Preparation and Determination Studies of Cobalt(III) and Nickel(II) Ions With New Reagent 2-[(6-Nitro-2-benzothiazolyl)azo]-1-naphthol (α-NBTAN)by Spectrophotometric Methods

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Abstract:

New heterocyclic azo dye reagent 2-[(6-Nitro-2-benzothiazolyl)azo]-1-naphtha(α-NBTAN=LH) and two complexes with Co(III) and Ni(II) have been prepared and characterized by using elemental analysis and vibrational spectra. A direct method has been developed for the spectrophotometric determination of microgram amounts of cobalt and nickel. This method sensitive, selective and rapid between Co(III) and Ni(II) with reagent (α-NBTAN) to form a color complexes. The molar absorptivity (Є) of the complexes are 2.51 × 10^3 L. $mol^{-1}.cm^{-1}$ and 1.03 x10^3 L. $mol^{-1}.cm^{-1}$ at maximum absorptions (λ_{max}) 629 nm and 625 nm for Co(III) and Ni(II) complexes respectively . The relative standard deviations, relative errors and recovery for Co(III) and Ni(II) complexes were : R.S.D%=1.16, 0.516, Re = 98.57, 97.14, D.L= 0.237, 0.537 and Erel % = 1.42, 1.12 respectively. The metal to ligand ratio (M : L) of complexes are (1 : 2) by using the mole ratio and slop ratio methods .

الخلاصة :

يتضمن البحث تحضير كاشف صبغة أزو غير متجانسة الحلقة جديدة 2 - [(6 - نايترو-2 - بنزوثيازوليل) أزو]-1 - نفثول (α –NBTAN=LH) مع معقد الكوبلت (III) والنيكل (II) وتم تشخيصهما في الحالة الصلبة بواسطة تحليل العناصر الدقيق والأطياف الاهتزازية ثم تقدير كميات مايكرو غرامية من أيون الكوبلت (III) والنيكل (II) بطريقة تحليلية طيفية وهي طريقة حساسة وانتقائية وسريعة لإنتاج معقدات ملونة .معاملات الامتصاص المولاري للمعقدين هي10^3 x 2.51 لتر . مول $^{-1}$. سم $^{-1}$ و10^3 x 1.03 لتر . مول $^{-1}$. سم $^{-1}$ عند الأطوال الموجية للامتصاص الأعظم 629 نانومتر و 625 نانومتر لمعقدي الكوبلت (III) والنيكل (II) على التوالي . قيمة % R . S . D هي 1.16 و 0.516 وقيمة % Re هي 98.57 و 97.141 وقيمة D . L هي 0.237 و 0.537 وقيمة % E_{rel} هي 1.42 و 1.12 على التوالي . نسبة (الليكاند : الفلز) هي (2 : 1) للمعقدين باستعمال طريقتي النسبة المولية والميل النسبي .

1.Introduction:

A large number of thiazolylazo compounds have been prepared and proposed as highly sensitive chromogenic reagents for determination of several metal ions[1–4]. Thiazolylazophenols and its derivatives have attracted much attention as analytical reagents awing to the high sensitivity and selectivity[5–9]. Many of organic reagents are used for determination of cobalt(II) and nickel(II) ions by using many techniques, such as the chromogenic 1-[(2-Pyridylazo)]-2-naphthol as a complexing reagent in aqueous phase using nonionic surfactant[10]. Also the reagent 2-[2-Qunolylazo]-5-diethylamino aniline (QADEAA) used as a chromogenic reagent for determination of cobalt based on the color reaction of (QADEAA) with cobalt and the solid phase extraction of the colored chelate with C_{18} disks [11].

In this work, a new heterocyclic azo dye reagent 2-[(6-Nitro-2-benzothiazolyl)azo]-1-naphthol (α-NBTAN) has been synthesized and used spectrophotometric determination of micrograms quantities of cobalt(III) and nickel(II) ions.

2. Experimental

2.1- Apparatus and materials

Absorption spectra were recorded with Shimadzu UV-Vis spectrophotometer UV-1650 double beam spectrometer using 1cm quartz cells with absolute ethanol as solvent. Elemental analysis were

carried out by means of micro analytical unit of 1108 C.H.N Elemental analyzer. IR spectra were recorded with FTIR-8000 Shimadzu spectrometer, by CsI discs. The metal content of the complexes was measured using atomic absorption technique by Shimadzu -AA-160. The conductance measurements were carried out at room temperature and 10^{-3}M concentration using conductivity bridge model Ec219. pH measurements were carried out using a Philips PW 9421 pH meter . Electro thermal melting point, Gowllands was used to measure the melting point of reagent and its complexes . All chemicals were of highest Purity and used as supplied by the manufactures except of 2-amino-6-nitrobenzothiazole was prepared as described in the literature[12]. All solutions were prepared using de- ionized water.

