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 analy tical 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 .

الخلاصة

تم تحضير المركب1- [2- (6 - مثيل بنزوثيا زوليل) ازو] - 2 - هايدروكسي - 3 - حامض النفثويك (6-Me BTANA) وهو مركب جديد من نوع مركبات الازو ذات الحلقة غير المتجانسة ويمكن أستخدامه ككاشف تحليلي في التفاعلات التعقيدية . وتم تعيين ثوابت التأين له طيفياً وجهدياً وكذلك تعيين ثوابت الاستقرارية لمعقداته مع الايونات الانتقالية (Ni^{2+},Pd^{2+},Pt^{2+},Pt^{4+}) طيفياً في درجة 25° م في خليط 20% من الماء – الايثانول وتم تعيين التوصيلية المولارية لهذه المعقدات في محاليلها الكحولية وعينت أيضاً الحساسية المغناطيسية للمعقدات الصلبة لهذا الكاشف مع الايونات أعلاه . أستخدمت دراسات طيفية مثل IR و Uv.Visb. لتعيين الصيغة الجزيئية لليكاند ومعقداته .وأخيراً إقترحنا الصيغ التركيبية لهذه المعقدات المحضرة .

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 from coordination complexes with high selectivity and high sensitivity such as DMG which is uses 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_2H_5OH	B.D.H	98%
Sodium nitrite	$NaNO_2$	Merck	99%
Paratoluidine	C_7H_9N	B.D.H	99%
Nickel nitrate	$N_2(NO_3)_2H_2O$	B.D.H	99%
Paladium nitrate	$Pd(NO_3)_2.2H_2O$	B.D.H	99%
Hexa Chloro Platonic Acid	H_2PtCl_6	B.D.H	99%
2- Hydroxy 3- Naphthoic Acid	$C_{11}H_8O_3$	B.D.H	90%

Apparatus

The electronic spectra and absarbances 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

