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Research Article

Interactions of Celestine Blue, (Phenoxazine Dye) with Solvents and Metal Ions: Spectrophotometric and Computational Studies

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Abstract

Background and Objective: Research into the design of materials and strategies for the detection of metal ions continues to increase because of the need for a clean environment and better life opportunities. Dyes are applied in all areas of life for painting, dyeing paper, skin and clothing. Solvatochromic dyes are used as fluorescent sensors and imaging agents. A number of these applications of dyes are based upon their ability to form soluble complexes with metal ions. This study is to investigate the interactions of Celestine Blue (CB) with different solvents and the transition metal ions at different pH values using UV/Visible Spectrophotometry and Computational Analyses. **Materials and Methods:** Reagents used were Celestine Blue (CB), water, ethanol, acetonitrile, cyclohexane, copper (II), cobalt (II) and buffered solutions, (pH 2., 5, 8, 11). For the solvent effects, 0.20% of Celestine blue in different solvents were prepared. While for the chelating properties, 2×10^{-2} mol dm^{-3} of metal (II) acetate and Celestine blue were prepared in an aqueous solution. UV/Visible absorption measurements of the mixtures were taken. For the computational analyses, molecular structures of the CB ligand and its metal (II) complexes were modelled using Gauss View 5.0. **Results:** The study provided information on the solvatochromic nature of Celestine blue. A 1:1 metal:Dye species at pH 8 in an aqueous solution was established. The computational modelling also suggests the favourable disposition of CB to complex with these metal ions. **Conclusion:** Celestine blue is solvatochromic and also a potential chelating agent for metal ions.

Key words: Celestine blue, solvents, metal ions, spectrophotometry, computational analyses, chromophoric receptors, solvatochromism

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Dyes are applied practically in all areas of life for painting, dyeing paper and clothing. The colour properties of dyes have also been exploited in industries such as food, cosmetics, plastics, leather, reprographics, electronics, information technology and analytical chemistry. In analytical chemistry, basic dyestuff methods find importance in the monitoring of pollution problems to detect metals. Dyes have been useful in the medical, biochemical fields, for protein purification and as structural probes for investigating biochemical processes¹⁻³.

A number of these applications of dyes are based upon their ability to form soluble complexes with metal ions. Dyes form complexes with transition metals and thus serve as indicators since most of these dyes possess several ligand atoms suitably disposed of for coordination with a metal atom. Furthermore, some classes of dyes have been established to function as efficient sensors for metal ions. The resulting structures were found to depend on the coordination of the metal ions to the chromophoric receptors^{3,4}.

Not much information is available in the literature about the complexing properties of Celestine blue but there had been reports about the padding of Celestine blue with chromium acetate before being enlisted for use in dyeing cotton. There are also metal complex dyes that are prepared as complexes before being applied to fibre^{3,4}. Metal-complexes of some acid dyes have been synthesised through coordination of the dyes with transition metal ions and applied to wool, silk and nylon to achieve better wash fastness for dyed fabrics. The metal-complexed dyes, especially 1:2 chromium pre-metallised dyes, are commercially important to produce bright, wash-fast shades on natural protein and polyamide fibres without the risk of over dyeing and degradation of fibre⁵.

This study was therefore carried out to determine the complexing abilities of Celestine Blue, CB, 1-(aminocarbonyl)-7-(diethylamino) 3, 4-dihydroxy-1-phenoxazine-5-ium chloride with metal ions and thus, its possible applications to detect metal ions. Computational modelling studies on the interactions of CB with metal ions were also carried out to affirm the chelating atoms and thus the complexing properties. The study found strong agreement between the experimental and computational studies on the complexing properties.

In carrying out investigations into these complexing properties, there was the need to select a proper solvent and pH suitable for the success of the reactions. This is because solvents have a strong influence on the position of chemical equilibria, reaction rates, the position and intensity of spectral

absorptions. The influences of the solvents on chemical reactivity are measured in terms of the "solvent polarity" or solvatochromism. Solvatochromic dyes are used to detect the polarity of solvents^{6,7}.

Solvatochromic dyes have been successfully applied to biological membranes for studying lipid domains (rafts), apoptosis and endocytosis due to their sensitivity to polarity and hydration. As fluorescent labels, solvatochromic dyes can detect practically any type of biomolecular interactions, involving proteins, nucleic acids and biomembranes⁸.

Celestine blue is found in this study to be sensitive to the nature of the solvents influencing the position of the wavelength of maximum absorption, λ_{max} .

MATERIALS AND METHODS

Study area: The conception and preliminary work on the interactions of CB with various solvents started while L.M. Durosinmi was on a Postdoctoral Programme at the Department of Chemistry, Loughborough University of Technology, Loughborough, Leics, UK, 1995/96. While the studies on metal interactions with phenoxazine dyes were in 2019/2020 at the Obafemi Awolowo University, Ile-Ife, Nigeria. The computational analyses were carried out in 2020 at the same University.

Reagents: Celestine blue, water, ethanol, acetonitrile, cyclohexane, copper (II), cobalt (II), buffered solutions of pH ranging from 2.0-11.0.

All chemicals were of analytical grade and were used without further purification. All solutions were prepared using distilled water.

Preparation of the reagents: For the determination of the metal: CB stoichiometric ratio, 2×10^{-2} mol dm⁻³ of copper (II) acetate, cobalt (II) acetate and Celestine blue were prepared in an aqueous solution. Buffered solutions of pH ranging from 2.0-11.0 were also prepared.

Solvent effects on CB: A total of 0.20% of Celestine blue in different solvents, namely water, ethanol, acetonitrile were prepared and UV/Visible absorption spectra were taken. CB was insoluble in cyclohexane.

Interactions of CB with copper (II) and cobalt (II) ions and determination of the stoichiometric ratio of the metal

CB species in aqueous solutions: The possible metal-dye complex species in solutions were determined by the mole-ratio method which is varying the ratio of the metal ion

concentration to that of the dye and then taking the absorbance values of the different mixtures of solutions^{9,10}.

Instrumentation: The UV/Visible absorption spectra of the solid Celestine blue and solutions of Celestine blue in different solvents as well as those of the metal-CB mixtures, were obtained on Pye-Unicam SP8-400 and the Pye-Unicam 8700 series UV/Visible spectrophotometer/ Unicam colour plotter.

RESULTS AND DISCUSSION

Solvent effect on Celestine blue: Celestine Blue, (CB) is a cationic dye and hence a polar molecule. The non-solubility,

of CB in cyclohexane, attests to the polar nature of CB. The solid UV-Visible spectrum of CB, Fig. 1, indicates the wavelength of maximum absorption, λ_{\max} of 550 nm.