2.2- Preparation and characterization of reagent (α-NBTAN)

The azo reagent (α-NBTAN) fig.1, has been synthesized by the diazotization coupling reaction using the general procedure (with some modifications) for synthesis this kinds of compounds[13]. A 2-amino-6-nitrobenzothiazo (1.95 gm, 0.01 mole) was dissolved in 50 ml of distilled water and 10 ml of concentrated hydrochloric acid . The filtered solution was cooled to 0 ºC. To this solution was added drop wise a solution of (0.75 gm, 0.01 mole) of sodium nitrite in 15 ml of distilled water at 0–5 ºC and the mixture was stirred at below 5 ºC .The diazonium chloride solution was added drop wise in to 500 ml beaker containing (1.44 gm, 0.01 mole) of α-naphthol dissolved in 200 ml alkaline ethanol. The mixture was stirred for additional 2 hrs, in an ice-bath and allowed to stand overnight and acidified with dilute hydrochloric acid until pH=6.0. The precipitate formed was filtered off and recrystallized twice from hot ethanol and then dried in the oven at 60 ºC for 24 hrs, and dried in a desiccator over an hydrous $CaCl_2$.

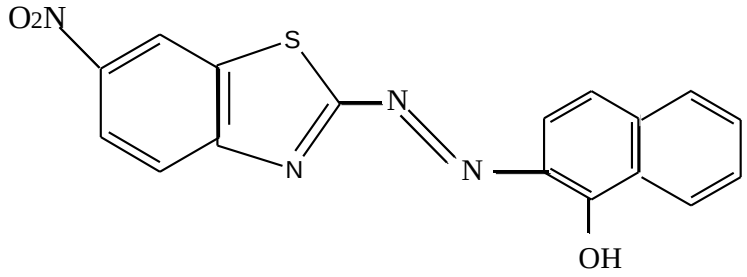


Fig .1: Structure of the reagent (α-NBTAN = LH)

2.3- Preparation of complexes

The complexes were prepared by adding (1.75gm, 0.005 mole) from reagent dissolved in 70 ml hot ethanol and added drop wise with stirring a stoiciometric amount (0.0025 mole) of 1:2 ratio (M:L) for Co(II) and Ni(II) chloride salt dissolved in 25 ml hot buffer solution (ammonium acetate) at optimal pH for each metal ions. The mixture was stirred and heated to 50 ºC for 40 min, then the solution left at room temperature for 24 hrs, the precipitate was filtrate off, washed with ethanol, distilled water and dried in a desiccator over anhydrous $CaCl_2$. The analytical and physical data for the synthesized reagent and their metal complexes are listed in table1.

Table.1: Physical properties and analysis of reagent and their metal complexes

No.	Compound	pH	Color	M P C°	Yield %	Molecular formula (M . wt)	Found (Cacl) %			
							C	H	N	M
1	LH	6.0	Dark brown	136	78	$C_{17}H_{10}N_4O_3S$ (350.35)	58.28 (58.16)	2.88 (2.97)	15.99 (15.84)	—
2	$[CoL_2]Cl.H_2O$	7.0	Green	237d.	71	$C_{34}H_{20}N_8O_7S_2CoCl$ (811.08)	50.35 (50.26)	2.48 (2.48)	13.81 (13.93)	7.26 (7.45)
3	$[NiL_2].H_2O$	8.5	Dark green	226	67	$C_{34}H_{20}N_8O_7S_2Ni$ (775.39)	52.67 52.80	2.60 (2.71)	14.45 (14.32)	7.57 (7.41)

LH = Reagent (α-NBTAN) ; d = complex melt with decomposition

2.4- Standard metal ions solutions

A solutions of Co(II) and Ni(II) (1000 ppm) were prepared by dissolving (0.4038 gm) of $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ in 100 ml of distilled water, working solutions prepared freshly by appropriate dilution of the stock solutions .

2.5- Standard reagent solution

In absolute ethanolic solution was prepared from the pure of reagent (α-NBTAN) (10^{-3} M) by dissolving (0.0087gm) in 25 ml of absolute ethanol. The stock solution of reagent were stable for several months if stored in amber bottle .

2.6- Buffer solution

0.01 M ammonium acetate (0.771 gm) was dissolved in 1 liter of distilled water. 0.2 M acetic acid and 0.2 M ammonium solution were used for pH adjustment .

