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Preparation, Photoluminescent Behaviour, Antimicrobial and Antioxidant Properties of New Orange Light Emitting Sm(III) Complex, $Sm(CHME)_3.Dmphen$

P. Nandal[1], R. Kumar[2], Sheetal[1], S. P. Khatkar[1], V. B. Taxak[1]*
[1]Department of Chemistry, Maharshi Dayanand University, Rohtak, Haryana, India
[2]Department of Chemistry, UIET, Maharshi Dayanand University, Rohtak, Haryana , India
*Corresponding Author: E-mail address: v_taxak@yahoomail.com

ABSTRACT

The photoluminescent properties of lanthanide complexes with organic ligand have been the subject of great interest as these functional complexes have potential applications in various fields from quantum cutting materials to photonic devices [1-13]. Most of these applications are based on the efficient emission of lanthanide complexes in the UV region to IR regions. However, the lanthanide ions have very low absorption coefficient which prevents direct excitation due to Laporte-forbidden 4f-4f transitions. To overcome this disadvantage and obtain intense lanthanide luminescence, there are two specific ways to sensitize lanthanide emission. Firstly, the use of metal ion in the heteromettalic system where energy can be transferred from the metal ion to lanthanide ion which results in enhanced luminescence of lanthanide ion. Secondly, to choose a suitable organic chromophore moiety which excite and transfers the energy to the lanthanide ion through antenna affects. For the second option numerous organic ligands such β-hydroxyketone, β-diketone, carboxylic acids and various heterocyclic derivatives have been introduced to develop and designed new luminescent lanthanide-based materials [14-20].

Keywords : Laporte-Forbidden, Photoluminescent, Antimicrobial, Antioxidant, Sm(CHME)3.Dmphen, UV Region, IR Regions, Organic Chromophore Moiety, B-Hydroxyketone, B-Diketone, Carboxylic Acids, CHME, OLEDs

I. INTRODUCTION

The β-hydroxyketones and its derivatives serve as excellent antennas or sensitizers, absorbing the excitation light and transferring the energy to the trivalent lanthanide ions [21-24]. The choice of β-hydroxyketone ligand is based on its strong ability to coordinate lanthanide ion which can have many practical usage. To the best of the author knowledge, Eu^{3+} and Tb^{3+} ions are of particular interest but investigations on Sm^{3+} complexes containing β-hydroxyketone ligand are still rare. This present work deals with the synthesis of a new Sm(III) complex employing β-hydroxyketone ligand 2-(4-chlorophenyl)-1-(2-hydroxy-4- ethoxyphenyl)ethan-1-one (CHME) as main ligand and 5,6-dimethyl-1,10-phenanthroline as ancillary ligands. The investigation of photoluminescent properties has also done for possible use in OLEDs as emitting materials. The author also explicated in vitro antimicrobial activities and antioxidant activities of ligand and its corresponding Sm(III) complex employing tube dilution method and DPPH method respectively in detail.