In water, the wavelength of maximum absorption, λ_{\max} depends on the concentration of the dye. At high concentration, the λ_{\max} is 550 nm, the same as the λ_{\max} in the solid CB but with two shoulder absorption bands, Fig. 2. In dilute solutions, the λ_{\max} is 600 nm within five minutes of mixing, Fig. 3a. The λ_{\max} however shifts to a longer wavelength with an increase in time, 650 nm at 30 min, Fig. 3b.

In ethanol, the wavelength of maximum absorption is independent of concentration with a constant value at 620

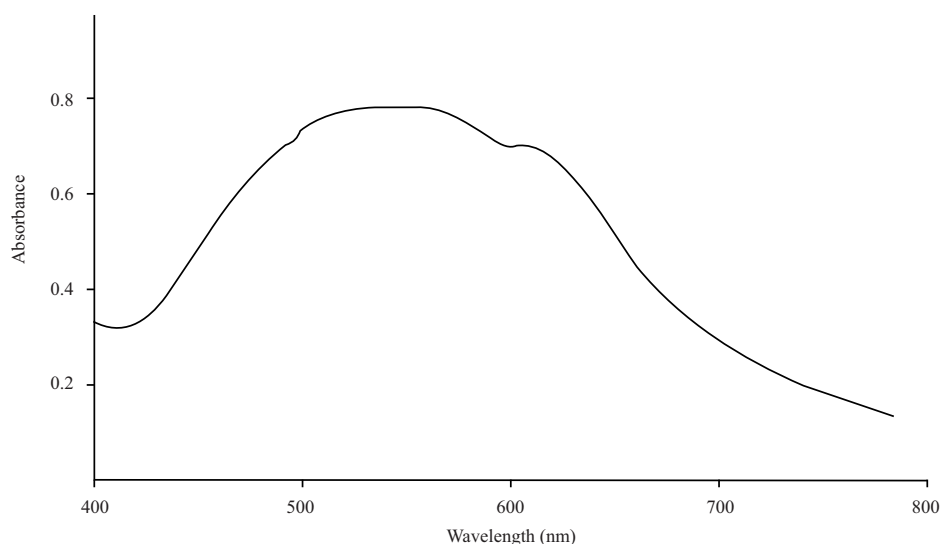


Fig. 1: Solid UV-Visible spectrum of celestine blue, (λ_{\max} 550 nm)

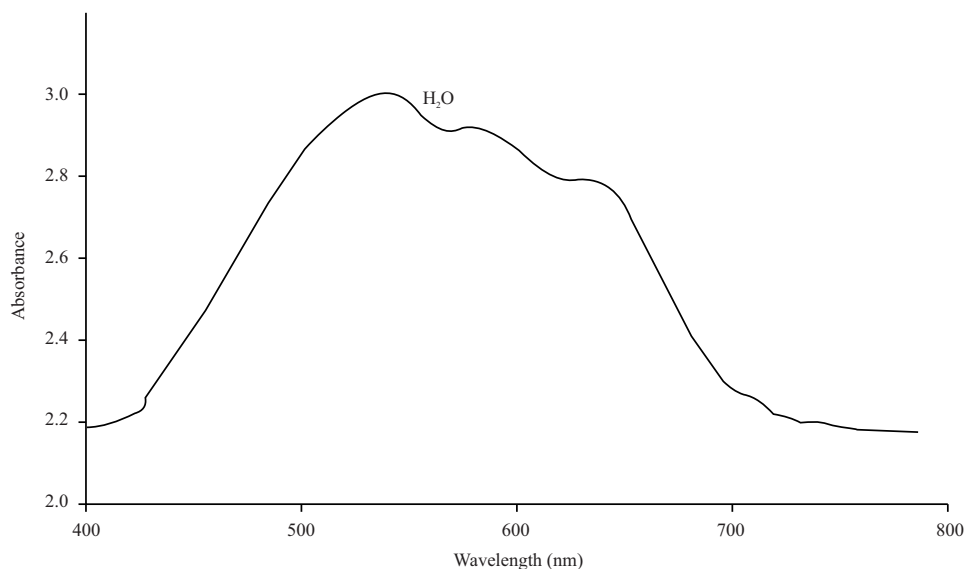


Fig. 2: UV-Visible spectrum of celestine blue in an aqueous medium, (high concentration), (λ_{\max} 550 nm)