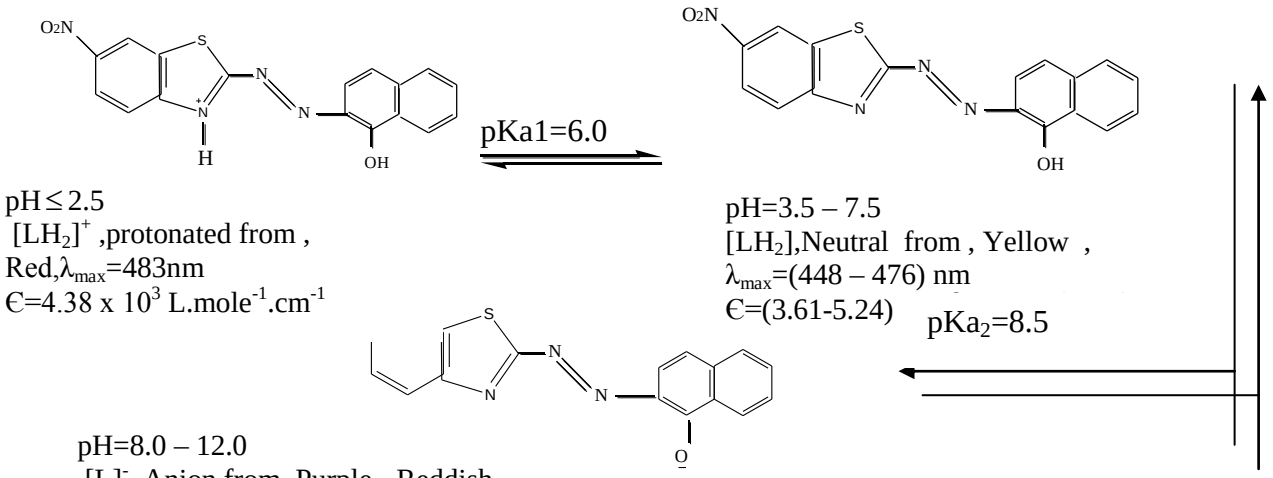
2.7- General procedure of Co(II) and Ni(II) ions

1 ml from each Co(II) and Ni(II) ions solutions (10 ppm) was mixed with (1–10 ml) (10^{-4} M) from (α-NBTAN) then diluted to 10 ml by buffer solutions at pH 7.0 and 8.5 for determination the concentration of the reagent also, 1 ml from each ions solutions (10 ppm) was mixed with the favored volume (6 ml) (10^{-4} M) from (α-NBTAN) to determination the stability of complexes with a period of time (10–60) min and temperature (10–70 ºC). Although , the ratio of ions to reagent were determined by using mole ratio and slop ratio methods. The calibration curves for Co(III) and Ni(II) solutions was determined by preparing (1–30), (1–25) ppm. at pH 7.0 and 8.5 respectively

3-Results and Discussion

3.1- Acid - base dissociation behavior

The reagent (α-NBTAN) and their complexes insoluble in water but soluble in organic solvent such as methanol, ethanol, acetone, chloroform and DMF. The reagent showed acid-base indicator properties and was red in strongly acidic solution, yellow in neutral solution but purple- reddish in strongly alkaline solution. Three species of the reagent, $[LH_2]^+$, [LH] and $[L]^-$ [14,15]. The pka values obtained by spectrophotometric method, and the dissociation of reagent (α-NBTAN) may formulate as follows :-



pH ≤ 2.5
$[LH_2]^+$,protonated from ,
Red,λ_{max}=483nm
Є=4.38 x 10^3 L.mole^{-1}.cm^{-1}

pH=3.5 – 7.5
$[LH_2]$,Neutral from , Yellow ,
λ_{max}=(448 – 476) nm
Є=(3.61-5.24)

pH=8.0 – 12.0
$[L]^-$,Anion from, Purple - Reddish ,
λ_{max}=(496 – 523) nm
Є=(5.87-6.94) x 10^3 L.mole^{-1}.cm^{-1}

3.2- Infrared spectra of reagent and complexes

The FTIR absorption bands of reagent (α-NBTAN = LH) and their complexes are summarized in table.2. These spectra are complicated due to the extensive overlap of a number of bands arising from υ (O–H), υ (C=N) and other bands originated from phenyl and thiazole rings appeared in the region below 1620 cm^{-1}. The shifts in the positions of those bands compared with those due to free reagent suggest the probable modes of bonding in the complexes. Some of these main shifts along with the conclusions are given below :-

1. The spectrum of the reagent shows a broad weak band around(3560–3590)cm^{-1} due to naptholic υ(O–H). This suggests a strong intermolecular hydrogen bonding[16–18]. In the spectra of Co(III)–Complex and Ni(II)–Complex the broad weak absorption band around 3630 cm^{-1} and 3580 cm^{-1} respectively indicates the presence of water in these complexes [19].
2. The weak bands observed at 3110 cm^{-1} and 2895 cm^{-1} in the spectrum of reagent which are due to υ (C–H) aromatic and aliphatic respectively. These bands are stable in position in both reagent and metal complexes.
3. Reagent spectrum show another band at 1610 cm^{-1}, which is considered to be υ (C=N) of thiazole ring[20]. This band was shifted to a lower frequencies 1590 cm^{-1} and 1595 cm^{-1} in the complexes spectra of Co(III) and Ni(II) respectively with a little change in shape in the spectra of its complexes. These differences suggest a linkage of metal ions with nitrogen of hetero cyclic thiazole ring [21].
4. Two absorption bands are observed at 1480 cm^{-1} and 1420 cm^{-1} in the reagent spectrum , which are due to the azo group υ (N=N). These bands shifted to a lower frequencies at (1465–1475) cm^{-1} and (1415–1425) cm^{-1} in the spectra of the prepared complexes Co(III) and Ni(II) respectively, which suggest coordination of this group to the metal ions[17, 21, 22] .
5. A band at 1225 cm^{-1} has also appeared in the reagent spectrum, this absorption band is due to υ (C–S) of thiazole ring [23]. The unchanged of this band in metal spectra complexes means that the sulfur atom of hetero cyclic ring does not participate in coordination[21].
6. The far infrared spectra of complexes showed a new bands in the region of (285–540) cm^{-1} which are not present in the spectrum of reagent may be attributed to υ (M–O) and υ (M–N) [24, 25]. Thus the above IR spectra data leads to suggest that the reagent behaves as a tridentate chelating agent coordinating through the position of naptholic oxygen ,nitrogen of azo group and thiazole ring nitrogen. Fig .2 shows the spectra of reagent (α-NBTAN) and $[CoL_2]Cl.H_2O$.

