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Research Article

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Synthesis, Quantification and Speciation of Copper (I) and Manganese (VII) in Micellar Media using the Schiff Base 2-[(E)-[3-[(E)-(2-Hydroxyphenyl) Ethylene amino] Phenyl] Iminomethyl] Phenol in Environmental Samples

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Abstract

The Schiff base ligand H2L and its Cu(I) and Mn (VII) complexes were synthesized. The yield of the ligand and the complexes were within the range of 86.5 – 89.6 %. The synthesized complexes were stable below 270 °C. The electronic spectra of the H2L, [CuIL] and [MnVIIL] complexes were 325, 470 and 570 nm, respectively with molar absorptivity's (dm3 mol-1cm-1) of 1683, 29733 and 26366 respectively. The infrared spectra of the ligand showed v(O-H) at 3442 cm-1; v(C=N) at 1612 cm-1; and v (C-O) at 1276 cm-1. Proton NMR spectra of the ligand showed chemical shifts (ppm) at 12.92; 8.82 and 7.52 – 7.398. The Carbon-13 NMR spectra revealed signals (ppm) at 164.55, 160.93 and 120.00. The Mass Spectroscopy results gave the molecular weight of H2L, [CuIL] and [MnVIIL] complexes as 339.1, 403.967 and 369.027 g/mol, respectively. Beer-Lambert's law was obeyed in micelle media between 0.36 – 1.12 ppm. Analytical sensitivity, calibration sensitivity, limit of detection, limit of quantification and correlation coefficient (R2) were in the range 0.088 – 0.220 ppm, 0.175 - 0.308 ppm, 0.752 - 1.384 ppm, 2.507 - 4.613 ppm and 0.996 - 0.998, respectively.

Keywords: Spectrophotometry, Speciation, Micelle, Manganese (VII) and Copper (I) Complexes.

Introduction

Trace analysis and speciation of metals is a major area of study due to the dangers posed by heavy metals to man and the environment even in the minutest amount. Accumulation of heavy metals in the human body has been linked to diseases like Parkinson, cancer of the liver, blood and skin; and muscular dystrophy. Many protocols like atomic absorption spectrophotometry, chromatographic techniques, electronic tongue and x ray fluorescence, have been developed and applied to a very high degree of success in detecting and quantifying heavy metals [1]. However, due to existence of heavy metals in various oxidation states with different biological implications, existing methods have not fully satisfied the requirement of speciating and isolating heavy metals [2]. It is still a big challenge to find robust, cheap and easy methods of speciating metal ions in aqueous medium. Spectrophotometric methods have been applied for the purpose of speciating metal ions in aqueous media and scarcely in micellar media. Tetradentate Schiff base complexes have been employed as catalyst for many reactions and as biological models in understanding the structure of bio-molecules and biological process. Only a few metal ions have been probed but speciation of Cu, Mn have not been studied in micellar media using the Schiff base ligand 2-[(E)-[3-[(E)-(2-hydroxyphenyl) ethyleneamino] phenyl] iminoethyl] phenol (H2L).

Materials and Method

All the reagents used were of analytical grade. The synthesized Schiff base and the compounds were characterized by means of a Jetway 6305 UV/visible spectrophotometer for measuring the absorbance of the solutions. The infrared spectra were measured in the range of 4000 – 200 cm-1 using Shimadzu infrared spectrophotometer, Proton and Carbon- 13 Nuclear Magnetic Resonance spectra were determined on Mercury- 200BB spectrophotometer, Mass spectra were obtained using micro OTOF ESI-MS II spectrophotometer at University of Waikito, New Zealand. The conductivity of the ligand and the complexes were measured with WTW LF90 (model)-conductivity meter. Buffer solutions of pH 1-13 were prepared according to literature [3]. The formations of the complexes in aqueous and micelle media were studied using Cetyl Trimethyl Ammonium Bromide (CTAB) as a cationic surfactant, Sodium Dodecyl Sulphate (SDS) as anionic surfactant and Triton X - 100 as non-ionic surfactant.

Synthesis of the Ligand and Metal Complexes

Synthesis of the Schiff base ligand and metal complexes were carried out according to reported methods from literature 5.41 g of (0.05mole) of 1,3 diamino benzene was dissolved in dimethyl formamide (50 cm3) and 2 cm3 of 1.0 M NaOH was added and stirred to dissolve. 10.44 g (0.1mole) of 2-hydroxy benzaldehyde (salicyaldehyde) was added to the resulting solution at room temperature [3]. The reaction mixture was refluxed for 2 hours at 60-65oC. There was a color change from reddish green to orange. The mixture was cooled and the product formed collected, washed with cold ethanol (99.8%) and the dried sample recrystallized, kept in desiccator over for further use. The copper(I) and manganese (VII) complexes of 2-[(E)-[3-[(E)-(2-hydroxyphenyl) methylene amino] phenyl] iminomethyl] phenol was synthesized according to literature [3].

