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ORGANIC FUNCTIONAL DYES HETEROCYCLIC METAL COMPLEXES AS TYPICAL PRECURSORS IN CYANINE DYES SYNTHESIS, SPECTRAL BEHAVIOURS"[1]

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Abstract:

Our synthetic approaches of unsymmetrical (symmetrical) (bis mono) N-bridgehead heterotricyclic methine cyanine dyes (**5a-g**, **8Aa-c)** were started by the preparation of key reaction intermediate compounds 4-arylideno-3-methyl-1-phenyl pyrazol-5-one (imine) (2a-f) and/or 3,3`-dimethyl-1,1`-diphenyl-bis pyrazolo-5,5`- one-4,4`-formylidin (6) with urea under acidic conditions to give the corresponding 6-arylideno-4-[3-methyl-5-one (imine)-1-phenyl-pyrazol-4-yl] - pyrimidin-2-one **(3Aa-f)** and/or 3-methyl-1-phenyl-6-one-4[3-methyl-5-one-1-phenyl-pyrazol-4-yl]- pyrazolino- [4,5-d] pyrimidin **(7)** Further reaction of the later compounds with metal divalent chlorides in ethanol as a solvent afforded 5-arylideno 3-methyl -1-phenyl-pyrazolino- [4, 5-d] 1, 3-oxazine-2-metallo–[3,4-a] pyrimidin-7-one chloride metal chelate complexes (4a-e) and/or 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino- [4,5-d,4`,5`-d`]pyrimidino-[3,4-a]-1,3-oxazine-2-metallo chloride metal chelate complexes **( 8Ba-c).** The later compound on ethanol extraction achieved the corresponding 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino-[4,5-d,4`,5`-d`]pyrimidino-[3,4-a]-1,3-oxazine-2-metallo chloride metal chelate complexes **(9a-c).** Reaction of equimolar ratios of both latter compounds **(4a-e, 9a-c))** with N-methyl –and/or 2(4)-methyl Heterocyclic quaternary iodide salts under thermal/ piperidine conditions afforded the corresponding unsymmetrical 5-arylideno 3-methyl -1-phenyl-pyrazolin-7-one - [4, 5-d] 1, 3-oxazine-2-metallo–[3,4-a] pyrimidino zero- 4- [4(1)]-methine cyanine dyes **(5a-g)** and/or 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino-[4,5-d,4`,5`-d`] pyrimidino-[3,4-a]-1,3-oxazine-2-metallo–mono-9[2(4)]-methine cyanine dyes **(10a-e)**. The new synthesized Heterotricyclic cyanine dye metal complexes were identified by elemental and spectral analyses. The UV-visible absorption spectra of some selected dyes were investigated in pure organic solvents, as well as in aqueous universal buffer solutions. The photometrical and metallochromic Behaviour of some selected cyanine dyes were studies.

Keywords: Heterocyclic Metal Complexes, Cyanine Dyes, Synthesis, Solvatochromic and Mediachromic Behaviour

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Introduction

The purpose of the present article was to compare and evaluate synthesis of new N-Bridge head Heterocyclic Metal Chelator derivatives as synthetic precursor's alternative entities to their related cyanine dye derivatives with the hope to consider their spectral studies with the aim to permit an improvement of their synthetic routes. The most traditional and promising approach is how to reach the goal and trend in order to systematize such dyes according to their quite different physico-chemical features. There remains great interest in emerging optimal and unique opportunity to the molecular design of such heterocyclic moieties to be susceptible chelating reagents material combining several properties in molecular N-bridge head heterocyclic cyanine dye metal complexes, **[1, 2].** One of the main bottlenecks to the development of such multi-property material is to pertain and search of new methodology for direct initial attempts for cyanine dyes synthesis, deeping the color and increasing the intensity of spectral bands as a criterion of photosensitization effect. The absorption spectra of methine cyanine dyes incorporating heterocyclic metal complex anhydro base moieties would extend an available range of long wavelength absorbing material and taken as a criterion for their photo-sensitizing effect. Pyrimidines metal complexes derivatives have been performed **[3]** and play a dominant role in many biochemical systems. It is important to consider the synthetic routes for an easier and stable heterocyclic reagents under the reaction conditions. There are several advantages in using such routes than conventional methods. The present method produce the products in a good yield. Dyes of interesting heterocyclic metal chelate might be used as better sensitizers than cyanine dyes having the same heterocyclic moieties with no metal incorporation. Dye composition containing metal chelate cyanine dye is used as an optical recording medium capable of writing and/or reading information laser light and shows excellent resistance against light and humidity, **[4].** Heterocyclic metal chelate complex might be influenced on near infrared absorbing cyanine dyes, **[5]**.

Results and Discussions

Our synthetic approaches of unsymmetrical (symmetrical) (bis mono) N-bridgehead heterotricyclic condensed methine cyanine dyes **5a-g** was started by the synthesis of 6-arylideno-4-[3-methyl-5-one (imine)-1-phenyl-pyrazol-4-yl] - pyrimidin-2-one derivatives **(3Aa-f)** as key reaction intermediate compounds which prepared by reaction of 4-acetyl-3-methyl-5-one(imine)-1-phenyl pyrazole **(1a,b)** with aromatic aldehyde derivative under piperdine conditions to afford the corresponding 4-arylideno-3-methyl-1-phenyl pyrazol-5-one (imine) **(2a-f).** Cyclocondensation reaction of the later compounds with urea in absolute ethanol containing concentrated HCl acid afforded 6-arylideno-4-[3-methyl-5-one (imine)-1-phenyl-pyrazol-4-yl] - pyrimidin-2-one **(3Aa-f)**, **[6-10],Scheme 1**. The cyclo-condensation process seems to be an easier for the orientation towards acyclic α, β-unsaturated carbonyl

substituent **(3Aa-f)** in the former more than cyclic β-Dicarbonyl analogous **(3Ba-f)** in the later compound to give suggested desired pyrimidinone derivatives. The pyrimidinone derivatives **(3Aa-f)** consider as an interest ligands to react with metal divalent chlorides.

The structure of **3Aa** and **3Ad** was characterized and identified by elemental analysis **Table 10**, IR, ^{1H}-NMR and Mass spectral data. Thus, IR (ν^{KBr} cm^{-1}) of **3Aa** and **3Ad** showed the disappearance of α,β-unsaturated carbonyl group at 1755 characterized for compound **(2a-f)**,, in addition to, general absorption bands at 1497 cm^{-1} (C=N), 1592 cm^{-1} (C=C), 1708 cm-1 (C=O), the appearance of cyclic pyrazolino (C=O, C=NH) at 1708, This is criterion of the formation of pyrimidinone of the type **(3Aa-f) [*11*]**, ^{1}H-NMR (CD_3OD, 250 MHz) spectra of compounds **3Aa** and **3Ad** showed the general singlet and multiplet signals at δ 1.19-1.29 (s, CH_3, of pyrazol), 3.86-5.55 (s, 1H, pyrimidine nucleus), 7.25-7.90 (m, 13H, Ar +Het + =CH + NH), **[*12*],** Mass spectra of **3Aa** and **3Ad** confirmed a molecular formula agree with a molecular ion peaks at m/z =389, and base peak at m/z =134 for compound **3Aa**, a molecular ion peaks at m/z =388, and base peak at m/z =148 for compound **3Ad [13]**.

The synthesis of novel heterocyclic metal cyanine dye complexes were started by the reaction of an equimolar amounts of 6-arylideno-4-[3-methyl-5-one-1-phenyl-pyrazol-4-yl] -pyrimidin-2-one **(3Aa-c)** and metal divalent chlorides (Cu^{++}, Ni^{++} Co^{++}) in ethanol as a solvent to afford 5-arylideno 3-methyl -1-phenyl-pyrazolino- [4, 5-d] 1, 3-oxazine-2-metallo–[3,4-a] pyrimidin-7-one chloride metal chelate complex **(4a-e)**.The reaction seems to be in two possibilities metal complex formation, one of them represented as **(4Aa-e)** and other as **(4Ba-e)**. To determine which will be formed, on triturating compound **(4a)** (as a representative example) with sodium sulphide solution gave the corresponding 5-arylideno 3-methyl -1-phenyl-pyrazolino- [4, 5-d] 1, 3-thiazine-2-metallo–[3,4-a] pyrimidin-7-one chloride metal chelate complex **(4Af).** This is a criterion for the co-ordination was conducted from pyrazolin-5-one and not form C=N of pyrimidinone. This is due to the great in electron pyrazoline -5-one cloud if compared with pyrimidinone C=N which affected by the electron withdrawing C=O of pyrimidinone. On triturating of such compound **(4Aa-e)** with saturated solution of KI followed by dissolving of the resulted in conc. H_2SO_4 liberated iodine vapour on warming. This is a criterion for the presence of the chloride anion replaced by iodide analogous. Reaction of equimolar ratios of the latter compound **(4Aa-e)** with N-methyl heterocyclic iodide salts under piperidine catalysis afforded the corresponding unsymmetrical 5-arylideno 3-methyl -1-phenyl-pyrazolin-7-one - [4, 5-d] 1, 3-oxazine-2-metallo–[3,4-a] pyrimidino zero- 4- [4(1)]-methine cyanine dyes **(5a-g).(Scheme2).** Chemical dye confirmation was conducted by the direct reaction of equimolar ratios of (**3Aa-e)** and N-methyl quinolinium iodide, as represented example under basic condition to give the corresponding 4-supstituted pyrazolino pyrimidinone zero-5(4(1)) methine cyanine **(4Ca-**

e) which on addition with metal divalent chlorides achieved the desired N-bridge head heterocyclic metal complex cyanine dyes **(5a-g).** It was obvious that during the formation of such N-bridge head heterocyclic metal complex cyanine dyes **(5a-g)**, the reaction undergoes oxidative elimination followed by dehydrochlorination to give the involved anhydro base of N-bridge head heterocyclic metal complex. The formation of metal complex **(4Aa-e)** and dyes incorporating metalo Pyrazolo quinone nuclei were suggested to proceed through formation of one form **(A)** which was easier to be available than those of isomeric structure analogous **(B).** Such latter isomeric structure does not reacted with sodium sulphide solution (1%) in EtOH/H_2O. This indicated that the replacement process of sulphur in place of oxygen not take place. Such reaction disclose which of the two-isomeric products **(A) or (B)** was isolated **(Equation 1).** Meanwhile**,** The formation of dyes was suggested to proceed according to relative stability of both reactants either 5-arylideno 3-methyl -1-phenyl-pyrazolino-7-one-[4,5-d] 1,3-oxazine-2-metallo–[3,4-a] pyrimidino chloride metal chelate complex **(4Aa-e)** and/or heterocyclic quaternary salts. Thus, the reaction was suggested to proceed through oxidative elimination process followed by rearrangement with dehydro halogenated HCl to give the desired dyes (**equation 2).**

