

Research Article

Synthesis and Characterization of Heteronuclear Copper(II)-Lanthanide(III) Complexes of N,N' -1,3-Propylenebis(Salicylaldiminato) Where Lanthanide(III) = Gd or Eu

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Three complexes, namely, $[Cu(salbn)]$ (1), $[Cu(salbn)Gd(NO_3)_3 \cdot H_2O]$ (2), and $[Cu(salbn)Eu(NO_3)_3 \cdot H_2O]$ (3) where $salbn = N,N'$ -1,3-propylenebis(salicylaldiminato) have been synthesized and characterized by elemental analyses, ICP-AES, IR, UV, NMR, MS, EDX, powder XRD, and EPR spectroscopies. The EDX results suggest the presence of two different metal ions in heteronuclear complexes (2) and (3). The ligand($salbn$), complex (1), and complex (3) crystallize in triclinic system while complex (2) crystallizes in monoclinic system. The EPR studies suggest that $[Cu(salbn)]$ complex is tetragonally coordinated monomeric copper(II) complex with unpaired electron in the $d_{x^2-y^2}$ orbital and spectral features that are the characteristics of axial symmetry while complex (2) in DMF solution at liquid nitrogen temperature exhibits an anisotropic broad signal around $g \sim 2.03$ which may suggest a weak magnetic spin-exchange interaction between Gd(III) and Cu(II) ions. The fluorescence intensity of Eu(III) decreased markedly in the complex (3).

1. Introduction

The spectroscopic and unique properties of copper(II)-lanthanide(III) complexes have become a subject of intense research interest with coordination chemists because of their wide arrays of applications in electroluminescent devices, biomedicine, MRI, magneto magnets, and many more [1–5]. The coordination chemistry of lanthanide(III) ions is also increasing day by day, owing to the relevance of these compounds in basic and applied research in various fields to chemistry, material science, life science, and so forth [6–8]. Lanthanide complexes possessing higher stability are especially important in two different fields of research where inert complexes are potentially useful, namely, for the design of Gd(III) contrast agents for NMR imaging and for the separation of the lanthanides as a set of metals [9]. Most of the heteronuclear copper(II)-lanthanide(III) complexes have been synthesized with heterodonor ligands of N and

O which are coordinated to copper and lanthanide atoms. The structural chemistry of the lanthanides is interesting as they have a strong tendency to form complexes with higher coordination numbers up to twelve. Because of their large size and their tendency to form ionic bonds rather than covalent bonds, lanthanide(III) ions may form complexes having higher coordination numbers with monodentate, simple bidentate or polydentate ligands possessing small chains [10]. The structural versatility arises from the lack of strong crystal efforts for the 4f electronic configurations as well as from the large ionic radii of these lanthanide metal ions, which change markedly with atomic number or oxidation number of the lanthanides. The chemistry of lanthanides with N,N/O donor ligands and their thermal properties has been intensively investigated [11]. Very recently, Akine made a review on design of novel ion recognition systems based on salen ($H_2\text{salen} = N,N'$ -disalicylideneethylenediamine) or related ligands [12]. These ligands are versatile and important

compounds that have been widely used in coordination chemistry. In general, salen-type ligands coordinate to a transition or typical metals as a doubly form in a tetradentate fashion [13]. Heteronuclear copper(II)-lanthanide(III) complexes have attracted increasing interest because of their different coordination capabilities. Thus, heteronuclear copper(II)-lanthanide(III) compounds have commonly been synthesized with heterodonor ligands of N and O which are good building blocks for the formation of different lanthanide coordination compounds [14–16].

In view of the above observations, it seemed interesting to synthesize heteronuclear copper(II)-lanthanide(III) complexes from heterodonor ligands like N,N'-1,3-propylenebis(salicylaldiminato), salbn in order to investigate the spectroscopic and their magnetic properties. In this paper, the synthesis and characterization of [Cu(salbn)] (1), [Cu(salbn)Gd(NO₃)₃·H₂O] (2) and [Cu(salbn)Eu(NO₃)₃·H₂O] (3) complexes from heterodonor ligand; that is, N,N'-1,3-propylenebis(salicylaldiminato) have been described.

2. Experimental

2.1. Materials and Methods. The commercially available AR grade chemicals were used without further purification. The solvents were used as either AR or spectroscopic grade. Gadolinium nitrate pentahydrate [Gd(NO₃)₃·5H₂O] was obtained from Sigma Aldrich, europium nitrate pentahydrate [Eu(NO₃)₃·5H₂O] from Fluka, and copper acetate monohydrate, Salicylaldehyde (C₇H₆O₂), and 1,3-diaminopropane from Merck (India).

