

Physical Studies of BTZ Azo Naphthoic Acid And Its Complexes with Heavy Metal Ions

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Abstract

A new heterocyclic azo compound, 1 - [2 - (6 - methyl benzothiazolyl) azo] - 2 - hydroxy - 3 - naphthoic acid, (6 - Me BTANA), was synthesized to use it as analytical reagent in complexing reactions. Its ionization constants were obtained spectrophotometrically and potentiometrically. The stability constants of the ions (Ni^{2+} , Pd^{2+} , Pt^{2+} , Pt^{4+}) complexes have determined spectro ophotometrically at 25°C in ethanol-water mixture 20% by volume. The molar conductivity of these complexes have determined in its alcoholic solutions, also the magnetic susceptibility of the solid complexes of this reagent with above ions have determined. Spectro photometric studies such as IR and Uv.Visb. were used to determine the molecular formulas of the ligand and complexes. Finally, structural formulas of the complexes were suggested.



—	%20	25	(Pt ⁴⁺ , Pt ²⁺ , Pd ²⁺ , Ni ²⁺)
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Uv.Visb. IR

Introduction

Many organic reagents have been synthesizing and using as photometric reagents in analytical chemistry ^(1,3). They have good ability to coordinate with many metal ions ⁽⁴⁾. Others are recommended as metal indicators such as EDTA ⁽⁵⁾. These reagents have high selectivity, high molecular weight,

strong colores and high dissolution in organic solvents⁽⁶⁾

In analytical chemistry^(7,8), these reagents have ability to form coordination complexes with high selectivity and high sensitivity such as DMG which is used as a reagent to detect and evaluate Ni⁽⁹⁾ and alizarine to detect and evaluate Al⁽⁶⁾.

In clinical chemistry , these reagents use as inhibitors for many metal ions in human body ⁽⁸⁾ , while many metal ions have important role in human metabolism such as Fe , Co and Mg. ^(10,11)

There are two types of these ligands :

1- Homocyclic azo compounds , such as HPAP ⁽¹²⁾

2- Heterocyclic azo compounds , such as PAN ⁽¹³⁾

Our ligand belongs to the second type and it classifies as a tridentate ligand ^(14,15).

Material

Substance	Formula	Company	Purity
Bromin water	Br ₂	B.D.H	98%
Ethenol	C ₂ H ₅ OH	B.D.H	98%
Sodium nitrite	NaNO ₂	Merck	99%
Paratoluidine	C ₇ H ₉ N	B.D.H	99%
Nickel nitrate	N ₂ (NO ₃) ₂ H ₂ O	B.D.H	99%
Paladium nitrate	Pd(NO ₃) ₂ .2H ₂ O	B.D.H	99%
Hexa Chloro Platonic Acid	H ₂ PtCl ₆	B.D.H	99%
2- Hydroxy 3-Naphthoic Acid	C ₁₁ H ₈ O ₃	B.D.H	90%

Apparatus

The electronic spectra and absarbanes were determind on a cintra 5 GBC-Uv.Visb. spectrophotometer , IR analysis was carried out by testscan Shimadzu in frarad spectrophotometer , while the pH measurement were carried out by a Bechman pH meter. The molar conductivity measurements were carried out by a digital conductivity meter (Alpha-800) , while the magnetic susceptibility measurments were carried out by a magnetic susceptibility balance (MSB-MK1).

Experimental

1- Preparation of the primary material (2-amino-6-methy benzothiazol) :

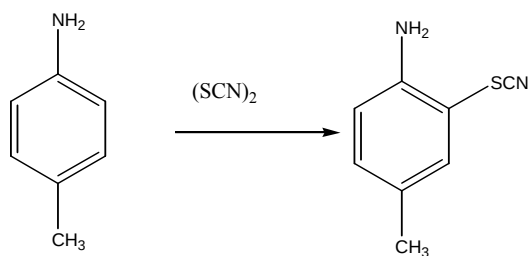
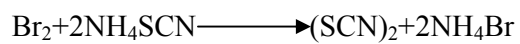
It was synthesized from paratoluidine and amonium thiocyanate as it was described previously . ⁽¹⁶⁻¹⁷⁾

2- Preparation of 6-MeBTANA : It was synthesized by cauplling diazotised 2-

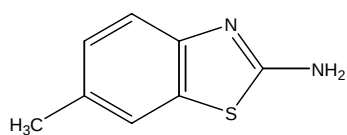
amino -6-methyl benzo thiazol with 2-hydroxy - 3 - naphthoic acid in an ethanolic solution at 20-40°C as it was described previously. ^(18,19) Its m.p.=190-192°C

It was identified by IR and Uv.Visb.spectroscopy. Its percentage yield was 72%. It has a red color with molar extinction coefficient $E=1.07 \times 10^3 \text{ L.mol}^{-1}\text{cm}^{-1}$ at wavelength max. = 460 nm. Scheme 1shows all these reactions .

