposed a mono-nuclear structure based on the analytical and spectral studies discussed above. The Ln(III) in the proposed structure was coordinated with two C = O oxygen atoms and two C = N nitrogen atoms of L. The coordination sphere of Ln(III) was completed by two bi-dentate nitrate ions for a total coordination number of eight (Figure 5).

tion band that appeared at 1385 cm^{-1} was attributed to D_{3h} of free

3.4 | Computational

ionic nitrate^[38] (Figure 1i).

DFT calculations were carried out to investigate the structure, energy and properties of the title L ligand and its cationic monoligated lanthanide species $[LnL(NO_3)_2]^+$ at the B3LYP/6–31G(d) level of theory. The

TABLE 5 Infrared spectral data of the L ligand and its Ln-L complexes

| | | | | | | | v(NO ₃ ⁻) | v(M-N) | v(M-O) | | | |
|---------|--------|----------|------------------|--------|------------------|--------|----------------------------------|----------------|---------------------------------|----------------|--------|--------|
| Complex | v(N-H) | v(C = O) | $v(C = N)_{azo}$ | v(C-N) | $v(C = N)_{pyr}$ | v(N-N) | v ₁ | v ₄ | v ₁ - v ₄ | V ₀ | v(M-N) | v(M-O) |
| L | 3170 | 1677 | 1659 | 1159 | 1572 | 1078 | - | - | - | - | - | - |
| La-L | 3162 | 1645 | 1545 | 1166 | 1573 | 1080 | 1495 | 1284 | 211 | 1384 | 476 | 425 |
| Pr-L | 3165 | 1642 | 1549 | 1164 | 1572 | 1074 | 1489 | 1287 | 202 | 1386 | 477 | 429 |
| Nd-L | 3164 | 1644 | 1547 | 1162 | 1573 | 1079 | 1492 | 1888 | 204 | 1384 | 475 | 424 |
| Sm-L | 3164 | 1645 | 1543 | 1162 | 1575 | 1075 | 1498 | 1285 | 213 | 1385 | 477 | 428 |
| Eu-L | 3176 | 1645 | 1546 | 1164 | 1574 | 1079 | 1495 | 1295 | 200 | 1385 | 477 | 430 |
| Gd-L | 3169 | 1642 | 1547 | 1165 | 1571 | 1078 | 1495 | 1289 | 206 | 1384 | 475 | 428 |
| Tb-L | 3174 | 1641 | 1545 | 1163 | 1573 | 1076 | 1493 | 1288 | 205 | 1385 | 479 | 431 |
| Dy-L | 3172 | 1643 | 1549 | 1161 | 1572 | 1079 | 1490 | 1285 | 205 | 1384 | 477 | 427 |
| Er-L | 3163 | 1677 | 1546 | 1159 | 1573 | 1075 | 1493 | 1887 | 206 | 1384 | 477 | 426 |

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FIGURE 5 The optimized ground state geometry for the $[LnL(NO_3)_2]^{1+}$ complexes at the B3LYP/631G(d) level of theory showing th atom-numbering scheme around the lanthanide ion

optimized ground state geometries of L and its Ln(III) complexes at the B3LYP/6–31G(d) level of theory are shown in Figures 6 and 5, respectively. Selected structural parameters for the optimized L ligand along with the experimentally determined values are listed in Table 2. Considering the noticeably small percent differences Δ % (0.06–1.8%) between the observed and calculated structural parameters, it can be appropriately noted that there is a good agreement between the X-ray crystal structure and the theoretically predicted geometry.

The outcome for the geometrical optimization supports octadentate coordination of the L and nitro groups to the lanthanide ion. This proposal is feasible through four binding sites provided by the two nitro groups along with four coordination sites for the L ligand depicted in two Ln–O(carbonyl) and two Ln–N(imine) bonds. Selected calculated bond lengths (Å) for the $[LnL(NO_3)_2]^{1+}$ complexes at the B3LYP/631G(d) level of theory are listed in Table 6. The computed FT-IR vibrational analysis of the L ligand revealed several bands at 3483, 1760, 1677, 1647 1620, 1288, 1139 and 1110 cm⁻¹. These bands are associated with N–H and C = O of amide, C = N of

azomethine, C = C of phenyl, C = N of pyridine, phenolic C–O, C–N and N–N groups, respectively. The medium bands observed in the 3100–2800 cm⁻¹ region in the IR spectrum and assigned to C–H stretching vibrations of aromatic and methoxy groups were theoretically predicted in the 3000–3229 cm⁻¹ range. The computed FT-IR vibrational frequency analysis of Ln–L complexes supported the coordination of Ln to two C = O oxygen atoms of the L ligand. This result was well predicted by the shift in the u(C = O) to a lower frequency calculated in the range 1683–1691 cm⁻¹ for complexes.