2.2. Physical Measurements. FT-IR spectra were recorded on a Shimadzu FT-IR 8400S model spectrometer in the range of 4000–400 cm⁻¹ using KBr disks. Electronic spectra of the ligand and complexes were recorded at room temperature on a Perkin Elmer UV-Vis Lambda 35 spectrophotometer. The fluorescence spectra were recorded by a Perkin Elmer LS55 fluorescence spectrophotometer. The elemental analyses (C, H, N) were performed on a Perkin Elmer 2400 series II analytical instrument. Lanthanide(III) metals were estimated from Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) by using ARCOS Spectrometer (Germany). MS spectra were recorded on MS Waters ZQ-4000. Energy-dispersive X-ray spectroscopy (EDX) spectra were recorded on JEOL and JEM-7600F models. The powder X-ray diffraction pattern was recorded on PAN analytical Philips diffractometer with Cu-K α radiation of wavelength 1.54056 Å operating at a voltage of 40 kV and a current of 20 mA. The 2 θ range used was from 5° to 65° at a step of 0.02°. The peak positions of the various complexes were obtained by fitting Lorentzian function. The peak positions so obtained were used to index the pattern and compute the cell parameters using the programme DICVOL and P-INDEX. Thermogravimetric analyses (TGA/DTA) of the compounds were carried out in the temperature from 40°C to 900°C with Perkin Elmer STA 6000. The experimental conditions were platinum crucible, nitrogen atmosphere with 20 mL/min flow rate, and a heating rate 5°C/min. Magnetic moment

at room temperature (μ_{eff}) was measured using Sherwood Scientific susceptibility balance (MSB). EPR experiments were conducted on a VARIAN-E-112 spectrometer X-band frequency (9.5 GHz) with sensitivity of 5×10^{10} Δ H spins using tetracyanoethylene (TCNE). ¹H NMR and ¹³C NMR spectra were recorded on FT-NMR spectrometer BRUKER AVANCE II 400 in CDCl₃ solution, using TMS as the internal standard chemical shifts, and were reported in δ units downfield from TMS.

2.3. Synthesis of Ligand and Complexes. The ligand N,N'-1,3-propylenebis(salicylaldiminato) was prepared by employing the procedure [17], but we use 1,3-diaminopropane instead of 1,4-diaminobutane. The ligand (salbn) was used for the synthesis of following copper(II) and heteronuclear copper(II)-lanthanide(III) complexes.

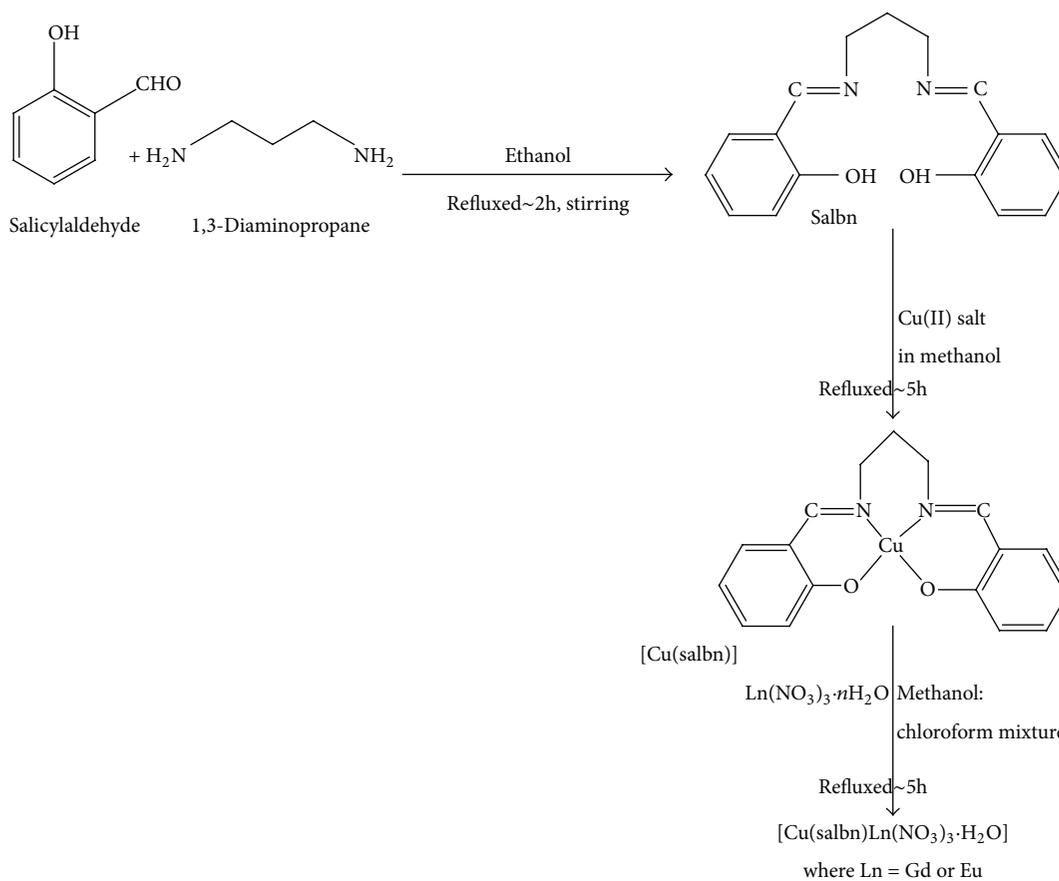
[Cu(salbn)] (1) was synthesized by adding the methanolic solution of copper acetate (0.01 mole) to the methanolic solution of the yellow ligand (0.01 mole) under constant stirring. The reaction mixture was subsequently allowed to stir and refluxed for 5 hours giving green precipitate. After cooling, the green precipitate was filtered and washed with methanol and finally dried in air. [Cu(salbn)] complex is found to be soluble in DMF, chloroform, and ethanol solvents.

