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Role of Metal Ions on Laser Interaction with a Conjugated Organic System

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1,1,4,4-Buta-1,3-diene tetrasalicylocarbohydrazone H_8BTSTCH and its metal complexes with Co(II), Cu(II), Zn(II) and Pb(II) ions were synthesized. The stoichiometry and structure of the ligand and its complexes were elucidated by elemental analysis as well as GC, IR and ^{1}H-NMR spectroscopic techniques. Solution absorption spectra, (in DMF), of the isolated compounds showed absorption manifold in the UV region with some tailing extending into the visible. Laser excitation of these solutions at 410 nm resulted in a laser induced fluorescence, (LIF), arround 510 nm with the lead complex showing double the fluorescence intensity of both the ligand and the Zn complex. The observed emissions from all the compounds had similar features. In acidic buffer solutions, all isolated compounds showed enhanced emission intensities. Such enhancement may be attributed to an increased coplanarity and the formation of molecular aggregates through H-bonding.

INTRODUCTION

The conjugated organic compounds have drawn the attention of many researchers because of their industrial applications in synthesis of electroconducting polymers[1], light emitting diaods[2] and their importance in non-linear optics.[3]

Laser induced fluorescence, (LIF), is a well known method for studying the optical properties of new chemical compounds.[4] Such method is used to extract information about bonding and structure.[5,6] In the present work, we have studied the fluorescence behaviour of 1,1,4,4-buta-1,3-diene tetrasalicylocarbohydrazone (H_8 BTSTCH) and its Zn(II) and Pb(II) metal complexes. In addition, the effect of pH on the fluorescence has been studied.[7–9]

EXPERIMENTAL

Synthesis of the ligand

Molar ratio of 4 : 1 salicylaldehyde to 1,1,4,4-buta-1,3-diene tetracarbohydrazide[10] were mixed in ethanolic solution with continuous stirring. The reaction mixture was refluxed on a water bath for 1 h. The white precipitate thus formed was filtered, washed with ethanol and dried over P_2O_5. The structure of

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the ligand was elucidated by elemental analysis, IR and ^{1}H-NMR spectroscopic data.[11]

Preparation of the metal complexes

A hot ethanolic solution of the ligand (0.01 mol) was mixed with an aqueous ethanolic solution of the acetate salts (0.04 mol) of Cu(II), Co(II), Zn(II) and Pb(II) ions. The mixture was refluxed on a water bath for 2 h and was reduced to one third of its initial volume. The product thus formed was filtered, washed with ethanol and dried in vacuum over P_2O_5.

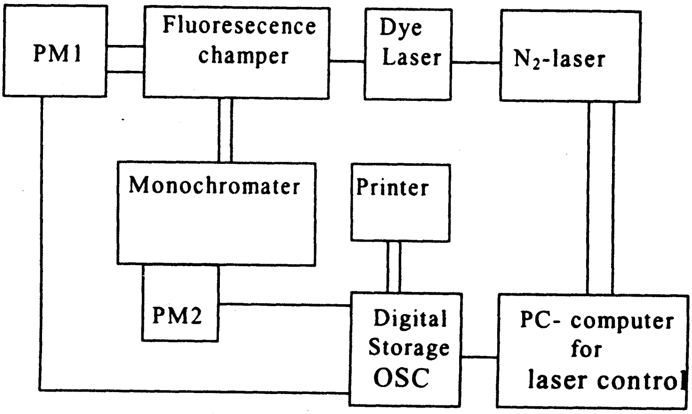
Physical Measurements

Metal ions were determined by the standard methods. Carbon and hydrogen analyses were carried out in the microanalytical centre of Cairo University, Giza, Egypt. IR spectra were recorded (4000-400 cm^{-1}) on a FTIR Perkin-Elmer 1605 model using KBr pellets. The ^{1}H-NMR spectrum of the ligand was carried out in School of Chemical Sciences, University of Illinois, USA. The thermal analysis for all complexes was done on a TGA7 thermogravimetric analyzer.