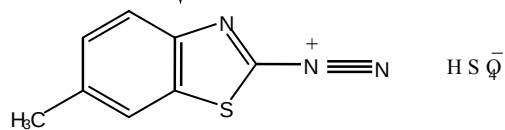
The electronic spectra of the ligand and its complexes are shown in figer 1. IR analysis is shown in table 6 .



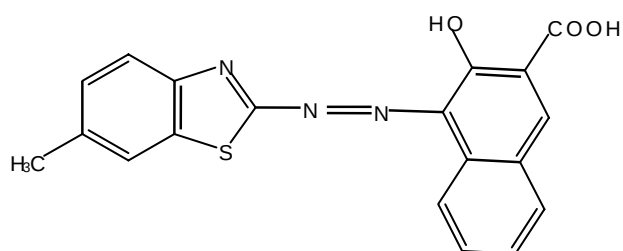
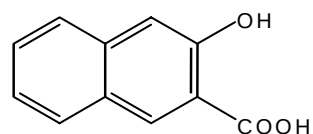
NaOH



NaNO_2
 H^+



HS^-

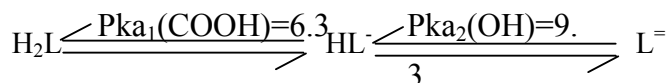


6-MeBATNA

Determination of acid dissociation constants of the ligand :^(20,21)

The acid dissociation constants determined by both the potentiometric and spectrophotometric methods in 20% aqueous ethanolic solution at

25°C , the ionic strength of the mixture was adjusted with 0.1M sodium nitrate solution . The results are shown in table 4. The proton dissociation constants , scheme of 6-Me BTANA (H₂L) were found to be



Determination of the stability constants of the complexes :^(22,23)

The stability constants of the metal-6-MeBTANA complexes were determined spectrophotometrically by

using the mole ratio and the job methods .

Table 1 shows the stability constants for the complexes under study.