[Cu(salbn)Ln(NO₃)₃·H₂O] where Ln = Gd or Eu was synthesized by slowly adding a methanolic solution of Ln(III) nitrate salts to a solution of [Cu(salbn)] dissolved in hot chloroform under constant stirring. The reaction mixture was subsequently allowed to stir and refluxed for 5 hours giving dark green precipitate. Then the volume of the dark green precipitate solution was reduced to half of the initial volume and recrystallized in hot chloroform-methanol mixture. The dark green precipitate so obtained was filtered and finally dried in air. [Cu(salbn)Gd(NO₃)₃·H₂O] (2) and [Cu(salbn)Eu(NO₃)₃·H₂O] (3) complexes were soluble in chloroform, DMF, methanol, and ethanol solvents. The following reaction scheme (Scheme 1) affords the synthesis of [Cu(salbn)] and [Cu(salbn)Ln(NO₃)₃·H₂O] where Ln = Gd or Eu complexes from the ligand(salbn).

3. Results and Discussion

3.1. Characterization of the Complexes. Some analytical data of the ligand(salbn), [Cu(salbn)], and [Cu(salbn)Ln(NO₃)₃·H₂O] where Ln = Gd or Eu are tabulated in Table 1 which are in close agreement with theoretical and experimental values. All the complexes are soluble in chloroform, DMF, ethanol, and methanol.

3.2. X-Ray Diffraction Studies. Since single crystal of the complexes could not be obtained, the exact crystal structure could not be determined. In order to provide a typical idea about the single phasic nature of the complexes, we have carried out powder X-ray diffraction pattern for the ligand, [Cu(salbn)] (1), [Cu(salbn)Gd(NO₃)₃·H₂O] (2), and [Cu(salbn)Eu(NO₃)₃·H₂O] (3) complexes as shown in Figure 1. Lattice parameters of the XRD spectra were determined using a set of DICVOL and P-INDEX programs [18].



SCHEME 1: Reaction scheme showing the synthesis of [Cu(salbn)] and [Cu(salbn)Ln(NO₃)₃·H₂O] (where Ln = Gd or Eu) complexes from the ligand(salbn).

TABLE 1: Analytical data, magnetic moment, and electronic spectral data of ligand(salbn), [Cu(salbn)], and [Cu(salbn)Ln(NO₃)₃·H₂O] complexes where Ln = Eu or Gd.

Compound	Complex	Colour	dp (°C)	Analytical found/(calc) (%)					λ_{max} (nm)	^a μ_{eff} [#] (BM)	Yield (%)
				C	H	N	Cu	Ln			
N,N'-1,3-propylenebis (salicylaldiminato), salbn		Yellow	*105	71.98 (72.34)	6.32 (6.38)	9.70 (9.92)	—	—		89	
[Cu(II)(salbn)]	1	Green	*(187)	59.36 (59.38)	5.00 (4.65)	7.88 (8.15)	18.90 (18.49)	—	597	1.73	87
[Cu(II)(salbn)Gd(NO ₃) ₃ ·H ₂ O]	2	Dark green	(295)	29.09 (28.95)	2.75 (2.55)	10.10 (9.93)	9.20 (9.01)	21.79 (22.28)	615	8.06	80
[Cu(II)(salbn)Eu(NO ₃) ₃ ·H ₂ O]	3	Dark green	(287)	29.06 (29.16)	2.49 (2.57)	9.90 (10.00)	8.89 (9.08)	21.38 (21.72)	613	3.84	77

Salbn: N,N'-1,3-propylenebis(salicylaldiminato); Ln: lanthanide; * mp (°C): melting point; dp: decomposition point; ^a susceptibility values of the respective complexes were measured at 298 K; [#] magnetic moments can be calculated by using the equation $\mu_{\text{M}}^{\text{Calc}} = [(\mu_{\text{Cu}})^2 + (\mu_{\text{Ln}})^2]^{1/2}$.