Laser Induced Fluorescence (LIF) Experiments

The experimenttal apparatus for LIF techniques is shown in the following diagram.

Nitrogen laser has been used for pumping dye laser type (PL 202) tunable from 350–800 nm. The system has been controlled by PC-computer and the laser transmitted intensity monitored by photomultiplier (PM1). The flurorescence intensity as a function of wavelength has been measured by monochromator and a type (54501A) HP-Digital Storage Oscilloscope.



RESULTS AND DISCUSSION

(a) Spectral studies for the compounds

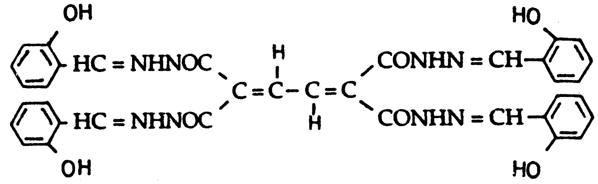
The reaction of the ligand H_8 BTSTCH with the acetate salts of cobalt(II), copper(II), zinc(II) and lead(II) gives two types of complexes: a binuclear complex in which the metal ion Co(II) or Zn(II) coordinates *via the phenolic* oxygen and azomethine nitrogen of the salicylo moieties of the organic compound forming $[Zn_2(L)]$ and $[Co_2(L)(H_2O)_4]$ complex. The a polynuclear complexes formed with Cu(II) and Pb(II) in which the metal coordinates through the azomethine nitrogen, the phenolic oxygen and enolic carbonyl oxygen atoms forming $[Cu_4(L)(H_2O)_4]$ and $[Pb_4(L)(H_2O)_4]\cdot 4H_2O$ complexes.

The isolated complexes are quite stable in air, insoluble in most organic solvents, *i. e.*, non-electrolyte complexes. The analytical data and some physical properties were collected in Table-1.

TABLE-1
ANALYTICAL DATA FOR THE PREPARED ORGANIC COMPOUND AND ITS METAL COMPLEXES

Compound	Color	% Analysis, Found (Calcd)		
		C	H	Metal oxide
$C_{36}H_{30}O_8N_8$, (H_8L)	pale yellow	61.50 (59.80)	4.30 (4.70)	—
$[Zn_2(H_4L)]$	yellow	52.10 (51.90)	3.44 (4.00)	18.70 (18.80)
$[Pb_4(L)_4H_2O]\cdot 4H_2O$	dark yellow	25.92 (25.90)	2.30 (2.90)	53.54 (54.60)
$[Cu_4(L)\cdot 4H_2O]$	dark brown	42.35 (42.50)	3.00 (3.50)	31.10 (30.50)
$[Co_2(L)\cdot 4H_2O]$	brown	48.66 (48.50)	3.40 (3.70)	16.86 (16.70)