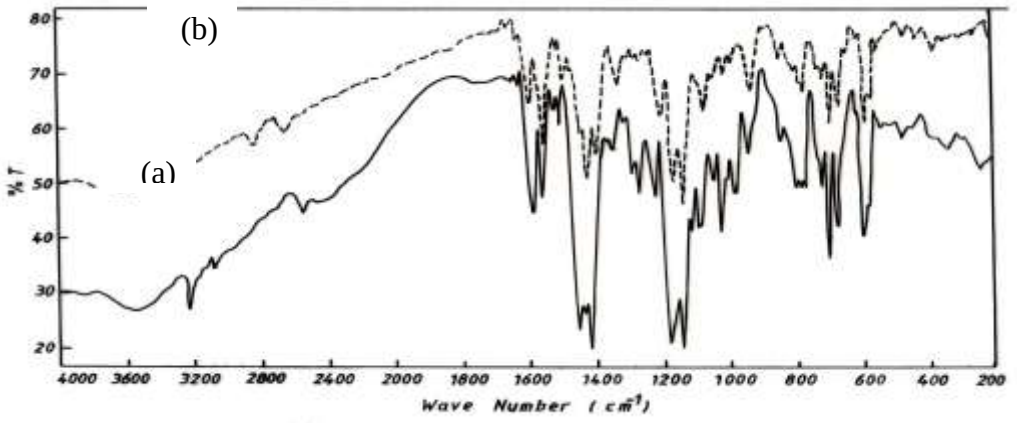


Fig.2: FTIR spectra of ;(a) the reagent(α-NBTAN) and (b)[CoL_2]Cl.H_2O

Table.2: FTIR absorption bands of the reagent and their complexes in cm $^{-1}$ units

Compound	υ (O – H)	υ (C = N)	υ (N = N)	υ (C – S)	υ (M – O)	υ (M – N)
LH	3560 w.br.	1610 m.	1480 m. 1420 ssh.	1225 m. 820 msh	___	____
[CoL_2]Cl.H_2O	3630 w.br.	1590 m.	1475 m. 1415 m.	1220 w. 815 w.	540 w.	320 w.
[NiL_2].H_2O	3580 w.br.	1595 S.	1465 m. 1425 m.	1225 m 820 m.	535 w.	285 w.

LH = reagent (α-NBTAN) , w = weak , m = medium , s = strong, sh = sholder, br = broad

3.3- Magnatic properties and electronic spectra

The magnetic moment values and electronic spectral data are listed in table 3**.**

3.3.1- Cobalt(III) complex

The magnetic moment of the Co(III) complex has been found to be diamagnetic and the low spin behavior of this complex indicates that Co(II) is oxidized to Co(III) during complexation. The change of the oxidation state agrees with earlier observation that the aqueous solution of Co(II) salts are spontaneously oxidized to Co(III) in the presence of strong reagent such as benzothiazolylazo compounds[21,26,27]. The electronic spectrum of this complex showed two absorption bands at 15898 cm^{-1}(υ_1) and 28571 cm^{-1}(υ_2) characteristic of octahedral stereo chemistry[26–28]. They were assigned to the transitions $^1A_1g \rightarrow {}^1T_1g$ (υ_1) and $^1A_1g \rightarrow {}^1T_2g$ (υ_2) respectively.

3.3.2. Nickel (II) complex

The value of magnetic moment for Ni(II) complex was found to be 3.27 B.M, which can be a normal value for octahedral high–spin Ni(II) complex. The electronic spectrum of Ni(II) complex showed three absorption bands at 10309 cm^{-1}, 16025 cm^{-1} and 31949 cm^{-1} corresponding to $^3A_2g \rightarrow {}^3T_2g$ (υ_1), $^3A_2g \rightarrow {}^3T_1g$ (F) (υ_2), and $^3A_2g \rightarrow {}^3T_1g$ (P) (υ_3), transitions with an octahedral spatial configuration[24, 25].