The structure of cyanine dyes **4Aa** and **5a, b, e, f, g** were characterized and identified by elemental analysis **Table 10**, **11,** IR, ^{1}H-NMR and Mass spectral data. Thus, IR (ν^{KBr}) of compounds **4a** and **5a, b, e, f, g** showed, in addition to, general absorption bands at 1465-1499 cm^{-1} (C=N), 1528-1599 cm^{-1} (C=C), 1704 cm-1 (C=O), 510-530 cm-1 (M-O), well defined absorption band at 2923 cm-1 (heterocyclic quaternary salt),510-530 cm-1 (M-O) for compounds **5a, b, e, f, g**, **[11]**, ^{1}H-NMR (CD_3OD, 250 MHz) spectra of compounds **4Aa** and **5a, b, e, f, g** showed, in addition to, the general single and multiple signals at δ 1.19-1.29 (s, CH_3, of pyrazol), 3.1 (s, 3H, CH_3 of Aromatic aldehyde), 7.16-7.97 (m, 25H, Ar. + Het. +NH+), Well define signals at 3.21-3.32 (s, 2H, N-CH_2), 3.79 (s, 3H, CH_3-CH_2-N^+I), 7.16-7.97 (m, 25H, Ar. + Het. +NH+CH=) for compounds **5a, b, e, f, g, [*12*],**

The high resolution mass spectrum of compounds **4Aa** confirmed a molecular formula with a base peak at m/z =305, **[13]**

5-Arylideno 3-methyl-7-one -1-phenyl-pyrazolino- [4, 5-d] 1, 3-oxazine-2-metallo–[3,4-a] pyrimidino zero- 4- [4(1)]-methine cyanine dyes **(5a-g)** in 95% ethanol possess (dark green to reddish violet), in colour, and easily (partially) soluble in polar (non) organic solvents and concentrated sulphuric acid from which iodine vapour was liberated on warming. Their ethanolic solutions gave permanent colour in basic media which reversibly discharge on acidification, it posses interachargable colour solution (brown- reddish brown) in acid and basic medium. The absorption spectra of unsymmetrical 5-arylideno 3-methyl -1-phenyl-pyrazolino- [4, 5-d] 1, 3-oxazine-2-metallo–[3,4-a] pyrimidino-7-one zero- 4- [4(1)]-methine

cyanine dyes **(5a-g)** in 95 % ethanol showed different absorption bands, their position and molar extinction coefficient being influenced by the type of heterocyclic quaternary residue (A), the nature of metal and aryl substituents (Ar). Thus, the absorption spectra of dye **5a** [M=Co, Ar **=** p-N-dimethyl benzaldehyde, A= quinolinum-4- ium ethiodide] exhibit (λ_{max} =367-405 nm; ε_{max}= 21072 $mol^{-1}cm^2$). Substitution of (A= quinolinum-4- ium ethiodide) in dye **5a** by [A= pyridine-4-ium ethiodide] in compound **5c** causes hypsochromic shift of $\Delta\lambda_{max}$ = 33 nm. **5c,** λ_{max} =438 nm; ε_{max}=15574 $mol^{-1}cm^2$. This is due to the more extensive π-delocalization or conjugation in dye **5c**. Changing the linkage position of quinoline residue from 4-ium in dye **5a** [A= quinolinium -4- ium ethiodide] to 1-ium in dye **5b** [A= isoquinolinum-1- ium ethiodide] resulted in hypsochromic shift in absorption band exhibit (λ_{max} 403 nm; ε_{max} 23731 $mol^{-1}cm^2$) **.** On the other hand, substitution of (M=Co) in dye **5a** by (M=Ni) in dye **5a** causes hypsochromic shift than those of **5d** exhibit (**5d**, λ_{max} = 404 nm; ε_{max} =17870 $mol^{-1}cm^2$). Also, substitution of (M=Co) in dye **5a** by (M= Cu) in dye **5e** resulted in hypsochromic shift of $\Delta\lambda_{max}$ = 6 nm than those of **5a**. This is due to the vacant orbital increasing gradually from Copper to Nickel or Cobalt, leading to the more extensive π-conjugation. Additionally, substitution of (Ar **=** p-N-dimethyl benzaldehyde) in dye **5a** by (Ar **=** m-Nitro benzaldehyde) in dye **5f,** the electronic absorption spectra of **5f** exhibited λ_{max} = 371nm; ε_{max}= 21072 $mol^{-1}cm^2$ causes bathochromic shift due to the more electron donating character of N-dimethyl substituted than NO_2 group. Also, substitution of (Ar **=** m-Nitro dimethyl benzaldehyde) in dye **5f** by (Ar **=** benzaldehyde) in dye **5g,** the electronic absorption spectra of **5f** exhibited λ_{max} = 467-494nm; ε_{max}= 20407 $mol^{-1}cm^2$ causes bathochromic shift due to the more electron donating character of the NO_2 group. **Table (1).** Our approaches in the synthesis of the titled mono N-bridgehead hetero tricyclic -condensed methine cyanine dyes **(10a-e)** was started by the synthesis of 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino- [4,5-d,4`,5`-d`]pyrimidino-[3,4-a]-1,3-oxazine-2-metallo chloride metal chelate complex **(9a-e)** as a new key reaction intermediate compounds. Thus, such preparation was proceeded via cyclocondensation reaction of reference compound 3,3`-dimethyl-1,1`-diphenyl-bis pyrazolo-5,5`- one-4,4`-formylidin **(6) [5]** with urea in absolute ethanol containing concentrated HCl acid **[20] to** afford the corresponding 3-methyl-1-phenyl-6-one-4[3-methyl-5-one-1-phenyl-pyrazol-4-yl]-pyrazolino- [4,5-d] pyrimidin (**7**), **Scheme 3**. Reaction of equimolar ratio of compounds **(7)** with metal divalent chlorides ($CuCl_2$, $NiCl_2$, $CoCl_2$) in absolute ethanol gave an intermediate **(8Ba-c)**, which refluxed with ethanol extraction to give the corresponding 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino-[4,5-d,4`,5`-d`]pyrimidino-[3,4-a]-1,3-oxazine-2-metallo chloride metal chelate complexes **(9a-c).** The reaction was suggested to proceed through rearrangement with dehydrogenation to give compounds **(9a-c)** which consider as a key intermediate compounds in the synthesis of metal complex cyanine dyes. On triturating of such **(9a-c)** with saturated solution of KI followed by dissolving of the resulted in conc.

H_2SO_4 liberated iodine vapour. This is a criterion for the presence of the chloride anion replaced by iodide analogous. Thus, reaction of equimolar ratios of compounds **(9a-c)** with 2(4)-methyl heterocyclic quaternary salts [α (γ)-picoline and quinaldine] methyl iodide under thermal condition in presence of piperidine as basic catalyst gave the corresponding unsymmetrical 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino-[4,5-d,4`,5`-d`]pyrimidino-[3,4-a]-1,3-oxazine-2-metallo–mono-9[2(4)]-methine cyanine dyes **(10a-e)**. The reaction was preceded through nucleophilic addition reaction between active methyl group in heterocyclic quaternary salts and carbonyl group in heterocyclic compounds **(9a-c)** involving dehydration (-H_2O) process to give the corresponding compounds **(10a-e)**, **Scheme 3**. Such dyes **(10a-e)** were soluble in Conc. H_2SO_4 acid liberating iodine vapour on warming.