Additionally, the calculated u(C = N) frequency of the pyridine ring at 1620 cm⁻¹ in the free ligand was not much changed upon complexation (1616–1614 cm⁻¹). This result matches well with the experimental IR data and confirms that the pyridine N atom was not involved in the coordination. The two non-ligand absorption bands attributed to u(Ln-N) and u(Ln-O) in the calculated IR spectrum appeared at 489– 491 cm⁻¹ and 421–427 cm⁻¹, respectively. This result further supports the coordination of Ln(III) to L through the N and O atoms. Moreover, the calculated absorption bands in the 1674–1682 cm⁻¹, 1041–



FIGURE 6 The optimized ground state geometry for the L ligand at the B3LYP/ 631G(d) level of theory

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TABLE 6Calculated bond lengths (Å) for the $[SmL(NO_3)_2]^{1+}$ complexat the B3LYP/631G(d) level of theory

| Bond | Length (Å) | Bond | Length (Å) |
|--------------|------------|-----------------|------------|
| Sm-O1(nitro) | 2.347 | Sm–O5(carbonyl) | 2.653 |
| Sm-O2(nitro) | 2.368 | Sm–O6(carbonyl) | 2.653 |
| Sm-O3(nitro) | 2.368 | Sm-N1(imine) | 2.751 |
| Sm-O4(nitro) | 2.347 | Sm-N2(imine) | 2.751 |

1044 cm⁻¹, 248–251 cm⁻¹ and 1275–1304 cm⁻¹ ranges are assigned to the stretching modes of the two coordinated nitrate groups, which is consistent with the obtained IR data for the complexes.

3.5 | Photophysical properties

The absorption spectrum of L in DMF exhibited three main absorption bands at 328 nm (ϵ = 2.42 × 10⁵ M⁻¹ cm⁻¹), 306 nm (ϵ = 1.50 × 10⁵ M⁻¹ cm^{-1}) and 284 nm ($\epsilon = 1.47 \times 10^5 M^{-1} cm^{-1}$), Figure 7. These bands may be attributed to $n \to \pi^*$ and $\pi \to \pi^*$ intra-ligand transitions. The molar absorptivity, ɛ, increased significantly upon complexation with none or minimum shifts in the maximum wavelengths of the two higherenergy absorption bands. The low-energy absorption band was red shifted by 10–12 nm (Figure 7). These changes implied coordination of L-to-Ln(III) ions. All complexes in DMF displayed almost identical absorption bands with a different increase in ε depending on the kind of Ln(III) ion. The electronic spectrum of L was attained theoretically at the B3LYP/6-31G(d) level of theory predicting a main absorption band at 333 nm and is in good correlation with the experimentally determined λ_{max} from the ligand spectrum. Additionally, all Ln(III)-L complexes exhibited similar calculated spectra with a main absorption band around 343 nm with minimal shifts in the absorption band across all complexes (Figure 8).

Upon UV irradiation ($\lambda_{ex} = 277$ nm), L in DMF emitted a strong luminescence with $\lambda_{max} = 436$ nm assigned to $\pi \rightarrow \pi^*$ intra-ligand transitions, Figure 9(inset). Excitation of Tb–L and Eu–L complexes in DMF at 283 and 281 nm revealed, in addition to the expected transitions of Tb(III) and Eu(III) ions, very weak broad emission bands peaking at 448 and 457 nm, respectively, due to the ligand centered luminance (Figures 9 and 10. The emission spectrum of Eu–L complex showed five peaks at 582, 597, (608, 619 and 626), 663, and 698 nm assigned



FIGURE 7 UV-Vis absorption spectra of (a) the L ligand and (b) the Sm-L complex recorded in DMF at room temperature



FIGURE 8 UV–Vis absorption spectra of L ligand (top) and Sm–L complex (bottom) attained theoretically at the B3LYP/6–31G() level of theory



FIGURE 9 Emission spectrum for Tb–L complex, λ_{ex} = 281 nm recorded in DMF at room temperature. Inset refers to the emissionspectra of (a) L, (b) Sm–L, (c) Dy–L, (d) Tb–L and (e) Eu–L complexes

to the transition of electrons from ${}^{5}D_{0}$ to ${}^{7}F_{J}$ (J = 0, 1, 2, 3, 4) (Figure 9). It is worth noting that the number of Stark components observed for the electric-dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is three and the first component intensity is the highest.^[39] In addition, the high intensity ratio of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and the presence of a single line for non-



FIGURE 10 Emission spectrum for Eu–L complex, λ_{ex} = 283 nm recorded in DMF at room temperature



FIGURE 11 The lifetime decay curves for (a) Tb-L, and (b) Eu-L complexes in DMF solution

degenerated ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition indicated that Ln(III) ions occupied sites with low symmetry and with no inversion center.^[40] In the emission spectrum of the Tb–L complex, the following ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ transitions could be detected: *J* = 6 (491 nm), 5 (547 nm), 4 (596 nm), 3 (623 nm) and 0 (678 nm) (Figure 9). The ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ had the highest intensity.

