

## Microwave assisted synthesis, spectroscopic characterization and luminescence property of transition metal complexes of 2-(3-phthalylhydrazidylazo)-ethylacetoacetate

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**Abstract :** A simple, efficient and green synthetic protocol of bivalent transition metal complexes of a luminol derivative namely (3-phthalylhydrazidylazo)ethylacetoacetate under microwave irradiation in the absence of solvent has been described. The complexes have been characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility measurements and various spectral studies. The spectral studies have revealed that the ligand acts as monobasic tridentate coordinating to the metal ion through acetyl carbonyl, hydrazo nitrogen and amido carbonyl of phthalylhydrazide moiety. The electron paramagnetic resonance spectra of copper(II) complex has shown that the metal-ligand bond has considerable covalent character. The ligand and nickel(II) complex have been subjected to powder X-ray diffraction study. The high degree of crystallinity of the ligand has been lost on complexation with metal ion. The electrochemical behavior of the copper(II) complex has been also examined. The luminescence properties of complexes have been compared with that of the free ligand.

**Keywords :** Microwave assisted synthesis, ethylacetoacetate, phthalylhydrazide, XRD, electrochemical behavior, luminescence.

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### Introduction

Luminol and its derivatives have been extensively used as chemiluminescent reagents. The chemiluminescence of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) was first described by Albrecht<sup>1</sup>. Since then, luminol and its derivatives have been extensively studied and applied for several analytical applications<sup>2-6</sup>. Electrogenenerated chemiluminescence is of growing importance in many areas of analytical interest. It can offer a number of advantages for the detection of a wide range of analyte<sup>7</sup>. Recently, chemiluminescence has been an attractive detection method for HPLC. With chemiluminescence detection, luminol related compounds have been widely utilized as chemiluminescence derivatization reagents, because of their high sensitivity and selectivity. However metal complexes of luminol and its derivatives have received only sporadic attention so far when compared to its analytical applications, presumably due to the poor solubility of luminol and its derivatives in common organic solvents used for synthetic purposes. From a safety and environmental point

of view, the synthetic protocol is saddled with a serious drawback, especially when the reactants are insoluble in common solvents used for the synthetic purposes. In the present work it has been overcome by microwave assisted solvent free synthesis. This new synthetic approach has got several advantages over the conventional method<sup>8</sup>. In this investigation luminol has been incorporated into a  $\beta$ -ketoester through azo coupling. Apart from the synthetic aspects, the structural diversities exhibited by arylazo derivatives of  $\beta$ -diketones and their metal complexes have evolved considerable interest. The structure of such coupling products, capable of existing in different tautomeric forms, has generated so much arguments and speculations as hardly any other topic in the whole realm of organic chemistry done so far<sup>9,10</sup>. Although several metal complexes of carbocyclic azo derivatives have been extensively investigated, those derived from heterocyclic systems have received comparatively less attention<sup>11</sup>. The present work deals with the synthesis and spectroscopic characterization of some complexes of some transition

metal ions with the host of a monobasic tridentate ligand derived from diazotized luminol and ethylacetoacetate. Microwave assisted synthetic technique has been used successfully for the preparation of metal complexes.

## Results and discussion

### *Microwave assisted synthesis :*

Microwave activation as a non-conventional energy source has become an important method that can be used to carry out a wide range of reactions within short time and with high yields, especially in the absence of solvents. Microwave treatment has also provided non-contact heating, an inverted temperature gradient, direct energy transfer, and selective heating of reaction mixture. Although microwave irradiation has been widely exploited in the last decades to carry out a striking number of organic syntheses, its application for the synthesis of metal complexes is very limited. Here, the product is obtained in high yield and purity.

### *Structure of ligand :*

The products obtained by coupling aryldiazonium salts with compounds containing active methylene group, have in fact, generated so much arguments and speculations. Systematic studies of such coupling products of benzene diazonium salts have been carried out by several investigators<sup>12</sup>. Although several tautomeric forms have been suggested for such coupling products, possibilities of resonance assisted hydrogen bonding are present in the hydrazone and azo-enol forms. Hence this type of coupling products gives rise to azo-hydrazone tautomerism. It has been reported that a bulk of information in this regard could be obtained from UV-Visible spectroscopy, a technique well suited to such investigations<sup>13</sup>. The tautomeric equilibrium depends on the extent of conjugation, nature and position of the substituents, polarity of the solvent etc. This phenomenon has drawn considerable attention by several investigators and characteristic spectral bands have been assigned to the individual tautomers; that is the monophenylazo and monophenylhydrazone derivatives. The former type of compounds gave a strong band in the range 270–284 nm while the monophenyl hydrazone exhibited a strong band above 320 nm<sup>13,14</sup>. The ultraviolet spectrum of the ligand under investigation showed a strong band (other than CT band) at 344 nm characteristic of the hydrazone form<sup>14,15</sup>.

