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Original scientific paper

Synthesis, fluorescent studies, antioxidative and α-amylase inhibitory activity evaluation of some lanthanide(III) complexes

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Abstract: A novel heterocyclic ligand, *viz*. 1,2-dihydro-1,5-dimethyl-4-[[1-2--oxo-2*H*-1-benzopyran-3-yl)ethylidene]amino]-2-phenyl-3*H*-pyrazol-3-one, was prepared by condensing 3-acetylcoumarin with 4-aminoantipyrine. This ligand is versatile in forming complexes with lanthanum(III), praseodymium(III), samarium(III), gadolinium(III) and dysprosium(III) ions. The ligand and the metal complexes were characterized through various physicochemical and spectral studies. The spectral studies revealed that the ligand is coordinated to the metal ion in a bidentate fashion, through the azomethine nitrogen and the oxygen atom of the pyrazolone ring. The powder XRD patterns of ligand and the dysprosium(III) complex were studied. The photoluminescent properties of ligand and metal complexes were evaluated and the relative quantum yields were determined. It was observed that in all cases the metal ions enhanced the luminescence intensity. The α-amylase inhibitory activity of the ligand and the metal complexes was evaluated using the method of Apostolidis. The metal complexes exhibited increased activity compared to the ligand. The antioxidant property was also examined using the DPPH assay and the metal complexes were found to be more potent antioxidants than the ligand.

Keywords: 3-acetylcoumarin; lanthanides; luminescence; DPPH assay; Schiff base; rare earths.

INTRODUCTION

The importance of lanthanide(III) complexes in modern technological applications is mainly associated with their spectroscopic, magnetic, photophysical and biological properties.[1] The coordination chemistry of lanthanide(III) complexes with Schiff base ligands has been investigated mainly due to their unique structures and potential pharmacological properties.[2] In recent years lanthanide(III) complexes also have attracted much attention, because of their use in various fields, such as organic light emitting diodes, fluorescent probes, sensors,

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MRI agents, laser materials, molecular optoelectronic devices, *etc*.[3–6] In view of their unique electronic and coordination properties, Schiff bases represent a group of organic ligands used for the preparation of coordination compounds showing interesting physical, chemical and biological properties. Based on the sharp f–f transitions and high quantum yields, it is often thought that lanthanide(III) complexes are the most important components in pursuit of new luminescence materials. These properties of lanthanide complexes and their potential applications were the encouragement to continue studies on some new lanthanide complexes with a Schiff base ligand. The Schiff base was prepared by condensing 3-acetylcoumarin with 4-aminoantipyrine possessing a wide spectrum of biological activity, such as antibacterial, antifungal, anti-inflammatory, anticoagulant, anti-HIV and antitumor properties.[7,8] The resulting Schiff base was expected to surpass either of the parent reagents in its effectiveness of complex formation and biological activities. Apart from this, coumarin derivatives have been used as antenna ligands to harvest the absorption of photon energy and to enhance the efficiency of emission. Considering these aspects, the particular ligand was selected and characterization of the ligand and the metal complexes were achieved on the basis of elemental analysis, molar conductance measurements, and IR, NMR and UV–Vis spectral studies. The luminescence property of ligand and its effect on metallation was also examined. In view of the biological significance of the parent compounds, the antioxidant property and α-amylase inhibitory activity of the ligand and the metal complexes were also investigated.

EXPERIMENTAL

Materials

All chemicals used in this work were of analytical reagent grade, purchased from Aldrich, Merck, Fischer, Sisco (India), *etc*. Solvents used for physicochemical measurements, were purified by standard methods. Elemental analysis for C, H and N were realised using microanalysis. The metal content was estimated by the oxalate-oxide method.[9] Molar conductance measurements were realised using 10^{-3} M solutions of the complexes in a suitable solvent at room temperatures using a Systronic direct reading conductivity meter Type 305. The infrared spectra were recorded using KBr discs on a Shimadzu FTIR 8000 spectrophotometer and electronic spectra were recorded on a Hitachi 320 UV–Vis spectrophometer. Powder X-ray diffraction studies were conducted using a Siemens D 5005 model X-ray spectrometer and indexing was performed using McMaille software. Proton NMR spectra were recorded using on a JEOL GSX 400 NB 400 MHz spectrometer in DMSO-d_6. The fluorescence property was measured using JASCO 8300 spectrofluorometer.