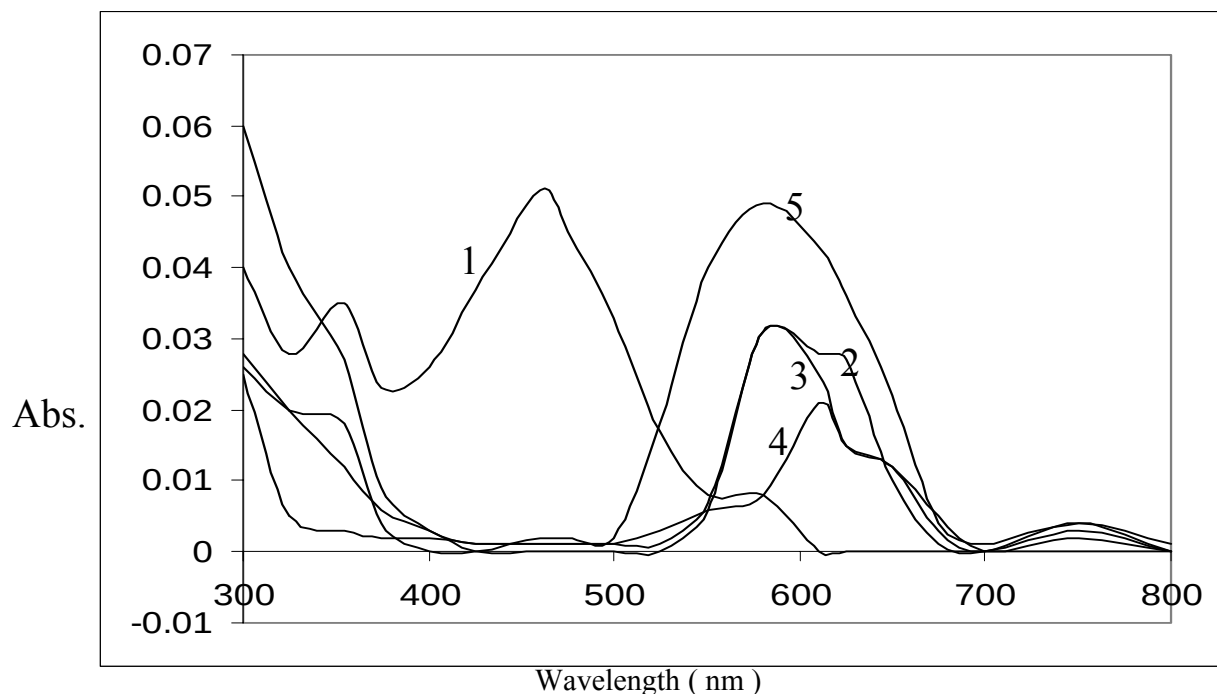


Fig. 1: Absorption spectra of , 1. 6-MeBTANA , 2. Ni⁺² + 6 -MeBTANA, 3. Pd⁺² + 6-MeBTANA, 4. Pt⁺² + 6 - MeBTANA, 5.Pt⁺⁴ + 6 -MeBTANA, all concentration 5* 10⁻⁵M.

Table 1:stability constants for the metal ionic complexes

Metal Ion Comp.	α	Ksta	logKsta.
[Ni(HL) ₂]	0.011	$6.6 \times 10^{13} \text{ L}^2 \cdot \text{Mol}^{-2}$	13.8
[Pd(HL) (H ₂ O)] NO ₃	0.018	$5.9 \times 10^7 \text{ L} \cdot \text{Mol}^{-1}$	7.7
[Pt(HL) (H ₂ O)] NO ₃	0.015	$8.4 \times 10^7 \text{ L} \cdot \text{Mol}^{-1}$	7.9
[Pt(HL) ₂] Cl ₂	0.023	$8.1 \times 10^{12} \text{ L}^2 \cdot \text{Mol}^{-2}$	12.9

Determination of Molar Conductivity of Complexes : (24)

The molar Conductivity was measured for the ligand and complexes

solution ($10^{-3}M$) $25^{\circ}C$ in ethanol and diformamide solvents , the results are listed in table 2.

Table2 :Molar conductivity for the ionic complexes solution ($10^{-3}M$) in ethanol and DMF.

Complexes	($S.mol^{-1} cm^2$) in Δm Ethanol	($S. mol^{-1} cm^2$) in Δm DMF
[Ni(HL) ₂]	2	5
[Pd(HL) (H ₂ O)] NO ₃	34	65
[Pt(HL) (H ₂ O)] NO ₃	33	64
[Pt(HL) ₂] Cl ₂	71	137

Determination of Magnetic Properties of Complexes : (25)

The magnetic properties were measured for the complexes according

to Gouy method . The results are listed in table 3.

Table 3 : Effective magnetic momentum for the prepared complexes in $25^{\circ}C$.

Complex	eff. (BM) μ
[Ni(HL) ₂]	3.13
[Pd(HL) (H ₂ O)] NO ₃	0.70
[Pt(HL) (H ₂ O)] NO ₃	0.80
[Pt(HL) ₂] Cl ₂	1.06

Result and Discussion

The ionization constants (pK_{a1}, pK_{a2}) of the COOH and OH groups of 6-

MeBTANA is found to be 6.2 and 9.2 , while those of the similar ligands are reported in table4 .

Table 4 : comparison of pKa values for the prepared ligand with similar ligands .

Ligand	pKa ₁	pKa ₂	Ref.
6- Me BTANA	6.2 pot . 6.5 Spe .	9.2 pot . 9.5 spe .	This work
B- BTANA	5.8 pot.	7.0 pot .	26
BTANA	----	8.5 pot .	27

The former values are significantly higher than the latter might due to the effects of CH₃ group which is an electron donating group in the sixth position of the benzothiazol ring leads to increasing the basicity of the ligand

because this group is a strong electron donating group . Inter molecular hydrogen bonding plays a well known role in the complexing properties of (6-MeBTANA) chelating might occur during OH, azo group and N of

heterocyclic ring. The stability constants ($\log K_{sta.}$) of the complexes (Ni^{+2} , Pd^{+2} , Pt^{+2} , Pt^{+4}) are 13.8, 7.7, 7.9, and 12.9 respectively. This values

are relatively high, and similar to many azo complexes as shown in table(5)

Table 5: compartion of $\log K_{sta.}$ values for the prepared complexes with similar complexes.