In agreement with the hydrazone form, infrared spec-

trum of the ligand showed three strong bands at 1680, 1650 and 1614  $\text{cm}^{-1}$ . The bands at 1680 and 1614  $\text{cm}^{-1}$  can be assigned to stretching of the free ethyl ester carbonyl and hydrogen bonded acetyl carbonyl groups respectively<sup>16</sup>. The slightly broad band at 1650  $\text{cm}^{-1}$  can be assigned to the amide carbonyl of the phthalylhydrazone moiety. A broad band spreading over the region 3500–3350  $\text{cm}^{-1}$  can be ascribed to ring NH group. The vibrational characteristic of internally hydrogen bonded NH group of hydrazone moiety is observed at 3192  $\text{cm}^{-1}$  and the band due to hydrazo (N-N) has been observed at 954  $\text{cm}^{-1}$ . Some authors have reported that the amide carbonyl group present in the phthalylhydrazone moiety enolises. However, the strong  $\alpha$ -effect due to two heterocyclic nitrogen atoms on the phthalylhydrazone moiety prevents the enolization of this carbonyl group of the luminol moiety. Proton NMR spectrum of the ligand adequately supported the observations drawn on the basis of UV and IR spectral data.

Proton NMR spectrum of the ligand recorded in  $\text{CDCl}_3$  displayed two methyl proton signals of equal intensity around  $\delta$  2.58 and 2.69 which show that the methyl protons are not equivalent. The low field broad single proton signal at  $\delta$  13.71 is indicative of the hydrogen bonded NH proton of the hydrazone moiety. Absence of the -CH- proton signal of the  $\beta$ -ketoester moiety and the presence of a low field broad signal at  $\delta$  13.71 adequately confirm that the ligand exists in the internally hydrogen bonded hydrazone form. The signal for the ring amido NH proton was observed at  $\delta$  9.95. The aromatic proton signals were observed in the range  $\delta$  6.85 to 7.74. On the basis of the above spectral data, an internally hydrogen bonded hydrazone structure has been assigned to the ligand (Fig. 1).

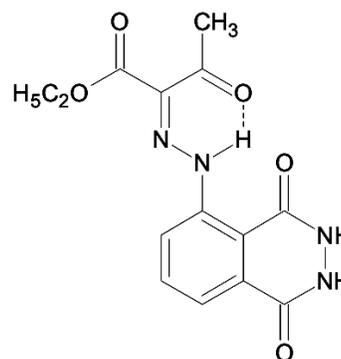
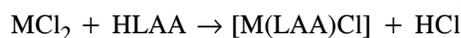
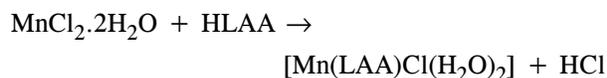


Fig.1. Structure of HLAA.

*Structure of the metal complexes :*

Analytical data of the complexes were in good agreement with their formulation (Table 1). Molar conductance measurements in different solvents adequately confirmed their non-electrolytic nature. Formation of the complexes can be represented by the following equations. It has showed that microwave assisted synthesis of metal complexes is an excellent synthetic route to metal complexes.



where M = Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> or Zn<sup>II</sup>

The ultraviolet spectral band of the ligand characteristic of the hydrazone form was only marginally red shifted in metal complexes indicating that no structural alteration of ligand took place on chelation with metal ion. In the infrared spectra of the metal complexes the band due to  $\nu(\text{NH})$  has been disappeared, indicated the coordination of hydrazone NH proton after deprotonation. This is further supported by the appearance of band due to  $\nu(\text{N-N})$