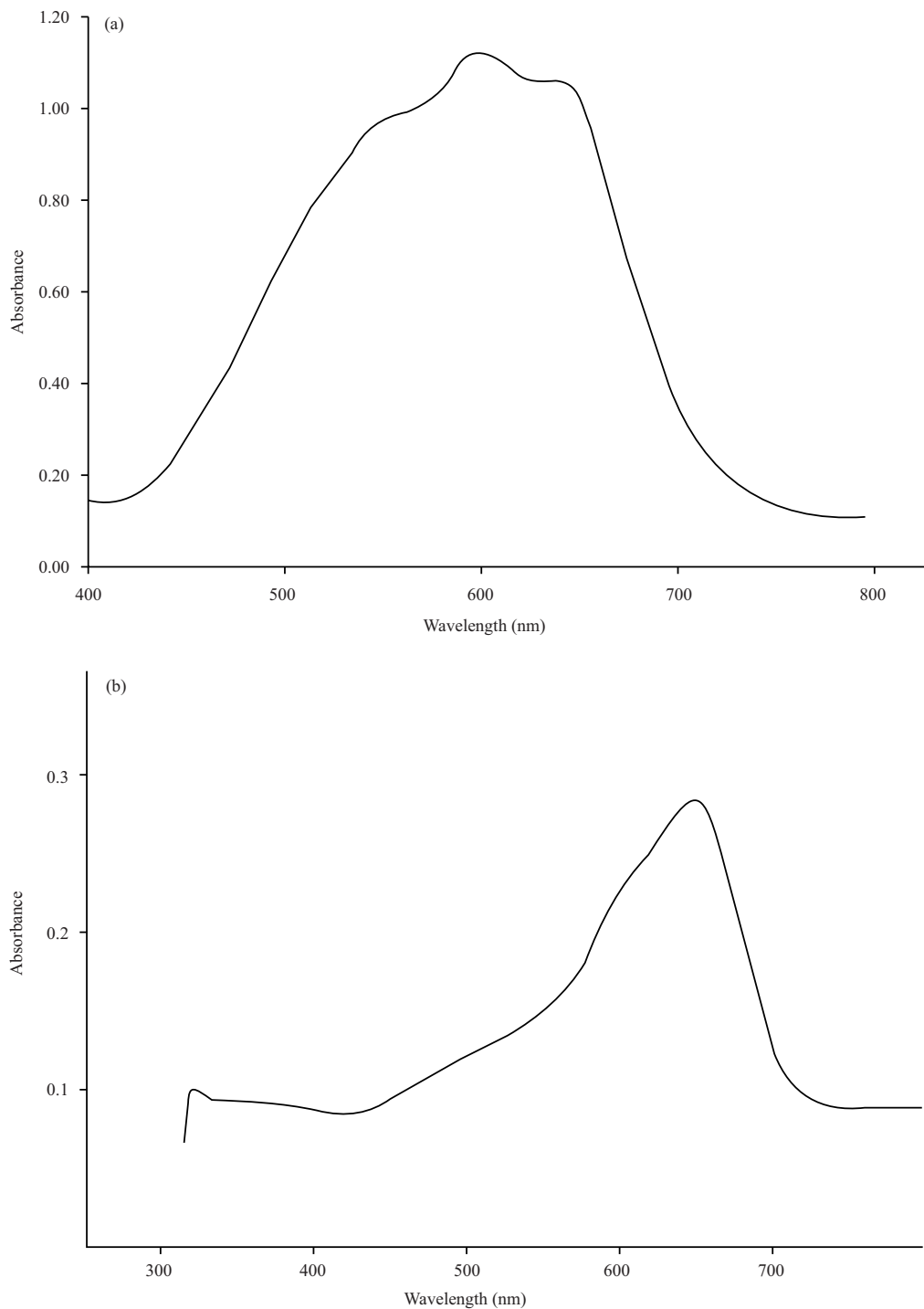


Fig. 3(a-b): UV-Visible spectrum of celestine blue in an aqueous medium. (a): After 5 min ($\lambda_{\text{max}} = 600$ nm) and (b): After 30 min ($\lambda_{\text{max}} = 650$ nm)

nm, Fig. 4. In acetonitrile, CH_3CN , Fig. 5, CB has a wavelength of maximum absorption, λ_{max} at 590 nm at 5 min of dissolution. The λ_{max} decreases to 550 nm with a shoulder band at 20 min. The absorbance values corresponding to these variations are listed in Table 1.

Thus, there are changes in the absorbance values and also a decrease in λ_{max} (a blue or hypsochromic shift) as the solvent changes from water to ethanol to acetonitrile.

The changes occur due to differences between the solvation energy of the initial and excited states in the various

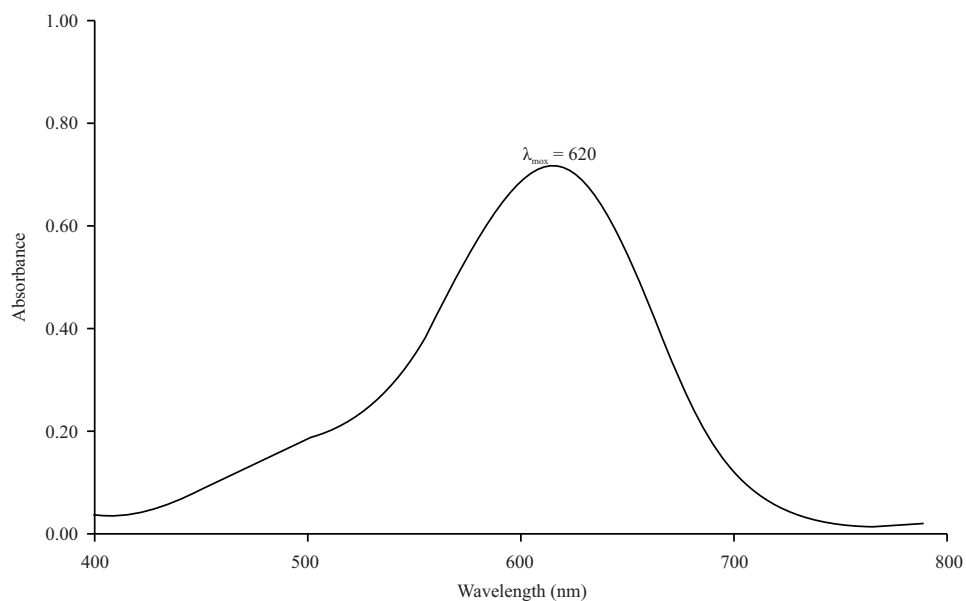


Fig. 4: UV-Visible spectra of celestine blue in Ethanol, (λ_{max} 620 nm)

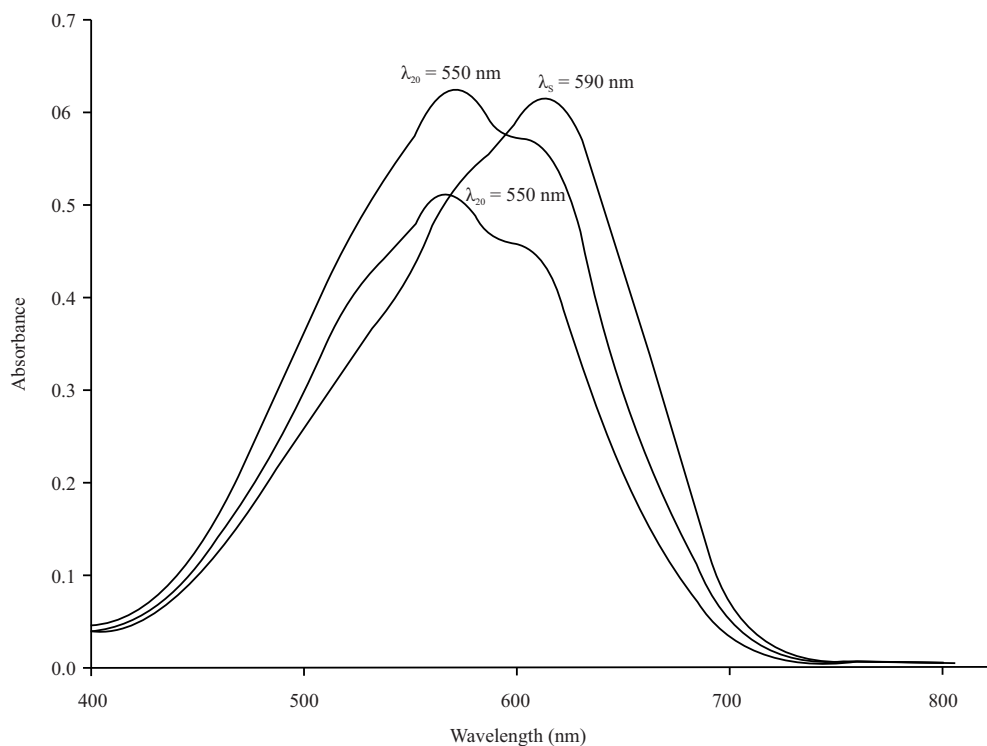


Fig. 5: UV-Visible spectra of celestine blue in acetonitrile at 5, 20 mins, (λ_{max} 590 and 550 nm, respectively)

solvents. The ground state is more polarized than the excited state resulting in a larger energy gap due to destabilization of the excited state in the presence of polar solvents and thus a shift to shorter wavelengths (hypsochromic shift). This occurs for $n \rightarrow \pi^*$ transitions.