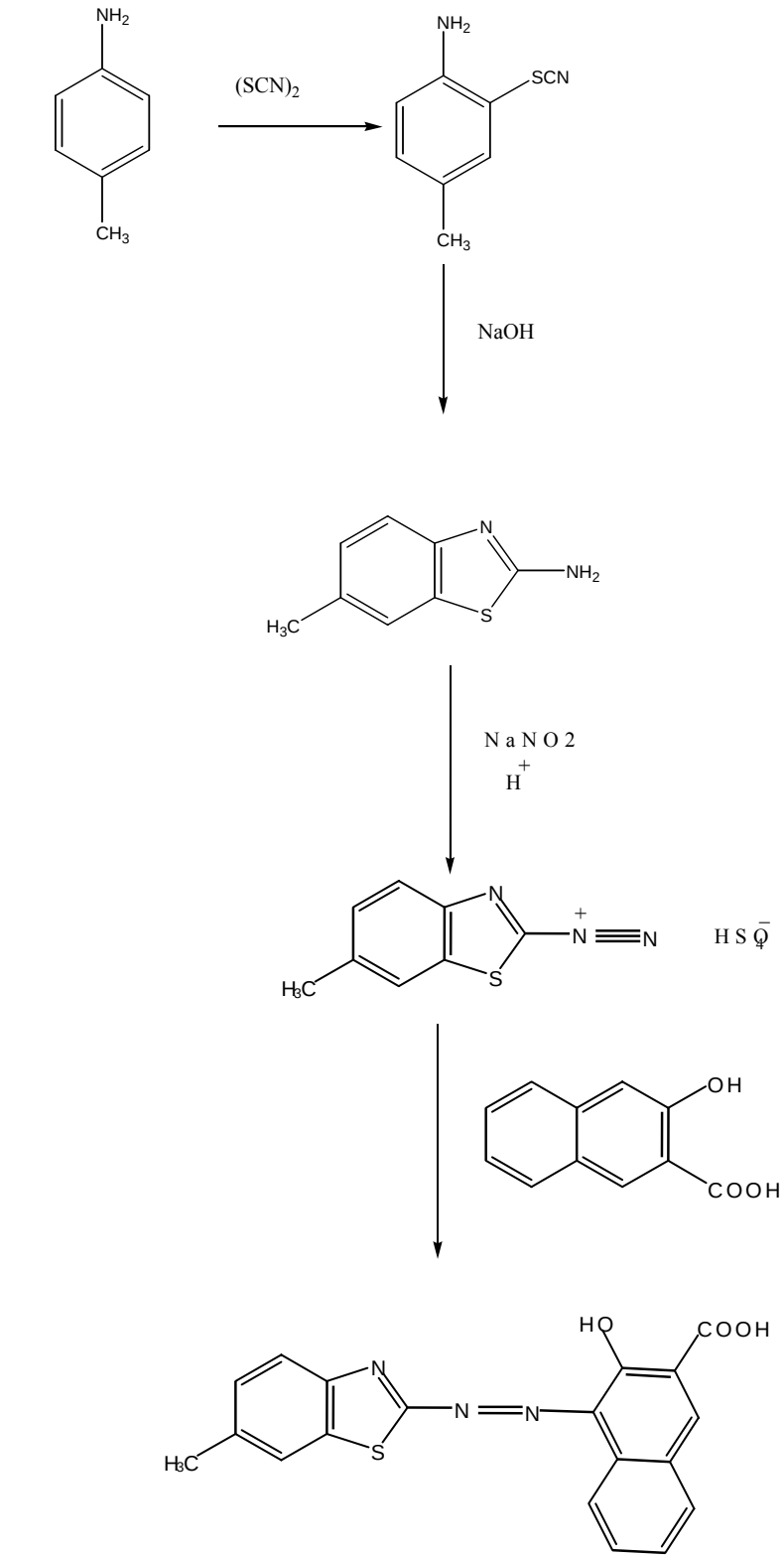
1- Preparation of the primary material (2-amino-6-methy benzothiazol) :

It was synthesized from paratoludine and amonium thiocyanate as it was described previously . [16-17]

2- Preparation of 6-MeBTANA : It was sunthesized 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 $E=1.07\times10^3$ $L.mol^{-1}cm^{-1}$ 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 .


Br2+2NH4SCN⟶(SCN)2+2NH4Br
NH2
CH3
(SCN)2
NH2
SCN
CH3
NaOH
N
NH2
S
H3C
N a N O 2
H+
N
+
N ≡ N
H S Q−
S
H3C
OH
COOH
HO
COOH
N
N ═ N
S
H3C

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 strenght of the mixture was adjusted with 0.1M sodium nitrate solution . The results are shown in table 4. The proton dissciation constants , scheme of 6-Me BTANA (H_2L) were found to be

$$H_2L \xrightarrow{Pka_1(COOH)=6.3} HL^- \xrightarrow{Pka_2(OH)=9.3} L^=$$

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.