The lattice parameters, volume, and figure of merit of ligand, complex (1), complex (2), and complex (3) are tabulated in Table 2. The ligand(salbn), complex (1), and complex (3) crystallize in triclinic system while complex (2) crystallizes in monoclinic system.

3.3. Electronic Spectral Study. The electronic spectra of the free ligand(salbn) exhibits two charge transfer (CT) bands

at 257 and 310 nm attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions within the ligand. In the spectrum of the complex, the CT band at 257 nm remains intact, in agreement with the $\pi \rightarrow \pi^*$ transition of the ligand. Another band at *ca.* 342 nm is observed in the spectrum of complex (1). The band at 310 nm observed in the spectrum of free ligand is red shifted to 342 nm in the form of ligand to metal charge transfer transition (LMCT). Unlike the spectrum of the free

TABLE 2: Lattice parameter, volume, and figure of merit of ligand(salbn), complex (1), complex (2), and complex (3).

Compound	System	Figure of merit (FOM)	Lattice parameters						Volume (\AA^3)
			a (\AA)	b (\AA)	c (\AA)	α ($^\circ$)	β ($^\circ$)	γ ($^\circ$)	
Ligand (salbn)	Triclinic	F(12) = 47.5(0.0097, 26)	15.469(5)	5.085(1)	4.775(9)	74.46	92.66	93.63	361.06
Complex (1)	Triclinic	F(12) = 14.0(0.0094, 91)	12.758(2)	10.523 (2)	3.595(8)	72.15	91.62	94.84	457.88
Complex (2)	Monoclinic	F(12) = 14.2(0.096, 89)	23.016(2)	7.037(7)	16.307(9)	144.31	90.00	90.00	640.87
Complex (3)	Triclinic	F(12) = 14.8(0.0092, 88)	11.331(1)	10.579(1)	7.010(4)	50.33	114.11	122.19	544.33

Salbn: N,N'-1,3-propylenebis(salicylaldiminato); F: figure of merit.

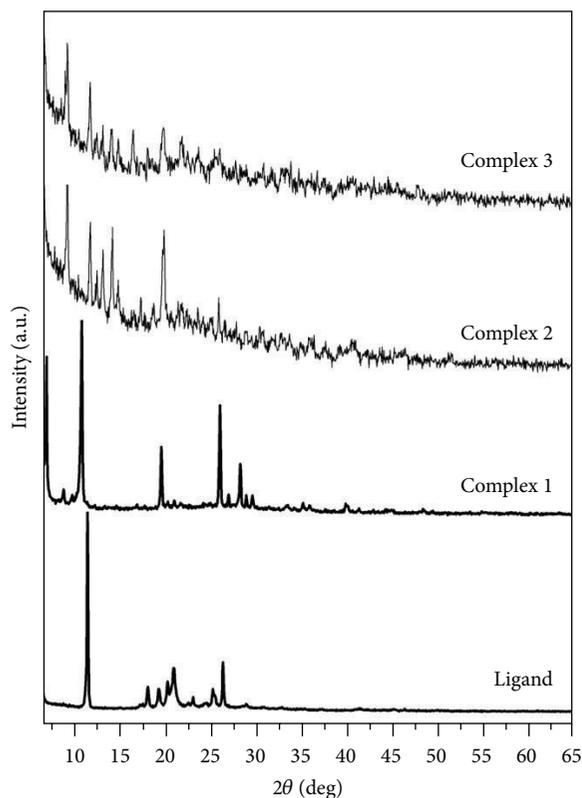


FIGURE 1: XRD patterns of ligand and complexes (1), (2), and (3).

ligand, broadband at *ca.* 597 nm is observed in the spectrum of complex (1) (see SFigure 1 in Supplementary Material available online at <http://dx.doi.org/10.1155/2013/281270>). The d-d transition at *ca.* 597 nm may be attributed to structurally well characterised square-planar copper(II) complexes [19]. The electronic spectrum of complex (1) in DMF exhibits a higher energy band at 597 nm, which has been shifted to lower energy at *ca.* 615 nm (SFigure 2) for the complex (2) seems to be due to a distortion of geometry occurring at the copper centre. Other f-f transitions, which are expected to appear, may be concealed by d-d, charge-transfer, or intraligand transitions. The electronic spectra taken in DMF have the higher absorbance and shifted to longer wavelength compared to the spectra taken in ethanol (EtOH) and methanol (MeOH) of complex (2) (SFigure 2).