There were three absorption bands appear at the free reagent (α-NBTAN) spectrum those are appearing at the position, 41152 cm^{-1}, 35587 cm^{-1} and 21598 cm^{-1}, the bands 41152 cm^{-1} and 35587 cm^{-1} due to the $\pi \rightarrow \pi^*$ transitions while the band at 21598 cm^{-1} is due to the charge

transfer characters[29]. The electronic spectra of the reagent, and the metal complexes of Co(III) and Ni(II) ions in absolute ethanol solution are given in fig .3.

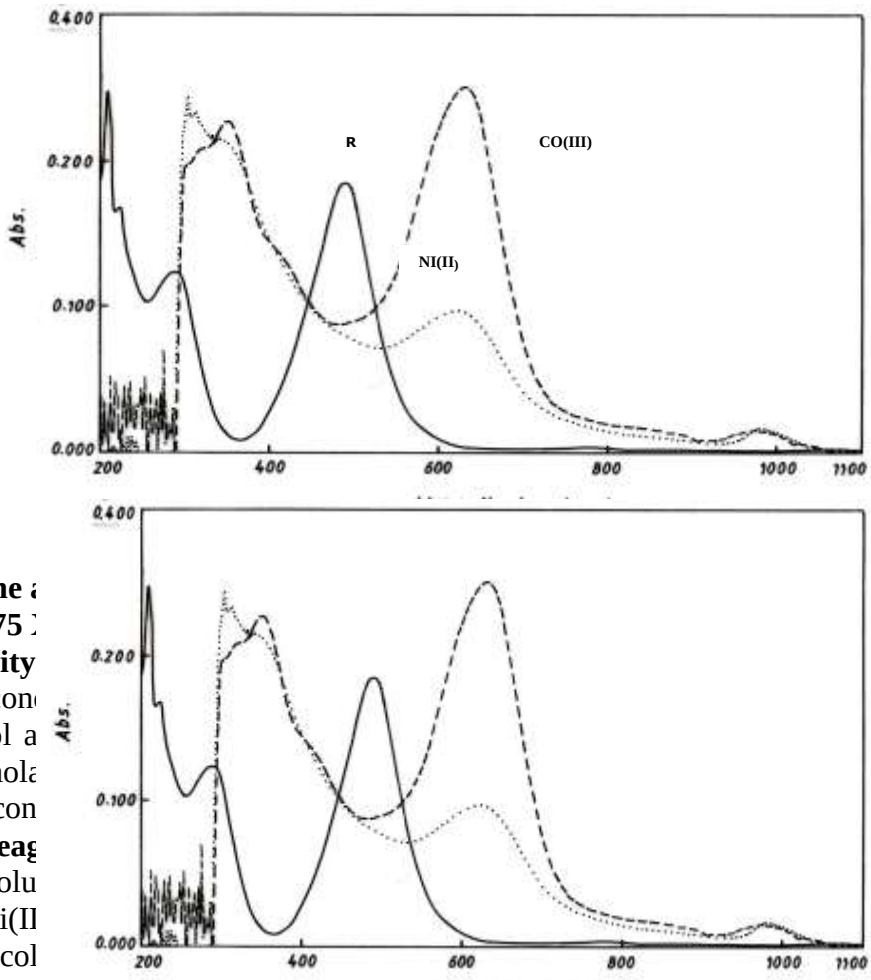


Fig. 3: The a **itable pH**
(1.75) AN)

3.4- Conductivity

The lower con ol^{-1}, table 3, in absolute ethanol a lectrolytes. But the value of mola e same solvent indicating non con

3.5- Effect of reag

Different volu affixed amount of Co(II) and Ni(II s found enough to develop the col onsidered to be optimum for the concentration range (1.00 x 10 M) of Co (II) and Ni (II) ions.

3.6- Effect of pH

The effect of pH value on the absorbance of the metal chelate solutions to determine the optimum pH in each case , the result are shown in fig.4. The optimal pH, optimal concentration and wavelength (λ_{max}) with molar absorpitivity (Є) of cobalt and nickel complexes are shown in table 4.

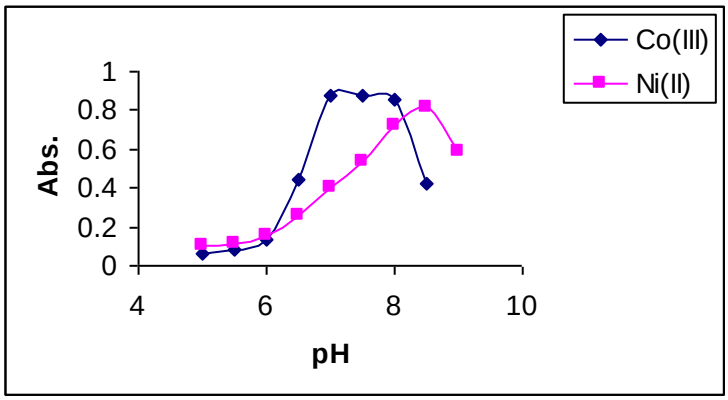


Fig. 4: Effect of pH on absorbance of (α-NBTAN) – metal chelates
Reagent conc . = 2 × 10^{-4} M ; Metal ion conc . = 1.25 × 10^{-4} M

3.7- Effect of time

It was found that the absorbance of the Co(III)– complex and Ni(II)– complex chromogenic system reaches a maximum value with in 10 min at room temperature and remains stable for at 24 hr, the result are shown in fig.5.