Determination of Cu(I) and Mn (VII) with H2L using UV-Visible Spectrophotometer in Non-ionic Triton- X 100 Micellar Media

Metal ions Cu(I) and Mn (VII)) solutions of fixed volume (0.5 cm3) [3.7 x 10-6 mol dm-3] were taken into various volumetric flask of 10 cm3, non-ionic Triton – X 100 surfactant solution of various concentrations [1.0 x 10-5 to 2.1x10-4 mol dm-3] and volumes (0.1 to 2.1 cm-3) was then added into the various marked volumetric flasks. Appropriate volumes of the requisite buffer solutions of varying pH were then added. Lastly, 0.5 cm3 the ligand (2-[(E)-[3-[(E)-(2-Hydroxyphenyl) methylene amino] phenyl] iminomethyl] phenol) [3.7 x 10-6 mol dm-3] was then added. The various volumetric flasks containing the mixture of solutions were shaken using a vortex mixer (Shar and Soomro, 2007) [4-6]. At the optimized conditions of the stable complexes, the spectra of the metal chelate were noted and absorbances were recorded at particular wavelengths λ max for various metal ions. The percentage efficiency was then calculated.

Results and Discussion

Table 1: Physical Properties and Molar Conductivity Data of the Ligand and its Copper(I) and Manganese (VII) Complexes.

Compound	Color	Texture	Melting Point (oC	Percent Yield	Stoichimetries (M:L)	Molar Conductyivity
Ligand	Orange	Crystalline	160 – 163	78.2		5.05
Copper(I) Complex	Orange Brown	Powdery	243 – 257	86.5	1 : 1	19.4
Manganese (VII) Complex	Indigo	Powdery	268 – 270	89.6	1 : 1	37.5

Table 2: UV- Visible Electronic Spectral Data of H2L and the Metal Complexe

S/N	Compound	U V Bands π → π*, n→ π*	d→d
1	H2L	260, 325	
2	[Cu^{II}L]	225, 325	360, 470
3	[Mn^{VII}L]	350	420, 435,570

In Table 2, the spectra of the [CuIL], the band in 225nm (37333 cm-1) was assigned to n→π* transition. While the bands in the region 360 nm (20000 cm-1), 325 nm (26366 cm-1) and 470nm (33455 cm-1) were assigned to π → π*, n→ π*, n→ π*, transitions respectively as contain Table 2. The UV - Visible electronic spectrum of the [MnVIIL], displayed four bands at 49,333 cm-1 (420 nm) and 28,660 cm-1 (435 nm) assigned to n→ π*, which are probably due to the electronic transition 6A1→4T2g and 6A1→ 4T1g in accordance with a square planar geometry around Mn (VII) ion as confirmed by the elemental analysis and suggested by Asha et al. [7].

Table 3: The Infrared Spectra and Electronic Spectral Data of the Schiff Base and Metal Complex

Metal complexes and Ligand	ν(C=N) cm^{-1}	ν(C-O) cm^{-1}	ν(O-H) cm^{-1}	ν(M-O) cm^{-1}	ν(M-N) cm^{-1}
H_2L	1612	1276	3442	501	-
[Cu_1L]	1608	1377	3418	536	506
[Mn^{VII}L]	1606	1311	3222	542	489

FTIR Spectra of H_2L and its Cu(I) and Mn (VII) Complexes. A Summary of the Bands and Comparism Between the Ligand and Complexes is Depicted in Table 3.

The ν (O - H) band appeared at 3442 cm-1 in the ligand but in the spectra of the metal complexes, the bands appear between 3370 - 3414 cm-1 indicating the ligand to be lignated to the metal complexes using the deprotonated oxygen atom or undeprotonated –OH group. ν (C=N) stretching which was observed at 1612 cm-1 in H2L was shifted to between 1604 – 1608 cm-1 in the complexes, indicating complexation through the azomethine group as shown in Table 3. The ν (C-O) was observed at 1276 cm-1 in H2L while in all the complexes, the band appeared at between 1314 – 1377 cm-1. This suggests that the H2L binds to the metals through the phenolic oxygen. This is confirmed by the presence of bands around 536 – 542 cm-1 in all the complexes assigned to M – O bonding. These results are in accord with has been reported for H2L and the complexes [8, 9].