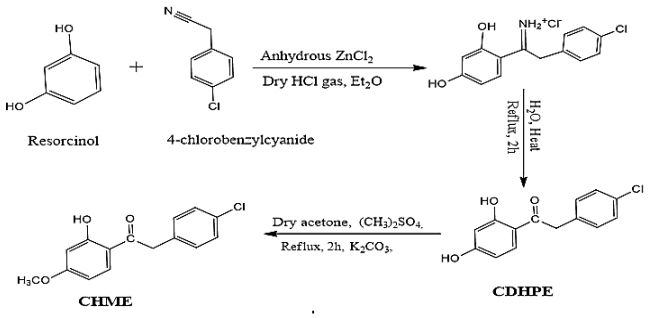
II. EXPERIMENTAL DETAILS

2-(4-chlorophenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (CHME) has been synthesized in 72% yield according to the Houben-Hoesch reaction mechanism. All starting materials were of analytical grade and were purchased from Sigma-Aldrich/Hi-Media Company and used without further purification. By using CHME novel ternary Sm(III) complex have been synthesized by adopting solution precipitation method. The synthesized ligand and its corresponding Sm(III) complex were investigated by various techniques. The C, H, N and O elemental analysis were carried out on thermo scientific flash 2000 elemental analyzer. The Samarium content in the complex was obtained by EDTA titration. ^{1}H-NMR spectra were recorded in DMSO using Bruker Avance II 400 spectrometer (400 MHZ). FT-IR spectra were obtained on Perkin Elmer spectrometer. The Fourier transform infrared spectra were recorded in the spectral range 4000–400 cm^{-1}at a maximum resolution at 4 cm^{-1} with KBr pellets technique. For the photoluminescent analysis, the excitation and emission spectra of the complex were measured in the UV-Visible region at room temperature by using (Hitachi F-7000) fluorescence spectrophotometer with xenon lamp as the excitation source.

2.2 Synthesis

2.2.1 Synthesis of ligand 2-(4-chlorophenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (CHME)

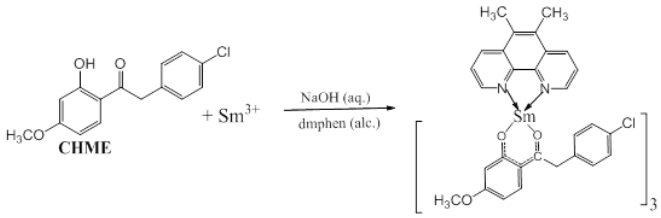
The ligand CHME was synthesized by adopting conventional method as per literature [25] and is given in Scheme 1 as follow:



Scheme 1. The synthetic route of ligand CHME.

2.2.2 Synthesis of complex Sm(CHME)$_3$.dmphen

The complex was prepared by adopting solution precipitation method as per Scheme 2. The mixture of CHME (1 mmol), 5,6-dimethyl-1,10-phenanthroline (1 mmol) in ethanol was dissolved in an aqueous solution of 1 mmol $Sm(NO_3)_3.6H_2O$ was stirred at 35 ^oC for 3 h. The pH value of the mixture was adjusted to 7-8 by adding 0.05 M NaOH aqueous solution. White precipitates appeared in the reaction mixture which were washed with distilled water and then with ethanol to remove the free ligand. Sm(CHME)$_3$.dmphen complex was obtained as white powder with 80% yield.



Scheme 2. The synthetic route and structure of Sm(CHME)$_3$.dmphen.

2.3 Biological evaluation of the ligand and its Sm(III) complex

2.3.1. Antimicrobial activity

In vitro antimicrobial activity activity of ligand and synthesized novel Sm(III) complex were investigated against Gram-negative bacterium: E. coli (MTCC 443), Gram-positive bacteria: B. subtilis (MTCC 441), S. aureus (MTCC 3160) and fungal strains: C. albicans (MTCC 227) and A. niger (MTCC 281). Tube dilution

method was adopted for screening these antimicrobial strains with respect to standard drugs ciprofloxacin and fluconazole.

2.3.2. Antioxidant activity

The antioxidant activity of the synthesized ligand CHME and its corresponding Sm(III) complex were evaluated by DPPH radical scavenging assay [26-30]. It is due to fact that odd electron present in the 2,2-diphenyl-2-picrylhyrazyl hydrate (DPPH) reacts with the antioxidant complexes, which can donate hydrogen, it gets reduced and its deep violet color in methanol bleaches to yellow, shows a significant absorption decrease at 517 nm. Stock solution of various concentrations is 25, 50, 75 and 100 µg/mL of the test ligands and complexes, dissolved in methanol were added to 5 mL of 0.004% methanol solution of DPPH. Then the mixture was shaked and allowed to stand for 30 min in the dark at room temperature for incubation.

III. RESULTS AND DISCUSSION

3.1. Solubility

The solubility of the complex was investigated in various solvents. As expected the Sm(III) complex were soluble in DMSO, DMF, chloroform, dichloromethane and acetone, sparingly soluble in methanol and ethanol but insoluble in hexane, benzene and dichloromethane. The ligand and its complex were stable under atmospheric condition.