Complexes	Log Ksta.	Ref.
$Ni^{+2}+6-MeBTANA$	13.8	This work
$Pd^{+2}+6-MeBTANA$	7.7	=
$Pt^{+2}+6-MeBTANA$	7.9	=
$Pt^{+4}+6-MeBTANA$	12.9	=
$Ni^{+2}+B.BTANA$	9.05	(26)
$Ni^{+2}+5-MeBTANB$	10.89	(21)
$Pd^{+2}+5-MeBTANB$	6.88	(21)
$Pt^{+2}+TRA$	12.00	(28)

IR spectrum for both ligand and its complexes inducts that there is binding, modifying and shifting in the peaks and their intensities of the ligand rather than these for its complexes. The shape of the complexes are shown in scheme (2) and table (6) listed the results obtained from IR studies. (29,30)

Molar conductivity results show that Ni^{+2} complex hasn't electrolyt feature, while the others have, these results are due to the charges present. Magnetic susceptibility results show that Ni^{+2} complex is paramagnetic while the other are diamagnetic

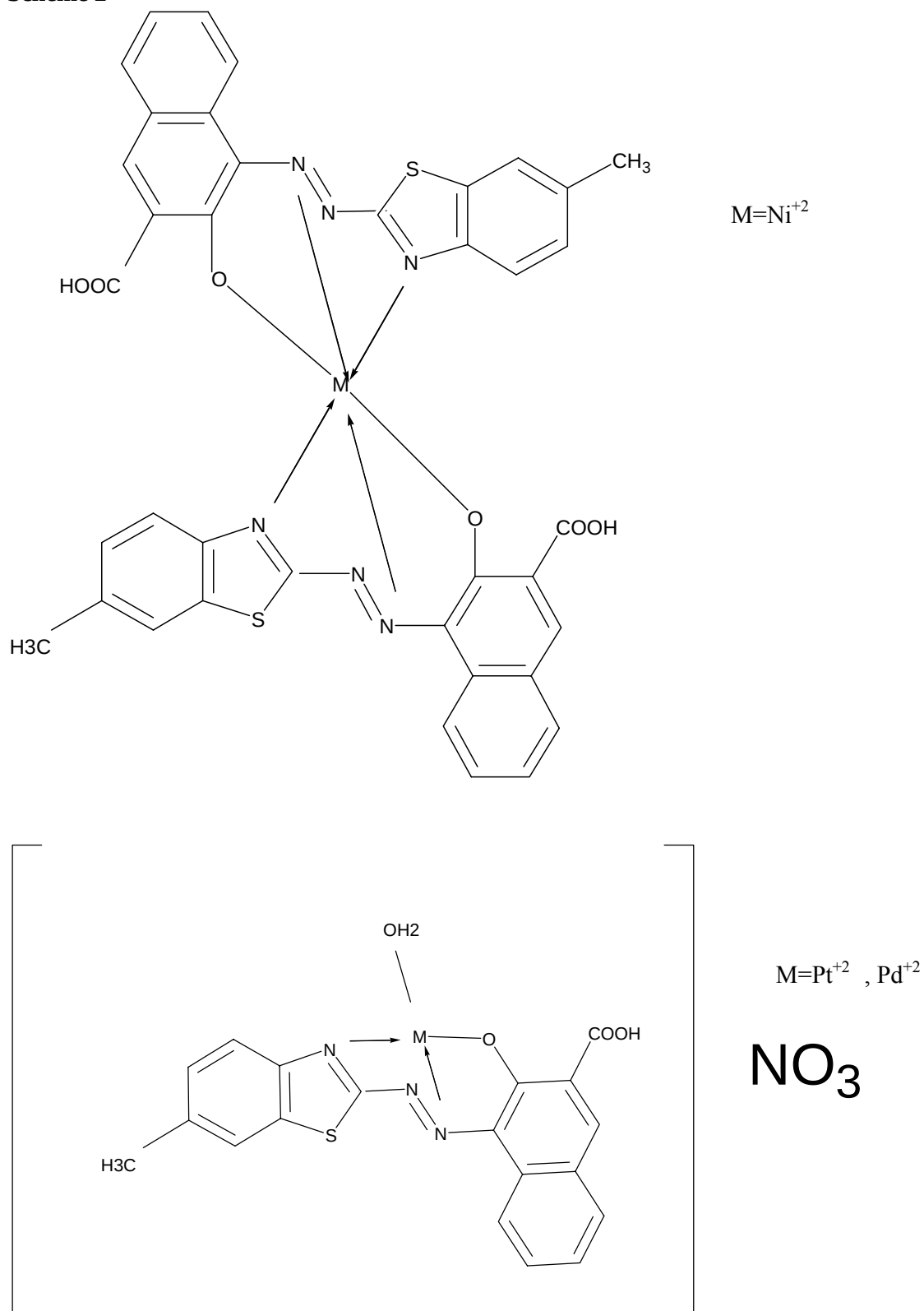
Table 6: IR spectral frequencies for the ligand 6-MeBTANA and the complexes