Celestine blue is thus a solvatochromic dye as the position, shape and intensity of the absorption bands of Celestine blue vary with the nature of the solvent.

Solvatochromism is a reversible change of the absorption or emission spectrum of a material that is induced by

Table 1: Celestine blue in different solvents

Solvents	λ_{max} (nm)	Time (mins)
(Solid)	550	5.0
Water (H ₂ O)	600	5.0
Water (H ₂ O)	650	30.0
Ethanol (EtOH)	620	5.0, 20.0, 30.0
Acetonitrile (CH ₃ CN)	590	5.0
Acetonitrile (CH ₃ CN)	550	20.0
Cyclohexane (C ₆ H ₆)	Insoluble	

the action of solvents. The absorption maximum shifts occur due to differences between the solvation energy of the initial and excited state in various solvents. The excited state, which is more polar than the initial state, is more stable in more polar solvents. Such systems require lower energy for excitement, which leads to a bathochromic shift of the absorption spectrum. This phenomenon is called positive solvatochromism. The less polar excited state than the initial state produces a counter-effect and a hypsochromic shift of the absorption maximum. This phenomenon is called negative solvatochromism¹¹.

Reichardt, in a review, provided information on the solvatochromic nature of solutions of zwitterionic betaine dye 4-(2,4,6-triphenylpyridinium-1-yl)-2,6-di-phenylphenolate. The position of its longest-wavelength intra-molecular charge-transfer absorption band was found to depend on solvent polarity¹¹.

Celestine blue in this study shows positive solvatochromism, λ_{max} 650 nm in water, 620 nm in ethanol and 550 nm in acetonitrile while the betaine dye 4-(2,4,6-tri phenyl pyridinium-1-yl)-2,6-di-phenylphenolate exhibits negative solvatochromism. The solvatochromic absorption band of the betaine dye is shifted from $\lambda_{\text{max}} = 810$ nm in diphenyl ether to $\lambda_{\text{max}} = 453$ nm in water.

Thus, when UV/Visible absorption spectra of suitable chromophores are measured in solvents of different polarities, the position, intensity and shape of their absorption (and emission) bands are usually modified to a greater or lesser extent. A pronounced hypsochromic band shift with increasing solvent polarity is called negative solvatochromism while a corresponding bathochromic band shift is termed positive solvatochromism¹¹.

Under their exceptional large negative solvatochromism, pyridinium-N-phenolate betaine dyes are particularly suitable as UV/Visible spectroscopic indicators of solvent polarity, using their long-wavelength intra-molecular Charge-Transfer (CT) visible absorption band to measure solvent-dependent reference process.

The extraordinary sensitivity of the UV/Visible spectra of solvatochromic betaine dyes to small polarity changes in

their molecular-microscopic surroundings makes them ideal optochemical materials to monitor polar substances in non-polar media. Optochemical sensors register spectral changes caused by contact of the analyte with immobilized indicator dyes, i.e., changes in the position and intensity of their absorption or fluorescence bands¹¹.

Generally, polar solvents tend to interact electro-statically and form H-bonds with various chromophores. This changes the charge distribution in the molecule and results in increased delocalization. For $\bar{n} \rightarrow \bar{n}^*$ transitions, both ground and excited states are stabilized and the absorption moves to a longer wavelength. For $n \rightarrow \bar{n}^*$ transition in the ground state, hydrogen bonding is with the lone pair of electrons, whereas in the excited state the H-bond involves only one electron of the lone pair, the other having been promoted to an upper energy state.

Hence, the ground state is more stabilized than the excited state and consequently absorption shifts to the shorter wavelength. This is in agreement with the findings in this study and other findings by Martínez-Martínez *et al.*⁷, Klymchenko, that solvatochromism occurs when solvent molecules interact with solute molecules and stabilize (or destabilize) one or both of the orbitals involved in the electronic transition, thus affecting the λ_{max} . The excited state in $\pi \rightarrow \pi^*$ transitions is often more polarized than the ground state. The polar solvent aids the stabilization of the excited state and thus a reduced energy gap. The effect of this is a bathochromic shift of λ_{max} to a longer wavelength by polar solvents such as ethanol (relative to hexane). In this study, λ_{max} shifts to a longer wavelength of 650 nm in water which is a more polar solvent to 620 nm in ethanol and 590 nm in acetonitrile.

In contrast, for $\bar{n} \rightarrow \pi^*$ transitions, the ground state is more polarized than the excited state resulting in a larger energy gap due to destabilization of the excited state in the presence of polar solvents and thus a shift to shorter wavelengths (hypsochromic shift)^{6-8,11-12}.

Other studies by Ali Hosseini *et al.*¹³ on solvent effects such as the spectrophotometric determination of stability constants for complexes of Co²⁺, Mn²⁺, Cd²⁺, Pb²⁺ and Zn²⁺ with 5, 7-diiodo-8-hydroxyquinoline, iodoquinol, using binary mixed solvents N, N-dimethylformamide/Methanol (DMF/MeOH), have established that the stability constants of the complexes were increased with an increasing amount of MeOH in the binary mixtures.

However, a reverse relationship between the stabilities of complexes and the amount of DMF in the binary mixed solvents¹³.

Table 2: Mole-ratio method for determination of stoichiometric ratios of copper (II): Celestine blue species in solution

CB	CuAc	pH	λ_{\max}	A
-	1.00	2.0	682	0.05
1.00	0.00	2.0	526	1.86
1.00	1.00	2.0	538	1.92
1.00	2.00	2.0	532	2.00
1.00	2.00	5.0	564	0.02
1.00	-	8.0	648	1.37
1.00	1.00	8.0	510	0.48
1.00	2.00	8.0	552	0.41
1.00	2.00	9.0	540	0.02
1.00	1.00	10.0	504	0.60
1.00	2.00	10.0	528	1.60

CB = CuAc = 2×10^{-2} mol dm⁻³

Table 3: Mole-ratio method for determination of stoichiometric ratios of cobalt (II): Celestine blue complex ion

CB	CoAc	pH	λ_{\max}	A
1.00	0.00	2.0	524	0.20
1.00	1.00	2.0	520	0.06
1.00	2.00	2.0	520	0.08
1.00	0.00	8.0	650	0.12
1.00	1.00	8.0	628	0.11
1.00	2.00	8.0	628	0.10
1.00	0.00	11.0	532	0.02
1.00	1.00	11.0	520	0.02
1.00	2.00	11.0	524	0.02

CB = CoAc = 2×10^{-2} mol dm⁻³

Effect of the medium (pH): The intensities of the bands are related to the resonance states of the CB molecule and also to the acidity and alkalinity of the medium of the reaction. The intensity of absorption of Celestine blue is enhanced in the acid medium, (pH 2) but with a shorter wavelength, λ_{\max} at 526 nm as compared to 648 nm in slightly alkaline solutions, pH 8.

