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Synthesis and Spectral Studies of Co (II), Cu (II) and Fe (III) Ions with 2(2`-Hydroxynaphthyl azo-) Benzothiazole

T.Y. Mohamed
Chemistry Department, Faculty of Science, Benha University, Benha, Egypt.

A NEW azo compound 2 (2`-hydroxy naphthyl azo-) benzo-thiazole (HNABT) has been synthesized. Bands of the ligand and the formed complexes of Co(II), Cu(II) and Fe(III) are assigned using FT-IR spectra. The electronic absorption spectra of the ligand in pure organic solvents of different polarity and also in buffer solution of varying pH are investigated. Acid ionization constant and stability formation constant of complexes were determined. A sensitive spectrophotometric method for the micro determination of metals using the azo compound, as a new chromogenic ligand is established. This method is successfully used for the determination of Co(II), Cu(II) and Fe(III) in the presence of foreign ions and in solutions .

Keywords: 2(2`-Hydroxynaphthylazo-) benzothiazole , Spectrophotometr, Micro-determination of Co(II) and Cu(II) and Fe(III) .

Azo compounds were the main subject of large research work due to their applications as textile dyes, acid-base and redox indicators, metalochromic reagents and histological stains[1-4] . Careful examination of the literature reveals that, considerable work has been reported on the spectrophotometric studies. The acid-base properties of the heterocyclic azo compounds, their metal complexes and their analytical applications have been reported[5-8]. Azo compounds derived from 3-amino1,2,4 triazole, their azo-azo methine derivatives and their metal complexes have been shown in the literature [9]. ^{60}Co isotope has a particular importance from radioactive waste view point, and is present as a component in steel used in nuclear facilities. Co (II), Cu (II) and Fe(III) complexes were determined with different azo compounds [10]. In the present work, a new azo compound 2(2`-hydroxynaphthyl azo)- benzothiazole has been prepared, characterized and utilized as a new chromogenic reagent for the spectrophotometric determination of Co(II), Cu(II) and Fe(III) in simple and sensitive method.

Email : dr_talaat2003@yahoo.com

Experimental

Reagents

All chemicals used were either of analytical grade or of high purity provided from BDH, Aldrich or Sigma. Bi-distilled water was used in all experiments.

Preparation of the ligand

A solution of 2-amino benzothiazole (0.01 mol) in phosphoric acid 10-20 ml (1.0 mol) was diazotized [11,12] at -5°C with 5 ml sodium nitrite (2 mol) over 1hr. A solution of β-naphthole (0.01 mole) dissolved in 20 ml   0.5 N sodium hydroxide , 40 ml ethanol and 300 ml Na_2CO_3 (1.0 mol) was added to the above solution. The diazo compound was added to 2N H_2SO_4 dropwise with stirring at -2°C to yield the azo dye, which completely precipitated and it was recrystalized from ethanol, elemental analysis of the ligand are given in Table 1.

TABLE 1. Physical data of the ligand and its elemental analysis .

Empirical formula	Elemental analysis cal (found)			λ_{max}(nm)	ε (lmol^{-1} cm^{-1})	m.p ^{o}c	Yield%
	%C	%H	%N				
$C_{18}H_{11}N_3OS$ (317)	68.13 (68.3)	3.47 (3.50)	13.2 (13. 4)	486	2.02×10^4	183	85

Preparation of solution

Stock solution (10^{-3}M) of the ligand (HNABT) was prepared by dissolving an appropriate weight in absolute ethanol and complete the volume till 100 ml measuring flask. Also, stock solutions of metal salts 5×10^{-3}M of each metal solution are prepared and standardized by EDTA solution [13]. Universal buffer solution of pH values 2.0-12 were prepared by the recommended method [14] .

Instrumentation

FT-IR analysis was performed using FT-IR spectrometer (Perkin Elmer-550) in the range 400-4000 cm^{-1} and elemental analysis of the ligand was performed in Micro Analytical Center, Cairo university. The pH was determined by using Jenway 3505 pH meter 9V AC power. All spectrophotometric measurements were performed using Jasco V 530 UV/Vis Spectrophotometer, equipped with 10 mm matched quartz cell.

