PREPARATION AND SPECTRAL CHARACTERIZATION OF NEW THIAZOLYL AZO LIGAND WITH SOME TRANSITION METAL Complexes

Khalid J. Al-Adely
Department of Chemistry, College of Science, University of Al-Qadisiya.

Abstract
Some transition metal complexes of Fe(III), Co(III), Ni(II), Cu(II), Zn(II) and Ag(I) with new benzothiazolylazo ligand 2-(6-nitro-2-benzothiazoylazo)-4-nitro phenol (6-NO₂BTAP = LH) were prepared and characterized by elemental analysis, magnetic susceptibility at room temperature, molar conductance measurements, infrared and electronic spectra. The isolated solid complexes are found to have the general formula [ML₂]Clₙ₋ₘH₂O, where n = 1, m = 1 when M = Fe(III), Co(II) and n = 0, m = 0 when M = Ni(II) and Cu(II) or [MLX]ₙH₂O when x = Cl, m = 1, M = Zn(II) and x = H₂O, m = 0, M = Ag(I). The electronic spectra and magnetic susceptibility data have supported the proposed octahedral geometry of Fe(III), Co(II), Ni(II) and Cu(II) complexes, but tetrahedral geometry of Zn(II) and Ag(I) complexes. The coordination number of all ions is found to be six, except of Zn(II) and Ag(I) which were found four, with bonding through the phenolate O, azo N and with thiazole N. The mole ratio method of the metal:ligand (M:L) has showed 1:2 for all the prepared complexes except of Zn(II) and Ag(I) complexes were found 1:1.

Introduction
Thiazolylazo phenols ligands and its derivatives are described as heterogenous compounds and investigated for many purposes.1-3 Thiazolyleazo and benzothiazolylazo dyes have attracted much attention as they are sensitive chromogenic reagents in addition to being important complexing agents.4-6 They have been used for spectrophotometric and extraction photometric determination of many metal ions.7-8 These dyes are applied for dyeing fibers9,10 and different biological industrial fields of life.11,12 The azo dyes give colored complexes with most metals, especially with some transition metal ions.13,14 Thiazolylazo molecule being a π-acidic azo imine group (−N=N=−C=N−) for this reason a number of these compounds were prepared as chelating ligands.15-18

This work describe the preparation and characterization of some transition metal complexes, using the new thiazolylazo ligand (6-NO₂BTAP).

Experimental
1- Materials and Instruments
All chemicals were of highest purity and used BDH, Aldrich and Fluk except of 2-amino-6-nitro benzothiazole was prepared as described in the literature.19

Electronic absorption spectra in the visible and ultraviolet regions were measured with a shimadzu UV-1650 spectrophotometer using ethanol as solvent. Infrared spectra were measured with FT-IR-8000 Shimadzu, in the 4000-400 cm⁻¹ range using CsI disc.

Atomic absorption spectrophotometer – AA-160 Shimadzu was used.

Elemental C.H.N analysis were carried out by Perkin–Elmer 2400 elemental analyzer. The magnetic susceptibility of the prepared complexes were obtained at room temperature using Farady method for this purpose; balance magnetic MSB-MI had been employed. The pH values were determined with a Philips PW 9421 pH meter (pH ± 0.001).

Electronic molar conductivity measurement were carried out at room temperature by conductivity bridge model Ec 219 with solute concentration (10⁻³ M) in DMF. Electro thermal melting point 9300 was used to measure the melting point of ligand and their complexes.

2. Preparation of ligand (6-NO₂BTAP)
The azo ligand (6-NO₂BTAP) was prepared by dissolving (1.95 gm, 0.01 mol) 2-amino-6-nitro benzothiazole in 50 ml of distilled water and 10 ml of concentrated hydrochloric acid. The filtered solution was cooled below 5°C. To this mixture a solution
of (0.75 gm, 0.01 mol) of sodium nitrate in 25 ml of distilled water was added dropwise at 0-5 °C and the mixture was stirred for 40 min. This diazonium chloride solution was added dropwise in 500 ml beaker containing (1.39 gm, 0.01 mol) of 4-nitro phenol dissolved in 200ml anhydrous ethanol and cooled to 0-50 °C. The mixture was stirred and heated to 50 °C for 4 hours, in ice-bath allowed to stand over night and acidified with dilute hydrochloric acid to pH =6.0. The precipitate crude dyes were collected by filtration and recrystallization from hot ethanol and dried in a vacuum desiccator over anhydrous CaCl₂. A dark red crystals melting at 102 °C. The preparation of this ligand is shown in Scheme (1).