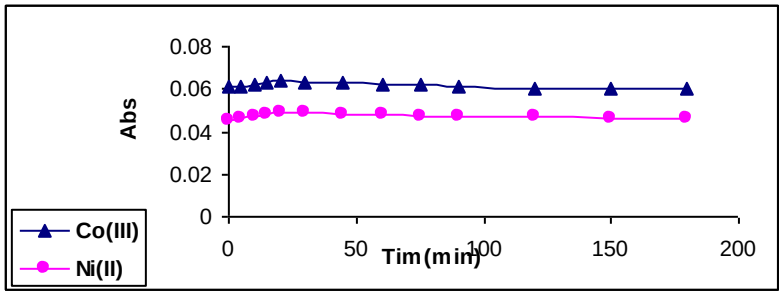


Fig. 5: Effect of time on the absorbance of Co(III)– complex and Ni(II)– complex

3.8- Effect of temperature

The effect of temperature on the absorbance of the Co(III)– complex and Ni(II)– complex were studied. The study was performed at temperature between 10 ºC and 70 ºC fig.6. The maximum absorption was obtained when the temperature was varied between 20 ºC and 30 ºC, at higher temperature than 30 ºCº the absorbance gradually decreased with increasing temperature until it reaches 80 ºC, which may be attributed to dissociation of the complexes.

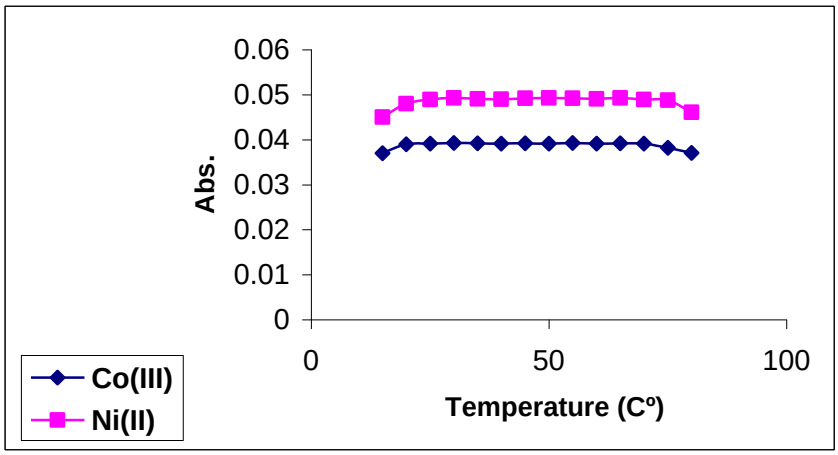


Fig. 6: Effect of temperature on the absorbance of Co(III) – complex and Ni(II) – complex

3.9- Composition and stability of complexes

The composition of the complexes was studied by mole ratio and slope ratio methods Both methods were showed that the mole ratio of Co(III)–complex and Ni(II)–complex are 1 : 2 (M : L) were obtained as shown in figs. 7 and 8. The stability constant are obtained spectrophotometrically by the mole ratio method. The degree of formation of the complexes are obtained from the relationship[31, 32], $\beta = (1 - \alpha) / (4 \alpha^3 c^2)$ and $\alpha = (A_m - A_s)/ A_m$ where A_s and A_m are the absorbance of the partially and fully formed complex respectively at optimum concentration. The calculated (β) and (log β) values for the prepared complexes are given in table 3.

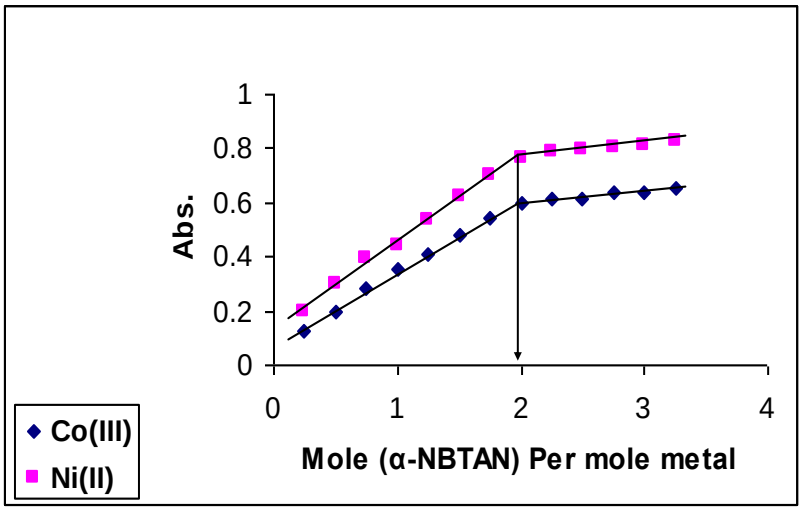


Fig. 7: Mole ratio (M : L) of (α-NBTAN) – metal chelats Co(III)– complex at pH = 7.0 ;Ni (II)– complex at pH = 8.5