The structure of compounds (**7, 9** & **10a, d, e)** was characterized and identified by elemental analysis **Table (3, 4)**, IR, ^{1}H-NMR and Mass spectral data. Thus, IR (ν^{KBr} cm^{-1}) of **7** and **9** showed, in addition to, the general absorption bands at 1497 cm^{-1} (C=N), 1592 cm^{-1} (C=C), 1704 cm-1 (C=O), well defined absorption band at 3058-3060 cm-1 (stretching CH) and 2923 cm-1 (CH3-N+I),510-530 cm-1 (M-O) for compounds **10a, d, e**, **[11]**. ^{1}H-NMR (CD_3OD, 250 MHz) spectra of compounds (**7, 9** and **10a, d, e)** showed, in addition to, the general singlet and multiplet signals at δ 1.19-1.29 (s, CH_3, of pyrazol), 2.20-2.32 (s, CH_3, of the other pyrazol), 7.16-7.97 (m, 13H, Ar. + Het. +NH) for **(7** and **9**) , well define signals at 3.21-3.32 (s, 2H, N-CH_2), 3.79 (s, 3H, CH_3-CH_2-N^+I), 7.16-7.97 (m, 25H, Ar. + Het. +NH+CH=) for compounds **10a, d, e, [*12*],** Mass spectra of compounds **(7** and **9)** reveals a molecular ion [M-42]$^+$ peaks at m/z =358,and base peak at m/z =77 for compound **7**, a molecular ion [M$^+$-42-(M+Cl)] peaks at m/z =358,and base peak at m/z =358 for compound **9 ,[13]** 3,4-Dimethyl-1,6-diphenyl-9-one-bispyrazolino-[4,5-d,4`,5`-d`] pyrimidino-[3,4-a]-1,3-oxazine-2-metallo–mono-9[2(4)]-methine cyanine dyes **(10a-e)** are highly coloured compounds (reddish violet-intense violet). They are fairly (partially) soluble in most polar (non polar) organic solvents exhibited coloured solutions accompanied with slight / strong green fluorescence depending upon solvent used. Their ethanolic solution turned yellow or became coloures on acidification; restore their permanent colour on basification. The visible absorption spectra of some selected of newly synthesized cyanine dyes are discussed. Such dyes are 5-arylideno 3-methyl-7-one -1-phenyl-pyrazolino- [4, 5-d] 1, 3-oxazine-2-metallo–[3,4-a] pyrimidino zero- 4- [4(1)]-methine cyanine dyes **(5a,c-g),** 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino- [4,5-d,4`,5`-d`]pyrimidino-[3,4-a]-1,3-oxazine-2-metallo–mono-9[2(4)] -methine cyanine dyes **(10a,b,d,e).** The absorption spectra of unsymmetrical 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino-[4,5-d,4`,5`-d`] pyrimidino-[3,4-a]-1,3-oxazine-2-metallo–mono-9[2(4)]-methine cyanine dyes **(10a-e)** in 95% ethanol undergo batho (hypso) chromically shifted depending upon the nature of heterocyclic residue A, their linkage

position, metal divalent M and heterocyclic nuclei moieties. Thus, the visible absorption maxima of **10a**, (A = quinolin-4-ium, M = Co^{++}) showed absorption band at λ_{max} =382-516 nm. Substitution of (A = quinolin-4-ium) in compound86 by (A = pyridin-4-ium) compound **10c** causes a bathochromic shift of the shorter (longer) wavelength of $\Delta\lambda_{max}$ = 56 nm. This is due to the more extensive π-conjugation within the quinolin-4-ium in **10a**. Additionally, changing the linkage position from (A = pyridin-4-ium)in compound **10c** to (A = pyridin-2-ium) in **10b** resulted in a hypsochromic shift of the shorter wavelength of $\Delta\lambda_{max}$ =16 nm. This is due to the decreasing of π-delocalization within-1-ium linkage relative to 4-ium analogue causing difficulty of charge transfer. On the other hand, Substitution of metal divalent M = Co^{++} in compound **10a** by M = Ni^{++} /Cu^{++} in **10d** and **10e** respectively, resulted in a bathochromic shift of $\Delta\lambda_{max}$ =5/30 nm. This is due to the vacant orbital increasing gradually from Copper to Nickel or Cobalt, leading to the more extensive π-conjugation. **Table 3**, The studies involve the absorption spectra of selected dyes in different pure organic solvents and examined in the visible region showing solvatochromism. This permits a selection of the optimal solvent (fractional solvent) when these dyes are applied as photosensitizes. The spectral behaviour of the selected cyanine dyes in aqueous universal buffer solutions and their dissociation (protonation) constants (pKa values) are described as a criteria for their use as photosensitizes to permit their acid-base properties or acido- baso chromic behaviour when these dyes are applied as photosensitizes. The metal ion concentration detection of some synthesized cyanine dyes is studied. The electronic absorption spectra of these cyanine dyes in different metal ion concentration using Ethanolic solution were examined in the visible region. This permits a selection of the optimal metal ion concentration when these dyes are applied as metal ion concentration detectors. Thus, the electronic absorption spectra of the cited cyanine dyes **(5a,c-g),(10a,b,d,e),** in the wavelength range 250-700 nm, have been studied in different organic solvents (H_2O, DMF, EtOH, MeOH, acetone, CCl_4, $CHCl_3$, and C_6H_6) **[14]**,. The colour changes of such dyes with solvents having different polarities are presented in **Tables (3, 4).** This is constructed with the intention to illustrate the solvatochromic behaviour of these dyes (λ_{max} and ε_{max}) values of the intramolecular charge transfer bands are given in **Tables (1, 2)**. These dyes are showed positive solvatochromism with increased solvent polarity, which depend on structure and type of dye. This indicates that the polar excited states of these cyanine dyes are stabilized by polarization interaction forces as the polarizability of the solvent is increased. This behaviour occurs as a result of electrostatic interactions of the distributed cationic charges with the dipoles of the solvated molecules which leads to formation of specific solvated forms of dyes. The relevant data in **Tables (1, 2)** as well as the representing graphs disclosed a hypsochromic shifts in ethanol relative to DMF, $CHCl_3$, and CCl_4. This shifts can be attributed to the following factors: The

bathochromic shift occurred in DMF relative to ethanol is mainly a result of the increase in solvent polarity due to increasing the dielectric constant of the former, **Tables (1,2) .** The hypsochromic shifts appeared in ethanol relative to $CHCl_3$, and CCl_4 is generated from the solute-solvent interaction through intermolecular hydrogen bonding between ethanol and the lone pair of electrons within the heterocyclic ring system. Otherwise, this decreases the mobility of the electron cloud over the conjugated pathway towards the positively charged centre, **Table (1, 2).** It was worth mentioning that the intermolecular hydrogen bonding between $CHCl_3$ molecules and the lone pair of electrons of nitrogen atoms of the heterocyclic ring system is difficult due to the sterric hindrance of the three bulk chlorines. Moreover, the solute solvent interactions in cases of $CHCl_3$, and CCl_4 generated a residual negative charge on the nitrogen atoms of the heterocyclic ring system which intern facilitated the electronic charge transfer to the positively charged centre and this explain the bathochromic shifts in these solvents relative to ethanol, **Table (1,2).** The unexpected hypsochromic shifts in the absorption spectral maxima in water relative to ethanol and its lower extinction coefficients were mainly ascribed to the ease of interactions of water molecules, through intermolecular hydrogen bonding, with the lone pair of electrons of the nitrogen atoms of the heterocyclic ring system, through intermolecular hydrogen bonding, which intern preclude the charge transfer from the heterocyclic ring system to the positively charged residue along the conjugated bridge**,Table (1, 2).** In point view of light absorption, it was obvious that most of the previous selected cyanine dyes, **(5a,c-g),(10a,b,d,e)** are absorbed the fundamental light absorption (violet-red) as they have got absorption values in the range 350-660 nm **Tables (1-4) [15]**. The selected cyanine dyes might be suggested to be used as photosensitizers in most polar and non polar organic solvents in the (violet-red). Thus, it was obvious that compounds **(5a, c-g),** absororbed green-blue light in EtOH, acetone, benzene, $CHCl_3$, CCl_4 and MeOH λ_{max} = 340-385 nm extended and improved to the absorption of green light in DMF. The ethanolic absorption spectra of selected cyanine dyes **(5a,c-g),(10a,b,d,e),** in aqueous universal buffer solution of different values of pH (2.09,4.10,6.09,7,8.36, 10.38,11.98) show regular changes with increasing the pH of the medium especially in the n-$\pi*$ and CT bands **Table (3).** Also The electronic spectra of selected cyanine dyes in aqueous universal buffer solutions of varying pH values showed bathochromic shifts with intensification of the absorption bands at high pH values (alkaline media), otherwise, hypsochromic shifts with quenching the intensity of the absorption bands at low pH values (acidic media) were recorded. Moreover, increasing the pH values of the medium intensified the electronic charge transfer due to deprotonation which intern support the lone pairs of electrons of the heterocyclic ring system and increase its mobility. In the other hand, decreasing pH values of the medium interrupted the charge transfer due to