Recommended procedure for spectrophotometric determination of metal ions

To a definite volume of the metal solution containing not more than 20 μg ml^{-1}, 2 ml of the ligand (10^{-3} M) and 2 ml buffer solution of the optimum pH , and 2 ml pure ethanol (40%v/v) were added and complete after that with bidistilled water till 10 ml in measuring flask. The blank solution was prepared by the same manner without metal solution. The mixture was allowed to stand for 5 min, where the absorbances were measured for Co(II), Cu(II) and Fe(III)-

ligand complexes at λ_{max} 652, 630 and 648 nm, respectively. The calibration graph was constructed by plotting the absorbance against metal concentration in μg ml^{-1}, the plots was straight line passing through the origin.

Results and Discussion

IR-Spectra

The IR spectra of the ligand and its complexes were studied and the data shown in Table 2. The ligand exhibited broad band within the range 3398 – 3340 cm^{-1} corresponding to the stretching vibration of OH group [15-17],while the stretching vibration of NH group gives a band at 3250 cm^{-1} and also N=N group gives a band at 1432 cm^{-1}, a strong peak at 1280 cm^{-1} due to vibration mode of σ_{OH}. Also, a weak intensity band in the range 1155-1164 cm^{-1} are assigned to the stretching vibration of ν_{C-OH} was reported. On the other hand , IR spectra of Co(II), Cu(II) and Fe (III) – ligand complexes showed bands at 3422, 3432 and 3425 cm^{-1} due to the stretching vibration of ν_{C-OH} groups and the presence of water molecules in coordinated complexes[15-17] . Also, bands appeared at 3240, 3220 and 3200 cm^{-1} are exhibited by the stretching vibration of ν_{NH} group. It was found that the bands appeared at 1522, 1528,and 1433 cm^{-1} due to the   stretching vibration of N=N group in the complexes above were shifted to higher values compared to band of ligand1432 cm^{-1}.This shift may be because of the bond stretching resulting from coordination between the Co (II), Cu (II) and Fe(III) with ligand to form complexes [18]. Bands at 1370 , 1316 and 1229 cm^{-1} due to the asymmetric stretching vibration of σ_{OH} group also reported (Table 2). New bands at 1189, 1202 ,1160 cm^{-1} and also at 747,741 and 675 cm^{-1} explained the stretching vibration of S-M bond formation and stretching of M-O bonds are reported, respectively. Finally, the frequency of C=N in thiazole ring exhibited bands at 1596, 1609 and 1601 cm^{-1} according to the order of complexes.

TABLE 2. IR spectra of ligand and metal complexes .

Compound	ν_{OH} cm^{-1}	ν_{NH}	$\nu_{N=N}$	δ_{OH}	$\nu_{C=N}$	δ_{M-O}
Ligand	3398	3250	1432	1280	1580	-
Co-ligand	3422	3240	1522	1310	1596	747
Cu-ligand	3432	3220	1528	1316	1609	741
Fe-ligand	3425	3200	1433	1229	1601	675

Electronic absorption spectra of the free ligand in organic solvents band assignment

The band located at the range 365 - 450 nm for the ligand corresponding to the (π-π*) transition involving the π-electrons of the azo group [19] .The very broad band observed in the range 465-600 nm can be assigned to an intermolecular charge transfer interaction involving the whole molecule. This band can be assigned to the existence of azo-hydrazone toutmeric equilibrium originating from the OH group and N=N group [20] which can be represented as given in Scheme 1.
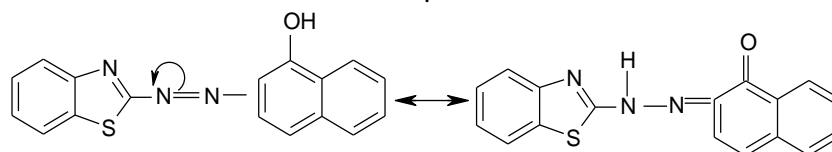
Scheme 1. Azo - hydrazo toutmerism in ligand.