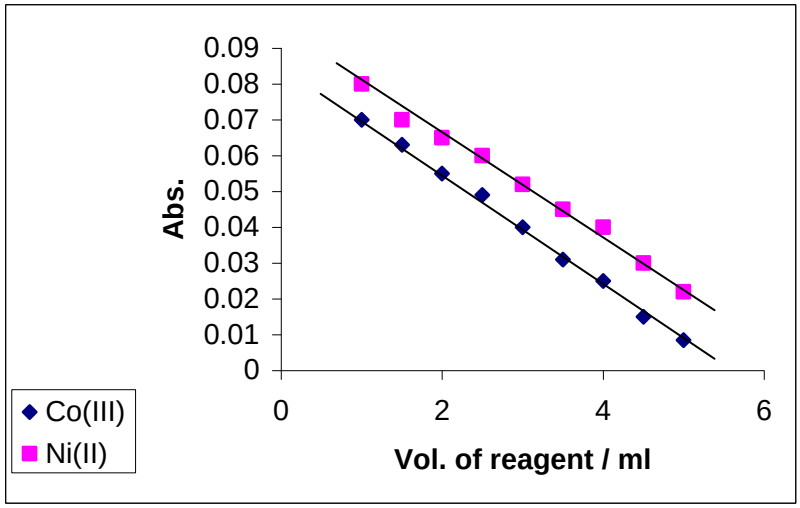


Fig. (8 A): Slope ratio of (α-NBTAN) – metal chelats Co (III)– complex at pH = 7.0 ;Ni (II) – complex at pH = 8.5

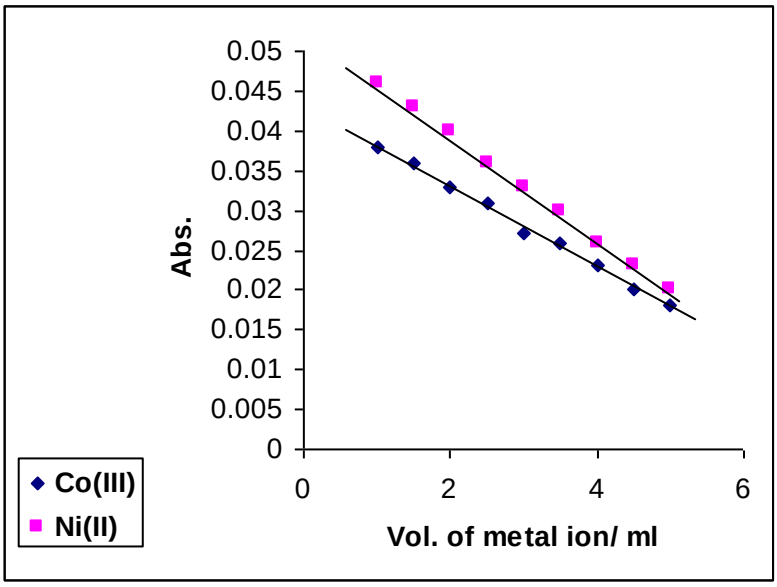


Fig. (8 B): Slope ratio of (α-NBTAN) – metal chelats Co (III) – complex at pH = 7.0 ;Ni (II) – complex at pH = 8.5

According to there results the structural formula of prepared complexes can be suggested and showing in fig. 9.