Synthesis of lanthanide(III) chlorides

Lanthanide(III) chlorides were prepared by dissolving the corresponding lanthanum oxide in 50 % hydrochloric acid and subsequently the salt formed was crystallised after concentrating the solution on a water-bath.

Synthesis of ligand

3-Acetylcoumarin, the starting material for the synthesis of the ligand (ACAP) was prepared by the Knoevenagel method. The ligand was prepared by condensing 3-acetylcoumarin with 4-aminoantipyrane in 1:1 mole ratio in methanolic medium. A hot methanolic solution (30 mL) of 3-acetylcoumarin (0.01 mol) was mixed with a hot methanolic solution (20 mL) of 4-aminoantipyrine (0.01 mol). The mixture was refluxed on a water-bath for 3 h. The resulting solution was concentrated to half of its initial volume and allowed to crystallise. The crystals formed were collected on a filter paper, washed with methanol and dried and further purified by recrystallization from methanol. The melting point was found to be 194 °C. More details are given in the Supplementary material to this paper.

Synthesis of metal complexes

All the lanthanide(III) complexes were prepared according to the following general procedure. To a hot methanolic solution (20 mL) of the ligand (0.01 mol), a methanolic solution (20 mL) of lanthanide(III) chloride (0.01 mol) was added and refluxed for 1h on a water bath. The pH of the solution was adjusted to 6.5–7.0 and the refluxing process was continued for 8––10 h. The resulting solution was concentrated to half of its initial volume. The solid mass separated was filtered, washed successively with small portions of water, methanol and ether and finally dried in vacuum over P_4O_{10}.

α-*Amylase inhibitory assay*

The *in vitro* α-amylase inhibitory activities of the ligand and metal complexes were determined. Different concentrations of sample were taken and made up to 100 µl using 25 mM phosphate buffer containing 25 µl of porcine *α*-amylase at a concentration of 0.5 mg ml^{-1} and were incubated at 25 °C for 10 min. After pre-incubation, 25 µl of 0.5 % starch solution in 25 mM phosphate buffer (pH 6.9) was added. The reaction mixtures were then incubated at 25 °C for 10 min. The reaction was stopped with 50 µl of 96 mM 3,5-dinitrosalicylic acid colour reagent. The microplate was then incubated in a boiling water bath for 5 min and cooled to room temperature. The solution thus prepared was taken as the test solution. Absorbance was measured at 540 nm using a microplate reader. A control was prepared using the same procedure replacing the sample with distilled water:

$$\text{Inhibition} = 100\frac{\text{Control} - \text{Test}}{\text{Control}} \tag{1}$$

Antioxidant assay

The radical scavenging activity of the ligand and the metal complexes were determined using DPPH assay. The decrease in the absorption of the DPPH solution after the addition of an antioxidant was measured at 517 nm. Ascorbic acid (10 mg ml^{-1} DMSO) was used as reference. 1,1-Diphenyl-2-picrylhydrazyl is a stable free radical with a red colour that turns yellow when scavenged. This property of DPPH is used in assessing free radical scavenging activity. The scavenging reaction between DPPH and an antioxidant (H–A) could be written as:

$$\text{DPPH} + [\text{H} - \text{A}] \rightarrow \text{DPPH} - \text{H} + \text{A} \tag{2}$$

Antioxidants react with DPPH and reduce it to DPPH–H and as a consequence the absorbance decreases. The degree of discoloration indicates the scavenging potential of the antioxidant compounds or extracts in terms of hydrogen donating ability. Different volumes (2.5–40 µl) of sample solutions (1.25, 2.5, 5.0, 10 and 20 mg/ml) were made up to a final volume of 40 µl with DMSO and 2.96 mL DPPH (0.1 mM) solution was added. The reaction

mixture was incubated in the dark at room temperature for 20 min, after which, the absorbance of the mixture was read at 517 nm. The DPPH was taken as the control. Percentage of inhibition was measured using Eq. (1).