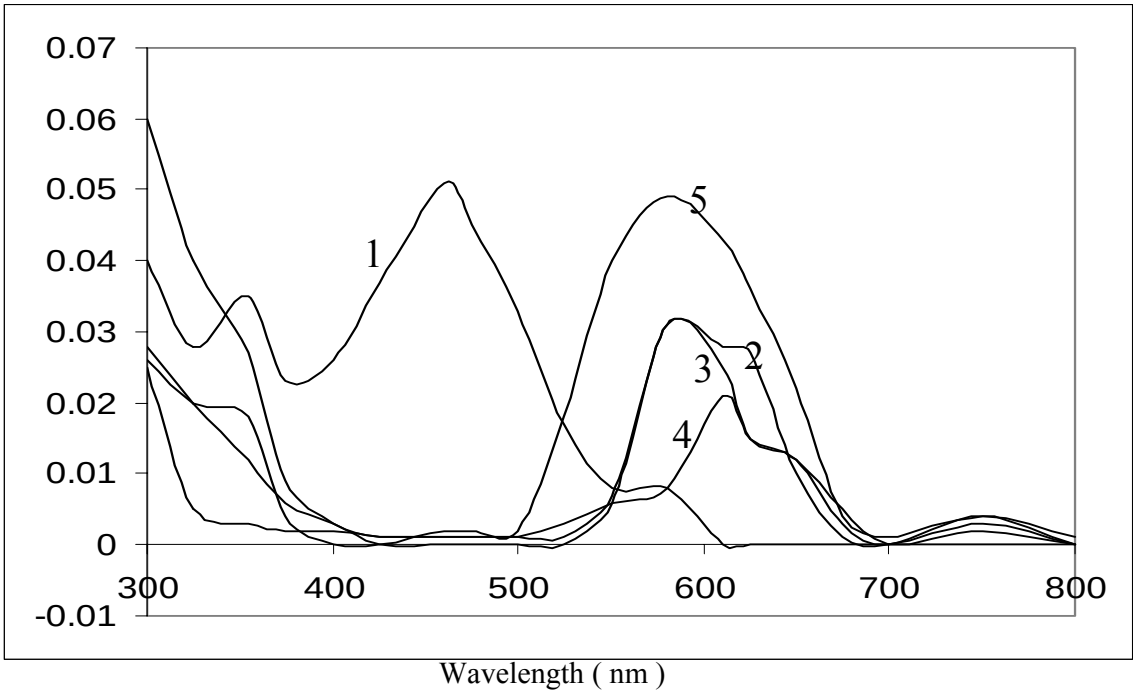


Fig. 1: Absorption spectra of , 1. 6-MeBTANA , 2. Ni^{+2} + 6 -MeBTANA, 3. Pd^{+2} + 6-MeBTANA, 4. Pt^{+2} + 6 - MeBTANA, 5.Pt^{+4} + 6 -MeBTANA, all concentration 5* 10^{-5}M.

Table 1:stability constants for the metal ionic complexes

Metal Ion Comp.	α	Ksta	logKsta.
$[Ni(HL)_2]$	0.011	6.6×10^{13} $L^2.Mol^{-2}$	13.8
$[Pd(HL)(H_2O)]NO_3$	0.018	5.9×10^{7} $L.Mol^{-1}$	7.7
$[Pt(HL)(H_2O)]NO_3$	0.015	8.4×10^{7} $L.Mol^{-1}$	7.9
$[Pt(HL)_2]Cl_2$	0.023	8.1×10^{12} $L^2.Mol^{-2}$	12.9

Determination of Molar Conductivity of Complexes : (24)

The molar Conductivity was measured for the ligand and complexes solution (10^{-3}M) 25°c in ethanol and diformanide 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 Λm Ethanol	(S. mol^{-1} cm^2) in Λm DMF
$[Ni(HL)_2]$	2	5
$[Pd(HL)(H_2O)]NO_3$	34	65
$[Pt(HL)(H_2O)]NO_3$	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 momentun for the prepared complexes in 25°C .

Complex	$_{eff.}$ (BM) μ
$[Ni(HL)_2]$	3.13
$[Pd(HL)(H_2O)]NO_3$	0.70
$[Pt(HL)(H_2O)]NO_3$	0.80
$[Pt(HL)_2]Cl_2$	1.06

Result and Discussion

The ionization constants (pka_1,pka_2) of the COOH and OH groups of 6-MeBTANA is found to be 6.2 and 9.2 , while thouse of the similar ligands are reported in table4 .