^{1}H NMR Spectra of the Ligand and its Metal Complexes

The proton NMR spectra of the ligand showed chemical shifts (ppm) at 11.9 assigned to the O-H; 8.82 assigned to azomethine proton and 7.4 ppm assigned to aromatic protons. The Carbon-13 NMR spectra revealed signals (ppm) at 164.549, 160.926 and 120 assigned to -C-OH, C=N and aromatic carbon. (H$_2$L)

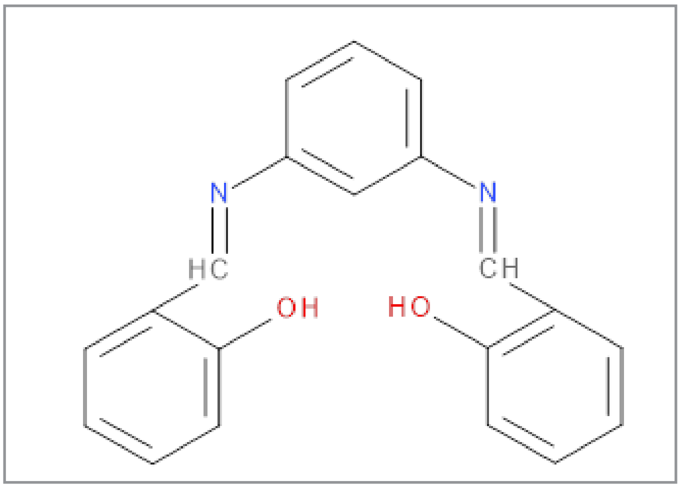

Figure 1: The structure of the Ligand

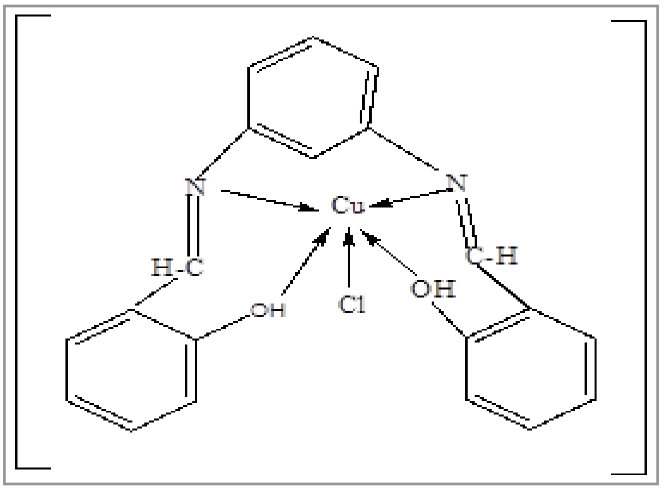

Figure 2: Copper (II) Complex [CuL]
(Square Pyramidal Geometry)

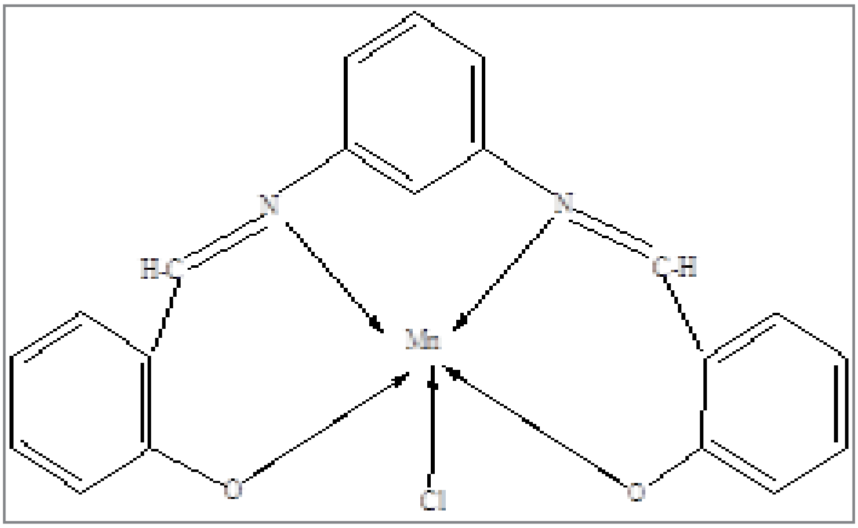

Figure 3: Manganese (VII) Complex [MnL]
(Square Pyramidal Geometry)