which has been shifted to higher frequencies by about 20  $\text{cm}^{-1}$  in the metal complexes. The broad band ranging from 3500–3350  $\text{cm}^{-1}$  centered at 3354  $\text{cm}^{-1}$ , attributable to the amide NH unaltered in the metal complexes. It indicated the non-participation of the amido NH of phthalylhydrazide moiety. The band due to the hydrogen bonded carbonyl of the acetyl acetone moiety occurring at 1614  $\text{cm}^{-1}$  has disappeared, but instead, another strong band appeared at  $\sim 1560 \text{ cm}^{-1}$ . This can be assigned to the coordinated carbonyl of the acetyl group. A medium intensity band observed at  $\sim 1610 \text{ cm}^{-1}$  in the spectra of the metal complexes is probably due to  $\nu(\text{C}=\text{N})$  which has been masked in the spectrum of the ligand by the high intensity of carbonyl band. However in the metal complexes this band become visible due to lowering of the  $>\text{C}=\text{O}$  stretching as a result of coordination. The band due to amide carbonyl group of phthalylhydrazide motif was shifted to lower frequency by about 40  $\text{cm}^{-1}$  showed the participation of this group on metal coordination. However, the other amido carbonyl group remained unaffected, as evidenced by the sharp carbonyl band in the metal complex (Table 2).

**Table 1.** Analytical data and other details of 3d metal complexes of HLAA

Complex	Analytical data <sup>a</sup> (%)				Molar conductance ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )			$\mu_{\text{eff}}$ (B.M.)
	M	C	H	N	DMF	Nitrobenzene	DMSO	
[Mn(LAA)Cl(H <sub>2</sub> O) <sub>2</sub> ]	12.42 (12.38)	37.88 (37.90)	3.84 (3.86)	12.59 (12.63)	10.7	3.5	8.8	5.85
[Co(LAA)Cl]	14.36 (14.32)	40.81 (40.85)	3.17 (3.18)	13.58 (13.61)	10.3	2.8	9.1	4.20
[Ni(LAA)Cl]	13.14 (13.12)	37.62 (37.58)	3.85 (3.83)	12.55 (12.52)	10.5	2.3	9.7	D
[Cu(LAA)Cl]	14.13 (14.05)	37.23 (37.18)	3.78 (3.79)	12.42 (12.39)	9.8	2.2	9.5	1.82
[Zn(LAA)Cl]	14.38 (14.40)	37.12 (37.02)	3.75 (3.77)	12.37 (12.34)	10.2	2.9	9.8	D

**Table 2.** Infrared and far infrared spectral details of ligand and metal complexes

Compd.	$\nu(\text{NH})$ Hydrogen bonded	$\nu(\text{NH})$ Phthalyl hydrazide	$\nu(\text{C}=\text{O})$ Amide carbonyl	$\nu(\text{C}=\text{O})$ Ethyl ester carbonyl	$\nu(\text{C}=\text{O})$ Hydrogen bonded	$\nu(\text{C}=\text{N})$	$\nu(\text{N-N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-Cl})$
HLAA	3192	3350	1650	1680	1614	–	954	–	–	–
[Mn(LAA)Cl(H <sub>2</sub> O) <sub>2</sub> ]	–	3356	1610	1678	1560	1610	976	415	520	390
[Co(LAA)Cl]	–	3360	1608	1680	1562	1612	976	412	515	388
[Ni(LAA)Cl]	–	3354	1605	1678	1565	1609	981	414	521	393
[Cu(LAA)Cl]	–	3352	1608	1675	1561	1610	980	415	517	392
[Zn(LAA)Cl]	–	3350	1604	1679	1560	1610	978	416	522	390

The proton NMR spectrum of the ligand indicated a low field broad signal at  $\delta$  13.71 for hydrogen bonded NH which disappeared in the spectra of the complexes indicating replacement of the NH proton during metal chelation. The signal due to the amide proton of the phthalylhydrazide ring is observed both in the case of ligand and complexes, have not registered any appreciable change.

In the far infrared spectra of all the complexes, the non-ligand bands observed at the 410–420  $\text{cm}^{-1}$  region can be assigned to  $\nu(\text{M-N})$  stretching vibration. Conclusive evidence regarding the bonding of oxygen to the metal ions is provided by the occurrence of bands at 515–525  $\text{cm}^{-1}$  as the result of  $\nu(\text{M-O})$ . The non-ligand bands appearing in the region 388–393  $\text{cm}^{-1}$  is due to the  $\nu(\text{M-Cl})$  vibration. Therefore it has been concluded that the ligand acts as monobasic tridentate to the metal ion through acetyl carbonyl, hydrazo nitrogen and amido carbonyl of the phthalylhydrazide moiety.