RESULTS AND DISCUSSION

Analytical data indicated that condensation of 3-acetylcoumarin with 4-aminoantipyrine occurred in 1:1 mole ratio. The ligand is soluble in common organic solvents, such as methanol, ethanol, benzene, toluene, *etc*. Analytical data of the complexes, given in Table S-I of the Supplementary material to this paper, are in good agreement with their formulation.

All the complexes possess 1:1 metal–ligand stoichiometry and possess good keeping qualities. They are non-hygroscopic solids, soluble in DMSO and DMF. The molar conductance values of the complexes, given in Table S-I, were in the range of 6.4–13.1 S cm^{-2} mol^{-1} in DMSO solution at room temperature. These values indicated that the complexes were non-electrolytes in nature.[10]

IR spectra

The relevant IR spectral data provide important information of coordination of ligand to the metal ion and are presented in Table S-II of the Supplementary material. The IR spectra of the ligand and its lanthanum(III) complex are given in the Figs. S-1 and S-2 of the Supplementary material. The ligand shows a medium intensity band at 1590 cm^{-1}, characteristic of ν(C=N) stretching vibration. This band in the complex is shifted to a lower frequency by ≈25 cm^{-1} indicating the involvement of the azomethine nitrogen in coordination to the metal ion.[11]

Apart from this, the stretching frequency of the carbonyl group on the antipyrine moiety showed ν(C=O) at 1654 cm^{-1} in the free ligand that was shifted in the IR spectra of complexes (≈15 cm^{-1}) to lower wave numbers. This indicated that the C=O was bonded to the metal ion.[12] A medium intensity band in the ligand at 1721 cm^{-1} was attributed to the carbonyl group of the coumarin moiety. The lactone carbonyl frequency of the complexes remain unchanged in the position and intensity, indicating the non-coordination of the lactonic oxygen.[13] The IR spectra of complexes showed a broad band in the region 3400–3460 cm^{-1} that was assigned to ν_{O-H} of co-ordinated water. This is further substantiated by the additional band occurring in the 850–840 cm^{-1} region.[14] The complexes showed non-ligand bands that occurred in the region of 432–441, 420–427 and 338–354 cm^{-1}, which were assigned to ν(M–O), ν(M–N) and ν(M–Cl) vibrations, respectively.[15] The IR spectral data indicated that the ligand behaves as a bidentate ligand with NO donor sites coordinated to the metal ions *via* the azomethine nitrogen and the pyrazolone oxygen.

NMR spectra

The ^{1}H-NMR and ^{13}C-NMR spectra of both the ligand and the lanthanum(III) complex were recorded in DMSO-d_6 (Figs. S-3 and S-4 of the Supplementary material). The ^{1}H-NMR spectrum of the ligand showed a multiplet at 7.25–7.57 ppm due to aromatic protons. The complex showed a slight upfield shift of the aromatic protons found in the range 7.23–7.54 ppm, which confirmed the bond formation. Two singlets at 2.55 and 3.21 ppm were attributed to pyrazolone ring methyl protons of C–CH_3 and N–CH_3, respectively.[16] A singlet was observed at 2.41 ppm in the spectrum of the ligand due to the C–CH_3 methyl proton of the coumarin moiety.[17] The ^{13}C-NMR spectra of the ligand and the corresponding metal complexes were recorded in DMSO-d_6 using TMS as the internal standard. In the case of the ^{13}C-NMR spectra, the aromatic carbons in the ligand showed signals in the range of 113–134 ppm that were slightly shifted to 109––129 ppm in the complexes. The considerable shifts in the position of the carbon atoms indicated the bonding of the azomethine nitrogen to the metal atom. The signal due to the lactone (C=O) carbon atom remained almost unchanged in the ^{13}C-NMR spectra of the metal complexes.[18] This is a clear indication of the non--coordination of the lactone (C=O).