Table 5: Mass Spectra Data and Molecular Formula of the Ligand and Complexes

Compounds	M+ Calculated	ES-MS (Found)	Molecular Formula
H2L	339.342	339.096	C20H16N2O2Na
[CuIL]	402.888	403.967	C20H16N2O2NaCu
[MnVIIL]	371.290	369.027	C20H16N2O2Mn

Optimization Studies

Optimization studies (Effect of Time, Effect of Temperature, Effect of pH on Complexation) was carried out on the ligand and complexes, Time (minutes) is a fundamental condition for the determination of Cu(I) and Mn (VII). Therefore 10 minutes and 20 minutes are the maximum time required for the reaction to take place, and was maintained throughout in the determination of the metal ions. The optimum temperature for the formation of Cu(I) and Mn (VII) Complexes are 40oC and 60oC. These established temperatures were maintained throughout the determination of the metal ions under study.

Effect of Micellar Medium on the Analysis of Metal Ions

The effect of all the three kinds of surfactants - Triton X-100 (non-ionic surfactant), SDS (anionic surfactant) and CTAB (cationic surfactant) and water, have also been studied to determine their effect on absorption properties of Cu(I) and Mn (VII) complexes.

The effect of surfactant concentration was studied within the range from 1×10-2 mol dm-3 to 8 ×10-1 mol dm-3. The absorbance at λmax of the complex shows a sharp increase with increasing surfactant concentration. The increase in absorbance in the presence of micelle was due to the binding of reactants in a small volume of stern layer of the micelle, thus leading to considerable concentration effect. The maximum in the plot of "absorbance against concentration of surfactant" was produced by two opposing effects. With increase in surfactant concentration, binding of reactants in the stern layer begins and they are transferred into small volume of the micellar pseudo phase. There was thus a concentration effect which is responsible for increase in absorbance. This concentration effect was opposed by continuous dilution of the reactants within the micellar pseudo phase with increasing surfactant concentration. The former effect is predominant at lower surfactant concentration, whereas the latter becomes important at higher concentrations of surfactant, resulting in a maximum in the absorbance against surfactant concentration level.

Determination of Cu(I) and Mn (VII) with H2L Using UV-Visible Spectrophotometer in Various Micellar Media

The Effect of various surfactants (Triton X, CTAB and SDS) on the different metal ions solutions under study was determined and percentage efficiency calculated. From the percentage effect of Triton X – 100 (nonionic surfactant) was remarkably obvious and highest in all the solutions of the metal ions under study. This was distantly followed by Cetyl Trimethyl Ammonium Bromide (CTAB) (Cationic surfactant) and lastly by Sodium Dodecyl sulphate (Anionic surfactant). Based on the result, Triton X – 100 (nonionic surfactant) was selected to be used for further study of the metal ions under study.

The variation of absorbance with the concentration of the reagent was studied by reacting fixed amount of 3.7 x 10-6 mol dm-3 stock solutions of the ligand (0.5 cm3) with a fixed amount 3.7 x 10-6 mol dm-3 solution of the various metal ions (0.5 cm3) Cu(I) and, Mn (VII) under study. While varying the volume and concentration of various surfactant solutions. The surfactant concentration was studied within the range from 1×10-5 mol dm-3 to 2.1 ×10-4 mol dm-3. The mixture were allowed to react for various given time and the absorbance taken at the specific wavelengths of the metal ions. The absorbances were plotted against the various concentration of the surfactants.