The electronic spectrum of manganese(II) complex exhibited three peaks around 14020  $\text{cm}^{-1}$ , 16510  $\text{cm}^{-1}$  and 19515  $\text{cm}^{-1}$  assignable to  ${}^6A_{1g} \rightarrow {}^4T_{1g}$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  and  ${}^6A_{1g} \rightarrow {}^4E_g$ ,  ${}^4A_{1g}$  transitions respectively. These data along with magnetic moment value are compatible with an octahedral geometry around the metal ion.

The cobalt(II) complex exhibited absorption band at 14880  $\text{cm}^{-1}$  which can be attributed to  ${}^4A_{2g} \rightarrow {}^4A_{1g}(P)$ , characteristic of tetrahedral geometry around the cobalt(II) ion. The magnetic moment value also supported this geometry.

Two absorptions characteristic of  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  and  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  transitions respectively are observed at 17270  $\text{cm}^{-1}$  and 24210  $\text{cm}^{-1}$  in the case of nickel(II) complex, assignable to a square planar geometry. The diamagnetic nature of the complex lends added support to the above geometry.

The copper(II) complex exhibited a broad band at 13865  $\text{cm}^{-1}$  which is assignable to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  transition. This observation is consistent with a square planar geometry with a magnetic moment value 1.82 B.M.

It has been reported that tetrahedral geometry is the most preferred structure for coordinated zinc(II) complexes. In this case the four coordination sites are occupied by ONO donor atoms of ligand and the remaining position by one chloride ion.

#### EPR spectra :

Electron spin paramagnetic spectral studies are particularly instructive in revealing the covalent character of the metal ligand bond. It has been reported that  $g$  values are sensitive to covalent nature of metal-ligand bond; values above 2.3 showing ionic character and lower values showing covalent character. Apart from this, the  $\alpha^2$  values also give information regarding the nature of metal-ligand bond<sup>17</sup>.

The EPR spectrum of copper(II) complex (Fig. 4) exhibited a resolved  $g_{\parallel}$  and broadened  $g_{\perp}$  regions. The trend  $g_{\parallel} > g_{\perp} > g_e$  indicates that the unpaired electron is most likely in the  $d_{x^2-y^2}$  orbital ( $g_{\parallel} = 2.263$ ,  $g_{\perp} = 2.110$ ,  $A_{\parallel} = 180$ )<sup>18</sup>. The covalent parameter ( $\alpha^2$ ) has been calculated using Kivelson and Neiman equation<sup>19</sup>.

$$\alpha^2_{\text{Cu}} = -(A_{\parallel})/0.036 + (g_{\parallel} - 2.002) + 3/7(g_{\perp} - 2.002) + 0.04$$

The value ( $\alpha^2 = 0.79$ ) adequately support the fact that the metal-ligand bonds have considerable covalent character. The spectrum showed four peaks evidently due to coupling of the electron spin with the spin of the  ${}^{63}\text{Cu}$  nucleus ( $I = 3/2$ ). The peaks are broad and have the appearance of ill-resolved triplets. The breadth and triplet appearance can be attributed to hyperfine splitting by the nitrogen atom ( $I=1$ ) of the ligand. The triplet appearance is adduced as an evidence for nitrogen coordination.

The structures of metal complexes are shown in Figs. 2 and 3.

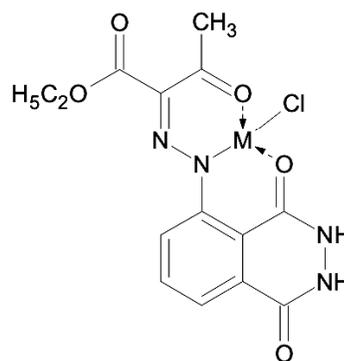


Fig. 2. Structure of  $[\text{M}(\text{LAA})\text{Cl}]$ , where  $\text{M} = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$  or  $\text{Zn}^{\text{II}}$ .