![Scheme (1) Methods of preparation of the ligand 2-[(6-Nitro-2-benzothiazolyl)azo]-4- nitro phenol (6-NO₂BTAP=LH).](image)

3- Preparion of Complexes

The complexes were prepared by adding (0.345gm, 0.001 mol) of ligand (6-NO₂BTAP) dissolved in 50 ml hot anhydrous ethanol to a hot solution of metal chloride(0.0005 mol); FeCl₃,6H₂O, CoCl₂.6H₂O, NiCl₂.6H₂O and CuCl₂ while (0.001 mol) of ZnCl₂ and AgNO₃ dissolved in 30ml buffer solution (ammonium acetate) at optimal pH for each metal ions. The mixture was stirring and heated to 50 °C for 1 hr., then left overnight where the solid complexes precipitated. They were filtered off, washed with ethanol 10 ml to remove the remaining unreacted substances and dried in a desiccators over anhydrous CaCl₂.

3.1-Result and Discussion

1- Characterization of ligand and

The azo dye ligand (6-NO₂BTAP) was drak red crystals but the coordination complexes of this ligand with Fe(III),Co(II),Ni(II),Cu(II), Zn(II) and Ag(I) ions vary in color from purple, green and blue .The ligand and their solid complexes are stable in air ,insoluble in water but soluble in most organic solvents such as methanol ,ethanol ,acetone ,DMF and MSO. The result of elemental analysis and physical properties of prepared ligand and their complexes are given in Table (1).
Table (1)
Physical properties and analytical data of the ligand (6-NO₂BTAP=LH) and their complexes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Color</th>
<th>m.P C°</th>
<th>Yield %</th>
<th>Molecular formula (Mol.Wt)</th>
<th>Found (Calc.)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LH</td>
<td>Dark red</td>
<td>102</td>
<td>67</td>
<td>C₁₃H₁₂N₂O₅S (345.29)</td>
<td>45.31 (45.22)</td>
</tr>
<tr>
<td>2</td>
<td>[FeL₂]Cl·H₂O</td>
<td>Blue</td>
<td>167</td>
<td>73</td>
<td>C₂₆H₁₄N₁₀O₁₁S₂ClFe (797.87)</td>
<td>39.23 (39.14)</td>
</tr>
<tr>
<td>3</td>
<td>[CoL₂] Cl·H₂O</td>
<td>Purple</td>
<td>194</td>
<td>61</td>
<td>C₂₆H₁₄N₁₀O₁₁S₂ClCo (800.96)</td>
<td>38.87 (38.99)</td>
</tr>
<tr>
<td>4</td>
<td>[NiL₂]</td>
<td>Dark Purple</td>
<td>210 d.</td>
<td>58</td>
<td>C₂₆H₁₂N₁₀O₁₀S₂Ni (747.25)</td>
<td>41.87 (41.79)</td>
</tr>
<tr>
<td>5</td>
<td>[CuL₂]</td>
<td>Green</td>
<td>186</td>
<td>72</td>
<td>C₂₆H₁₂N₁₀O₁₀S₂Cu (752.10)</td>
<td>41.43 (41.52)</td>
</tr>
<tr>
<td>6</td>
<td>[ZnCl₂]Cl·H₂O</td>
<td>Purple</td>
<td>218 d.</td>
<td>65</td>
<td>C₁₃H₁₂N₁₀O₅SCLZn (463.13)</td>
<td>33.85 (33.72)</td>
</tr>
<tr>
<td>7</td>
<td>[AgL(H₂O)]</td>
<td>Purple Redash</td>
<td>148</td>
<td>53</td>
<td>C₁₃H₁₂N₁₀O₅S₂Ag (470.16)</td>
<td>33.08 (33.21)</td>
</tr>
</tbody>
</table>

**d** = decompose

2- Acid base dissociation behavior of the ligand

The ligand (6-NO₂BTAP) showed acid-base indicator properties and were red in strongly acidic, orange in neutral solution but Violet–Reddish in strong alkaline solution.