3.2. Elemental analysis, ^{1}H-NMR and IR spectra

The elemental analysis data for CHME ($C_{15}H_{13}O_3Cl$) was found (calc.) % C, 65.18 (65.10); H, 4.76 (4.73); O, 17.29 (17.34). IR (KBr) cm^{-1}: 3429 (b), 3055 (m), 3022 (w), 2940 (w), 2842 (w), 1650 (s), 1633 (s), 1596 (s), 1567 (s), 1494 (s), 1439 (s), 1351 (s), 1310 (m), 1291 (s), 1229 (s), 1207 (s), 1197 (s), 1084 (s), 1028 (s), 994 (s), 822 (s), 810 (s), 777 (s), 600 (s), 581 (s). ^{1}H-NMR (400MHz, DMSO): δ 3.83 (s, 3H, OCH_3), 4.18 (s, 2H, CH_2), 6.42 (s, 1H, Ar-H), 6.43 (s, 1H, Ar-H), 7.24 (d, 2H, Ar-H), 7.30 (d, 2H, Ar-H), 7.57 (s, 1H, Ar-H), 12.61 (s, 1H, OH).

Sm(CHME)$_3$. dmphen

The obtained complex was white powder with 91 % yield. The elemental analysis data for Sm(CHME)$_3$.dmphen ($C_{59}H_{50}O_9Cl_3N_2Sm$) was found (calc.) % C, 59.63 (59.66); H, 4.19 (4.24); O, 12.19 (12.12); N, 2.34 (2.36); Sm, 12.72 (12.66). IR (KBr) cm^{-1}: 2930 (m), 2831 (m), 1956 (w), 1923 (w), 1624 (s), 1589 (s), 1545 (s), 1419 (s), 1372 (s), 1223 (s), 1167 (s), 1130 (s), 1092 (s), 1021 (s), 976 (m), 845 (m), 808 (s), 732 (s), 689 (m), 578 (m), 467 (m). ^{1}H-NMR (400MHz, DMSO): δ 2.57 (s, 6H, dmphenCH_3), 3.38 (s, 9H, OCH_3), 4.23 (s, 6H, CH_2), 6.45-6.59 (b, 6H, Ar-H), 7.21-7.64 (b, 12H, Ar-H), 7.93 (d, 2H, dmphen), 8.23 (s, 3H, Ar-H), 8.68 (d, 2H, dmphen), 9.28 (d, 2H, dmphen).

The experimental data of elemental analysis was well matched with the theoretical data. CHME shows a singlet at δ 13.84 due to phenolic proton in the ^{1}H-NMR spectrum. This proton signal is not observed in the spectrum of Sm(III) complex, indicating that oxygen atom of the phenolic OH coordinated with the Sm(III) ion. IR spectra shows a broad band appeared in the range 3500-3200 cm^{-1} centred at 3429 cm^{-1}, which was a typical peak of free OH stretching vibration in the ligand CHME, which was absent in the ternary complex (as tabulated in Table 1) resulted that ligand was coordinated with Sm(III) ion through oxygen atom of phenolic group. The C=O stretching vibration band of carbonyl group observed an intense band at 1633 cm^{-1} in the ligand which is red shifter by 9 cm^{-1} after complextation resulted that oxygen atoms in the carbonyl group were also coordinated with Sm(III) ion [31]. In the spectrum of the complex, a new absorption band appeared at 1589 cm^{-1} assigned to ν(C=N), indicating that nitrogen atom of 5,6-dimethyl-1,10-phenanthroline participated in the coordination with the central metal ion. Moreover, the presence of medium intensity band at 578 cm^{-1} and

467 cm^{-1} attributed to the ν(Sm-N) and ν(Sm-O) respectively due to introduction of ancillary ligand [32], supports the chelation through the oxygen atom of the free ligand [33, 34] and nitrogen atom of dmphen.

Table1. The characteristic IR bands (cm^{-1}) of the free ligand CHME and its corresponding Sm(III) complex $Sm(CHME)_3$.dmphen.