#### X-Ray diffraction study :

The ligand was subjected to X-ray diffraction study. The diffractogram (Fig. 5) showed 14 reflections with

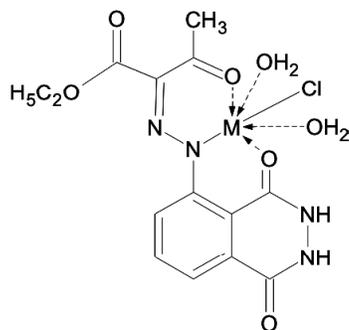


Fig. 3. Structure of [Mn(LAA)Cl(H<sub>2</sub>O)<sub>2</sub>].

lattice constants  $a = b = 6.6602 \text{ \AA}$  and  $c = 3.6176 \text{ \AA}$  and the cell volume has been  $160.4704 \text{ \AA}^3$ . The ligand has been indexed to tetragonal crystal system (Table 3). Thus the ligand exhibited high crystalline nature. The maximum peak recorded was at  $2\theta = 24.7790$  correspond to the  $d$ -spacing value  $3.5900 \text{ \AA}$ .

Table 3. X-Ray diffraction data of HLAA

Peak no.	$d$ ( $\text{\AA}$ )	$2\theta$	Relative intensity	$h k l$	$\sin^2 \theta$	
					Observed	Calcd.
1	7.4921	11.8170	93	100	0.0105	0.0112
2	6.7042	13.1970	37.1	010	0.0131	0.0132
3	5.2234	16.9480	26.5	011	0.0216	0.0221
4	4.4116	20.1430	27.8	110	0.0305	0.0267
5	3.5900	24.7790	100	001	0.0459	0.0453
6	3.3153	26.8980	87.3	200	0.0540	0.0534
7	3.1774	28.0060	68.8	101	0.0584	0.0586
8	2.9646	30.1110	53.4	210	0.0674	0.0668
9	2.6986	33.1060	39.3	120	0.0810	0.0812
10	2.4500	36.6050	30.7	201	0.0985	0.0987
11	2.2951	39.2450	27.2	211	0.1126	0.1121
12	2.0026	45.2180	21.9	221	0.1476	0.1522
13	1.8365	49.594	17.6	002	0.1757	0.1812

X-Ray diffraction pattern of the corresponding nickel(II) complex [Ni(LAA)Cl] not exhibited any prominent reflections and hence it could not be indexed to any crystalline form. Hence it can be concluded that the high degree of crystallinity of the ligand has been lost on complexation with metal ion.

#### Electrochemical behavior :

Electrochemical behavior of [Cu(LAA)Cl] was examined by means of cyclic voltammetry<sup>20</sup>. The CV profile of the complex is shown in Fig. 6. A single electron

transfer was identified at  $-937 \text{ mV}$  in the metal complex, which may be assigned to the reduction of the ligand. This observation was also seen in the free ligand at  $-752 \text{ mV}$ . The two peaks observed in the complex at  $E_{pa} +276.40 \text{ mV}$  and  $E_{pc}$  at  $218.75 \text{ mV}$  can be assigned to  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  couple.

The former reaction has been due to the reversible reaction of the ligand while the latter shows the reversible reaction in copper(II) ion. At slower scan rate the peak separation ( $\Delta E_p$ ) is less than  $60 \text{ mV}$ , indicating that the number of electron transfer is one. Also the ratio of the peak currents approach to one at this scan rate. Hence it can be concluded that the reaction is diffusion controlled and decomposition was not observed<sup>21</sup>.

#### Luminescence property of the ligand and its complexes :

Organic and coordination luminescent compounds have received intense attention due to their potential application in the area of chemical sensors and optoelectronic devices. Optical devices using various multichromophore compounds including organic polymers, small organic molecules and coordination compounds have been fabricated successfully<sup>22</sup>. Among these devices, luminescent transition metal complexes play a vital role in such optoelectronic devices mainly because of their relatively high thermal stability and flexibility in structure design and modification. Such types of organic/inorganic hybrid materials are currently receiving considerable attention, owing to their properties in magnetism, catalysis and nonlinear optical activity<sup>23,24</sup>.

The emission spectra of the ligand and metal complexes are measured in DMSO and the values obtained are presented in Table 4. The emission shown by the ligand is the result of interaction of the chromophores of the ligand. However, in the metal complexes this band is slightly red shifted, relative to the ligand due to the perturbation of the intraligand  $\pi-\pi^*$  transition of the hydrazone unit by the metal atom. The emission spectra of ligand and representative metal complexes recorded in DMSO solution ( $10^{-3} \text{ M}$ ) are presented in Fig. 7. The excitation wavelength was fixed at  $325 \text{ nm}$  and the emission spectra were recorded from  $350$  to  $600 \text{ nm}$ .