3.4. Infrared Spectral Study. A strong sharp absorption band around 1638 cm^{-1} in the spectrum of the ligand may be assigned to the C=N stretching. In the complex, this band is shifted to 1627 cm^{-1} upon complexation with the metal, which may be attributed to the coordination of the imine nitrogen to the metal centre [20–23]. The ligand shows band at 3539 cm^{-1} due to O–H stretching from phenolic group which disappears in the complexes (1), (2), and (3), indicating the deprotonation of the ligand upon complexation [5]. The strong phenolic C–O absorption band at 1212 cm^{-1} observed in the spectrum of ligand shifts to lower frequency at 1017 cm^{-1} , supporting the coordination of the deprotonated phenolic oxygen atoms to the metal centres in the complexes [22]. A broadband at *ca.* $3300\text{--}3450\text{ cm}^{-1}$ indicates that coordinated water is present in the heteronuclear Cu(II)-Ln(III) complexes which is also supported by thermal data. The IR spectra of the complexes (2) and (3) show weak bands at 860 and 897 cm^{-1} for ρ_r and at 550 cm^{-1} for ρ_{wagg} of coordinated water [21]. The ligand coordination to the metal centre is substantiated by a band appearing at 470 cm^{-1} which is mainly attributed to $\nu_{\text{Cu-N}}$ in the complexes.

The spectra of the heteronuclear copper(II)-lanthanide(III) complexes (2) (SFigure 3) and (3) exhibit characteristic vibrational frequencies of coordinated nitrate group, which is supported by two bands observed at *ca.* 1485 and 1301 cm^{-1} [24]. The medium band at 1030 cm^{-1} due to the ν_2 vibration of the nitrate group (C_{2v}) stands as additional evidence for the presence of coordinated nitrate group. The difference in wavenumbers between the two highest frequency bands ($\nu_4\text{--}\nu_1$) of nitrate (C_{2v}) is about 184 cm^{-1} , indicating the nature of bidentate nitrate bridging [21–26].

3.5. NMR and Mass Spectral Studies. ^1H and ^{13}C NMR spectra have been used to extract information regarding the coordination mode of the ligand(salbn) with the metal ion (SFigures 4 and 5). The ^1H NMR (400 MHz, CDCl_3) spectra of ligand within a range of 0 to +15 ppm have δ 8.31 (s, 2H, N=CH), 7.29 and 6.86 (*t* each, 2 : 2 H, aromatic CH), 7.21 and 6.96 (*d* each, $J = 7.2$ and 8.4 Hz , 2 : 2 H, aromatic CH), 5.31 (s, 2H, OH of salbn), 3.65 (s, 4H, methylene, α to --N=CH--), and 2.06 (s, 2H, methylene, β to --N=CH--), and ^{13}C NMR (100 MHz, CDCl_3) has δ 31.70(methylene, α to --N=CH--), 56.81(methylene, β to --N=CH--), 116.97, 116.68, 118.75, 131.34, and 132.30 (aromatic CH), 161.13(--HC=N--), and 165.48(--C--OH).

In the ^1H NMR spectrum of the free ligand no broad peak was observed due to free amine proton in the region

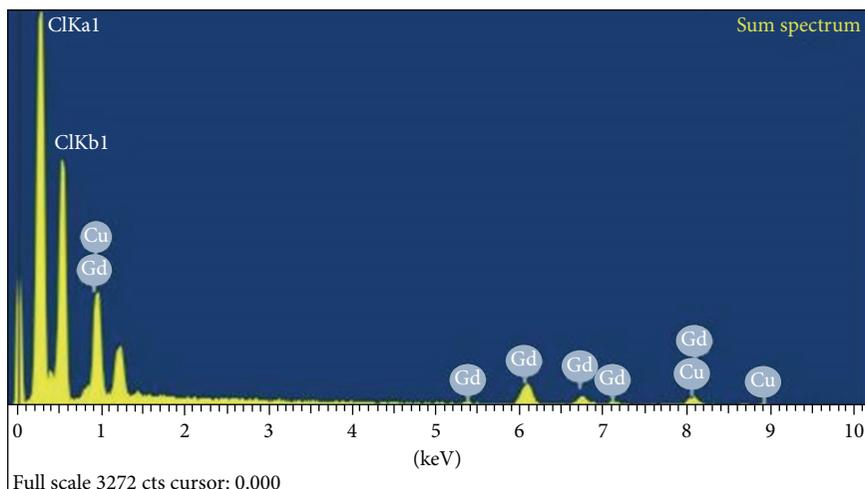


FIGURE 2: Energy-dispersive X-ray spectrum of heteronuclear Cu(II)-Gd(III) complex (2).