These changes can be attributed to changes in resonance states of the chromophoric or auxochromic character of the groups attached. The addition of acid either results in salt formation with auxochromic groups or the protonation of the potential donor groups. This leads to a reduction in colour intensity. At low pH, the dye is unionized. As the pH is raised, a proton is lost. In CB, no proton is expected to be lost until towards the pH 7-8 and that is from the phenolic OH group.

This loss of protons results in the formation of phenolate ions which can go into resonance with the ring and therefore stabilize and increase conjugation with a resultant increase in the wavelength of maximum absorption. Thus the λ_{\max} of 648 nm at pH 7,8 compared to the λ_{\max} of 526 nm at pH 2, 3.

Complexing properties of Celestine blue: The data in Table 2 and 3 shows the shifts in the values of the maximum wavelength, λ_{\max} and changes in the absorbance values of the metal (II)-CB mixtures when compared to that of the aquo metal ion alone. The shifts and the absorbance changes could be attributed to complexation¹⁰. The ability of Celestine blue

to complex with metal ions is not unexpected since they have capable donor atoms-the two hydroxyls (OH) groups. The mode of complexation by Celestine blue also satisfies the conditions necessary for chelation to occur. These conditions are the possession of more than one donor atom capable of combining with the metal and the location of these donor atoms in a way that permits the formation of rings.

Celestine blue and copper (II) ions: Absorption curves and changes in the wavelength of maximum absorption, λ_{\max} as well as absorbance values for the copper (II): CB mixtures in the mole ratios of 1:1, 1:2 at different pHs are given in Fig. 6 and 7 and Table 2, respectively. The shifts in the λ_{\max} are indications of interactions between Celestine blue and metal ions.

At pH of 2.0, the absorption maxima, λ_{\max} of the CB alone is at 526 nm and all the metal-dye composition mixtures in the ratios 1:1,1:2 gave rise to absorption bands in the visible region at about the same λ_{\max} , (538 and 532 nm), Table 2, Fig. 6. The non- appreciable change in the λ_{\max} value at pH of 2.0 with the addition of copper(II): CB mixtures is not surprising as all the potential coordinating groups are expected to be protonated. The OH groups also remain undissociated. Hence interaction between the dye and the metal ion becomes impossible.

At pH of 8, there is a pronounced shift in the wavelength of absorption maximum on the addition of copper (II) ion from 648-510 nm for copper (II): CB in the mole ratio 1:1. These are

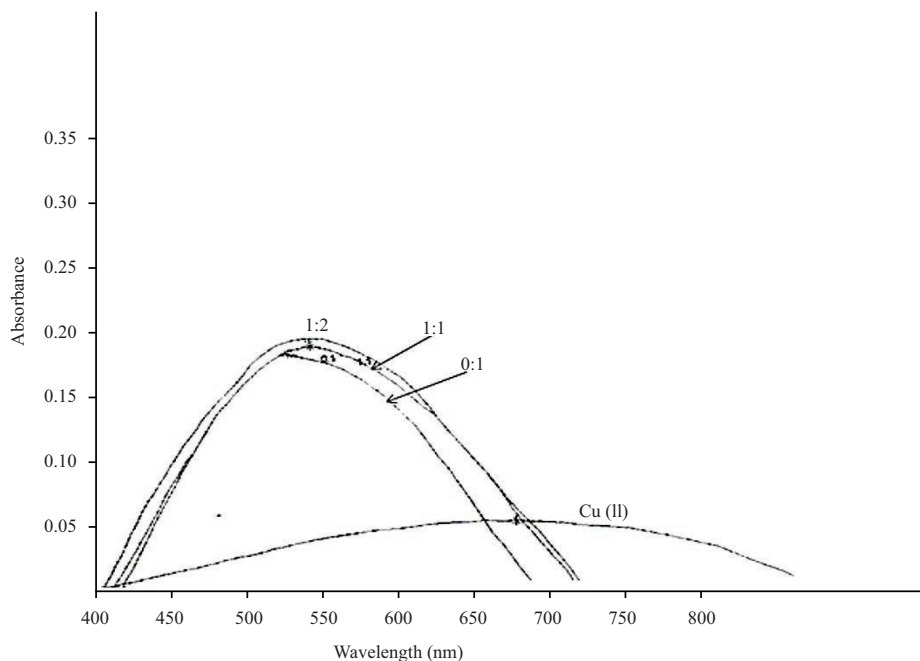


Fig. 6: Copper (II) alone and copper (II): Celestine mixtures in the ratios 1:1, 2:1 at pH 2.0

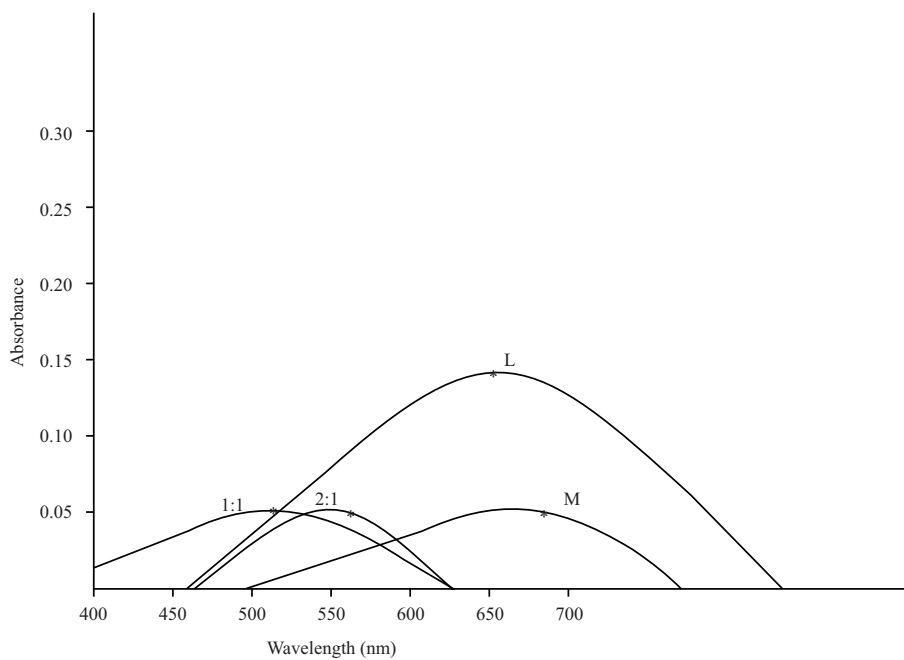


Fig. 7: Copper (II) alone and copper (II): Celestine mixtures in the ratios 1:1, 2:1 at pH 8.0