protonation and intermolecular hydrogen bonding which intern preclude the availability of the lone pairs of the heterocyclic ring system. Several methods had been adopted for spectrophotometric estimation of the dissociation constants of weak acids, the variation of absorbance at settled wavelength could be utilized. Thus, on plotting the absorbance at settled wave number versus pH values S-shaped curves were obtained. For all S-shaped curves, the horizontal portion to the left corresponded to the acidic form of the indicator, while the upper portion to the right corresponded to the basic form. Since the pKa value was defined as the pH value for which one half of the indicator (dye) is in the basic form and the other half in the acidic form. This point, (pKa value), was determined by the intersection of the S-curve with horizontal line midway between the left and right segments. The spectral behaviour of **(5a,c,d), (10a,b,d,e),** in 95% ethanol and/or in aqueous universal buffer solution showed that these compounds absorbed the blue light λ_{max} = 340-385 nm and the near violet light extended to the green light λ_{max} = 440-495 nm. In acid (pH $\geq$ 2.09) medium these dyes undergo a hypsochromic colour change due to the protonation of the heterocyclic nitrogen atom (oxygen) or the heterocyclic nitrogen atom of heterocyclic quaternary salts (quinolin-2-/ pyridin-4-) ium salts and other non-quaternize N-methyl (quinolin-2-/pyridin-4-) ium. In such cases the intramolecular charge transfer (CT) between the heterocyclic donor nitrogen (oxygen) and the heterocyclic acceptor nitrogen atoms does not occur, and the long wave length CT band disappears. A new short wave length band is observed, which could be assigned to a localized $\pi-\pi^*$ transition. On the other hand, the resulted bathochromic shift as the pH of the medium increases is due to that the protonated compounds becomes deprotonated and their mesomeric interaction with the rest of the molecule becomes high and consequently the CT interaction with the free base is facilitated, **Table (3).**. The pk_a values were obtained using the standard procedure **[16]**, the pKa values and spectral characteristics of the protonated forms of dyes are collected in Table 6. Thus, it was suggested that these dyes are sensitive as photosensitizers in both acidic and basic mediums. This may be due to the presence of N-methyl quinolin-2-/ pyridin-4-linkage and the other quinolin-2-/ pyridin-4-ium salts causing the high planarity of the dye molecule. It was interesting to study the photometrical and metallochromic and coordination behaviour of selected cyanine dyes such as 6-arylideno-4-[3-methyl-5-one-1-phenyl-pyrazol-4-yl] -pyrimidin-2-one- zero- 4- [4(1)]-methine cyanine dyes **(4Ca)** and 3-methyl-1-phenyl-6-one-4[3-methyl-5-one-1-phenyl-pyrazol-4-yl]-pyrazolino- [4,5-d] pyrimidin- mono-9[2(4)]-methine cyanine dyes (**8Ba)** towards the metal ions C(II), Co(II), and Ni(II). **T**he complexation equilibrium in solution, stoichiometry and stability of the formed complexes were determined by spectrophotometric measurements. The validity of Beer's law for the formed complexes was tested. **T**he electronic absorption spectra of the studied free dyes (ligands) **4Ca, 8Ba**

and their metal chelates in EtOH was recorded in the range 350-700 nm. Thus, **t**he spectra of the metal complexes were performed by using as blank the same concentration of the dye (ligand) as that in the test solution. This was done to overcome the interference of the dye (ligand) spectrum with that of the complex, which may leads to an inaccurate result. As was observed **in** electronic absorption spectra of the free dyes (ligands), it was obvious that dyes **4Ca, 8Ba** showed absorption bands located at λ_{max} = 420 nm, ε_{max} = 1927 cm^2 mol^{-1} for dye **4Ca**, λ_{max} = 490 nm, ε_{max} = 2120 cm^2 mol^{-1} for dye **8Ba** respectively. **T**he addition of the ethanolic solutions of metal ions to an ethanolic solutions of the free dyes at high concentrations of metal ions and ligands with respective fixed concentration of ligands solutions and different concentration of metal solutions causes generally an observed red shift of the main bands for all selected dyes. The observed bands shift suggests an instantaneous chelate formation between each of the ligands studied and metal ions used. This is attributed to the conjunction of heterocyclic metal chelator reveals an antagonistic effects increases the basicity and charge transfer from N-ethyl pyrazole as electron source towards heterocyclic quaternary iodide as electron sink. **O**n the other hand, the electronic absorption spectra of such formed complexes are influenced by nature of metal ion used. Thus, at fixed concentration of the dye **4Ca** [$0.5x10^{-3}$ mol], it was obvious that dye **4Ca** showed absorption bands at λ_{max} = 420 nm, ε_{max} = 1927 cm^2 mol^{-1} .An addition of the [0.13 x 10^{-4} mol] of Ni(II) solution to the above dye concentration resulted in formation of complex showed absorption band bathochromically shifted of $\Delta\lambda_{max}$ = 10 nm. Substitution the addition of Ni(II) solution [0.13 x 10^{-4} mol] by Cu(II) and/or Co(II) solution [0.13 x 10^{-4} mol] to the fixed dye concentration resulted in the formation of complexes exhibited absorption bands bathochromically shifted of $\Delta\lambda_{max}$ = 5 , 15 nm respectively relative to Ni(II) ion used. **A**lso, at fixed concentration of the dye [$0.5x10^{-3}$ mol], it was obvious that dye **8Ba** showed absorption band λ_{max} = 490 nm, ε_{max} = 2120 cm^2 mol^{-1} .Addition of Ni(II) solution [$0.5x10^{-4}$ mol] to the above dye concentration resulted in formation of complex showed absorption band bathochromically shifted of $\Delta\lambda_{max}$ = 40 nm. Substitution the addition of Ni(II) solution [$0.5x10^{-4}$ mol] by Cu(II) and/or Co(II) solution [$0.5x10^{-4}$ mol] the fixed dye concentration resulted in the formation of complexes exhibited absorption bands bathochromically shifted of $\Delta\lambda_{max}$ = 10 , 20 nm respectively relative to Ni(II) ion used. **O**n the other hand, addition of an ethanolic solution of metal ions to an ethanolic solution of the free dyes at low concentrations of metal ions and ligands with respective fixed concentration of ligands solutions and different concentration of metal solutions causes generally an observed hypsochromic shift of absorption intensities of the main bands for all selected dyes. It was found that the absorbance of charge transfer complexes formed are increased linearly with increasing of the metal divalent concentration. On examine the possibility for the spectrophotometric micro-determination of Cu(II), Ni(II), and Co(II) with cyanine dyes **4Ca,**

8Ba. at high concentration: Deviation of Beer's law**,** the concentration of free dyes **4Ca, 8Ba** was kept constant at [0.5 x 10^{-3} mol], whereas that of Cu(II), Ni(II), and Co(II) were varied from [2.44 x 10^{-6} mol] to [3.3 x10^{-5} mol]. The optical densities of such solutions were measured at λ_{max} = 450, 520 nm for dyes **4Ca, 8Ba** respectively and plotted as a function of concentration**.** Linear relationship is obtained for concentration of Cu (II), Ni (II), and Co (II) up to [0.4.6 x10^{-5} mol] above which negative deviations are observed. The slope of the curve **εmax** values of Cu(II), Ni(II), and Co(II) = 3.8 x 10^3, 3.62 x 10^3, 1.53 x 10^3 for dye **4Ca** , = 9.14 x 10^3, 5.49 x 10^3, 5.6 x 10^3 respectively, for dye **8Ba.** The high $\boldsymbol{\varepsilon_{max}}$ value permits the estimation of very small amounts of Cu(II), Ni(II), and Co(II). The lower limit that can be determined with satisfactory accuracy amounts to ~ [4 x 10^{-6} mol], [2 x 10^{-6} mol], [4 x 10^{-6} mol] for dye **4Ca**, [2 x 10^{-6} mol],[6 x 10^{-6} mol], [2 x 10^{-6} mol] for dye **8Ba**. Meanwhile, at low concentration, Validity of Beer's law**,** the concentration of the free dyes **4Ca, 8Ba** was kept constant at [1 x 10^{-4} mol], whereas that of Cu(II), Ni(II), and Co(II) were varied from [2 x 10^{-6} mol] to [1.6x10^{-4} mol]. The optical densities of such solutions were measured at λ_{max} = 430, 490 nm for dyes **4Ca, 8Ba** respectively and plotted as a function of concentration as shown in**.** Linear relationship is obtained for concentration of Cu(II), Ni(II), and Co(II) up to [1.3x10^{-5} mol] above which negative deviations are observed. The slope of the curve εmax values of Cu(II), Ni(II), and Co(II) = 4.43 x 10^3, 0.79 x 10^3, 2.36 x 10^3 for dye **4Ca** , = 6.45 x 10^3, 3.27 x 10^3, 0.398 x 10^3 respectively, for dye **8Ba.** The high $\boldsymbol{\varepsilon_{max}}$ value permits the estimation of very small amounts of Cu(II), Ni(II), and Co(II). The lower limit that can be determined with satisfactory accuracy amounts to ~ [9.1 x 10^{-6} mol], [2.44 x 10^{-6} mol], [2.44 x 10^{-6} mol] for dye **4Ca**, [1.3 x 10^{-5} mol],[2 x 10^{-5} mol], [1.7 x 10^{-5} mol] for dye **8Ba**.**Fig.(1A-D & E) & (2A-D & E).**

Experimental

All melting points are uncorrected. Elemental analysis was carried out at the Micro analytical center (Cairo-University). The IR (νKBr) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer (Cairo-University). ^{1}H–NMR spectra were recorded with a Bruker AMX-250 spectrometer. Mass spectra were recorded on a HpMs 6988 spectrometer (Cairo University). The electronic absorption spectra were recorded within the wavelength range (350-700) on 6405 UV/Visible recording spectrophotometer, Faculty of Science, Aswan.

Synthesis of 4-acetyl–3–methyl–1–phenyl pyrazol–5–one (imine) (1) & 4-arylideno-3-methyl-1-phenyl pyrazol-5-one (imine) (2a-f) 6-arylideno-4-[3-methyl-5-one (imine)-1-phenyl-pyrazol-4-yl] pyrimidin-2-one (3Aa-f)**,** Such compounds were carried out according to **[17] [6 -10]**. Characterization data are summarized in **Table (5)**.

Synthesis of 5-arylideno 3-methyl-7-one -1-phenyl-pyrazolino- [4, 5-d] 1, 3-oxazine-2-metallo–[3,4-a] pyrimidino zero- 4- [4(1)]-methine cyanine dyes (5a-g).