The CT band can be considered as a composite band resulting from the absorption of the two equilibrium species. The absorption region on the lower energy site would be due to the hydroxyl-azo form, while that at higher energy region can be attributed to the absorption by the o-quinone hydrazone species. This behavior seems to be quite common for azo or azomethine dyes having a hydroxyl group in o-position to the N=N on the aromatic ring [21,22].

Solvato chromic behavior

The electronic spectra of the free ligand in organic solvents of different polarity was investigated, and showed in Fig. 1. The results obtained indicate that the UV (π-π*) bands with high coefficient suffer small solvent shifts, this behavior is characteristics of the type of electronic transition. Also, the data showed that the intra- molecular CT band appearing in the range 500 -600 nm exhibited a red shift based on changing the solvent in the direction from non polar solvents to polar solvent. This behavior is observed with increasing the polarity of the solvent and can be explained on the principle that the excited state being more polar than the ground state in polar solvents, methanol and ethanol. Also, a weak intra-molecular H-bonding formed in a solvent molecules causes a blue shift [22,23].
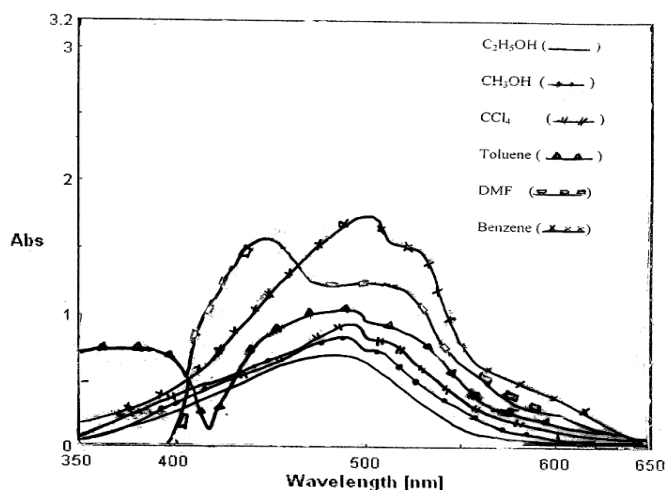
Fig. 1. The electronic absorption spectra of ligand in different organi solvents .

Analytical studies and the effect of pH

The protonation constant of the ligand under investigation is calculated by different methods of half height and modified limiting absorbance methods at different pH values ranged from 2.0-12 of buffer solution. It was found that the protonation constant pK_H of the reagent was 8.0 which is in satisfactory agreement with the value found for 1-(2- pyridyl azo) 2- naphthol (pK_H = 12.2) [24]. The absorption spectra of Co (II), Cu (II) and Fe(III)-ligand complexes were studied at different pH values using universal buffer solutions. Absorbance was found to be low at pH below 7 , increased in a basic medium at pH values from 9 -10.5, then decreased secondly after pH 10.5. The optimum conditions were found to be , for Co(II)- complex at pH 10.4 and λ_{max} 652 nm, for Cu (II)– complex at pH 10.0 and λ_{max} 630 and for Fe(III)– complex at pH 9.34 and λ_{max} 648 nm , data are listed in Table 3. As shown from values of absorption bands of the complexes, the bands were shifted to longer wavelengths compared to that of the free ligand (Fig. 2). This shift of λ_{max} of the complexes to red shift and longer wavelength can be attributed to increase in delocalization of the electrons due to complexation with the metal ions , leading to a decrease in the energy gap between the ground and excited state [25,26].