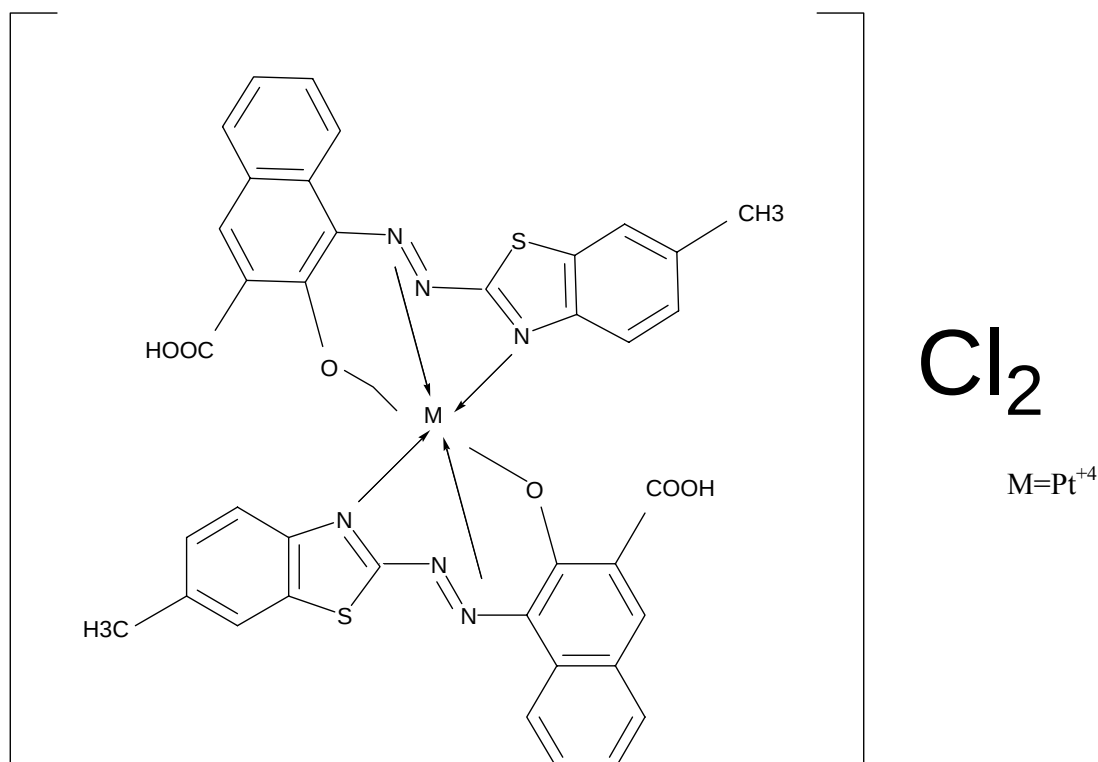
Bond	Ligand	$Ni^{(II)}$ Comp.	$Pd^{(II)}$ Comp.	$Pt^{(II)}$ Comp.	$Pt^{(IV)}$ Comp.
ν (OH)	3300 s	-	3300 br	3300 br	3300 w
ν (NH)	3090 m	3090 w	3090 br	3090 w	3090 w
ν (C=O)	1670 s	1670 s	1670 s	1670 s	1670 s
ν (C=N)	1630m.sh	1600 w	1620 s	1600 w	1630 w.sh
ν (C=C)	1520 m	1520 m	1520 m	1520 w	1520 m
ν (N=N)	1480 s	1460 s	1470 m	1470 w	1470 s
ν (=N-N=)	1442s.sh	-	1440 m	1400 w	1400 m
ν (C-S)	1257 m	1257 w	1257 w	1257 m	1257 w
(C-N) ν	1350 m 950 m	1400 w 950 w	1400 w 1050 m	1450 w 1100 m	1400 w 975 w
ν (M - O)	-	450 w	435 W	430 s	425 M
ν (M - N)	-	475 s	475 S	475 m	475 s

s = strong, w = weak, m = medium

ν = very, sh = shoulder, br = broad

Scheme 2





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