An ethanol solution of **(4a-e,** 0.01mol) and of pyridinum, quinolinium and isoquinolinium ethiodide (0.01mol) in the presence of few drops of piperidine was refluxed for 6-8 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol **Table (6)**. Synthesis of 3,3`-dimethyl-1,1`-diphenyl-bis pyrazolo-5,5`- one-4,4`-formylidin (6) & 3-methyl-1-phenyl-6-one-4[3-methyl-5-one-1-phenyl-pyrazol-4-yl]- pyrazolino[4,5-d] pyrimidin (7), was prepared according to reference.**[1, 6** and **9]..**

6: m.p.= 172°C, yield = 80 %, colour = Deep yellow, Molecular formula = $C_{21}H_{18}N_4O_2$, M.wt = 358, Analysis % calculated (found) : C = 70.39 (70.43) H = 5.02 (5.09) N = 15.64 (15.67), **7:** m. p. = 155 °C, yield = 62 %, colour = yellow, Molecular formula = $C_{22}H_{20}N_6O_2$, M.wt = 400 Analysis % calculated (found):C = 66(66.13), H = 5(5.20),N = 21(21.12)

Synthesis of 5-arylideno 3-methyl-7-one -1-phenyl-pyrazolino- [4, 5-d] 1, 3-oxazine-2-metallo–[3,4-a] pyrimidino chloride metal chelate complex (4a-e) and/or 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino- [4,5-d,4`,5`-d`] pyrimidino-[3,4-a]-1,3-oxazine-2-metallo chloride metal chelate complex (9a-c).

A mixture of (**3Aa-c and/or 7,** 0.01mol) and metal divalent (Cu^{++}, Ni^{++} Co^{++}) (0.01mol) were dissolved in ethanol and refluxed for 2-4 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cooled and recrystalised from aqueous ethanol to give an intermediate **(4Aa-e) and/or (8a-c).** The ethanolic solution of compounds **(4Aa-e)** was refluxed for 1hr with 1% Sodium sulphide to give compound (4f), The ethanolic products (8a-c) were refluxed for 2-4 hours in Ethanol containing few drops of piperidine to give **(9a-c)**. The filtrate was concentrated, cooled and dried to give **(9d) Table (3).**

Synthesis 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino- [4,5-d,4`,5`-d`]pyrimidino-[3,4-a]-1,3-oxazine-2-metallo–mono-9[2(4)]-methine cyanine dyes (10a-e):

A Mixture of **(9a-c)** (0.01mol) and 2(4)-methyl heterocyclic quaternary salts $\alpha(\gamma)$ picoline and quinaldine ethiodide salts (0.01mol) were refluxed in ethanol for 8 hr, in the presence of few drops of piperidine. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from the suitable solvent **Table (4).**

Solvatochromic and Acid -Base Properties:

The organic solvents were used of spectroscopic grade of purified according to the recommended methods **[18]**. The electronic absorption spectra of the studied dyes in different organic solvents were recorded within the wavelength (350-700 nm) on 6405 UV/Visible recording spectrophotometer using 1 cm cell. The stock solution of the dye was of

the order 10^{-3} M. Solution of low molarities used in spectral measurements were obtained by accurate dilution.

I-preparation of dyes solution:

1-For studying the effect of pure solvents in the UV and visible range: Accurate volumes of the stock solution of the dyes were diluted to appropriate volume in order to obtain the required concentrations. The spectra were recorded immediately after mixing in order to eliminate as much as possible the effect of time.2- For studying the spectral behaviour in mixed solvents in the visible region: An accurate volume of the stock solution (10^{-3} M in ethanol) of the dyes were placed in 10 ml measuring flask containing the required volume of ethanol, then completed to the mark with the other solvent. 3- For studying the spectral behaviour in aqueous universal buffer solutions: An accurate volume of the stock solution was added to 5 ml of the buffer solution in 10 ml measuring flask, then completed to the mark with redistilled water. The pH of such solution was checked before spectral measurements.

2-Preparation of Universal Buffer Solution:

A modified buffer series derived from that of, **[19]** was prepared for use in the present investigation. The constituents are as follows: A solution of 0.4 M of each phosphoric and acetic acid was prepared by accurate dilution of A. R. concentrated stock. A solution of 0.4 M of boric acid was obtained by dissolving the appropriate weight of the recrystallized acid in redistilled water. A stock acid mixture was prepared by mixing equal volumes of three acids in large bottle.

The total molarity of the acid was thus maintained at 0.4 M A series of buffer solutions with pH values ranging from (2.09-11.98) was prepared as recommended by **[19]**. This was done by mixing 150 ml of the acid mixture in a 250 ml measuring flask with the appropriate volume of 1.0 M NaOH and completed to the mark with redistilled water. This modification was performed in order to keep the ionic strength constant at all pH' s mixed with different proporations of organic solvents used. The pH's of the buffer solutions were checked using Orion pH-meter model (60, A), accurate to ± 0.005 pH units, at 25 °C.

3-Metal complex studies:

Spectral studies of Cu(II), Ni(II), and Co(II) chelates with the studied selected cyanine dyes.

Metal ion solution:

Stock solution ($1x10^{-3}$ mol-dm^{-3}) of metal ion studied Cu(II), Ni(II), and Co(II) [Merck or B.D.H products] were prepared by dissolving the accurately weighted amount of each metal in ethanol and the metal content was determined by complexmetric EDTA titration.

Dye (ligand) solution:

Stock solution of **(4Ca)** and **8Ba** ($1x10^{-3}$ mol-dm^{-3}) were dissolved in the quantity needed from the pure compound in ethanol.

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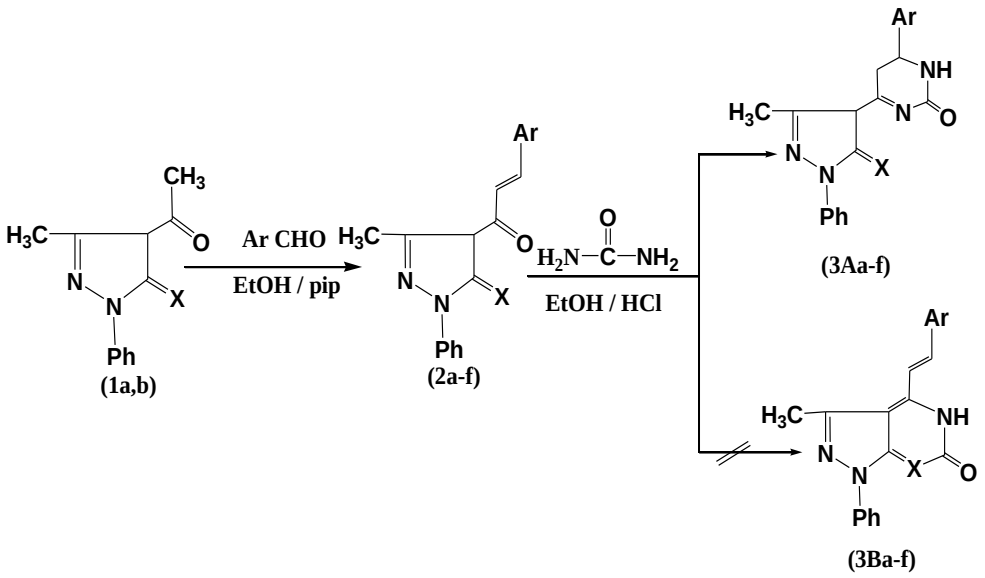
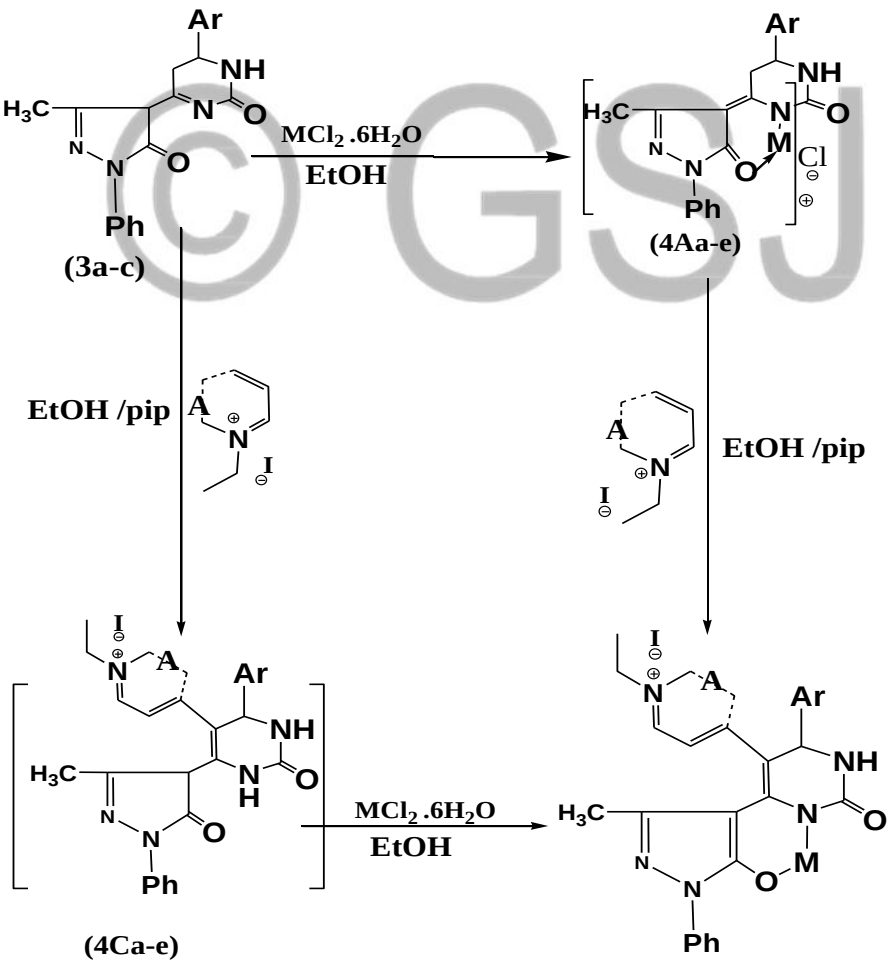