**TABLE 3. Absorption spectra and spectral data of Co(II), Cu(II) and Fe(III) chelates with ligand .**

Compound	pH	λ_{max}	Molar Ratio	Logβ_n	$-\Delta G^*$	Beer's law ($\mu g\ ml^{-1}$)	ε L $mol^{-1}\ cm^{-1}$	SS ($\mu g\ cm^{-2}$)	SD	CC	Ringbom ($\mu g\ ml^{-1}$)
Ligand	--	486	--	8.5							
Co-ligand	10.4	652	1:1 1:2	3.6 7.4	4.94 10.15	0.1-4.4	4 x 10^4	0.001475	0.0084	0.998	0.88-3.38
Cu-ligand	10.0	630	1:1 1:2	4.01 7.5	5.50 10.29	0.31-6.35	1.8 x 10^4	0.0035	0.0053	0.9993	0.54-5.94
Fe-ligand	9.34	648	1:1 1:2	5.65 7.8	7.6 10.70	1.4-8.4	1.2 x 10^4	0.00466	0.0077	0.9973	1.2-8.18

Effect of sequence of addition and organic solvent ratio

The sequence of addition was found to be (metal-ligand-buffer) for the best condition of forming the complex. Also, the effect of organic solvent ratio showed that ,the color of complexes attained amaximum value at a ratio of 40% (v/v) ethanol.

Effect of ligand concentration

The effect of reagent concentration on the intensity of the color for the complexes were obtained by varying the ligand volume from 1.5-2 ml of 10^{-3} M in 10 ml measuring flask.
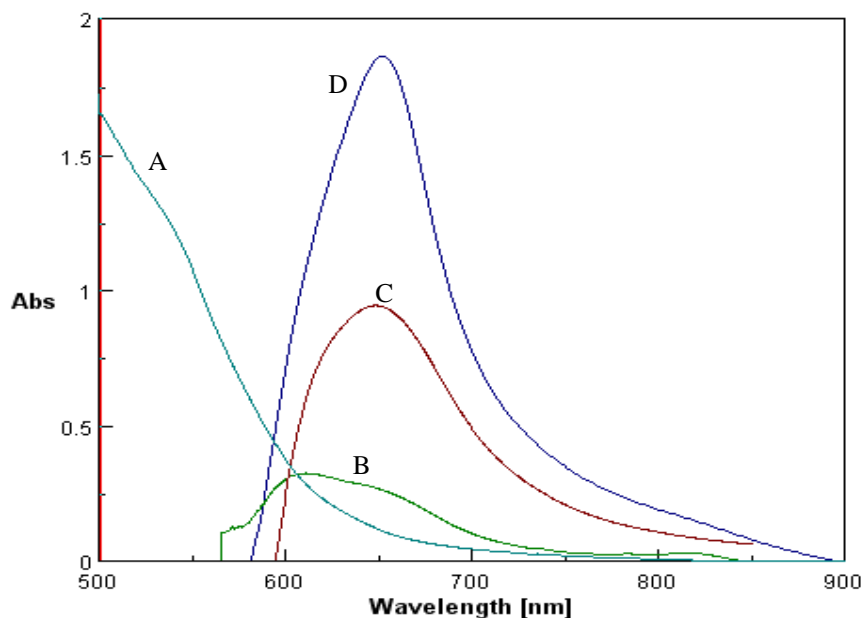
Fig . 2.   Absorption spectra of ligand with metal ion complex
(A) ligazand only against buffer blank
(B) Cu(II) - Ligand complex against ligand -buffer blank
(C) Fe(III) –Ligand complex against ligand -buffer blank
(D) Co(II) – Ligand Complex against ligand -buffer blank

Stoichiometry of the complexes

The composition of the metal-complexes was established by the continuous variation and molar ratio methods [24,25] which revealed the formation of (1:1) and (1:2) M:L complexes. The conditional and free energy change (ΔG^*) of formation of Co (II), Cu(II) and Fe (III) complexes were calculated according to the relationship [26] $\Delta G^* = - 2.303RT \log K$ (at 298) and are given in Table 3. The listed values showed that the stability of the complexes were increased with increasing the number of ligand molecules attached to the metal ion .