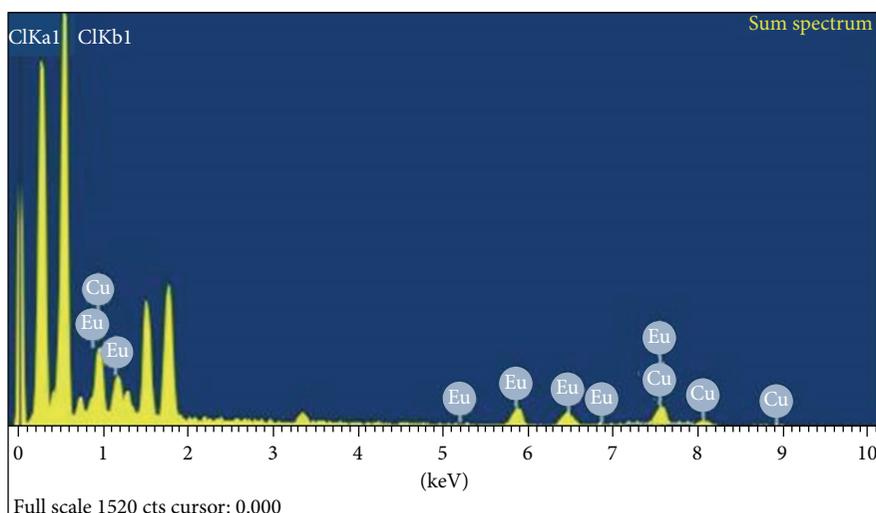


FIGURE 3: Energy-dispersive X-ray spectrum of heteronuclear Cu(II)-Eu(III) complex (3).

5.0–8.0 ppm indicating that both -NH_2 functions of the 1,3-diamine have undergone condensation with the carbonyl functional group of salicylaldehyde to give the Schiff base ligand [27, 28]. The ^{13}C NMR spectra of the ligand (SFigure 6) were recorded in CDCl_3 solution and revealed the presence of expected number of signals corresponding to different types of carbon atoms present in the ligand. In the free ligand, the aromatic carbons appear in the range 116–165 ppm. For the ligand, the azomethine carbon of the phenolic moiety appears at 161–165 ppm. Large chemical shift values for the carbon atoms attached to the azomethine nitrogen and phenolic oxygen suggest coordination of these atoms. The tetradentate nature of the ligand is confirmed from the spectral studies of ^1H NMR and ^{13}C NMR.

The FAB mass spectra of complex, $[\text{Cu}(\text{salbn})]$ with ligand (SFigures 7 and 8), play an important role in confirming the monomeric Cu(II) complex. The molecular ion peak of $[\text{Cu}(\text{salbn})]$ complex was observed at m/z 344, which is

equivalent to its molecular weight and that of ligand(salbn) was observed at m/z 282 which is also equivalent to its molecular weight. The other peaks like 336, 344, 346, 368, 369, 382, and 384 in $[\text{Cu}(\text{salbn})]$ complex correspond to various fragments. The stoichiometry of metal to ligand in the ratio 1 : 2 was supported by the observed molecular ion peaks in spectrum of complex (1). These observations confirm the stoichiometric composition of the complex formation. This is also supported by the FAB mass spectra of the other complexes [17]. The data of mass spectra was found in complete agreement with that of obtained via elemental analysis.

3.6. Energy-Dispersive X-Ray Spectroscopy Study. The composition of the heteronuclear copper(II)-lanthanide(III) complexes that is, complexes, (2) and (3), was defined by energy-dispersive X-ray spectrometer (EDX) analysis as shown in Figures 2 and 3, respectively. The analysis of the

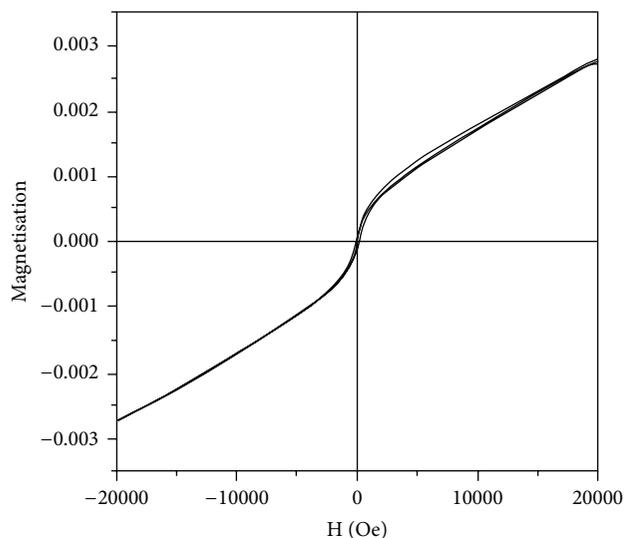


FIGURE 4: VSM hysteresis loop curve of complex (3) at room temperature.