The absorption band correspond to the most intense peak in the electronic spectrum is in accordance with the Franck-Condon principle and thermal relaxation of vi-

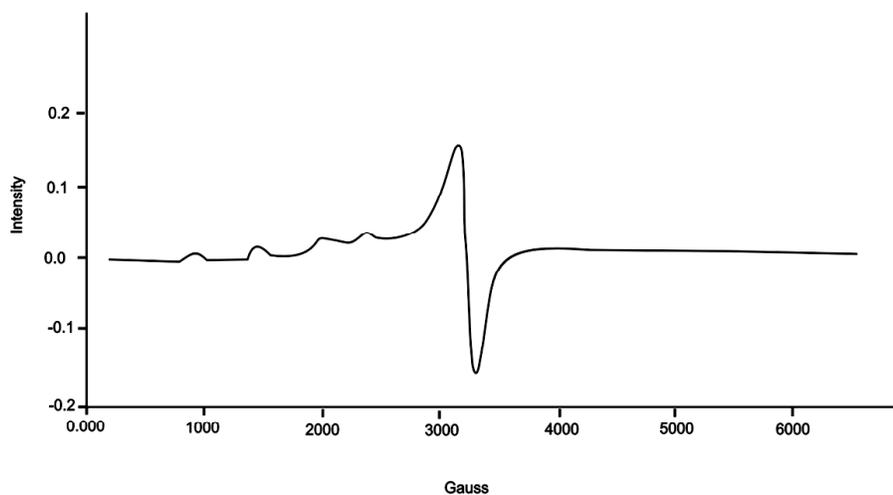


Fig. 4. EPR spectrum of [Cu(LAA)Cl].

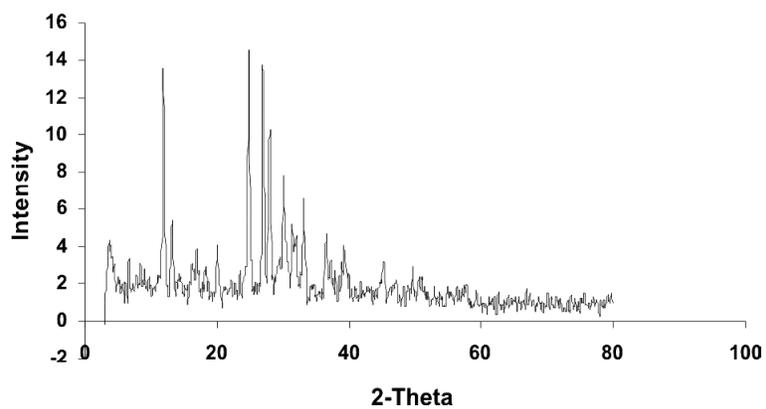


Fig. 5. X-Ray diffraction pattern of HLAA.

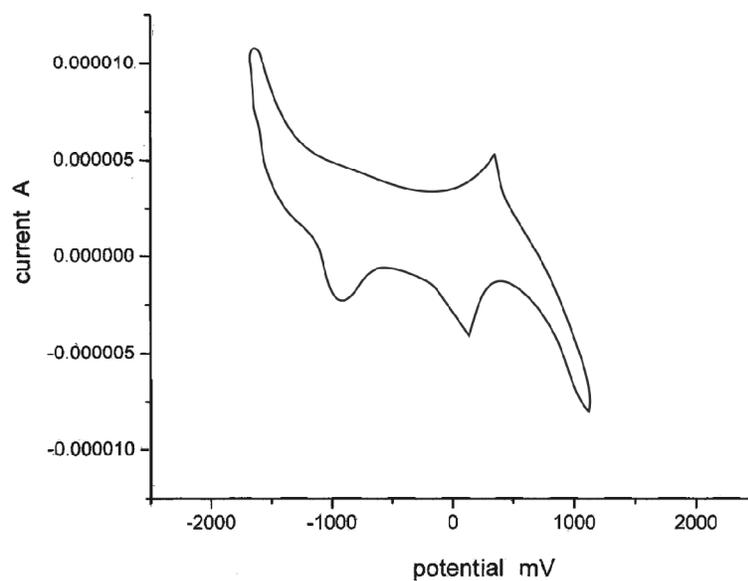
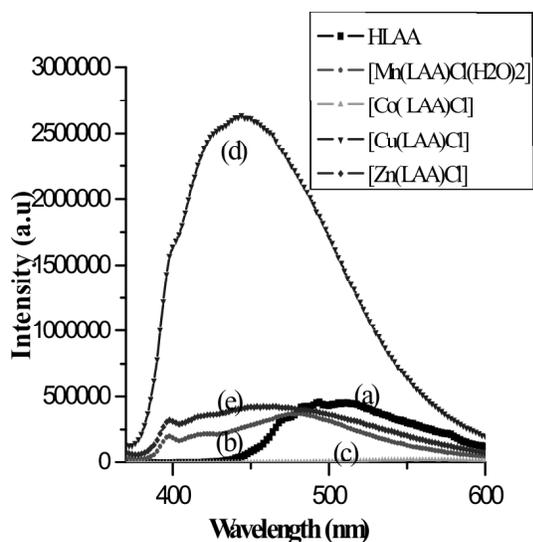