Table 4 : comportion 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 higer than the latters might due to the effects of CH_3 group which is an electron donating group in the sixth position of the benzothiazol ring leads to increasing the basicityof the ligand because this group is a strong electron donating group . Inter molecular hydrogen bonding plays a will known rule in the complexing properties of (6-MeBTANA) chelating might occure during OH, azo group and N of

heterocyclic ring. The stability constants (1logKsta.) 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 Ksta. 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]

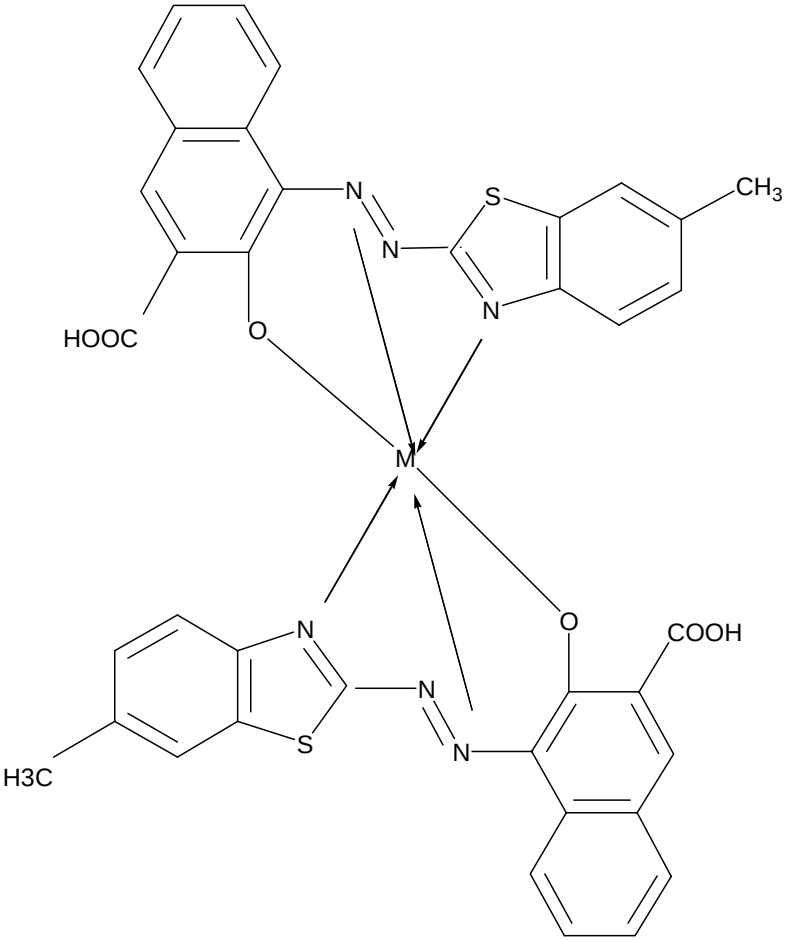
Molar conductivity results show that Ni^{+2} complex hasn't electrolyt feature, while the others have, these results are due to the charges present. Magnetic susceptibility results show that Ni^{+2} complex is paramagnetic while the other are diamagnetic