L: Ligand alone and M: Metal ion alone

listed in Table 2 and illustrated in Fig. 7. The marked change in λ_{max} indicates the existence of some species in solution. The protons of the OH groups are expected to be lost in this medium since de-protonation of the phenolic group occurs

from pH 7.5. This loss results in the formation of a phenolate ion that can interact electrostatically with the copper (II) ion and hence the appreciable change in wavelength of maximum absorption, λ_{max} .

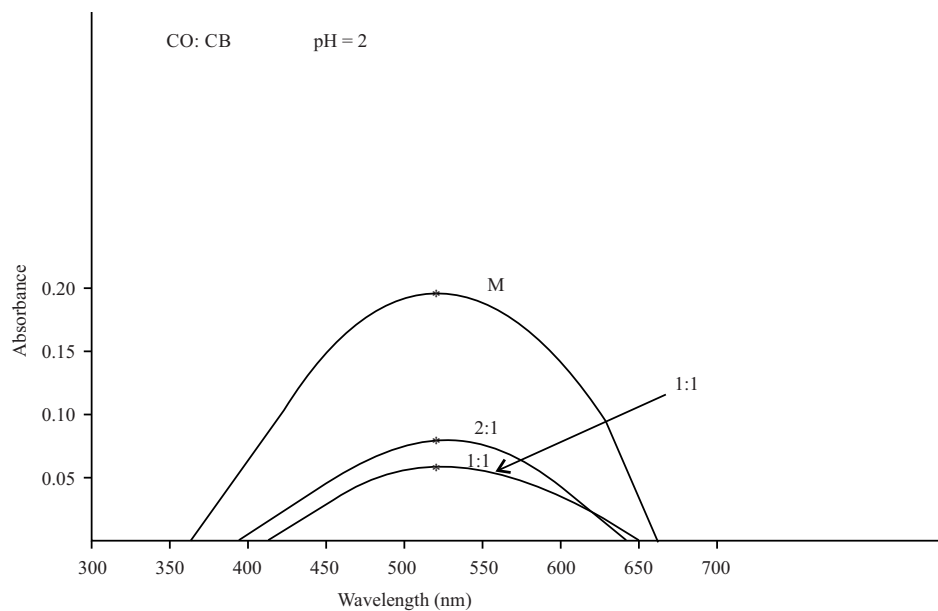


Fig. 8: Cobalt (II) alone and cobalt (II): Celestine blue in the ratios 1:1, 2:1 at pH 2
M: Metal ion alone

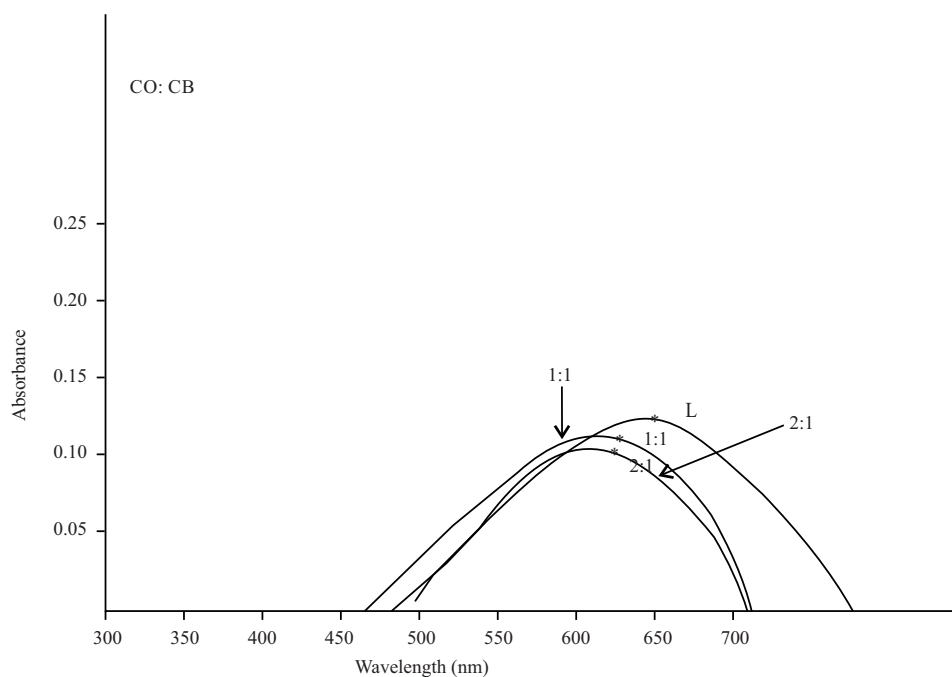


Fig. 9: Cobalt (II) ion and celestine blue in 1:1, 1:2 at pH 8.0
L: Ligand alone

Celestine blue and cobalt (II) ion: From Table 3 and Fig. 8, it can be seen that the absorption maxima remain almost constant for the 1:0, 1:1, 1:2 (Co(II):CB ratio) at pH of 2.0. This suggests that no complex

species are probably formed in this medium. However, the large decrease in intensity (0.20-0.060) on the addition of cobalt ions may be due to ion pair-association.