Fig. 6. Cyclic voltammogram of [Cu(LAA)Cl].

**Table 4.** Emission spectral data of ligand and its metal complexes (cm<sup>-1</sup>)

Compd.	Emission (cm <sup>-1</sup> )
HLAA	19,370
[Mn(LAA)Cl(H <sub>2</sub> O) <sub>2</sub> ]	19,530
[Co(LAA)Cl]	17,793
[Cu(LAA)H <sub>2</sub> O]	22,026
[Zn(LAA)Cl]	22,727

**Fig. 7.** Photoluminescence spectra of ligand and its complexes : (a) HLAA, (b) [Mn(LAA)Cl(H<sub>2</sub>O)<sub>2</sub>], (c) [Co(LAA)Cl], (d) [Cu(LAA)Cl] and (e) [Zn(LAA)Cl].

brational modes, the fluorescence spectra is observed on the red side of the absorption spectrum in an approximately mirror-image relationship. The spectrum is free from the anti-stoke's effect. The pattern of the spectrum indicates that the geometry of the excited state is not very different from that of the ground state<sup>25</sup>.

Complex of cobalt(II) exhibited a red shift by about 50 nm compared to the free ligand. In order to understand the effect on emission energy on going from the free ligand to the complex, a theoretic reason has been proposed<sup>26</sup>. The highest occupied molecular orbital (HOMO) of the complex is a  $\pi$ -orbital, localized on the non-coordinating nitrogen atom and carbon atom in the hydrazone moiety, owing to the low symmetry. On comparing with the free ligand, the energy of the HOMO level of the complex is much lower than that of the free ligand. The lower unoccupied molecular orbital (LUMO) of the com-

plex is a  $\pi^*$  orbital consisting mostly atomic orbitals from the luminol moiety. The role of the metal ion is to increase coplanarity and conformational rigidity in the molecular structure and increase the  $\pi$ - $\pi^*$  energy gap, reduce non-radiative decay of intraligand ( $\pi$ - $\pi^*$ ) transition excited state. Further this increase in coplanarity and conformational rigidity lead to a bathochromic shift. It is also assumed that the formation of covalent bonds between the metal and oxygen atoms via  $\pi$ -donation of a lone pair of electron of the oxygen atom to the metal atom changes the emission energy, due to the lowering of the energy gap between  $\pi^*$  and  $\pi$  orbitals. Coordination of the ligand with the metal ion increases the rigidity of the ligand, which can diminish the loss of energy via vibrational motion and increase the emission efficiency<sup>27,28</sup>.

In the case of manganese(II) and zinc(II) complexes the emission band has been blue shifted by about 50 nm, compared to the free ligand. It is due to the fact that the symmetry of the ligand enhanced after incorporation of the metal ion and the energy of the LUMO increased, resulting in the observed blue shift of the emission band. In contrast, zinc(II) has little electronic interaction with the ligand as the excited state energy of the zinc(II) complex cannot be released by the energy transfer from the ligand to the metal; hence the energy was released by fluorescence emission. However, the copper(II) complex, has a lesser blue shift than other complexes. This is a clear evidence that the metal ion play a key role in fluorescent emission of metal complexes, because copper(II) has one electron less than zinc(II) and hence copper(II) can accept electron from the ligand easily. There are also several reports on the effect of solvents on fluorescent emission by metal complexes. But this aspect could not be studied due to the poor solubility of the metal complexes in solvents suitable for such studies.

## Experimental

### Materials and methods :

All the chemicals used were of analytical grade, purchased from Aldrich, Fischer, Sisco (India) etc. Commercial solvents were distilled and used for synthesis, but for physico-chemical measurements, they were purified by standard methods.