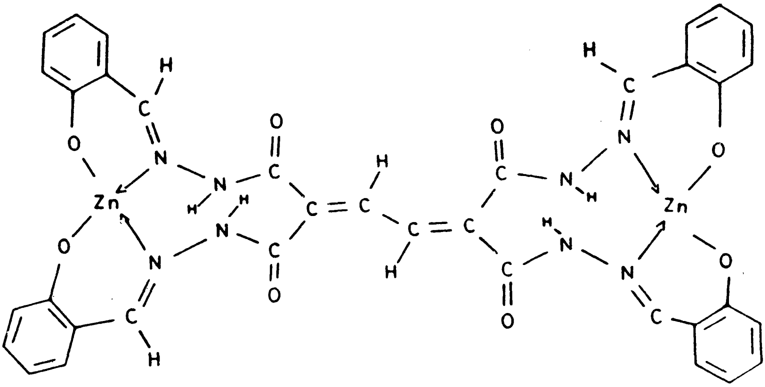
The IR spectra of compound (I) was carried out to elucidate its structure in addition to ^{1}H-NMR spectral studies. Two strong bands were observed at 1671 and 1655 cm^{-1} corresponding to the free and bonded carbonyl groups. The IR spectra shows the characteristic bands of the imino group (NH) at 3180, 1572 and 783 cm^{-1} assigned to stretching, bending and waging vibrations, respectively. A broad band was observed for the hydroxyl groups at 3445 cm^{-1} indicating the presence of intramolecular hydrogen bonding. New bands assigned to the =C—H alkene chain vibrations are observed at 2972 and 2860 cm^{-1} for the ν(CH), at 1421 and 1358 cm^{-1} for δ(CH) and at 683 cm^{-1} for δ(CH). In general the centrosymmetric arrangement of the hydrazone moieties around the central chain simplifies greatly the IR spectrum of such a highly complex molecule and renders the C=C vibrations IR inactive. The ν(C—H) aromatic bands are observed at 3048 cm^{-1}; its protons resonate in more complex profile consisting of two doublets at 6.98 and 7.86 ppm for the α and δ type protons encountering a triplet at 7.34, 7.37 and 7.39 ppm for β type protons. The spectrum reveals two strong singlets at 11.39 and 8.71 ppm for the phenolic and enolic protons of the imino group and the aldehydic protons at 6.94 ppm and 6.97 ppm. All these evidences support structure **I** for the conjugated organic compound. The IR spectra of polynuclear complexes $[Cu_4(L)\cdot 4H_2O]$ and $[Pb_4(L)\cdot 4H_2O]$ show the disappearance of NH and carbonyl groups with the appearance of new bands at 1612 and 1622 cm^{-1} respectively, which are related to the conjugated C═N—N═C system. The absence of ν(OH) and amide bands is taken as an evidence for the dissociation of their protons on complex formation. The lower shifts in ν(C—O) and ν(C═N) vibrations by 15-30 cm^{-1} in the IR spectra of the complexes indicate the participation of phenolic oxygen and the azomethine nitrogen in bonding with the metal atoms.[13] The characteristic bands of coordinated water molecules appear as a broad band in the regions 3445–3395, 880–870 cm^{-1} assigned to ν(OH) and $\rho r(H_2O)$ vibrations, respectively.



(I)

Thermal analysis studies

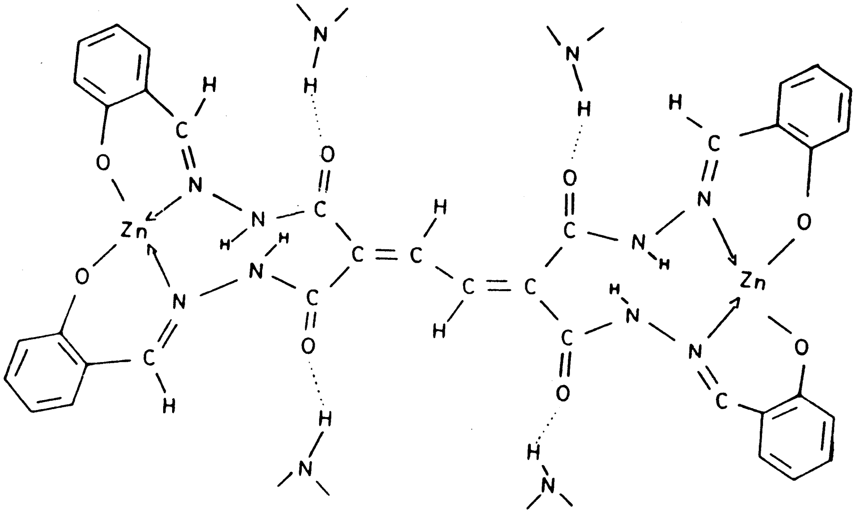
The thermal analysis of Co(II), Cu(II), Zn(II) and Pb(II) complexes were studied with the help of DTG and TG techniques. The thermograms of Pb(II) complex show an exothermic peak starting at 70, 105 and 130°C, a weight loss of 9.2% corresponding to the amount of water outside and inside the sphere (calc. 8.8%). The figure also shows a different exothermic peak starting from 205 to 527°C corresponding to the decomposition of the organic moiety. At higher temperature, a stable steady state observed starting at 600°C corresponding to the formation of lead oxide (calcd. 53.6%; found 54.1%). All the evidence gathered from elemental analysis, IR spectra and thermal analysis reveals structure **II** for $[Pb_4(L)(H_2O)_4]\cdot 4H_2O$ as an example for the polynuclear complexes.[14]