In contrast, no emission lnes characteristic of lanthanide ions could be detected in the emission spectra of Sm–L and Dy–L complexes in DMF. This finding may be interpreted as a proof of disabling any ligand-to-metal energy-transfer process that is supported by the appearance of large broad bands peaking at 466 and 465 nm for Sm–L and Dy–L complexes, respectively, and attributed to $\pi \rightarrow \pi^*$ intra-ligand transitions (Figure 9, inset). These data clearly demonstrated that the L-to–Ln energy-transfer process takes place more efficiently in the Eu–L and Tb–L complexes. This finding is most likely related to the energy gap between the lowest triplet energy level of L and the resonant energy level of Ln(III). The gap may be optimum for Eu–L and Tb–L complexes and not for Dy–L and Sm–L complexes and lead to less efficient energy transfer.^[41]

Luminescence decay and fit curves for the 5D_4 level of Tb obtained by monitoring the emission at 547 nm attributed to the hypersensitive ${}^5D_4 \rightarrow {}^7F_5$ transition with exciting at 281 nm are shown in Figure 11(a). The decay curve is best fit to multiple exponantial and the experimental lifetimes are obtained to be $\tau_1 = 1.221 \ \mu \text{sec} \ (15.6\%), \ \tau_2 = 5.341 \ \mu \text{sec} \ (38.8\%), \ \tau_3 = 18.45 \ \mu \text{sec} \ (45.6\%) \ (\chi^2 = 1.019) \ \text{and} \ \tau = 14.17 \ \mu \text{sec} \ [\tau = (A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2)].^{[19,42]}$ When the 5D_0 state of Eu(III) is exited



FIGURE 12 DPPH• radical scavenging activity of L and Ln-L complexes measured in DMF

at 582 nm the decay is also multi exponantial fit, Figure 11(b), with the lifetimes $\tau_1 = 0.48 \ \mu \text{sec} (22.3\%)$, $\tau_2 = 2.27 \ \mu \text{s} (36.5\%)$, $\tau_3 = 12.856 \ \mu \text{s} (41.2\%) (\chi^2 = 1.15)$ and $\tau = 11.2 \ \mu \text{sec}$. Luminescence quantum yields equal to 9.5% and 7.3% were determined for Tb-L and Eu-L complexes, respectively. The relatively low yields obtained may be due to non-radiative deactivation pathways through harmonics of O-H vibrations of H₂O molecules present in the coordination sphere. The higher quantum yield of the Tb-L complex compared with the Eu-L complex may be due to the effective match between the triplet state of L and the emitting level of Tb(III).

3.6 | Antioxidant activity

The DPH[•] assay was used to investigate the ability of the L ligand and Ln-L complexes to quench the stable DPPH* radical. DPPH* can be converted by antioxidant to 2,2-diphenyl-1-picryl hydrazine either by radical quenching via hydrogen atom transfer (HAT) or by direct reduction through electron transfer (EA) mechanisms.^[43] Figure 12 clearly shows that Ln-L complexes are more effective than L in quenching DPPH. This enhancement in the activity can be attributed to the formation of lanthanide-ligand complexes that enhances the HAT process.^[44] At the concentration of 312.5 µM, the Dy-L complex with activity of 34% was the strongest guencher and La-L complex with activity of 11% was the poorest effective guencher of all complexes. Notably, the antioxidant potential of the complexes could be seen even at lower concentrations (250, 187.5, 125, and 62.5 μ M). The effectiveness of the Dy-L complex over other complexes showed the significance of metal ion types in enhancing the antioxidant capability.

4 | CONCLUSION

An acyl-dihydazone pyridine ligand was synthesized and characterized by single X-ray diffraction. The ligand was explored for the first time as a coordinating ligand and sensitizer for Ln(III) luminescence. Ln–L complexes were prepared successfully, and their structures were determined by the means of elemental analysis, molar conductance, UV, MS and FT-IR spectra as well as TGA studies. Evidence was presented for the existence of mono-nuclear complexes with a 1:1 ligand-tometal ion stoichiometry. The optimized ground state geometries and FT-IR spectral data for L and its $[LnL(NO_3)_2]^+$ complexes were reported

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using DFT calculations at the B3LYP/6-31G(d) level of theory and the obtained results were in good agreement with the experimental data. The luminescence properties of L and Ln–L indicated that only Eu–L and Tb–L complexes showed corresponding metal luminescence, while the remaining complexes showed only the luminescence of the ligand. The scavenging activities of Ln–L complexes on the DPPH[•] were more effective than that of L, and the Dy–L complex was the most effective.

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