![Scheme (2) Acid–base dissociation behavior of ligand (6-NO₂BTAP).](image)

pH ≤ 2.5

[ LH⁺ ]⁺, protonated form, (strong acidic)
Red, λ max=493 nm
ε=5.96 x10³ L.mole⁻¹.cm⁻¹

pH = (3.5 - 7.5)

[ LH ], Natural form Orange
Orange, λ max=(453-462) nm
C= (7.07-10.65) x10³ L.mole⁻¹.cm⁻¹

pH = 8.0 - 12.0

[ LH ], Anion form, (strong alkaline)
Violet–Reddish, λ max = (521-537 nm)
ε=(6.37 – 9.48) x 10³ L.mole⁻¹.cm⁻¹
3- Infrared spectra

The infrared spectroscopic data of ligand and their complexes with Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Ag(I) are summarized in Table (2). These spectra are complicated owing to the extensive overlap of number of bands arising due to $\nu$(O–H), $\nu$(C= N), $\nu$(N= N) and other bands originate due to phenyl and thiazole rings appeared in the region below 1650 cm$^{-1}$, the comparison between spectra of the ligand with those of there coordination complexes have revealed certain characteristic:

1- The IR spectrum of ligand (6-NO$_2$BTAP) gives characteristic broad band at 3438 cm$^{-1}$ assigned to the phenolic $\nu$(O–H). This suggests a strong intermolecular hydrogen bonding (15,16). In the spectra of Fe(II), Co(II), Zn(II) and Ag(I) complexes show broad and weak bands around (3170-3417) cm$^{-1}$ indicate the presence of water molecule in these complexes (22-24). But this band was disappeared in the spectra of rest complexes.

2- This weak band had been observed at 3115 cm$^{-1}$ in the spectrum of the free ligand which was due to $\nu$(C–H) aromatic. This band was stable in position as well as in intensity in both ligand and metal complexes.

3- The spectrum of ligand shows absorption band at 1605 cm$^{-1}$ which is considered to be $\nu$(C= N) of thiazole ring (15,25). This band shifts to lower frequency (1550-1597) cm$^{-1}$ with a little change in shape in the metal complexes spectra. These different suggest the linkage of metal ion with nitrogen of hetrocyclic ring (23,26,27).

4- The azo group intens bands at 1519cm$^{-1}$ and 1345 cm$^{-1}$ are due to asymmetric and symmetri stretching vibrations of the $\equiv$N= N$\equiv$ group ,respectively (15). The band appearing at (1451-1493) cm$^{-1}$ and (1327-1350) cm$^{-1}$ respectively with some decrease in intensity of metal complexes spectra. Both band shift and reduced in intensity may indicate that azo group is coordinated to the metal ions to the formation complexes (27,28).

5- The $\nu$(C–S) of thiazole ring appear at 1248 cm$^{-1}$ and 854 cm$^{-1}$ in the spectrum of free ligand. this band unchanged in all complexes means that the sulfur atom of hetero cyclic ring does not participate in coordination (23,26,29,30).

6- The presence of coordinated water molecule in the Ag(I) complexes is further indicated by weak bands at 763 cm$^{-1}$ and 732 cm$^{-1}$.

7- New weak bands in the region (420-563) cm$^{-1}$ which are never been observed in the free ligand spectrum this may attributed to $\nu$(M–O), $\nu$(M–N) and $\nu$(M–Cl) bands (27,31,32).

The IR spectra data lead to suggest that ligand behaves as tridentate chelating agent coordinating through the positions of phenolic oxygen, nitrogen of azo group and thiazole ring nitrogen. Representative example for their spectra are given in Figs. (1-4).
Fig. (1) : IR spectrum of the ligand (6-NO₂BTAP=LH).

Fig. (2) : IR spectrum of the complex [FeL₂]Cl.H₂O.

Fig. (3) : IR spectrum of the complex [ZnLCl].H₂O.
Fig. (4) : IR spectrum of the complex [AgL(H₂O)].

**Table (2)**

Selected IR absorption bands of the ligand (6-NO₂BTAP) and their complexes in cm⁻¹ units (CsI disc).