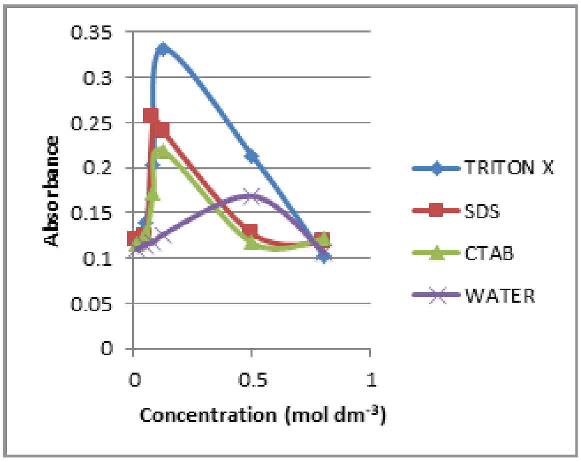

Figure 4: Effects of Surfactants on Absorbance of Copper(I) Complex

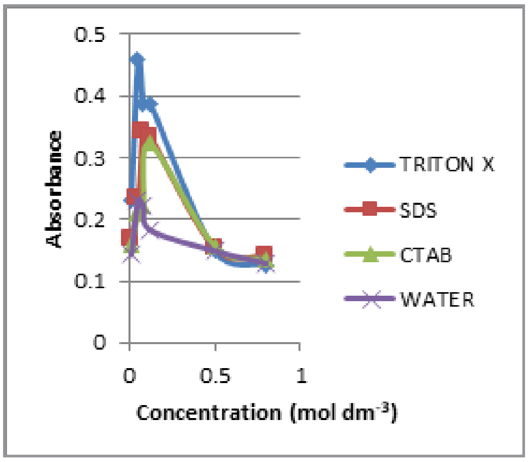

Figure 5: Effects of Surfactants on the Absorbance of Mn (VII) Complex

Table 6: Table 4.15: Effect of Various Micellar Media on Determination of Cu(I) @ [Cu(I)] = 3.76 x 10-6 mol dm3, [H2L] = 3.76 x 10-6 mol dm3, pH = 8.0, Temperature = 40oC, Time = 10 min.

Conc. of surfactant used. mol dm-	Average Abs. in CTAB (450 nm)	Average Abs. in SDS (435)	Average Abs. in Triton X (500nm)	Average Abs. in Water (480nm)
1.0x10-5	0.442	0.346	0.486	0.325
3.0x10-5	0.465	0.370	0.491	0.314
5.0x10-5	0.478	0.377	0.538	0.304
7.0x10-5	0.485	0.394	0.523	0.282
9.0x10-5	0.435	0.384	0.469	0.270
1.1x10-4	0.425	0.336	0.447	0.245
1.6x10-4	0.315	0.325	0.327	0.224
2.1x10-4	0.306	0.211	0.265	0.210
	72%	40%	77%***	

Table 7: Effect of Various Micellar Media on Determination of Mn (VII) @ [Mn (VII)] = 3.76 x 10-6 mol dm3, [H2L] = 3.76 x 10-6 mol dm3, pH = 11.0, Temperature = 60 oC, Time = 20 min.

Conc. of surfactant used. mol dm-3	Average Abs. in CTAB (570 nm)	Average Abs. in SDS (570 nm)	Average Abs. in Triton X (575 nm)	Average Abs. in Water (570 nm)
1.0x10-5	0.794	0.571	1.063	0.850
3.0x10-5	0.890	0.580	1.256	0.745
5.0x10-5	0.952	0.853	1.299	0.703
7.0x10-5	0.963	0.980	1.384	0.680
9.0x10-5	0.960	0.970	1.204	0.591
1.1x10-4	0.821	0.714	0.831	0.451
1.6x10-4	0.694	0.491	0.683	0.345
2.1x10-4	0.547	0.380	0.509	0.290
	42%	44%	104%***	

N.B: The average absorbance was obtaining after triplicate analysis

Table 8: Analytical Characteristics of the Procedures in Triton X – 100 Medium and in Aqua Medium.

Characteristics	Triton X – 100		Triton X – 100	
	Value of Cu(I) complex	Value of Mn (VI) complex	Value of Cu(I) complex	Value of Mn (VI) complex
ƛ (nm)	435	575	470	569
Molar Absorptivity (Lmol -1cm-1	48,933	21,400	20,000	4900
Calibration Sensitivity;(m)ppm	0.032	0.072	0.175	0.318
Analytical sensitivity; m/SA	0.088	0.22	0.870	1.096
Limit of Detection;3SA /R2	1.083	0.963	0.610	0.895
Limit of Quantification; CQ; 10SA/ R2 (ppm)	3.610	3.212	2.034	2.983
Correlation Coefficient, R2	0.997	0.996	0.988	0.972
Linear dynamic range (ppm)	0.042-0.56	0.07- 0.08	0.07-0.112	0.1 - 0.08

Conclusion

The ligand 2-[(E)-[3-[(E)-(2-Hydroxyphenyl) methyleneamino] phenyl] iminomethyl] phenol (H2L) and its Cu (II) and Mn (II) were successfully synthesized and characterized using Ultra Violet – Visible Spectroscopy (UV - Vis), Fourier Transform Infra-red spectroscopy (FTIR), Atomic Absorption Spectroscopy (AAS), Mass Spectroscopy (MS) in addition to other elemental analysis. The metal ions complexes were also determined in both aqueous and micellar media. The complexes crystallized out with the structures; tetrahedral and square planar.

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Conflict of Interest

The authors declare that there are no conflicts of interest in this work.

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