Electronic spectra

The electronic absorption spectra of the ligand and its complexes have been recorded in DMSO solution in the range of 200–800 nm and the results are presented in Table I. The electronic spectrum of ligand exhibited characteristic bands at 279 and 355 nm assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, respectively. Upon complexation, the absorption bands of the complexes were slightly blue shifted compared to those of the free ligand (Fig. 1). This is indirect evidence for coordination of the ligand with the lanthanide ion.[19] It also gives conclusive support that the same structural form of the ligand also exists in the metal complexes. The visible spectral bands of the lanthanide complexes are hypersensitive to stereochemistry.[20] An enhancement of the intensity of certain hypersensitive bands of the praseodymium(III) complex, compared to respective aquated ion was observed.[15] These variations could be attributed to the action of an inhomogeneous electromagnetic field and by changes in the symmetry of the field around the lanthanide ion. The spectra of the complexes exhibited alterations in intensity and shifted the positions of the absorption bands relative to the ligand. This slight shift was attributed to the effects of ligand field upon the inter-electronic repulsion between the 4f electrons.[21]

Various spectral parameters, such the nephelauxetic ratio (β), covalency factor ($b^{1/2}$), Sinha parameter (δ), covalency angular overlap parameter (η) were calculated (Table II) from the hypersensitive transitions of the spectrum of the

praseodymium(III) complex.[22] The β values being less than unity and the positive values of $b^{1/2}$ and δ indicate covalent metal–ligand bonding. In the case of the praseodymium(III) complex, an enhancement in the intensity of certain hypersensitive bands compared to the aquated ions was noted, Table II. This could be ascribed to quadrupolar effects owing to an inhomogeneous electrostatic field and changes in symmetry around the lanthanide(III) ion.

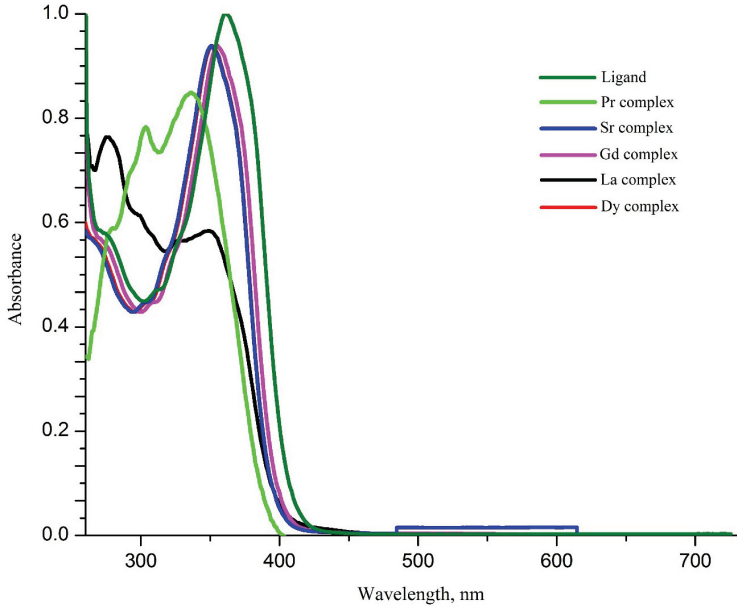

Fig. 1. Electronic absorption spectra of ligand and the complexes in 10^{-3}M DMSO.

TABLE I. Electronic spectral data of ligand and the metal complexes

Complex	λ_{abs} / nm	
	π-π*	n-π*
APAC	279	355
$[La(ACAP)(H_2O)_3Cl_3]$	276	348
$[Pr(ACAP)(H_2O)_3Cl_3]$	277	336
$[Gd(ACAP)(H_2O)_3Cl_3]$	258	350
$[Sm(ACAP)(H_2O)_3Cl_3]$	279	352
$[Dy(ACAP)(H_2O)_3Cl_3]$	271	351

$$\beta = \text{average value of} \left(\frac{B_{\text{complex}}}{B_{\text{aqua}}} \right) \quad (3)$$

$$b^{1/2} = \frac{(1-\beta)^{1/2}}{2} \quad (4)$$

$$\delta(\%) = 100\frac{(1-\beta)}{\beta} \quad (5)$$

$$\eta = \frac{1-\beta^{1/2}}{\beta^{1/2}} \quad (6)$$

TABLE II. Hypersensitive parameters of the praseodymium(III) complex

Complex	Wavelength, nm	Hypersensitive parameters			
		β	$b^{1/2}$	δ / %	η
$(Pr^{3+})_{aqua}$	340	0.9882	0.054	1.194	0.0595
$[Pr(ACAP)(H_2O)_3Cl_3]$	277, 336	–	–	–	–