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>v(O–H)</th>
<th>v(C=N)</th>
<th>v(N=N)</th>
<th>v(C–S)</th>
<th>v(M–OH₂)</th>
<th>v(M–O)</th>
<th>v(M–N)</th>
<th>v(M–Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LH</td>
<td>3438 w.br.</td>
<td>1605 m</td>
<td>1519 m.</td>
<td>1345 s.</td>
<td>1248 w.</td>
<td>854 m.</td>
<td>——</td>
<td>——</td>
</tr>
<tr>
<td>2</td>
<td>[FeL₂]ClH₂O</td>
<td>3170 w.br.</td>
<td>1597 s.</td>
<td>1480 m.</td>
<td>1340 w.</td>
<td>1252 m.</td>
<td>850 m.</td>
<td>——</td>
<td>535 w.</td>
</tr>
<tr>
<td>3</td>
<td>[CoL₂]ClH₂O</td>
<td>3235 w.br.</td>
<td>1578 s.</td>
<td>1485 S.</td>
<td>1335 w.</td>
<td>1247 m.</td>
<td>855 w.</td>
<td>——</td>
<td>540 w.</td>
</tr>
<tr>
<td>4</td>
<td>[NiL₂]</td>
<td>——</td>
<td>1583 m.</td>
<td>1470 m.</td>
<td>1327 w.</td>
<td>1250 m.</td>
<td>851 m.</td>
<td>——</td>
<td>557 w.</td>
</tr>
<tr>
<td>5</td>
<td>[CuL₂]</td>
<td>——</td>
<td>1595 s.</td>
<td>1487 S.</td>
<td>1345 m.</td>
<td>1248 w.</td>
<td>851 m.</td>
<td>——</td>
<td>545 w.</td>
</tr>
<tr>
<td>6</td>
<td>[ZnLCl].H₂O</td>
<td>3350 w.br.</td>
<td>1593 s.</td>
<td>1493 m.</td>
<td>1342 m.</td>
<td>1247 m.</td>
<td>850 s.</td>
<td>——</td>
<td>553 w.</td>
</tr>
<tr>
<td>7</td>
<td>[AgL(H₂O)]</td>
<td>3417 w.br.</td>
<td>1550 m.</td>
<td>1451 m.</td>
<td>1350 w.</td>
<td>1265 w.</td>
<td>857 m.</td>
<td>763 w.</td>
<td>732 w.</td>
</tr>
</tbody>
</table>

LH= ligand(6-NO₂BTAP),
W=weak,
S=strange,
m= medium,
br=broad,
sh= shoulder.
4-Absorption spectra

The absorption spectra of ligand (6-NO_2BTAP) and their complexes with Fe(III), Co(III), Ni(II), Cu(II), Zn(II), and Ag(I) ions were studied in an aqueous ethanolic solution 50% (V/V). The absorption maxima (λ max) of the free ligand is 457 nm.

A bathochromic shift ranging between (46-256) nm depending on the metal ion. The absorption spectra of the free ligand and their complexes are shown in Figs. (5 and 6).

Fig. (5): The absorption spectra of free ligand (LH) and their complexes in a suitable pH; Conc.=(1.75-2.50) x 10^{-4} M in aqueous ethanolic solution 50% (V/V); LH=(6-NO_2BTAP).

Fig. (6): The absorption spectra of free ligand (LH) and their complexes in a suitable pH; Conc.=(1.25-1.75) x 10^{-4} M in aqueous ethanolic solution 50% (V/V); LH=(6-NO_2BTAP).
5-Magnetic susceptibility measurements

Magnetic susceptibility for all metal complexes were measured except Zn(II) and Ag(I) complexes due to the configuration d^{10} gave ($\mu_{\text{eff}}=0.0\text{B.M}$) these complexes have diamagnetic moment. The other metal complex showed the following values of magnetic moment in Table (3).

1- Iron (III) complex absorbed magnetic moment value of $\mu_{\text{eff}}=1.83\;\text{B.M}$ which suggest a low spin octahedral geometry ($t_{2g}\; e\; g$)\textsuperscript{(33)}.