Scheme (1)



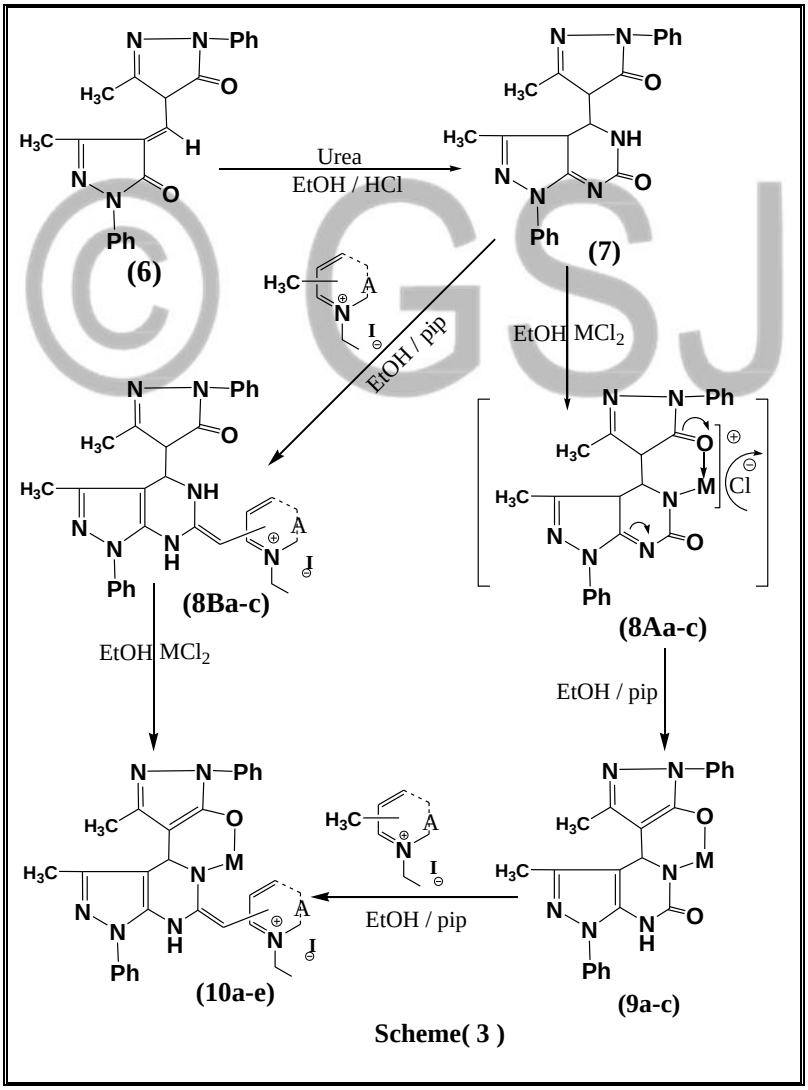
Scheme(2)

Scheme (1,2) Substituents:

(1a, b) X=O **(a);** X=NH **(b).(2a-f), (3Aa-f)** X=O , Ar=p-N-dimethyl benzaldehyde **(a);** X=O , Ar= m-Nitro benzaldehyde **(b);**X=O , Ar= benzaldehyde **(c);** X=NH , Ar= p-N-dimethyl benzaldehyde **(d);**X=NH,Ar= m-Nitro benzaldehyde **(e);** X=NH , Ar= benzaldehyde **(f). (4a-e):** Ar **=** p-N-dimethyl benzaldehyde, M= Co^{++} (a); Ar **=** p-N-dimethyl benzaldehyde, M= Ni^{++} (b); Ar **=** p-N-dimethyl benzaldehyde, M= Cu^{++} (c). Ar **=** m-Nitro benzaldehyde, M= Co^{++} (d) **,** Ar **=** benzaldehyde, M= Co^{++} (e)

(5a-g): Ar **=** benzaldehyde, M= Co^{++}, A=quinolin-4-ium salt (a). Ar **=** p-N-dimethyl benzaldehyde , M= Co^{++}, A=quinolin-4-ium salt (b); Ar **=** p-N-dimethyl benzaldehyde, M= Co^{++}, A=isoquinolin-1-ium salt (c); Ar **=** p-N-dimethyl benzaldehyde, M= Co^{++}, A=pyridin-4-ium salt (d); Ar **=** p-N-dimethyl benzaldehyde, M= Ni^{++}, A=quinolin-4-ium salt (e); Ar **=** p-N-dimethyl benzaldehyde, M= Cu^{++}, A=quinolin-4-ium salt (f);

Ar **=** m-Nitro benzaldehyde, M= Co^{++}, A=quinolin-4-ium-salt (g)



Scheme(3)

(8a-c, 9a-c): M = Co^{++} **(a)**; M = Ni^{++} **(b)**; M = Cu^{++} **(c)**; **(10a-e): A =** N-methyl-2-quinolinium methiodide, M = Co^{++} **(a)**; **A =** N-methyl-2-pyridinium methiodide, M = Co^{++} **(b)**; **A =** N-

methyl-4-pyridinium methiodide, M = Co^{++} **(c)**; **A =** N-methyl-2-quinolinium methiodide, M = Ni^{++} **(d)**; **A =** N-methyl-2-quinolinium methiodide, M = Cu^{++} **(e)**;

Table (1): Values of absorption (nm) and extinction coefficients ($mol^{-1}cm^{-1}$) of **(5a,c-g,10a,b)** in pure organic solvents.

Comp	Water		DMF		C_6H_6		$CHCl_3$		**CCl4**		Acetone		MeOH		
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ
5a	366	10347	364	12009	371	10861	371	14184	363	22462	363	11767	363	11646	3
	412	7809	404	8202	406	9229	406	12129	398	19018	454	10347	401	10226	4
	-	-	307	15725	307	15725	307	17870	-	-	-	-	304	15845	
5c	425	9864	307	15574	313	13549	310	10226	307	8716	463	5513	304	6661	3
	-	-	412	9592	430	7447	433	10105	417	7809	-	-	452	6419	3
	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4
5d	363	11495	364	14063	310	17990	371	13942	364	11888	363	15845	361	14305	3
	-	-	401	13429	371	11767	-	-	-	-	454	16601	409	15211	4
5e	404	39652	414	31616	414	32250	412	33398	409	35181	406	34425	412	33670	4
5f	354	20921	363	10740	355	12794	366	11646	358	2975	361	20166	361	13670	3
5g	454	8957	484	5906	471	5785	468	5664	457	7447	449	6782	463	6419	4
	-	-	500	5151	-	-	-	-	-	-	-	-	-	-	4
10a	492	33277	579	20407	524	16480	524	19410	519	39652	506	39018	511	39018	5
	-	-	409	16359	406	8836	401	9471	404	23972	-	-	385	14063	3
10b	401	23731	342	9592	401	8957	396	15453	404	13157	393	16993	412	15845	3
	-	-	440	12129	-	-	-	-	-	-	-	-	-	-	

Table (2): Values of absorption (nm) and extinction coefficients ($mol^{-1}cm^{-1}$) of **(10d, e)** in pure organic solvents

Comp	Water		DMF		C_6H_6		$CHCl_3$		**CCl4**		Acetone		MeOH		
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}
10d	497	39894	524	15845	527	6782	521	16601	524	6782	508	21193	511	20679	513
	358	26903	404	6419	398	3096	398	7054	401	3368	-	-	380	6299	385
10e	360	13773	406	28669	409	26975	404	28554	409	27951	390	32429	385	29042	393
	548	26717	560	27463	564	28410	551	28066	564	28898	548	29759	554	28181	548

Table (3): Values of absorption (nm) and extinction coefficients ($mol^{-1}cm^{-1}$) of compounds **(5a,c,d,10a,b,d,e)** in aqueous universal buffer solution.