Microwave reactions were performed on a Kenstar domestic multimode microwave oven with rotating platform tray and a power source of 230 V, 50 Hz and microwave energy output 800 W and the microwave frequency 2450 MHz. The microwave reactions were carried using on/off cycling to control the temperature. Inhomogeneity of the reaction mixture has been decreased by rotating the reaction platform. Carbon, hydrogen, and nitrogen analyses were carried out using a Heraeus Carlo Erba 1108-CHN Analyser. Molar conductance measurements of  $10^{-3}$  mol/L solutions were carried out at room temperature. Magnetic measurements were performed using a Gouy type magnetic balance. Infrared spectra were obtained from a Shimadzu FT IR 800 spectrophotometer and far infrared spectra were recorded on a Polytec FIR 30 Spectrometer using CsI discs. Proton NMR spectra were recorded in DMSO- $d_6$ , on a JEOL GSX 400NB 400 MHz FT NMR spectrometer using TMS as reference. The EPR spectrum of the copper(II) complex was recorded using a Varian E-112 EPR spectrometer using DPPH as standard. The electronic spectra of the complexes were recorded in suitable solvents in the range of 200–900 nm on a Hitachi 320 UV-Visible spectrophotometer.

*Synthesis of 2-(3-phthalylhydrazidylazo)ethylacetate :*

Luminol (1.77 g, 0.01 mol) dissolved in 2 M HCl was kept below 5 °C in an ice-salt bath. Then it was added to a stoichiometric excess aqueous solution of sodium nitrite (0.69 g, 0.01 mol) and stirred for another one hour. The excess nitrous acid in it was destroyed by adding urea. A temperature of 0 °C was maintained throughout the preparation. Luminol was sparingly soluble in water, but as the reaction proceeds, the maroon-coloured diazonium species was developed. The solution was filtered to remove any unreacted luminol. The resulting diazonium chloride solution was coupled with an alcoholic ethyl acetate (1.23 mL, 0.01 mol) and the pH was adjusted to 7 using 1 : 1 sodium acetate solution. The solution was kept for one hour in an ice-bath. The solid product formed was separated by filtration, purified by crystallization from alcohol and dried in vacuum over anhydrous calcium chloride. Yield 95%.

*Synthesis of Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> metal complexes :*

A mixture of the metal chloride and the ligand in 1 : 1 ratio was taken in a beaker and mixed well. It was then irradiated with microwave on the rotating platform. However, for the copper(II) complex the irradiation time was only 2 min and for the zinc(II) complex it was 20 min. After irradiation, the reaction mixture was allowed to attain room temperature. Then, added about 30 mL of ethanol and stirred well. The metal complex was collected on a filter, washed repeatedly with small portions of ethanol, finally with ether and dried over P<sub>4</sub>O<sub>10</sub> in a vacuum desiccator. Yield 80–85%.

*Cyclic voltammetry :*

Electrochemical behavior of ligand and its copper(II) complex were examined by employing glassy carbon working electrode, Ag/AgCl as reference electrode and platinum wire as auxiliary electrode. The working media consisted of DMSO and Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte.

*X-Ray powder diffraction :*

The X-ray diffraction data of the ligands and their metal complexes were recorded on Siemens D 5005 model X-ray spectrometer. Copper X-ray tubes, for which the wavelength of the strongest radiation (K $\alpha$ ) is approximately 1.54 angstroms (Å) are used for X-ray diffraction studies.

*Luminescence measurements :*

Luminescence property was measured using Horiba Jobin Fluorolog III modular spectrofluorometer equipped with 450 W xenon lamp and Hamatsu R 928-28 photomultiplier at room temperature in DMSO solution using 1 cm path length quartz cell. The ligand and complexes were excited at 325 nm and the emission spectra were recorded from 350 to 600 nm.

## Conclusion

The insolubility of the ligand has been overcome by efficient microwave assisted solvent free synthesis of complexes. The ligational behavior of ligand towards some bivalent transition metal ions was examined using various physicochemical studies. The cyclic voltammogram of copper(II) complex showed that the reaction is diffusion controlled and decomposition is not observed.

The luminescence property of the ligand and its complexes has been studied in DMSO solution. It has been observed that complexes of manganese(II), copper(II), and zinc(II) exhibited a blue shift; while cobalt(II) complex exhibited red shift compared to the free ligand.

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