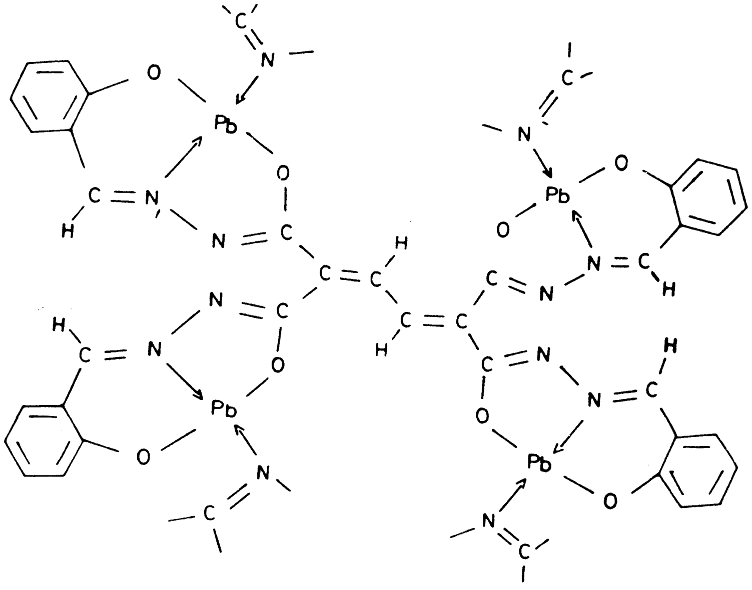
(II)

Emission Properties

The ligand and Zn-complex fluorescence are approximately similar as shown in Fig. 1, since Zn methal ions form a tetrahedral structure. This fluorescence behaviour could be attributed due to the presence of hydrogen bonding that formed between molecules in solution[8, 9] (structure III).



(III)



(IV)