Compounds	ν(O-H)	ν(C=O)	ν(C=N)	ν(C=C)	ν(Ph-O)	ν(Sm-N)	ν(Sm-O)
CHME	3429	1633	---	1567	1229	---	---
Sm(CHME)3.dmphen	---	1624	1589	1545	1223	578	467

3.3 Photoluminescent properties

3.3.1. Excitation spectra

The experimental data from photoluminescent properties of free ligand CHME and its corresponding Sm(III) complex were investigated in the solid state at room temperature, collected data are tabulated in Table 2. The solid state excitation spectrum of complex was investigated by monitoring emission at λ_{em} = 601 nm as depicted in Fig.1. In the inset, the two band in the region 300-440 nm, with peak maxima centred at 382 nm due to π-π* transition in the ligand, this excitation band red shifted by 3 nm with an enhanced intensity due to chelation between the Sm^{3+} ion and ligand. This suggest that the electronic transitions are mainly responsible for the excitation of the Sm(III) ion which are forbidden due to low molar extinction coefficient.

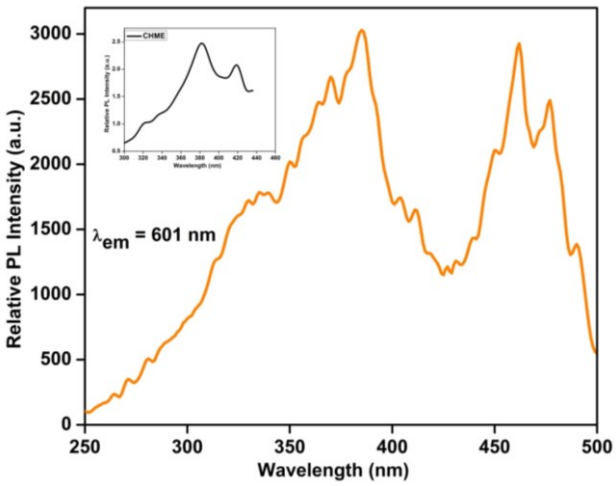


Figure 1. Photoluminescence excitation spectra of $Sm(CHME)_3$.dmphen, monitored at λ_{em} = 601 nm in solid state at room temperature and inset shows the excitation spectrum of ligand CHME.

3.3.2 Emission spectra

The photoluminescence emission spectra for solid $Sm(CHME)_3$.dmphen consists of three main emission peaks with different intensity at 564 nm, 601 nm and 646 nm which belong to the transitions of ($^4G_{5/2}\rightarrow{}^6H_{5/2}$), ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) and ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) respectively of Sm^{3+} ion [35].

Among these three characteristic transitions, the magnetic–electric dipole transition of Sm^{3+} ion $^4G_{5/2}\rightarrow{}^6H_{7/2}$ at 601 nm exhibits an intense orange emission. It is important to mention that the photoluminescence intensity of the Sm^{3+} ion was further enhanced after the introduction of N-donors ancillary ligand in the ternary Sm(III) complex.

Table 2. Photoluminescence data, decay time and color coordinates of Sm(III) complex, $Sm(CHME)_3$.dmphen.

Sm(CHME)$_3$.dmphen	λ_{ex} (nm)	λ_{em} (nm)	Assignment	τ (ms)	x and y coordinates
	385	546	$^4G_{5/2}\rightarrow{}^6H_{5/2}$	01.010	0.5274,
		600	$^4G_{5/2}\rightarrow{}^6H_{7/2}$		0.4703
		646	$^4G_{5/2}\rightarrow{}^6H_{9/2}$		

3.3.3. Luminescence decay curve

The photoluminescence decay curves for rare earth Sm(III) complex was monitored at λ_{em} = 601 nm and λ_{ex} = 385 nm of the Sm^{3+} ion. Fig.3 depicts the decay curve of complex in solid state at room temperature. The lifetime value were calculated by applying the equation $I=I_o \exp(-t/\tau)$, where τ is the radiative decay time, I and I_o are the luminescence intensities at time t and 0, respectively. The life time values calculated for complex was found to be 1.010 ms. The decay curves of this luminescent complex shows monoexponential behaviour, which suggests the presence of single Sm^{3+} ion luminescent species in the chemical environment of the complex and having only one site symmetry.