Table 6: IR spectral frequencies for the ligand 6-MeBTANAand the complexes

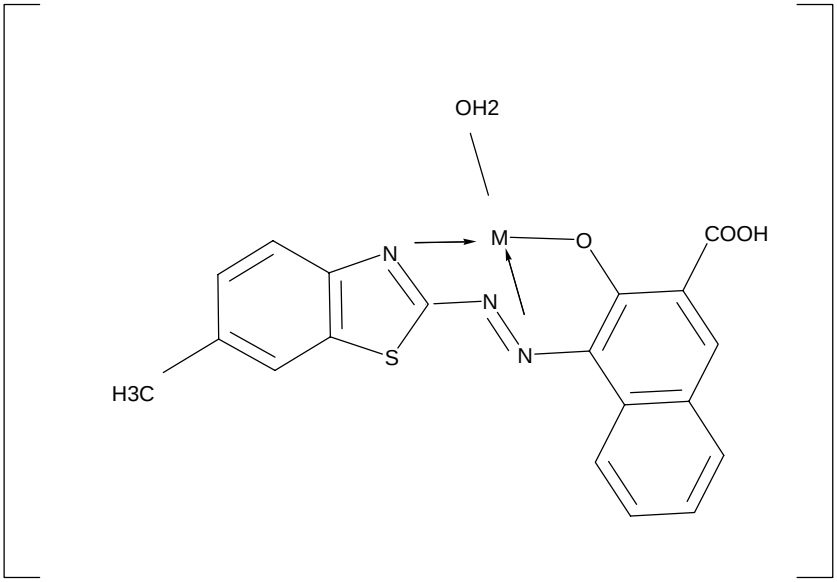
Bond	Ligand	$Ni^{(II)}$ Comp.	$Pd^{(II)}$ Comp.	$Pt^{(II)}$ Comp.	$Pt^{(IV)}$ Comp.
ν **(OH)**	3300 s	-	3300 br	3300 br	3300 w
ν **(NH)**	3090 m	3090 w	3090 br	3090 w	3090 w
ν **(C=O)**	1670 s	1670 s	1670 s	1670 s	1670 s
ν **(C=N)**	1630m.sh	1600 w	1620 s	1600 w	1630 w.sh
ν **(C=C)**	1520 m	1520 m	1520 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
v = very , sh = shoulder , br = broad

Scheme 2

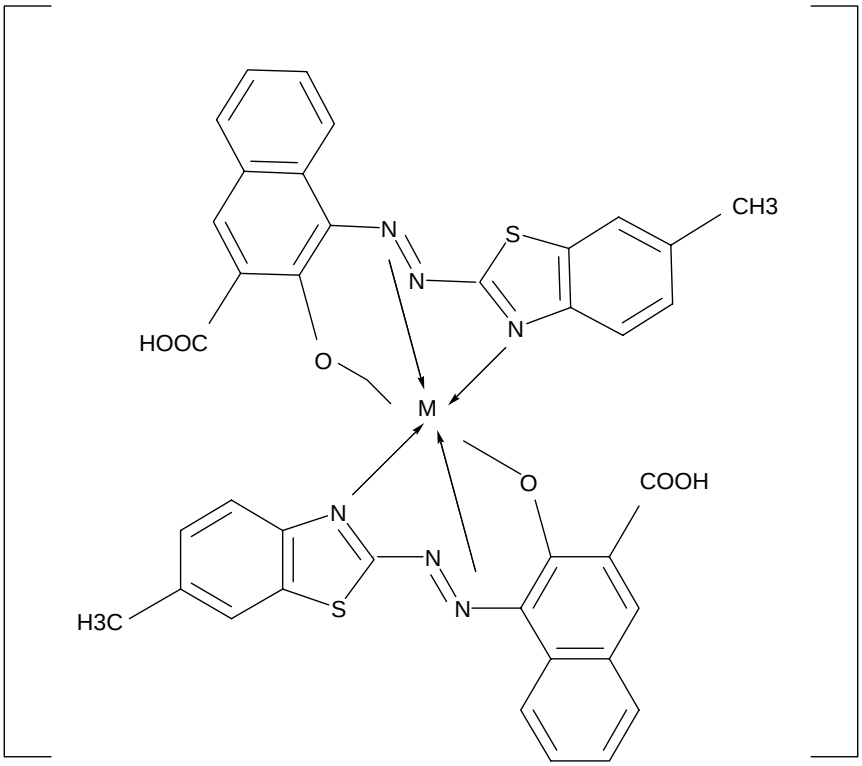


$M=Ni^{+2}$



$M=Pt^{+2}$, Pd^{+2}

NO_3



Cl_2

$M=Pt^{+4}$

References

1-L.Sieron and M.B. Strzyewska, ***Acta Cryst.*** **,**1999, **55** , 169.

2- B.M.Alsaadi, ***Acta Chem..Scand .*** **,**1982, **36** , 137.