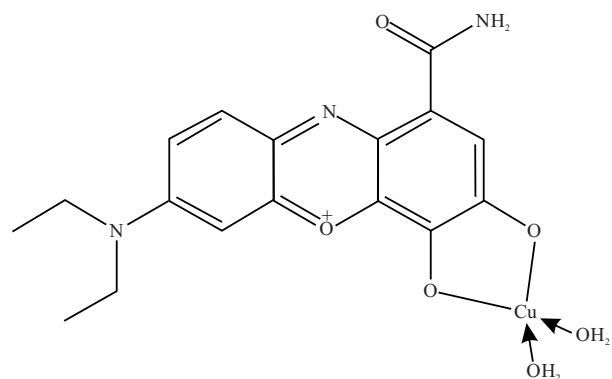


Fig. 10: Proposed structure for 1:1 copper (II): Celestine blue complex

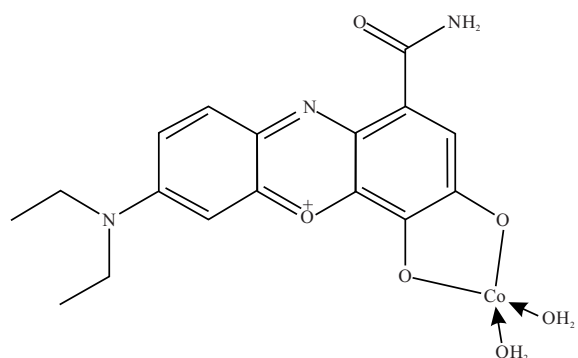


Fig. 11: Proposed structure for 1:1 cobalt (II): Celestine blue complex

However, the addition of cobalt (II) ion to CB caused a shift in λ_{max} from 650–628 nm at pH 8.0, Fig. 9. This suggests some kind of interaction between cobalt (II) ion and Celestine blue. The similarity in the values of λ_{max} and the spectra of the metal: CB mixtures suggest that a single compound is probably formed in solution at pH 7–8¹⁰. The existence of other species are not excluded since the determination of the coordination number and formulae of metal complex species of some systems shows that a single method does not reveal the existence of all possible complex species.

Possible structures For The metal(II): Celestine blue complexes: The changes in the absorbance values of the metal (II)-CB mixtures when compared to that of the aquo metal ion alone and the shifts in the values of maximum wavelength, λ_{max} could be attributed to complexation. This ability of Celestine blue to complex with metal ions is not unexpected since they have capable donor atoms—the two hydroxyls (OH) groups. The mode of complexation by Celestine blue also satisfies the conditions necessary for

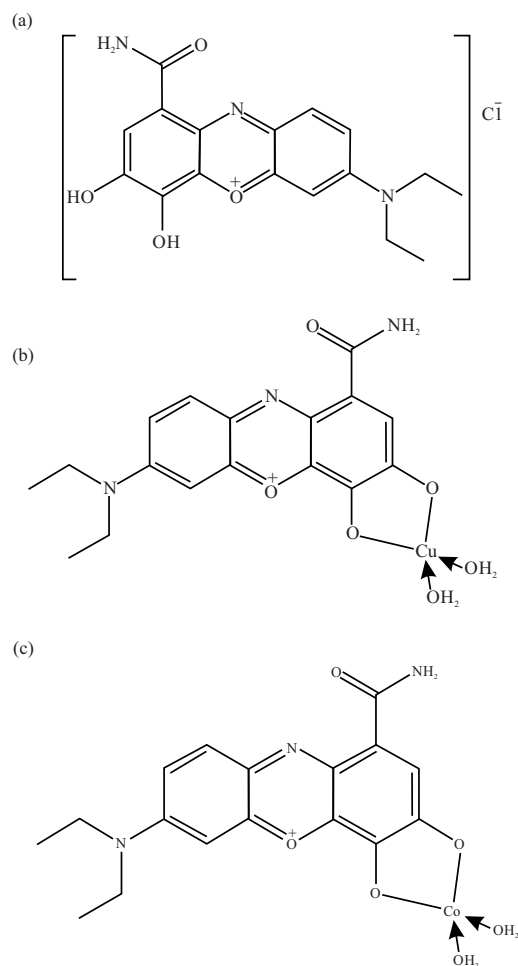


Fig. 12(a-c): 2D (unoptimized) molecular structures of (a) CB, (b) Cu-CB complex and (c) Co-CB complex

chelation to occur. These conditions are the possession of more than one donor atom capable of combining with the metal and the location of these donor atoms in a way that permits the formation of rings.

Thus, from the UV-Visible spectroscopic data, the following structures, Fig. 10 and 11 can be proposed for the metal (II): CB complex species. UV-visible spectroscopy has been applied in numerous ways to facilitate qualitative and quantitative analysis as well as structure determination¹².

Computational study: Initial molecular structures of the CB ligand and its Cu(II) and Co(II) complexes were modelled with the aid of GaussView 5.0. Full geometry optimization of force constant calculations was carried out with the aid of Gaussian 16, which is a widely used computational chemistry software and had been successfully utilized in previous study¹⁴. DFT method with B3LYP/LANL2DZ//6-31G+(d,p) was employed in

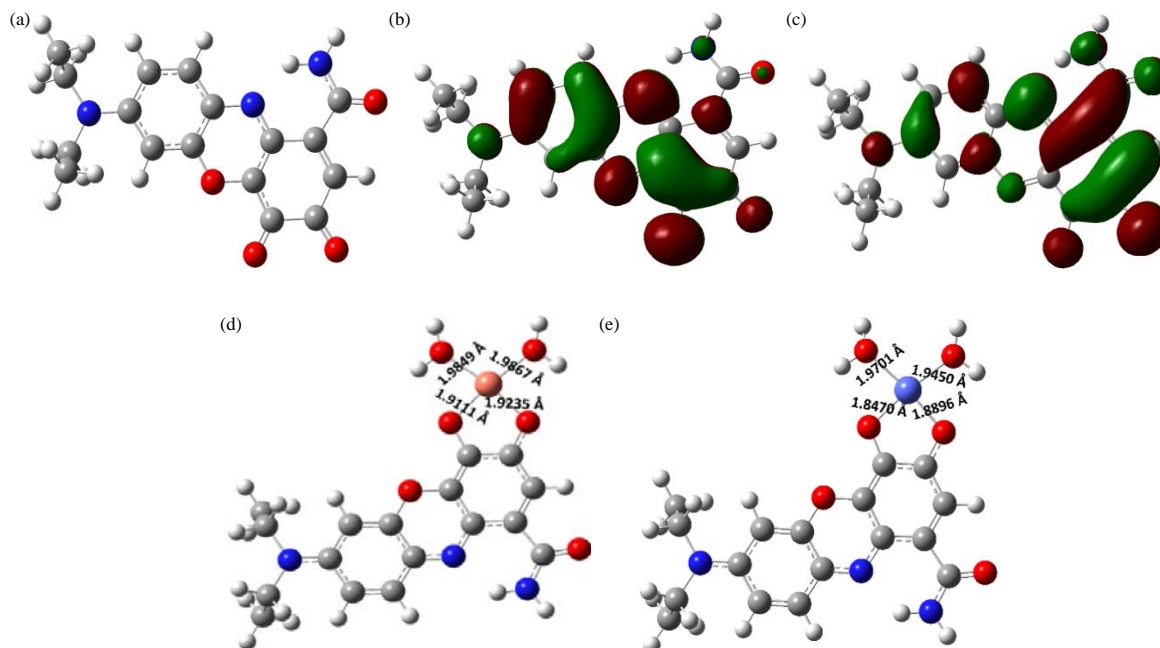


Fig. 13(a-e): Optimized structure, HOMO and LUMO electron isosurfaces of CB and optimized structures of Cu-CB and Co-CB complexes. (a) Optimized structure of CB, (b) HOMO isosurface of CB, (c) LUMO isosurface of CB, (d) Cu-CB complex showing salient ligand-metal bond lengths and (e) Co-CB complex showing salient ligand-metal bond lengths