The nephelauxetic parameter is close to unity evidencing only a slight covalent character of the metal–ligand bond interaction. The low $b^{1/2}$ value suggested a small participation of the 4f orbitals in the bonding and along with the δ value indicated the relatively low covalent character of the bond.[23] The lanthanide(III) ions possess unique spectral properties resulting from electronic f–f transitions within the 4f shells, which is shielded by the filled 5s and 5p orbitals. The shielding leads to minimal interactions with the field of surrounding molecules, so there were only weak perturbations of the electronic transition between the energy levels of the f electrons.[24]

Luminescence properties

The excitation and emission spectra of all the lanthanide(III) complexes and the ligand in DMSO at room temperature were recorded. The emission spectra were recorded in the range of 320–600 nm with an excitation wavelength of 300 nm. The excitation spectra of the complexes were obtained by observing characteristic emission of the lanthanide(III) ion. The maximum of the excitation spectra showed similar features to those of the absorption spectra of the related complexes. The luminescent properties of lanthanide complexes are due to the efficient intramolecular energy transfer from the lowest energy level of the triplet state of the organic ligand to the resonance energy level of the lanthanide ions. The corresponding emission spectra of all the complexes of lanthanum(III), praseodymium(III), gadolinium(III), dysprosium(III) and samarium(III) ions were recorded (Fig. 2).

In the case of ligand, two peaks were observed at 402 and 334 nm due to the presence of ligand chromophore moieties. All the lanthanide(III) complexes showed an enhancement in the emission intensity compared to that of the ligand. The enhancement of luminescence intensity depends on the nature of the lanthanide ion that was in the order Sm(III)>Dy(III)>Pr(III)>La(III)>Gd(III). The enhancement of the emission intensity of all metal complexes was clear evidence of metal–ligand complexation. Enhancement of luminescence intensity might be

attributed to the coordination of the ligand to the lanthanide(III) ion, which effectively increases the rigidity of the complexes and reduces the loss of energy by radiationless decay.[25] Due to intraligand $\pi \rightarrow \pi^*$ transitions, the emission spectra of La(III), Pr(III), Sm(III), Dy(III) and Gd(III) complexes exhibited ligand emission bands. The luminescence emission bands were slightly blue shifted in the complexes compared to that of the free ligand. The blue-shift emission originated

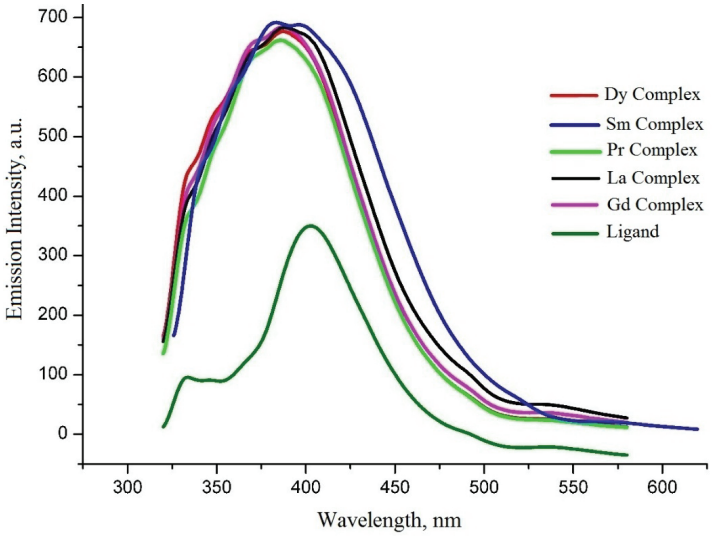

Fig. 2. Fluorescence emission spectra of the ligand ACAP and its lanthanide complexes.