3- T.Poand G.H.Nancollas , ***Inorg.Chem.,*** 1972, **11**, 2414.

4- A.Al-Kadhumi . H.A.Saleh, J.M. Abdula and F.N.Al-Obaidi,***J. of the College of Eduction, Salahaddin University,***1990, **2 ,** 121.

5- K.L.Cheng, ***Anal. Chem .,*** 1955, **27**,15872.

6- J.F.Flagg,***Organic Reagents Used in Gravimetric and Volumetric Analys***, New York , Interscience Publishers , Inc. (1948).

7- T.Yotsuyanagi , H.Hoshino and K.Aomura***, Anal. Chem., Acta,*** 1974, **71**, 349 .

8- N.S.A.Al-Nuaimy. ***Natio .J.of Chem .,***2002, **5,** 1.

9- H.F.Walton , ***Princuples and Methods of Chemical Analysis 2nd Ed .,*** Prentice –Hall , Inc . (1964).

10- F .A . Cotton and G . Wilkinson **,** ***Basic Inorganic Chemistry*** , John Wiley and Sons , Inc . (1976).

11- R . K Murray , D . K . Granner , p . A . Mayes and V . W . Rodwell **,** ***Harper's Biochemistry*** , Appleton and Lange (1993).

12 - G . W . Latlmer and j . R **.** ***Talanta*** **,**1968, **15 ,** 1.

13 - B . F . Peaseand M . B . Willams , ***Anal . Chem . ,*** 1959, **31** , 1044 .

14 - I . Mellan , ***Organic Reagent in Inorganic Analysis*** , Blakiston philadelphia , (1940) .

15 - H Diehl **,** ***Chem .,Rvs . ,***1937, **21** , 39.

16 - A . S . Hamad , K . M . Al-Janabi and H . J . Fawzi , ***Tikrit*** J **.** ***for pure Science ,*** 2003, **9** , 228.

17- R . Q . Brewester and F . B . Dains , ***J . Amer . Chem . Soc .,*** 1936, **58 ,** 1364 .

18 - S . Sibata , M . Furukawa and K . Toei , ***Anal . Chem . Acta . ,*** 1973, **66 ,** 397.

19 -P By abrtta , S . Pal , T . K . Misra , C . Sinha , F . Liao , K . Panneerselvam and T . H . Lu , ***J . Coord . Chem . ,***2002, **55 ,** 479.
20 - K . G . Al-Adely and F . H . Hussein **,** ***Natio . J . of Chem . ,*** 2001, **1 ,** 87.
21 -X . Fan , G . Zhang and C . Zhu , ***Anal . ,*** 1998, **123** , 109.
22 - J . B . Sendra , E . A . Lopez , A . M . G . Campana and L . C . Rodriguez ***, Anal Science ,*** 2003, **19** , 1431.
23 - R . Al-Hasani , ***ph . D . Sc Thesis*** , Al-Nahraain Univrsity (2004) .
24 - W . J . Geary , ***Coord .Chem*** . Revs , 1971, **7**,81.
25 - K . Burger , ***Coordination Chemistry Experimental Methods***, London,Ball / Worth's and Coupublishers Ltd .,(1973)
26 - J . M . Ab dula , H . A . saleh, F. N . Al-obaidi and A.Al-Kadhum , ***Iraqi J . of Chem .,*** 1998**, 24**, 96.
27 - F. N . Al-obaidi , H. A. M.Saleh , A. AL-Kadhumi and J. Abdulla , ***Zanco ,*** 1989**, 2** , 53.
28 - K . L . Cheng, K. Ueno and T. Imamura, ***CRC Hand book of organic Analytical Reagent***, CRC press , Inc., (1982).
29- J. Mc . Murry , ***Fundamental of Organic Chemistry*** , Books , Cole Publishing Company (1998) .
30- R . Chang , ***Physical Chemistry*** , University Science Books (2000) .