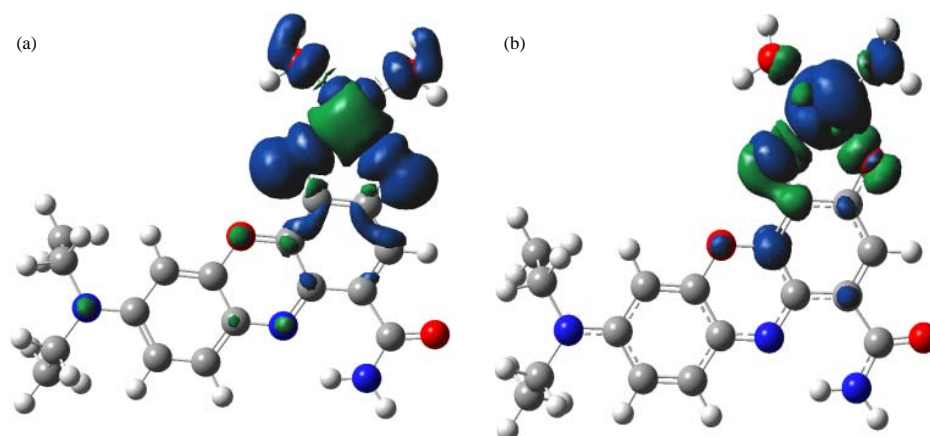


Fig. 14(a-b): Spin density distribution for the Cu-CB and Co-CB complexes. (a) Cu-CB complex and (b) Co-CB complex

the study, where the LANL2DZ relativistic pseudopotential was applied to the metal atoms (Cu and Co) and a 6-31G+(d,p) basis set was employed for all non-metallic atoms. The adopted model was used based on its successful application in previous similar studies that involved modelling of metal complexes¹⁵⁻¹⁸.

DFT study on Cu and Co complexes of CB—structure, relative stability and reactivity: The result of Fig. 12a-c shows the 2D (un-optimized) structures of the CB ligand and its Cu(II) and

Co(II) complexes. The optimized structure of the CB ligand is shown in Fig. 13a. The Frontier Molecular Orbitals (FMOs) isosurfaces of the ligand are shown in Fig. 13b,c. The CB ligand is essentially planar, except for the -CH₃ moieties of the -N(CH₂CH₃) group that are sticking out-of-plane at ca. 80° relative to the CB ring. This planarity of the CB ligand could confer a good spread of electron density over the fused rings and the bonding atoms to the metals. Electron density distribution of the FMOs of CB suggests relatively high electron density on the ring atoms and the anionic O-atoms

Table 4: Spin density distributions (%)

Distributions	Cu/Co	O _{1(CB)}	O _{2(CB)}	O _{1(H₂O)}	O _{2(H₂O)}
CuCB	82.635	7.369	9.593	0.195	0.167
CoCB	99.903	0.025	0.001	0.001	0.002

(of the O-H). Both the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) electron density isosurfaces shown in Fig. 13 suggest favourable forward and retro-donation of charges between CB and the metals, via the O-atoms of the ligand. The optimized structures of the metal complexes (Cu-CB and Co-CB) are shown in Fig. 13d-e, respectively. Both Cu(II) and Co(II) complexes of CB are also planar. The metal-ligand bond lengths revealed shorter metal-oxygen (M-O) bond lengths with the O-atoms of CB than those of H₂O. The M-O bonds compare favourably with literature values for similar bonds^{14,18,19}. Co-O bonds were observed to be shorter than their corresponding Cu-O bonds. A similar observation has been reported in literature¹⁵. However, this might not be enough to judge the relative stability of the complexes. Being odd electron systems, spin density distribution could be used to describe the degree of the covalent character of the M-O bonds. The spin density distribution for both Cu (II) and Co (II) complexes of CB is shown in Fig. 14a-b, respectively. The number of unpaired electrons in the valence orbitals of the metal ion characterizes the molecular orbitals of the metal ion in a complex. Usually, the central metal ion has the highest percentage of the charge density of the Singly Occupied Molecular Orbital (SOMO) in a complex. Though, some fractions of the charge density (attributed to the unpaired electrons) are spread/delocalized to the molecular orbitals of the ligand atoms. The more the spin density is delocalized to the ligand atoms, the higher the covalent character of the M-O bond, the stronger the bond and the more stable the complex. The data in Fig. 14 shows a more delocalized spin density for Cu-CB compared to Co-CB. The percentages of the resultant spin density on the atoms as listed in Table 4 also show higher percentages of the resultant spin density being delocalized onto the ligand atoms in Cu-CB compared to Co-CB. This suggests that the Cu-CB bonds are more covalent than the Co-CB bonds. Similar results have been reported in the literature.

CONCLUSION

This work has provided information on the chelating properties of Celestine blue and established a 1:1 Metal: CB species for copper (II) and cobalt (II), at pH 8 in an aqueous solution. The computational modelling also suggests the

favourable disposition of CB to complex with these metal ions. Thus, celestine blue can be used for the detection of metal ions. The solvatochromic nature of Celestine blue was also established as Celestine blue is sensitive to the nature of the solvents influencing the position of the wavelength of maximum absorption, λ_{max} . Solvatochromic dyes are used to detect the polarity of solvents.

SIGNIFICANCE STATEMENT

This study provided information on the chelating potentials of Celestine blue for possible applications to detect metal ions in an aqueous solution. The information reported herein could be beneficial in biomedical applications, possible use in the industries and analytical chemistry. It is important to note that several important applications of dyes are based upon their ability to form soluble complexes with metal ions. Information on the metal complexing properties of CB is relatively scanty. Thus, there is a new contribution to knowledge with regards to the chelating ability of CB as well as its solvatochromic nature for the detection of the polarity of solvents. Solvatochromic dyes could also be used as fluorescent sensors and imaging agents. Research into the design of materials and strategies for the detection of metal ions shall continue to increase because of the need for a clean environment and better life opportunities.

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