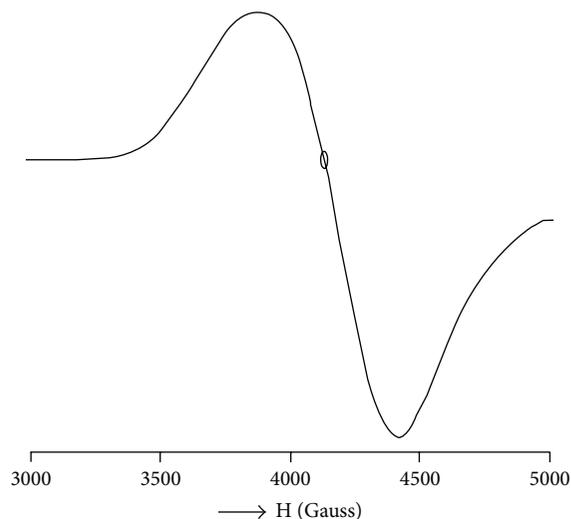


FIGURE 6: Powder EPR spectrum of complex (2) at 300 K.

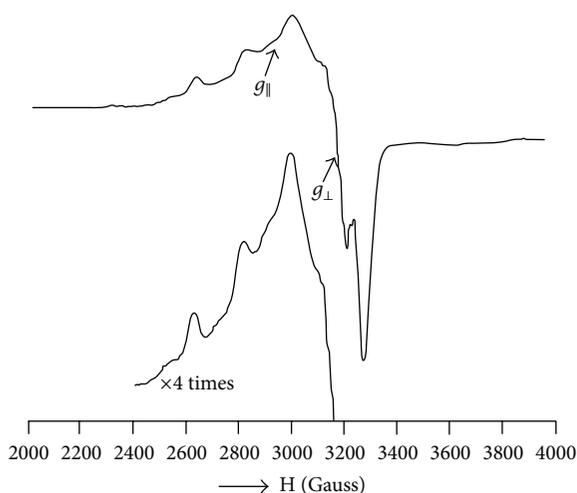


FIGURE 5: EPR spectrum of [Cu(salbn)] complex in DMF at liquid nitrogen temperature.

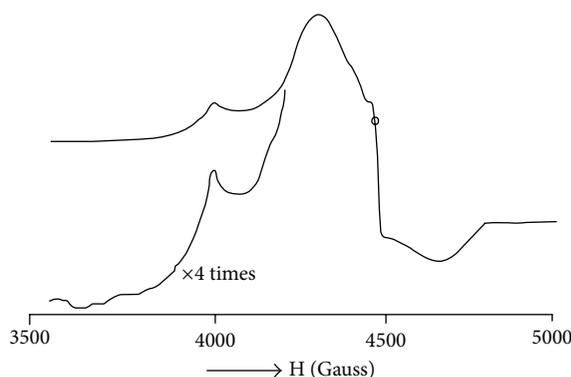


FIGURE 7: EPR spectrum of complex (2) in DMF at liquid nitrogen temperature.

EDX spectra indicates the presence of two kinds of different metals ions in heteronuclear complexes (2) and (3). Thus, from the EDX analysis, it can be proved that complexes (2) and (3) are heterobinuclear complex [29].

3.7. Thermal Analysis of the Complexes. The thermogravimetric studies show that all lanthanide(III) nitrate complexes undergo a series of weight loss starting from 40 to 820°C range (SFigure 9). TG curve of complex (2) shows the three steps of decomposition. The first weight loss corresponds to coordinated one water molecule at around 241°C vide IR while the second weight loss correspond to decomposition of ligand and anion in temperature around 330°C with a significant sharp endothermic peak. Finally the third step

corresponds to decomposition in the Ln_2O_3 oxides in temperature around 680°C. The residue obtained after heating up to 820°C to constant weight is very close to those expected for the lanthanide(III) oxides [5, 29, 30].

3.8. VSM Study. The magnetic hysteresis loop of the complex (3) taken at room temperature is shown in Figure 4. Saturation magnetization is not observed as the applied magnetic field is raised, and hence there is no coercivity and remanence in the hysteresis loop of complex (3) [31].