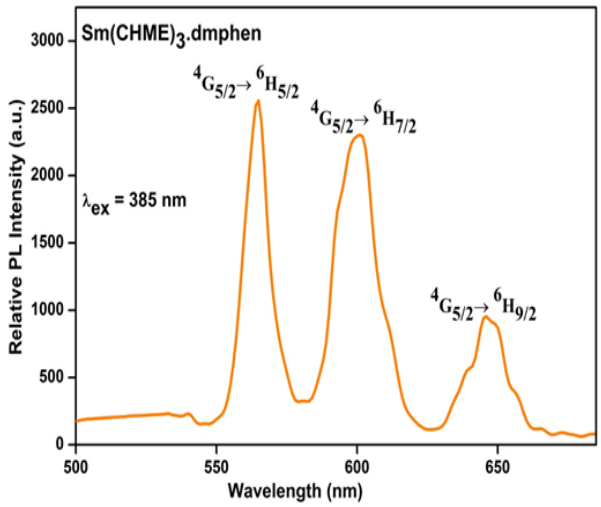


Figure 2. Photoluminescence emission spectra of Sm(CHME)$_3$.dmphen in solid state at room temperature, monitored at λ_{ex} = 385 nm.

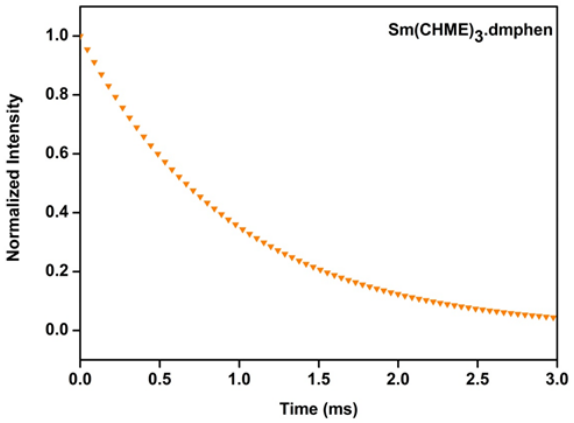


Figure 3. Luminescence decay curves for Sm(CHME)$_3$.dmphen complex in solid state at room temperature, monitored at λ_{ex} = 385 nm and λ_{em} = 601 nm.

3.3.4 Color coordinates

The CIE color coordinates (x, y) of the Sm(III) complex are located at 0.5274, 0.4703 which lie in orange spectral region as shown in Fig.4, suggesting promising application of the complex in display devices.

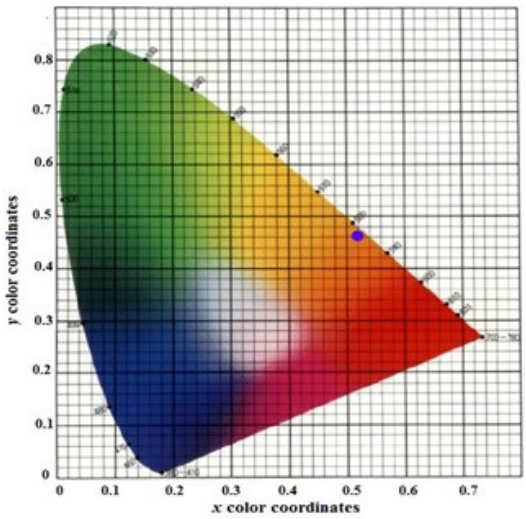


Figure 4. CIE colour coordinates of Sm(CHME)$_3$.dmphen

3.4. Antimicrobial activity Biological evaluation

3.4.1. Antimicrobial activity

In vitro antimicrobial activity activity of ligand and synthesized novel Sm(III) complex were investigated against bacterial strain: E. coli, B. subtilis, S. aureus and fungal strains: C. albicans and A. niger. Tube dilution method was adopted for screening these antimicrobial strains. Inhibition zone were measured and recorded in Table 3, whereas the bar diagram Fig.5 represented the antimicrobial activity of Sm(III) complex with respect to standard drugs ciprofloxacin and fluconazole. $Sm(CHME)_3$.dmphen showed excellent whereas ligand shows insignificant activity against all the investigated microbes. The tested complex exhibited better activity against S. aureus and E.coli than the standard drug ciprofloxacin used in the test. In case of C. albicans and A. niger, remarkable activity was observed for the complex and it is worth mentioning that complex, $Sm(CHME)_3$.dmphen showed better activity than the standard drug fluconazole.

Table 3. Minimum inhibitory concentration of CHME and $SM(CHME)_3$.dmphen. The bold values indicate highest values of the respective properties.