from the emission of a ligand-to-metal charge transfer.[26] The lanthanide complexes do not exhibit typical emission in the visible region, which could be attributed to the energy gap between the triplet level of the organic ligand and the lowest resonance energy level for lanthanide ions. This gap may not favour the energy transfer process from organic ligand to the lanthanide ion. Another possible reason is the fluorescence quenching effect of coordinated water molecules in these complexes. The samarium(III) complex exhibited an increase in intensity compared to the ligand and a marginal blue shift in wavelength (376 nm) and the peak around 334 nm disappeared. The enhanced intensity of the samarium(III) complex suggested a more efficient energy transfer from the lowest triplet state energy level (T1) of the ligand to the lowest resonance energy level of samarium(III). The lanthanum(III) complex showed a decrease in fluorescence intensity as the La(III) ion has a completely empty 4f shell and no suitable level that could receive energy from the triplet state energy level of the ligand. For Gd^{3+}, the lowest lying resonance level lies far above triplet level of the ligand and energy transfer from the triplet to the rare earth ion does not take place, resulting in ligand fluorescence. The efficiency of triplet to ion energy transfer is con-

trolled by the covalent nature of ligand-metal bonding. The enhancement of fluorescence through complexation opens up the opportunity for photochemical applications of these complexes. The fluorescence of the ligand was quenched by the photo-induced electron transfer process due to the presence of lone pair of electrons of the donor atoms in the ligand. This process was prevented by complexation of ligand with the metal ion. The ligand-to-lanthanide energy transfer was confirmed by the quantum yield values. The relative quantum yield of the ligand and the metal complexes were determined with reference to 2-aminopyridine, as given in Table III.

TABLE III. Photoluminescence data for the ligand and its metal complexes

Compound	λ_{em} / nm	Max emission intensity, nm	Quantum yield, Φ
ACAP	402	374	0.22
$[La(ACAP)(H_2O)_3Cl_3]$	376	590	0.24
$[Pr(ACAP)(H_2O)_3Cl_3]$	385	622	0.31
$[Sm(ACAP)(H_2O)_3Cl_3]$	387	733	0.35
$[Gd(ACAP)(H_2O)_3Cl_3]$	382	595	0.28
$[Dy(ACAP)(H_2O)_3Cl_3]$	422	676	0.34

The relative quantum yields were determined using the equation:

$$\Phi = \left[\frac{A_R}{A_X}\right]\left[\frac{E_X}{E_R}\right]\left[\frac{\eta_X}{\eta_R}\right]^2 \quad (7)$$

In this case, the quantum yield of the unknown was compared with that of a reference sample: where Φ is the luminescence quantum yield, A is the absorbance at the excitation wavenumber, E is the area under the corrected emission curve (expressed in number of photons), and η is the refractive index of the solvents used. The subscripts R and X refer to the reference and the unknown samples, respectively. Samarium(III) complex showed a higher quantum yield than that of the ligand. The stronger emission intensity was obtained by the photoexcitation of the coumarin-based ligand at a wavelength of 325 nm rather than by the direct photoexcitation of the lanthanide ions. For the lanthanide complexes, the quantum yield depends on the excited state of the ligand or metal ion because sensitization of the lanthanide ion can go through several energy migration paths, the efficiency of which depends on the particular levels involved.

X-Ray diffraction study

The X-ray diffraction pattern of the ligand was recorded (Fig. S-5), and the details are presented in Table S-III of the Supplementary material. The Bragg angles and the set of interplanar spacing obtained were related to the unit cell parameters and Miller indices and these values were assigned to the individual

reflections with the aid of expressions involving sin 2θ. The diffractogram of ligand recorded 20 reflections between 2θ ranging from 6 to 54° with a maxima at 2θ = 25°, which corresponds to an interplanar spacing d = 3.53 Å.[27]

However the X-ray diffraction pattern of the corresponding dysprosium(III) complex did not exhibit any prominent reflections and hence it could not be indexed to any crystalline form. Hence it could be concluded that the dysprosium(III) complex is amorphous in nature. The grain size was estimated using the Scherer formula, $d_{XRD} = 0.9\lambda/(\beta\cos\theta)$ and average particle size of the ligand was found to be 30 nm.[28]

Structure of the ligand and the complexes

Based on all the above physicochemical and spectral data, the structure of ligand and metal complexes were assigned and are given in Figs. 3 and 4, respectively.

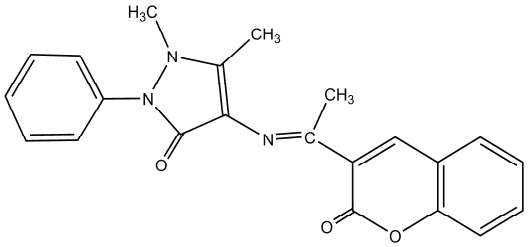

Fig. 3. Structure of the ligand.