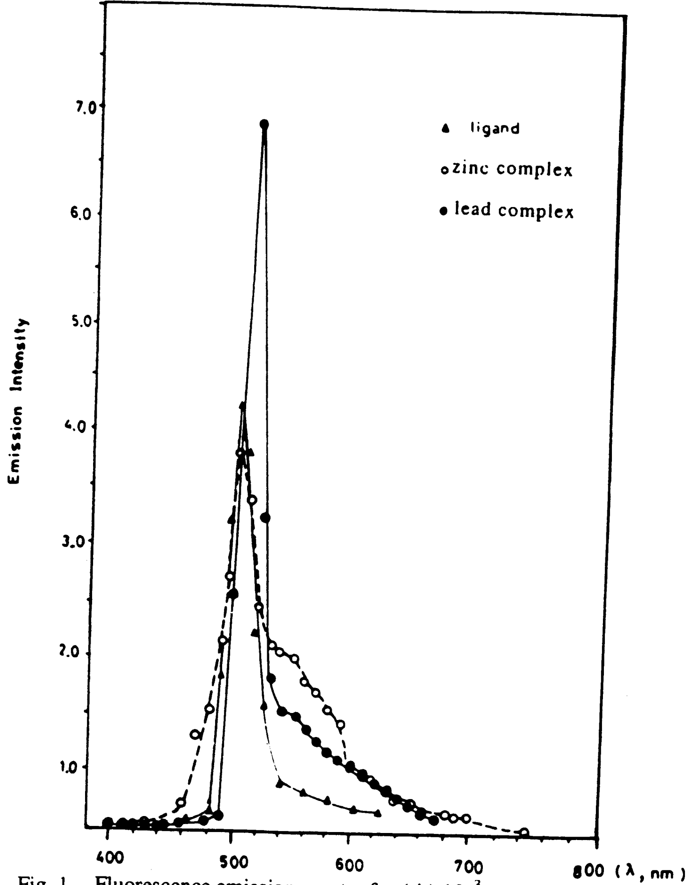


Fig. 1. Fluorescence emission spectra for (▲) 10^{-3} M of the organic compound solution, (○) 10^{-3} M zinc complex solution and (●) 10^{-3} M lead complex solution.

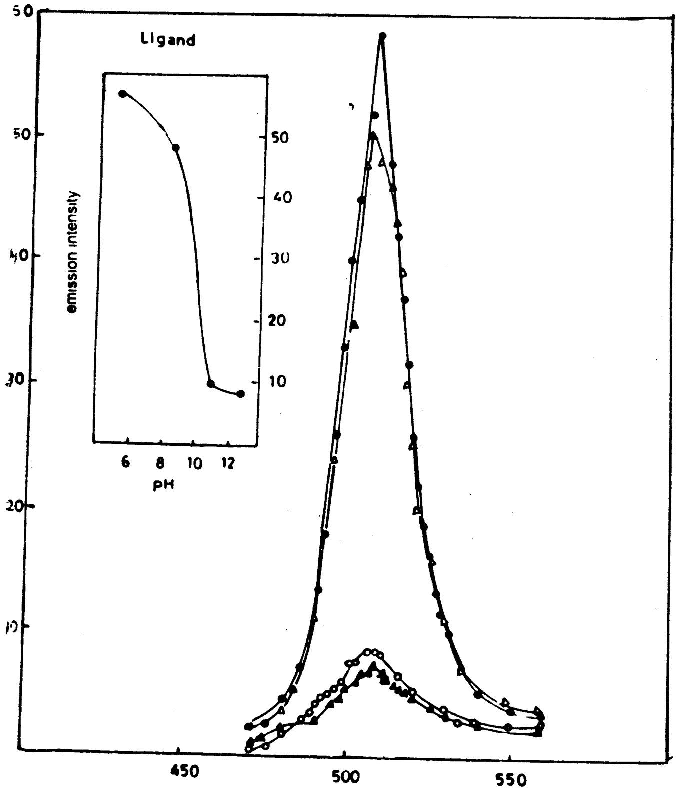


Fig. 2. Effect of aqueous buffer solutions on the fluorescence emission spectra for the conjugated organic compound.

The enhancement of fluorescence intensities in case of lead complex could be interpreted as a role of the lead ion to accept electrons from a free lone pair of imino group from another molecule which may form a conjugated polymeric structure in solution[15] (structure IV).

Fluorescence and pH-effect

Further investigation have been carried out to assure the behaviour of ligand and Zn complex. Aqueous solutions for both have been measured with pH = 5.6, 8.3, 11 and 13 as shown in Figures 1–3. Hydrogen bonding between molecules results in increased fluorescence, although to a lesser extent than metal ion complexation. In case of Pb complex fluorescence shows a different behaviour as a function of pH as shown in Fig. 4, which can be attributed to the presence of imino group and binding of its free electron to another molecule of Pb-complex which enhances fluorescence.[16]

As a conclusion, the prepared compounds may be considered as good candidates as a laser amplifier specially at the wavelength 510 nm.