Complexes	Minimum Inhibitory Concentration (µM/mL)				
	B. subtillis	S.aureus	E.coli	C.albicans	A.niger
CHME	22.5	22.5	22.5	45.2	45.2
$SM(CHME)_3$.dmphen	10.5	**5.26**	**5.26**	10.5	10.5
Std.	8.71 [a]	8.71 [a]	8.71 [a]	10.09 [b]	10.09 [b]

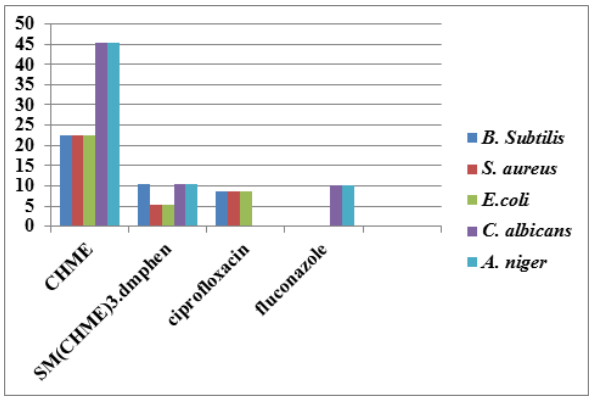


Figure 5. Bar diagram of Sm(III) complex with ligand CHME showing the antimicrobial activities with respect to standard drugs.

3.4.2 Antioxidant activity

The IC_{50} was calculated and summarized in Table 4 and graphically represented in Fig. 6. The IC_{50} values of ligand as well as the Sm(III) complex were comparatively higher than standard ascorbic acid and found to be insignificant antioxidant compared to standard ascorbic acid used.

Table 4. Percentage inhibition and IC_{50} values of DPPH radical scavenging activity of synthesized CHME and its corresponding Sm(III) complex, $Sm(CHME)_3$.dmphen.

Compound	Concentration (µg/mL)				
	25	**50**	**75**	**100**	**IC_{50}**
CHME	21.56	40.21	58.23	73.46	64.84
$Sm(CHME)_3$. dmphen	20.65	43.52	65.48	87.62	57.65
Std.	34.02	56.22	76.12	92.01	43.78

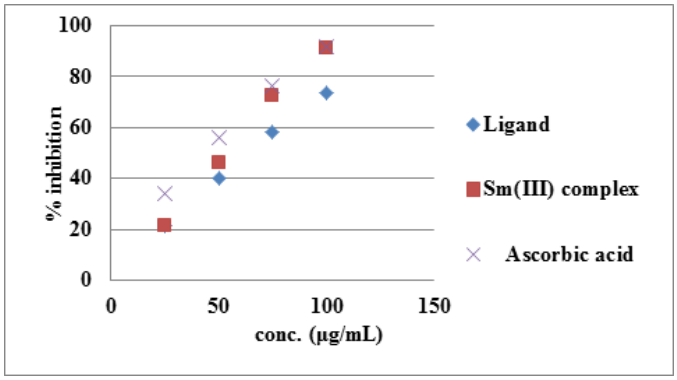


Figure 6. Percentage inhibition values of ligand CHME, Sm(III) complex, $Sm(CHME)_3.dmphen$ with respect to standard ascorbic acid.

IV. CONCLUSION

New ternary Sm(III) complex, Sm(CHME)3.dmphen have been successfully synthesized by employing 2-(4-chlorophenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (CHME) as main ligand and 5,6-dimethyl-1,10-phenanthroline(dmphen) as ancillary ligands by adopting solution precipitation method. The complex was further characterized through various techniques like elemental analysis, FT-IR, ^{1}H-NMR spectroscopy, photoluminescence spectroscopy, antimicrobial and antioxidant activity. In these synthesized complexes Tb(III) ion is wrapped with three CHME molecules and one ancillary ligand molecule. Hence the ligand can well sensitise Sm(III) ion in presence of dmphen. This ternary complex might be promising photoluminescent materials for fabrication of display devices. The antimicrobial properties of complex showed that it might be used as potent antimicrobial agents.

V. ACKNOWLEDGEMENTS

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