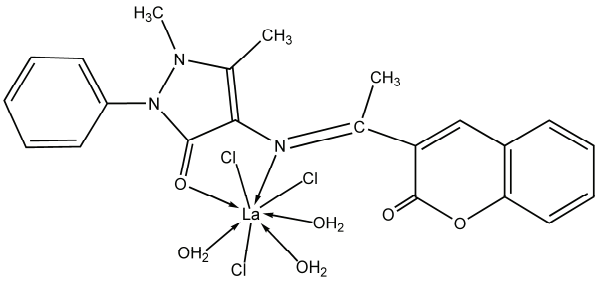

Fig. 4. Structure of [La(ACAP)$(H_2O)_3Cl_3$].

α-*Amylase inhibitory activity*

An α-amylase inhibition assay was performed for the ligand and metal complexes using the method of Apostolidis.[29] Pyrazole derivatives were used as synthetic hypoglycemic agents that reduced the formation and absorption of glucose in the intestine. As a result, the development of postprandial hyperglycemia was prevented. The α-amylase inhibitory activity of the ligand and the metal complexes are given in Table IV. The ligand and the complexes inhibited the α-amylase activity in a dose dependent manner.

The IC_{50} values of the ligand and metal complexes are given in Table IV. The IC_{50} value for ligand was found to be 2.32 mg mL^{-1}. Among the complexes, gadolinium(III) showed an IC_{50} value of 0.29 mg mL^{-1} which is close to that of the standard acarbose. It was observed that the α-amylase inhibitory activity of the ligand was enhanced on complexation with metal ions. The gadolinium(III) complex had a significantly higher percentage α-amylase inhibition, *i.e.*, 62.16 % at 0.5 mg mL^{-1}. The observed reduction in enzyme activity was presumably due to enzyme deactivation through chelation. The insulin-like capacity of a metal complex is generally related to its ability to lower the blood glucose level by activating glucose transport into the cells of peripheral tissues.[30]

TABLE IV. IC_{50} values for the α-amylase inhibitory activity of the ligand and metal complexes

Compound	IC_{50} / mg mL^{-1}
ACAP	2.32
[La(ACAP)Cl_3(H2O)$_3$]	0.31
[Pr(ACAP)Cl_3(H2O)$_3$]	0.78
[Sm(ACAP)Cl_3(H2O)$_3$]	0.36
[Gd(ACAP)Cl_3(H2O)$_3$]	0.29
Dy(ACAP)Cl_3(H2O)$_3$]	0.68
Acarbose	0.112

An increased α-amylase inhibition activity would decrease the rate of glucose absorption and concentration of postprandial serum glucose.[31,32] This effect would delay the degradation of starch and oligosaccharides, which would cause a decrease in the absorption of glucose and consequently inhibit an increase in postprandial blood glucose.

Antioxidant activity

Oxidative stress is the basis of many serious diseases and one of its primary characteristics is the cellular imbalance between endogenous antioxidant defences and ROS generation inside the cells. The antiradical properties of chromones have attracted increased interest and consequently, have been extensively investigated. The Schiff base ligand and its lanthanide(III) complexes were screened for free radical scavenging activity using the DPPH method. DPPH is a relatively stable nitrogen-centred free radical that easily accepts an electron or hydrogen radical to become a stable diamagnetic molecule. DPPH radicals react with suitable reducing agents as a result of which the electrons become paired off and the solutions lose colour stoichiometrically depending on the incoming electron.

The scavenging activity of the ligand and its metal complexes were compared with that of ascorbic acid. The results showed that the complexes exhibited scavenging effects with increasing concentration in the range of 1.25–20 μg mL^{-1}. The IC_{50} values of the ligand and metal complexes were determined (Table V).