Comp	Universal buffer													
	2.09		4.10		6.09		7		**8.36**		10.38		11.98	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
5a	454 361	2860 1429 0	422 363	2790 6790	412 363	2250 3340	414 366	5800 7390	406 363	6500 6660	401 -	1301 0 -	404 -	2370 0 -
5c	476 304 - -	2780 9570 - -	452 307 - -	6760 1024 - -	460 307 251 -	3560 8500 1691 0 -	430 320 248 -	3200 1540 6390 -	487 404 304 248	2200 3390 4620 2980	484 401 347 251	1170 5170 3620 1500 0	406 346 353 -	1014 0 1755 0 6430 -
5d	430 361 244	1240 0 2142 0 2377 0	414 361 264	1138 19110 4000	363 254 -	9130 2536 0 -	356 - -	2445 0 - -	406 358 -	2339 0 2650 0 -	404 361 - -	2161 0 2408 -	412 358 -	2812 0 2500 0 -
10a	425 460	2498 0 4000	442 433	16100 1796	495 -	3068 0 -	497 -	3175 0 -	484 -	3957 0 -	500 -	3913 0 -	492 -	3612 0 -
10b	401 - - -	1964 - - -	404 - - -	19270 - - -	420 345 - -	1834 0 1727 0 - -	284 215 436 347	3763 0 4000 0 1.427 0 1056 0	246 216 440 342	4000 0 3.957 17.66 0 1281 0	433 345 - -	1536 0 1111 0 - -	213 438 302 248	3457 0 1378 0 9640 3135 0
10d	428	1569 0	495	17530	497	1890 0	492	1957 0	497	1896 0	489	1040 0	492	1282 0
10e	463 412 358	3913 0 3910 0 3763 0	449 406 361	39570 39500 32630	476 - -	4000 0 - -	460 - -	4000 - -	473 - -	4000 0 - -	481 - -	4000 - -	455 413 442	4000 0 3913 0 3957 0

Table (4): The variation of absorbance in λ_{max} characteristic for each Selected (**5a, c, d, 10a, b , d , e)** in different buffer solutions

Comp. No. λ_{max} **pH**	**5a** λ_{490}	**5c** λ_{430}	**5d** λ_{430}	**10a** λ_{540}	**10b** λ_{470}	**10d** λ_{530}	**10e** λ_{560}
2.09	0.206	0.342	0.835	0.227	1.123	0.459	0.639
4.10	0.532	0.271	1.136	0.775	1.292	1.114	1.798
6.09	0.284	0.172	0.646	1.291	1.185	1.056	1.862
7	0.128	0.49	2.033	1.274	0.858	1.011	2.066
8.36	0.027	0.351	2.408	1.446	1.06	0.936	1.676
10.38	0.118	0.722	2.181	1.281	0.896	0.528	1.825
11.98	0.374	1.186	2.709	1.03	0.768	0.618	2.834
pKa	11.3 - -	10.1 - -	5.8 - -	4.3 - -	6.5 8.2 8.7	9.0 - -	8.1 9.2 -

Table (5): Characterization data of Pyrazol-4-yl] - pyrimidin-2-one **(3Aa-f)** and their 2-metallo–[3,4-a] pyrimidino chloride metal chelate complex **(4a-e).**

Comp. No.	M.P. °C	Yield %	Colour	Mol. Formula (Mol.wt)	Calcd.% (Found)% C	H	N
3a	125	45	Violet	$C_{22}H_{23}N_5O_2$ (389)	67.87 (67.91)	5.91 (5.95)	17.99 (17.98)
3b	155	58	Brown	$C_{20}H_{17}N_5O_4$ (391)	61.38 (61.42)	4.35 (4.38)	17.90 (17.93)
3c	130	64	Yellow	$C_{20}H_{18}N_4O_2$ (346)	69.36 (69.41)	5.20 (5.27)	16.18 (16.23)
3d	70	38	Deep red	$C_{22}H_{24}N_6O$ (388)	68.04 (68.10)	6.19 (6.21)	21.65 (21.69)
3e	110	49	Yellowish brown	$C_{20}H_{18}N_6O_3$ (390)	61.54 (21.68)	4.62 (4.67)	21.54 (21.58)
3f	80	36	Brown	$C_{20}H_{19}N_5O$ (345)	69.57 (69.59)	5.51 (5.56)	20.29 (20.25)
4a	220	78	Deep red	$C_{22}H_{22}N_5O_2CoCl$ (482.43)	54.72 (54.75)	54.72 (54.69)	14.51 (14.59)
4b	265	73	Pal red	$C_{22}H_{23}N_5O_2NiCl$ (482.21)	54.75 (54.72)	4.56 (4.59)	14.52 (14.55)
4c	240	68	Deep red	$C_{22}H_{23}N_5O_2CuCl$ (487.04)	54.20 (54.26)	4.52 (4.57)	14.37 (14.39)
4d	190	43	Pale brown	$C_{20}H_{16}N_5O_4CoCl$ (484.43)	49.54 (49.59)	3.30 (3.35)	14.45 (14.47)
4e	280	57	Deep red	$C_{20}H_{17}N_4O_2CoCl$ (439.43)	54.62 (54.67)	3.87 (3.83)	12.74 (12.78)

Table (6): Characterization data of Pyrazolino- [4, 5-d] 1, 3-oxazine-2-metallo–[3, 4-a] pyrimidino zero- 4- [4(1)]-methine cyanine dyes **(5a-g)**.

Comp. No.	M.P. °C	Yield %	Colour	Mol.Formula (Mol.wt)	Calcd.% (Found)% C	H	N	Absorption spectra in EtOH λ_{max} (nm)	ε_{max} ($cm^2 mol^{-1}$)
5a	145	38	Deep red	$C_{30}H_{25}N_5O_2CoClI$ (708.43)	50.82 (50.86)	3.53 (3.57)	9.88 (9.89)	467 494	21072 20407
5b	170	63	Brown	$C_{32}H_{30}N_6O_2CoClI$	51.10 (51.14	3.99 (3.95	11.18	367 405	17235 21072

				(751.43)	)	)	(11.21)		
5c	185	58	Yellowish brown	$C_{33}H_{32}N_6O_2CoClI$ (765.43)	51.74 (51.77)	4.18 (4.22)	10.97 (10.99)	403	23731
5d	90	68	Pal yellow	$C_{28}H_{28}N_6O_2CoClI$ (701.43)	47.90 (47.94)	3.99 (3.98)	11.98 (11.96)	304 342 438	19138 11767 15574
5e	225	71	Yellowish brown	$C_{32}H_{30}N_6O_2NiClI$ (751.21)	51.12 (51.16)	3.99 (3.96)	11.18 (11.20)	366 404	16993 17870
5f	145	76	Greenish brown	$C_{32}H_{30}N_6O_2CuClI$ (756.04)	50.79 (50.76)	3.97 (3.98)	11.11 (11.15)	411	12794
5g	130	43	Red	$C_{30}H_{24}N_6O_4CoClI$ (753.43)	47.78 (47.79)	3.19 (3.21)	11.15 (11.18)	371	21072

Table (7): Characterization data of the intermediate **(8a-c)** and 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino- [4,5-d,4`,5`-d`]pyrimidino-[3,4-a]-1,3-oxazine-2-metallo chloride metal chelate complex **(9a-c)** .

Comp. No.	**M.P. °C**	**Yield %**	**Colour**	**Mol. Formula (Mol.wt)**	**Calcd.% (Found)%**		
					C	**H**	**N**
8a	240	76	Green	$C_{22}H_{19}N_6O_2CoCl$ (493.43)	53.50 (53.56)	3.85 (3.89)	17.02 (17.08)
8b	180	78	Brown	$C_{22}H_{19}N_6O_2NiCl$ (493.21)	53.53 (53.58)	3.85 (3.89)	17.03 (17.08)
8c	120	67	Yellowish brown	$C_{22}H_{19}N_6O_2CuCl$ (498.04)	53.01 (53.07)	3.81 (3.85)	16.87 (16.89)
9a	240	76	Green	$C_{22}H_{17}N_6O_2CoCl$ (491.43)	53.72 (53.78)	3.46 (3.49)	17.09 (17.11)
9b	180	78	Brown	$C_{22}H_{17}N_6O_2NiCl$ (491.21)	53.74 (53.78)	3.46 (3.49)	17.10 (17.16)
9c	120	67	Yellowish brown	$C_{22}H_{17}N_6O_2CuCl$ (496.04)	53.22 (53.27)	3.43 (3.45)	16.93 (16.96)

Table (8): Characterization data of 3,4-dimethyl-1,6-diphenyl-9-one- bis pyrazolino- [4,5-d,4`,5`-d`]pyrimidino-[3,4-a]-1,3-oxazine-2-metallo–mono-9[2(4)] -methine cyanine dyes **(10a-e).**

Comp. No.	M.P. °C	Yield %	Colour	Mol. Formula (Mol.wt)	Calcd.% (Found)% C	H	N	Absorption spectra in EtOH λ_{max} (nm)	ε_{max} ($cm^2 mol^{-1}$)
10a	120	65	Violet	$C_{34}H_{29}N_7OCoClI$ (772.43)	52.82 (52.85)	3.75 (3.76)	12.69 (12.67)	516 382	36208 17235
10b	140	54	Yellowish brown	$C_{30}H_{27}N_7OCoClI$ (722.43)	49.83 (49.87)	3.74 (3.78)	13.57 (13.59)	398 -	32522 -
10c	180	46	Brown	$C_{29}H_{25}N_7OCoClI$ (708.43)	49.12 (49.16)	3.53 (3.57)	13.83 (13.86)	347 438	9078 9350
10d	130	38	Violet	$C_{34}H_{29}N_7ONiClI$ (772.21)	52.84 (52.87)	3.76 (3.78)	12.69 (12.72)	513 385	31495 9471
10e	170	70	Violet	$C_{34}H_{29}N_7OCuClI$ (777.04)	52.51 (52.56)	3.73 (3.77)	12.61 (12.64)	393 548	34839 29042