2- The magnetic moment of the cobalt(II) complex gave a value of $\mu_{\text{eff}}=0.0\text{B.M}$ because the low spin behavior of this complex indicates that Co(II) is oxidized to Co(III) during complexation to produce a diamagnetic properties and octahedral geometry($t_{2g}\; e\; g$). The change of the oxidation state agrees with earlier absorption that the aqueous solution of Co(II)salts are spontaneously oxidized to Co(III) in the presence of strong ligand such as thiazolylazo compounds\textsuperscript{(23,26)}.

3- Nickel(II) complex showed a magnetic moment value of $\mu_{\text{eff}}=2.97\;\text{B.M}$ which can be a normal value for octahedral geometry high-spin($t_{2g}\; e\; g$)\textsuperscript{(23,33)}.

4- Copper(II) complex gave a value of magnetic moment $\mu_{\text{eff}}=1.76\;\text{B.M}$ which suggest the presence of one unpaired electron in this complex and that suggest octahedral geometry ($t_{2g}\; e\; g$)\textsuperscript{(34)}.

6-Electronic Spectra

The prepared free ligand (6-NO\textsubscript{2}BTAP), three absorption bands were detected, first and second bands located at 264 nm (37879 cm\textsuperscript{-1}) and 296 nm (33784 cm\textsuperscript{-1}) respectively referring to the $\pi\to\pi^*$ transitions while the third band located at 457 nm (21882 cm\textsuperscript{-1}) is due to the charge transfer characters\textsuperscript{(16,27,40)}. For the spectra of metal complexes the following results were obtained:

1- Iron(III) Complex

The electronic spectrum of Fe(III)-complex showed three bands at 979 nm (10214 cm\textsuperscript{-1}), 713 nm (14025 cm\textsuperscript{-1}) and 536 nm (18657 cm\textsuperscript{-1}) attributed to $A_1 \to T_1\; g(G)$, $A_1 \to T_2\; g(E)$

And

$A_1 \to T_1\; g(P)$

transitions respectively. These bands suggest low spin octahedral geometry\textsuperscript{(37)} and that agree with the value of magnetic moment (1.83 B.M).

2- Cobalt(III) Complex

The Cobalt(III) complex, two bands were observed at 561 nm (17825 cm\textsuperscript{-1}) and 306 nm (32680 cm\textsuperscript{-1}) corresponding to $A_1 \to T_1\; g(G)$

And

$A_1 \to T_2\; g(E)$

transitions respectively. The complex was found to be diamagnetic behavior of this complex indicates that Co(III) is oxidized to Co(III) during complication. These result with (0.0 B.M) suggest a low spin octahedral geometry\textsuperscript{(23,38)}.

3- Nickel (II) Complex:

The electronic spectrum of this complex showed a three bands at 973 nm (10277 cm\textsuperscript{-1}), 559 nm (17889 cm\textsuperscript{-1}) and 440 nm (22727 cm\textsuperscript{-1}) attributed to $A_2 \to T_2\; g(F)$, $A_2 \to T_1\; g(F)$

And

$A_2 \to T_1\; g(P)$

transitions with an octahedral geometry\textsuperscript{(23,35,39)}.

4- Copper (II) Complex

The electronic spectrum of Cu(II) complex show abroad band at around 637(15698 cm\textsuperscript{-1}) due to $E\; g\to T_2\; g$ transition. It is reasonable to assign distorted octahedral structure\textsuperscript{(16,27,40)}.

5-Zinc(II) and Silver(I) Complexes

The electronic spectra of these complexes do not show any d-d transition band. The spectral data and magnetic moments are listed in Table (3).
7-Molar conductivity measurements
The molar conductivity were measured for all complexes using DMF as a solvent with the concentration of 10^{-3} M at room temperature. Most complexes showed no or very weak conductance which means non ionic nature\(^{(16,17,41)}\). But the lower conductivity values for the Fe(III) and Co (III) complexes appeared to be a good electrolyte 1:1 with ionic nature Table (3) and that was approved by using a solution of silver nitrate and a white colloidal precipitate of silver chloride obtained.

8-Calculation of the metal complexes stability constant (β)
Stability constants of all complexes prepared are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelength (λ max) and pH values.