3.9. Fluorescence Study. In order to investigate the effect of an adjacent metal ion on fluorescence of Eu(III), fluorescence spectra of complex (3) were recorded. The complex (3) showed no significant fluorescence in the range of 550–750 nm by the maximum excitation wavelength, while $[\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ gave the well-known five typical fluorescence bands at ~592, ~618, ~649, ~685, and ~698 nm when excitation monitored at 395 nm corresponding to

characteristic emission transitions $^5D_0 \rightarrow ^7F_J$ ($J = 0, 1, 2, 3, 4$) [32, 33]. This significant decrease in fluorescence intensity may be due to the energy transfer from the excited Eu(III) to the adjacent Cu(II) complex moiety (intramolecular energy transfer), followed by the radiationless energy loss through the Cu(II) complex moiety [34].

3.10. Magnetic Moment and EPR Studies of the Complex. The magnetic susceptibility measurement of the [Cu(salbn)] complex showed a magnetic moment value of 1.73 B.M (Table 1) corresponding to one unpaired electron, indicating that the Cu(II) complex is mononuclear. The heteronuclear copper(II)-lanthanide(III) complexes (2) and (3) under study showed a magnetic moment, μ_{eff} value at room temperature of 8.06 and 3.84 B.M (Table 1), respectively. The magnetic moments observed are compared with the theoretical spin orbital coupling values (the Hund's values) and the values calculated from Van Vleck formula of the respective lanthanide ion. These values agree well with each other for the copper(II)-lanthanide(III) complexes [35].

The solid and DMF solution EPR spectra of [Cu(salbn)] complex were recorded at 300 K and liquid nitrogen temperature by using tetracyanoethylene ($g = 2.0027$) as reference. According to $I_{\text{Cu}} = 3/2$ and calculation expression $(2I + 1)$, four hyperfine splitting lines can be expected. Indeed four weak peaks are observed giving parameters $g_{\perp} = 2.072$ and $g_{\parallel} = 2.183$ which is a normal axial symmetric EPR spectrum as shown in Figure 5. This is typical of tetragonally coordinated monomeric copper(II) complex with unpaired electron in the $d_{x^2-y^2}$ orbital and spectral features which are the characteristics of axial symmetry [36]. The g_{\parallel} and g_{\perp} values are >2.0023 indicating that the complexes are largely covalent [37].

EPR spectra of complex (2) were recorded at X-band in the solid and solution state at room temperature and liquid nitrogen temperature. The room temperature polycrystalline powder EPR spectrum of complex (2) shows a unique quasi-isotropic broad signal centred at $g = 2.1$ (Figure 6) but shows no clear characteristic peak in the $g = 2$ region [17, 38]. Little information is obtained from the room temperature polycrystalline powder EPR spectrum. The EPR spectrum of liquid nitrogen temperature in DMF solution of complex (2) exhibits an anisotropic broad signal around $g \sim 2.03$ which may suggest a weak magnetic spin-exchange interaction between Gd(III) and Cu(II) ions [39] as shown in Figure 7.

In the EPR spectrum of complex (2) in DMF solution at liquid nitrogen temperature, the fine structure exhibits the seven expected transitions around 2380, 2680, 3000, 3220, 3300, 3480, and 4000 G which may be generated by zero field splitting [17, 40]. This spectrum corresponds to the superposition of the signals of the copper(II) and gadolinium(III) ions. These results suggest that the copper(II) ($S = 1/2$) and gadolinium(III) ($S = 7/2$) spins are coupled to yield the total spin states $S = 3$ (low lying excited state) and $S = 4$ (ground state) which is a weak interaction between copper(II) and gadolinium(III) ions [41].

4. Conclusions

Three complexes, namely, [Cu(salbn)] (1), [Cu(salbn)Gd(NO₃)₃·H₂O] (2), and [Cu(salbn)Eu(NO₃)₃·H₂O] (3) where salbn = N,N'-1,3-propylenebis (salicylaldiminato) have been synthesized and characterized. The EDX results suggest the presence of two different metal ions in heteronuclear complexes (2) and (3). The ligand(salbn), complex (1), and complex (3) crystallize in triclinic system while complex (2) crystallizes in monoclinic system. The EPR studies suggest that [Cu(salbn)] complex is tetragonally coordinated monomeric copper(II) complex with unpaired electron in the $d_{x^2-y^2}$ orbital and spectral features that are the characteristics of axial symmetry while complex (2) in DMF solution at liquid nitrogen temperature exhibits an anisotropic broad signal around $g \sim 2.03$ which may suggest a weak magnetic spin-exchange interaction between Gd(III) and Cu(II) ions. The fluorescence intensity of Eu(III) decreased markedly in the complex (3).

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