Effect of foreign ions

The interference of various ions was examined by introducing the foreign ions into a solution containing 20 µg ml^{-1} of metal solution. The data concluded that the following metal ions Na^+, K^+, Li^+, Ca^{2+}, Ba^{2+}, CO_3^{-2}, PO_4^{-3} , SO_4^{-2} , Cl^-, Br^- did not interfere till 500 times of metal ion concentration. On the other hand , Cd^{+2}, Hg^{+2} and Ni^{+2} ions cause a positive deviation due to their ability to form colored complexes with excess of the ligand. Also, anions such as CN^-, SCN^- and EDTA cause a negative deviation based on the tendency to form complexes with the metal ions in the work.

Beer's law and sensitivity

The ranges of linearity of absorbance as a function of metal ion concentration (μg ml^{-1}) obeys Beer's law and provide a satisfactory measuring of the sensitivity of the ligand in direction to the metal ion for accurate results. Ringbom optimum concentration range was determined [27] by plotting log [M] in μgml^{-1} against %T and the linear portion of Z-shaped curve gives the accurate range of analysis. It was observed that Co (II)-ligand complex is the most sensitive complex since its molar absorptivity (4×10^4 mol^{-1}L cm^{-1}) is the highest value compared to the other complexes. Sandell sensitivity (SS), standard deviation (SD) and correlation coefficient (CC) for each complex were calculated and summarized in Table 3. It was found that the correlation coefficient is close to unity and standard deviation is small, confirming the possible application of the method for micro determination of the metals by a simple, accurate and sensitive spectrophotometric method.

Application and reproducibility

To determine the accuracy and precision of the present method for determination of Co (II) and Cu(II) in mixing solutions with small quantities of Pb (II), Mg(II) salts with a known concentration of Co(II) and Cu (II) using the ligand as a chromogenic reagent . All measurements were performed as the recommended method , the reproducibility deviation was found to be 0.00513, 0.00322 and the percentage recovery was 99.86 and 99.42% for Co (II) and Cu (II) ions.

Conclusion

This spectrophotometric method has been developed for the determination of Co (II), Cu (II) and Fe (III) by using a chromogenic ligand in aqueous solutions containing (40% (v/v) ethanol. Deep coloured complexes are formed at the optimum conditions and micro determination of the metals is obtained by applying Beer's law method. The method has several advantages mainly, good selectivity, and high sensitivity. Molar absorptivities are 4×10^4, 1.8×10^4 and 1.2×10^4 mol^{-1}cm^{-1} for Co (II), Cu (II) and Fe (III) -complex simultaneously, also sandell sensitivity is recorded for each complex as follow: 0.001475, 0.0035 and 0.00466 μg cm^{-2}, respectively. This method is successfully performed without extraction or pretreatment of the sample in presence of foreign ions.

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دراسات تحليلية و طيفية لعناصر الكوبلت والنحاس والحديد مع 2, 2– هيدروكسى نافثيل ازو بنزو ثيازول

طلعت يونس محمد

قسم الكيمياء – كلية العلوم – جامعة بنها – بنها – مصر .

تم تحضير مركب 2,2- هيدروكسى نافثيل ازو بنزو ثيازول , تم دراسة الامتصاص الطيفى لهذا المركب وأيضا متراكباته مع عناصر الكوبلت والنحاس والحديد . ثم تم القيام بتحليل المركب والمتراكبات المحضرة باستخدام الاشعة تحت الحمراء , وأيضا دراسة الانتقال الالكترونى فى المذيبات العضوية ذات القطبية المختلفة , وأيضا فى وجود محاليل منظمة مختلفة الاس الهيدروجينى .

من هذه الدراسة أمكن تعيين ثابت التاين وثابت التكوين للمتراكبات المختلفة , وقد تم تعيين القيم الدقيقة للعناصر فى المحاليل بواسطة طريقة سهلة وبسيطة فى وجود عناصر غريبة .