The complexes showed enhanced antioxidant activity at high concentrations than the ligand.[33] The synthesized compounds scavenged DPPH radicals in a concentration-dependent manner. The IC_{50} values of the complexes were found to be close to that of the standard ascorbic acid (Table V). The increased activity of the complexes might be attributed to chelation of the organic molecules to the lanthanide ions that exert different and selective effects on the radicals of biological systems. Electron-donating substituents to an aromatic ring can increase the radical scavenging activity as a result of increased electron density at the carbon atoms in the ring. In addition to this, the metal binding is also attributed to the antioxidant activities. Generally, chelation prevents metal-catalyzed free radical generation and their subsequent reactions and accordingly protects very important biologically active molecules from oxidative stress.[34]

TABLE V. IC_{50} values for the antioxidant activity of the ligand and metal complexes

Compound	IC_{50} / mg mL^{-1}
ACAP	8
[La(ACAP)Cl_3(H2O)$_3$]	4.9
[Pr(ACAP)Cl_3(H2O)$_3$]	5.7
[Sm(ACAP)Cl_3(H2O)$_3$]	4.7
[Gd(ACAP)Cl_3(H2O)$_3$]	4.2
Dy(ACAP)Cl_3(H2O)$_3$]	5.9
Ascorbic acid	2.5

Thus, lanthanide (III)complexes were found to be more effective free radical scavengers than their corresponding ligand. This study may be useful for the synthesis of lanthanide(III) complexes that prevent oxidative damage because in the body, many free radicals are generated that produce diseases such as aging, cancer, and cardiovascular and neurodegenerative diseases.

CONCLUSIONS

A novel heterocyclic Schiff base, 1,2-dihydro-1,5-dimethyl-4-[[1-2-oxo-2*H*--1-benzopyran-3-yl)ethylidene]amino]-2-phenyl-3*H*-pyrazol-3-one, and its corresponding lanthanide(III) complexes were synthesized and characterized based on various physicochemical spectral studies. Elemental analysis, and ^{1}H-NMR and ^{13}C-NMR spectroscopy confirmed the compositions of the compounds. IR and UV–visible spectroscopy confirmed the suggested coordination of the ligand through the azomethine nitrogen and oxygen of the pyrozoline ring. The XRD patterns of the ligand and the dysprosium(III) complex were recorded. The luminescence studies showed enhancement of the luminescence intensities for the complexes when compared to that of the ligand. From the α-amylase inhibitory assay, it was observed that the metal complexes, especially the gadolinium(III) complex, showed greater inhibitory activity than that of the ligand. The antioxi-

dant activity assay also evidenced the better antioxidant activity of the lanthanide complexes than that of the ligand.

SUPPLEMENTARY MATERIAL

The spectral data of the synthesized compounds are available electronically at the pages of the journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

СИНТЕЗА, ФЛУОРОСЦЕНТНА И АНТИОКСИДАТИВНА СВОЈСТВА НЕКИХ КОМПЛЕКСА ЛАНТАНОИДА(III) И ИСПИТИВАЊЕ ЊИХОВОГ УТИЦАЈА НА ИНХИБИТОРСКУ АКТИВНОСТ α-АМИЛАЗЕ

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Кондензационом методом, полазећи од 3-ацетилкумарина и 4-аминоантипирина, синтетисан је нови хетероциклични лиганд, 1,2-дихидро-1,5-диметил-4-[[1-2-оксо-2*H*-1--бензопиран-3-ил)етилиден]амино]-2-фенил-3*H*-пиразол-3-он. Овај лиганд се показао као веома погодан за комплексирање лантана(III), празеодијума(III), самаријума(III), гадолинијума(III) и диспросијума(III). Лиганд и одговарајући комплекси су окарактерисани помоћу различитих физичко–хемијских и спектроскопских метода. На основу спектроскопских мерења нађено је да се лиганд бидентатно координује преко азометинског атома азота и кисеониковог атома из пиразоловог прстена. Структура лиганда и одговарајућег диспросијум(III) комплекса одређена је дифракцијом X-зрака са прахова. Испитиване су фотолуминисцентне особине лиганда и комплекса метала и одређени су релативни квантни приноси. Нађено је да у свим случајевима јони метала повећавају луминесцентни интензитет. Применом методе Апостолидиса (Apostolidis), испитиван је утицај лиганда и одговарајућих комплекса на активност α-амилазе, при чему је нађено да комплекси метала показују већу активност у односу на лиганд. На основу DPPH тестова нађено је да су антиоксидативна својства комплекса израженија у односу на одговарајућа својства некоординованог лиганда.

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