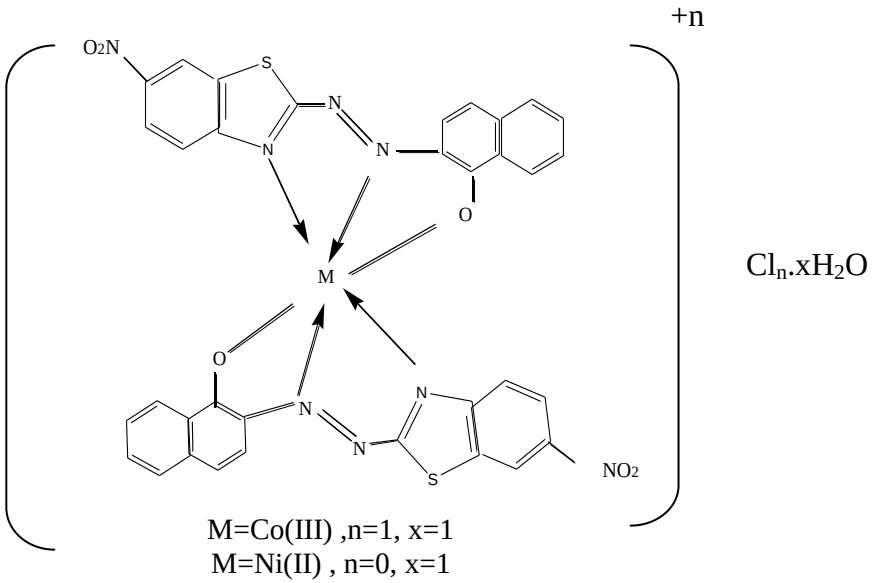


Fig. 9: The proposed structural formula of Co(III) and Ni(II) complexes

3.10- Calibration curve and sensitivity

The calibration curve was obey Beer's law Beer's law in the concentration (1–30) ppm and (1–25) ppm of Co(III)– complex and Ni(II)– complex respectively. The sandell sensitivity, relative error (%Re), percentage relative standard deviation (R.S.D%) and detection limit (D.L) for complexes were shown in table.5. These results indicate that this method is high accuracy and precision as shown in Fig .10.

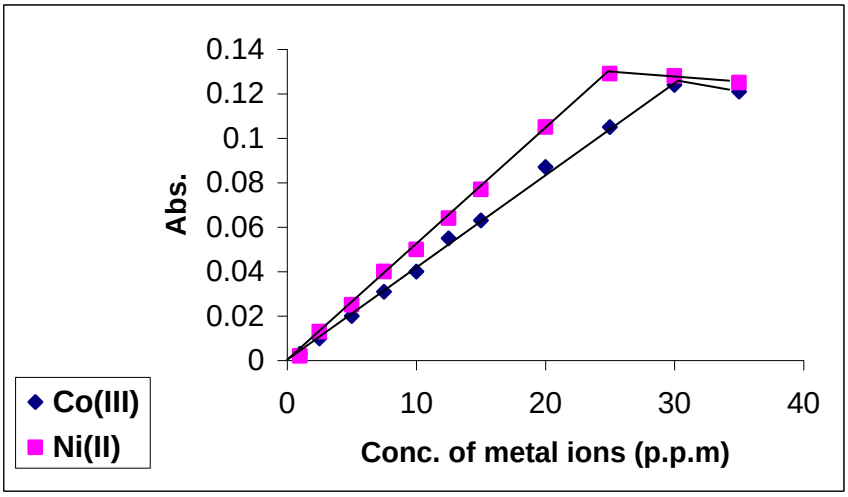


Fig. 10: Calibration curve of Co(II) and Ni (II) complexes

Table. 3: Electronic spectra, conductivity, magnetic moment data of complexes and the calculated stability constant values

Complex	Absorption bands (cm^{-1})	Transition	Conductivity S. cm^2. mol^{-1}	μeff (B.M)	β (mol^{-1}.L)	Log β
[CoL_2]Cl.H_2O	15898 28571	$^1A_1g \xrightarrow{\upsilon_1} {}^1T_1g$ $^1A_1g \xrightarrow{\upsilon_2} {}^1T_2g$	41.83	Dia	2.30 x 10^{11}	11.361
[NiL_2].H_2O	10309 16025 31949	$^3A_2g \xrightarrow{\upsilon_1} {}^3T_2g$ $^3A_2g \xrightarrow{\upsilon_2} {}^3T_1g(F)$ $^3A_2g \xrightarrow{\upsilon_3} {}^3T_1g(P)$	8.54	3.27	2.88 x 10^{11}	11.459

Table. 4: The optimal pH values, optimal concentration and wavelength (λ_{max}) with molar absorpitivity (Є) of metal ions in aqueous ethanol solution 50% (V / V)

Reagent	Metal ions	Optimal pH	Optimal conc.×10^{-4} M	Molar abosorptivity Є × 10^3 L.mol^{-1}. cm^{-1}	Optimal wave length (λ_{max}) n.m
(α–NBTAN) λ_{max} :=463 nm	Co (III)	7.0	1.25	2.51	629
	Ni (II)	8.5	1.75	1.03	625

Table. 5: The sandell's sensitivity, accuracy and precision of the method

Complex	Sandell's sensitivity	R.S.D %	Re %	D . L .	E_{rel} %	Sensitivity mg / L.
[CoL_2] Cl. H_2O	0.0016	1.16	98.57	0.237	1.42	2.40×10^{-3}
[NiL_2] . H_2O	0.0063	0.516	97.14	0.537	1.12	2.62×10^{-3}

Conclusion

The synthesis of reagent (α-NBTAN) is very simple. The reaction of reagent with Co(II) and Ni(II) ions which form water insoluble complexes can be easily dissolved in ethanol. The proposed method is more simple, rapid, selective and sensitive comparing with other methods used for determination of cobalt and Nickel ions in samples of different matrixes.

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