The degree of formation of the complexes is obtained from the relationship\(^{(42)}\), β=\((1-\alpha)/(\alpha^2c)\) for Ag(І) and Zn(II) complex (1:1=M:L), but β=\((1-\alpha)/(4\alpha^2c^2)\), for remaining metal complexes (1:2=M:L), and α =A_m – A_s /A_m , where A_m and A_s are the absorbance of the partially and fully formed complex respectively at optimum concentration.

The calculated log β values for the prepared complexes are given in Table (3). The stability constants follows the sequence Cu(II)>Co(III)>Fe(III)>Ni(II)>Ag(I)>Zn(II). The high stability constant of ligand (6-NO_2 BTAP) toward Cu(II) is remarkable over the other ions. This implies a considerably higher affinity toward this ion.

<table>
<thead>
<tr>
<th>No.</th>
<th>Complexes</th>
<th>λmax n.m</th>
<th>Absorption bands v cm(^{-1})</th>
<th>Transition</th>
<th>Conductivity S.mol(^{-1}).cm(^2)μ</th>
<th>μeff (B.M)</th>
<th>β L(^2).Mol(^{-2})</th>
<th>Logβ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[FeL(_2)]Cl.H(_2)O</td>
<td>979</td>
<td>10214</td>
<td>(^{4}A_1) g (\rightarrow)(^{4}T_1)g(G)</td>
<td>85.31</td>
<td>1.83</td>
<td>4.266x10(^9)</td>
<td>9.630</td>
</tr>
<tr>
<td></td>
<td></td>
<td>713</td>
<td>14025</td>
<td>(^{4}A_1) g (\rightarrow)(^{4}Eg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>536</td>
<td>18657</td>
<td>(^{4}A_1) g (\rightarrow)(^{4}T_1)g(P)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>[CoL(_2)] Cl.H(_2)O</td>
<td>561</td>
<td>17825</td>
<td>(^{1}A_1) g (\rightarrow)(^{1}T_1)g(G)</td>
<td>79.53</td>
<td>dia</td>
<td>5.364x10(^9)</td>
<td>9.729</td>
</tr>
<tr>
<td></td>
<td></td>
<td>306</td>
<td>32680</td>
<td>(^{1}A_1) g (\rightarrow)(^{1}T_2)g(G)</td>
<td></td>
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</tr>
<tr>
<td>3</td>
<td>[NiL(_2)]</td>
<td>973</td>
<td>10277</td>
<td>(^{3}A_2) g (\rightarrow)(^{3}T_2)g(F)</td>
<td>9.25</td>
<td>2.97</td>
<td>1.583x10(^9)</td>
<td>9.199</td>
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<tr>
<td></td>
<td></td>
<td>559</td>
<td>17889</td>
<td>(^{3}A_2) g (\rightarrow)(^{3}T_1)g(F)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>440</td>
<td>22727</td>
<td>(^{3}A_2) g (\rightarrow)(^{3}T_1)g(P)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>[CuL(_2)]</td>
<td>637</td>
<td>15698</td>
<td>(^{2}Eg) (\rightarrow)(^{2}T_2)g</td>
<td>8.12</td>
<td>1.76</td>
<td>8.992 x 10(^6)</td>
<td>10.953</td>
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<tr>
<td>5</td>
<td>[ZnLCl].H(_2)O</td>
<td>529</td>
<td>—</td>
<td>—</td>
<td>7.53</td>
<td>(0)dia</td>
<td>7.095 x 10(^5)</td>
<td>5.850</td>
</tr>
<tr>
<td>6</td>
<td>[AgL(H(_2)O)]</td>
<td>503</td>
<td>—</td>
<td>—</td>
<td>5.93</td>
<td>(0)dia</td>
<td>8.394 x 10(^5)</td>
<td>5.924</td>
</tr>
</tbody>
</table>
To evaluate optimal pH values on the absorbance for the metal complexes solution were studied in the 50% (V/V) ethanolic solution as shown in Figs. (7 and 8). The ligand (6-NO₂BTAP) formed a very stable complex with metal ions Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Ag(I) a wide pH range.

The absorption spectra did not change over the whole range. The optimal pH, optimal concentration and wavelength (λmax) with molar absorptivity (ε) of Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Ag(I) complexes are shown in Table (4).