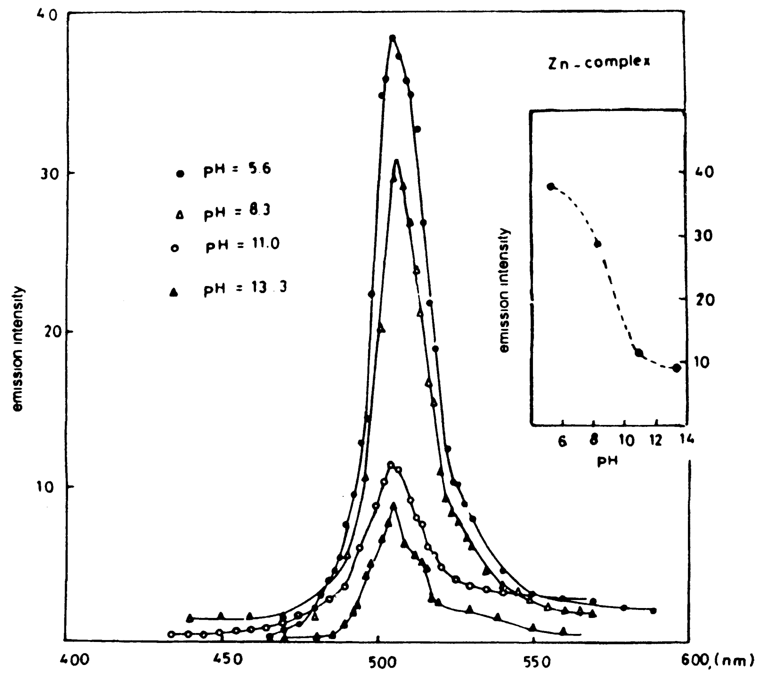


Fig. 3. Effect of aqueous buffer solutions on the fluorescence emission spectra for zinc complex solution.

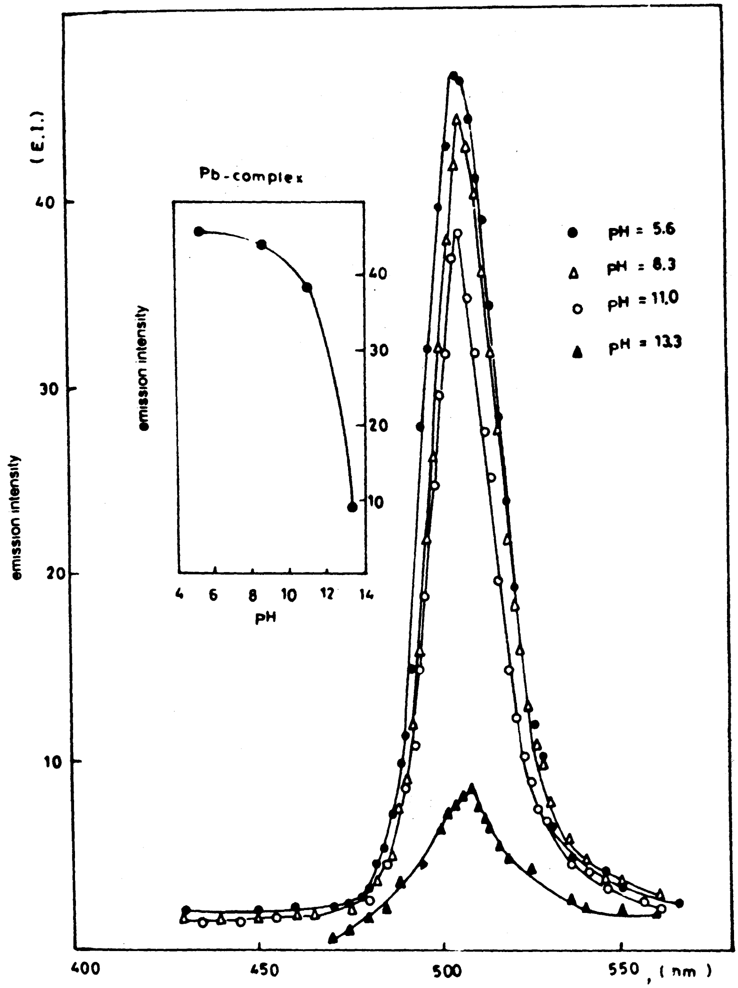


Fig. 4 Effect of aqueous buffer solutions on the fluorescence emission spectra for lead complex solution.

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