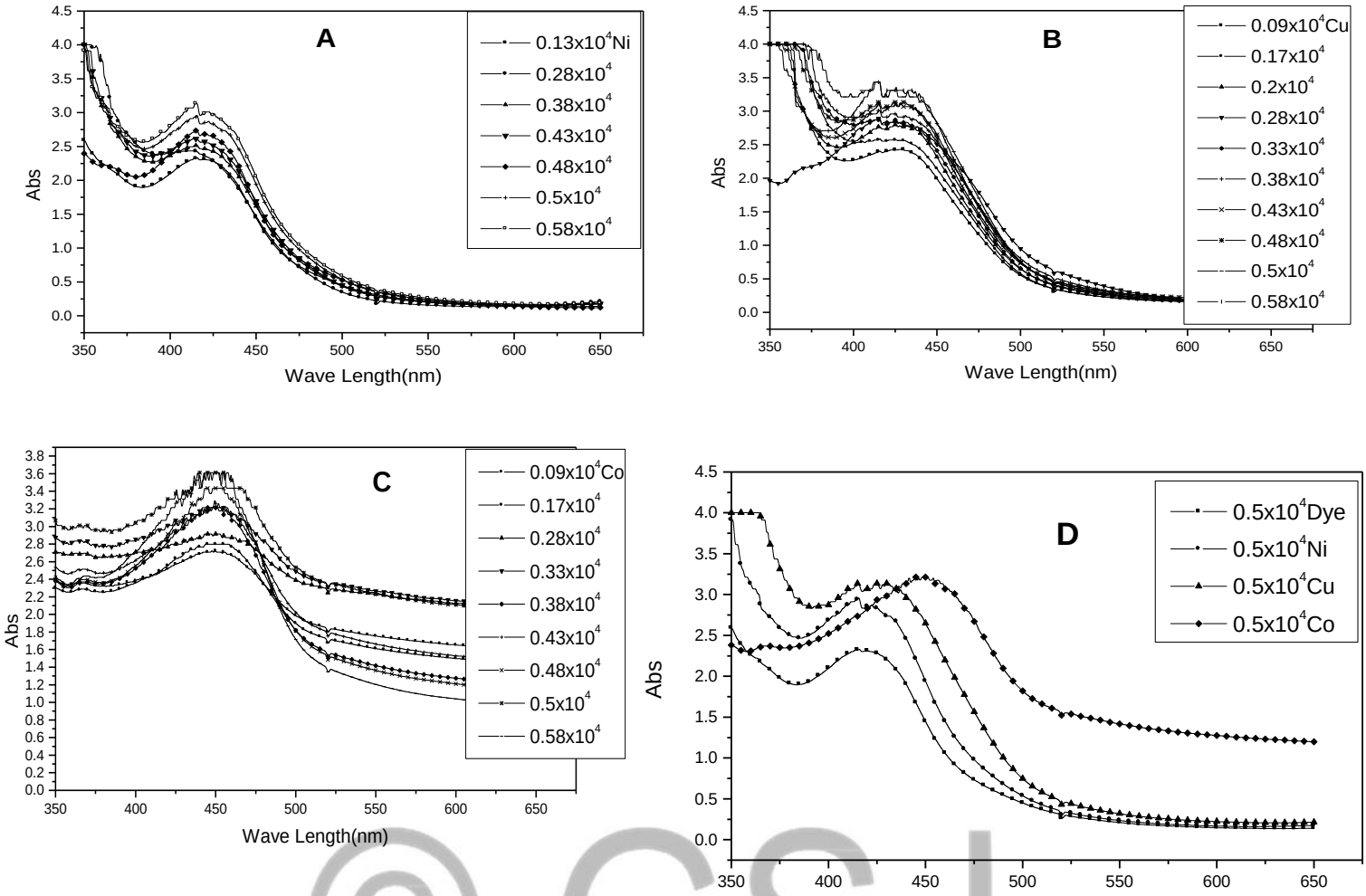


Fig. 1A-D: Absorption spectra of 4Ca 0.5x10-3 mol and **4Ca** With Cu(II), Ni(II), and Co(II) at different concentration and at fixed concentration 0.5x10-4 mol

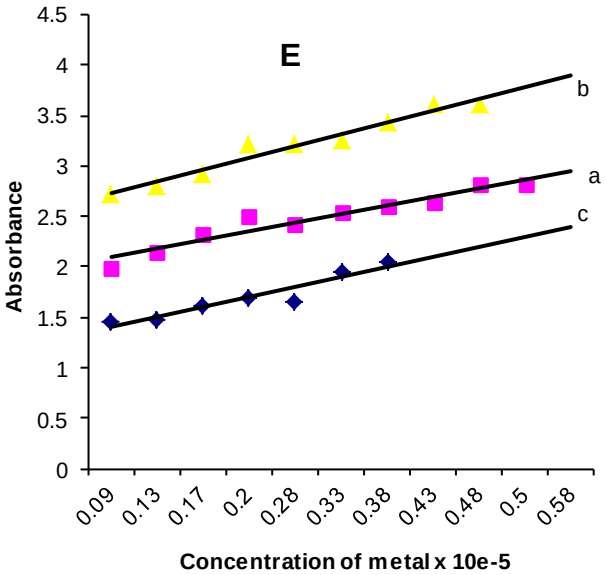


Fig. 1E: Validity of Beer's law of **4Ca** (1x10e-4M), λ=450nm with (a) Cu(II), (b) Ni(II), and (c) Co(II)

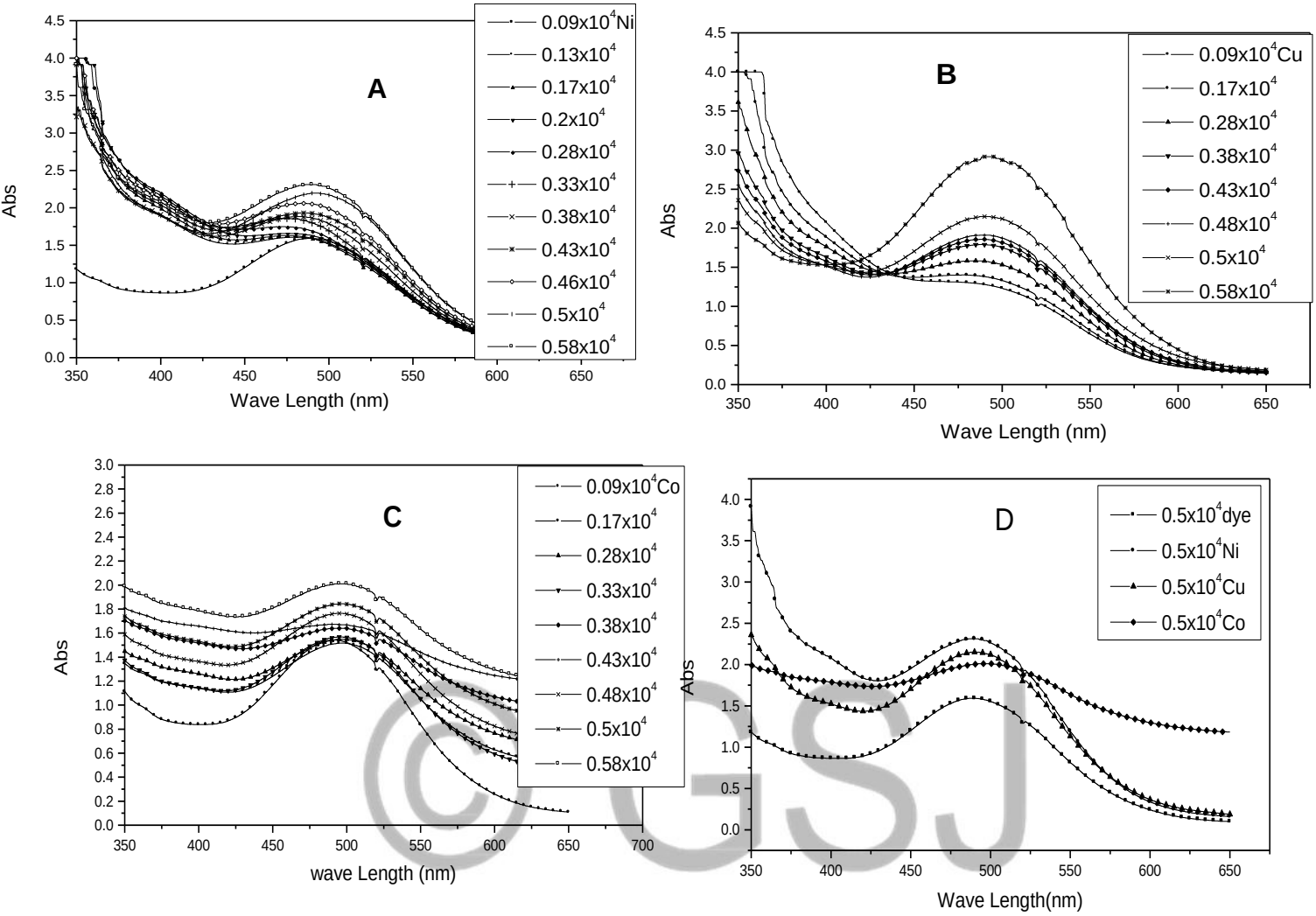


Fig. 2A-D: Absorption spectra of **8Ba** 0.5x10-3 mol and comp. **8Ba**
With Cu (II), Ni(II), and Co(II) at different concentration and at fixed concentration 0.5x10-4 mol

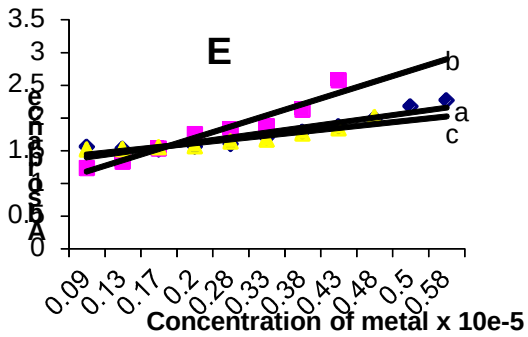


Fig. 2E: Validity of Beer's law of **8Ba**(1x10e-4M), λ=500nm with (a) Cu(II), (b)Ni(II), and (c) Co(II).