### Table (4)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Metal Ions</th>
<th>Optimal pH</th>
<th>Optimal molar conc. ( \times 10^{-4} ) M</th>
<th>Metal: ligand</th>
<th>Molar absorptivity ( (\varepsilon) \times 10^{3} ) L.mol⁻¹.cm⁻¹</th>
<th>Optimal wavelength (λmax) nm</th>
<th>( \Delta \lambda_{a max} ) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-NO₂BTAP, ( \lambda_{max}=457 \text{ nm} ) ( \varepsilon=2.41 \times 10^{3} ) L.mol⁻¹.cm⁻¹</td>
<td>Fe(III)</td>
<td>7.5</td>
<td>1.75</td>
<td>1:2</td>
<td>1.15</td>
<td>713</td>
<td>256</td>
</tr>
<tr>
<td></td>
<td>Co(II)</td>
<td>7.0</td>
<td>2.50</td>
<td>1:2</td>
<td>1.72</td>
<td>561</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>Ni(II)</td>
<td>8.0</td>
<td>2.25</td>
<td>1:2</td>
<td>1.6</td>
<td>559</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>Cu(II)</td>
<td>7.5</td>
<td>1.5</td>
<td>1:2</td>
<td>0.64</td>
<td>637</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>Zn(II)</td>
<td>8.5</td>
<td>1.25</td>
<td>1:1</td>
<td>0.86</td>
<td>529</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>Ag(I)</td>
<td>6.5</td>
<td>1.75</td>
<td>1:1</td>
<td>0.35</td>
<td>503</td>
<td>46</td>
</tr>
</tbody>
</table>

### 10. Effect of time

The effect of time on the absorbance of the metal complexes were studied in ethanolic solution maximum value within 10 min at room temperature and remains stable for about 24 hour. The result are shown in Figs. (9 and 10).
11- Effect of temperature

The effect of temperature on the absorbance of the metal complex were studied Figs.(11 and 12) show this effect the study was performed at temperature at the range (10-70) °C and the maximum absorption was obtained when the temperature was varied between 10 °C and 30 °C at temperature higher than 30 °C the absorbance gradually decreased with increasing temperature until it reaches 70 °C which may be due to dissociation of the metal complexes.

These results are in agreement with values reported for some thiazolylazo phenol complexes.\(^{16,17,21,23,27}\)

12- Metal :Ligand Ratios

The metal :ligand ratios(M:L) of complexes were determined by the method of molar ratio at the wavelength of maximum absorption ,molar concentration and fixed pH in aqueous ethanolic solution50% (V/V). The result are summarized in Table (4).

The ligand (6-NO\(_2\)BTAP) was found to from 1:2 (M:L) chelates with all metal ions except of Zn(II) and Ag(I) complexes was found 1:1 chelates as shown in Figs.(13 & 14).

According to these results the structural formula of prepared complexes in this work may be proposed composition of the complexes in the following Figs.(15, 16 and 17).
Fig. (15) : The proposed structural formula of Fe(III), Co(III), Ni(II), and Cu(II) complexes.

Fig. (16) : The proposed structural formula of Zn(n) complex.

Fig. (17) : The proposed structural formula of Ag(I) complex.
13-Conclusions
The preparation of ligand (6-NO2BTAP) and their complexes are simple. After combining all the physical measurement, the following molecular formula for Fe(III), Co(II), Ni(II) and Cu(II) complexes, but tetrahedral for Zn(II) and Ag(I) complexes. Stability constants refer to the high stability of all complexes. These complexes under optimum conditions are stable to more than 24 hours.

14-References


[39] Mohamed G. G, Nadia Gamel and Teixider, F, "Complexes of 2-(2-benzimidazolyl azo)-4-Acetamido phenol, O.phenol diazenyl-containing ligand could this be aMoiety for Zn
الخلاصـة

تم تحضير بعض معقدات العناصر الانتقالية لأيونات الحديد (II) والنيكل (II) والناحاس (III) والكولوت (IV) المحمض على النحو التالي:

1. 

我々これらの化合物を用いた実験によると、これらの化合物が化学的に安定であることが示唆され、それらの応用が期待される。

2. 

我々の研究では、これらの化合物が化学的に安定であることが示唆され、それらの応用が期待される。