Synthisis of Metal Complexes of Novel Heterocyclic Azo Dyes 1-nitro5-azo-(4N(2`,4`-dichloro-6-yl-δ-triazine)-anilino) acridine NADTAA and study Suggested Geometries

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Abstract

In this work,we synthesized a new azo complexes dye by bringing together three important chemical compounds, Acridine, (2`,4`-dichloro-6-yl-δ -triazine)-anilino and metal(I ,II , III, IV). Complexes by using this dye. The chemical structures of both nitro5-azo-(4N(2`,4`-dichloro-6-yl-δ-triazine)-anilino)-acridine NADTAA and azo metal complexes were studied.The preparation and structural identification of novel

(Ag^{+}, Cr^{+2} , Pd^{+2} , Cu^{+2} , Co^{+2} Cd^{+2} , Ni^{+2} , Zn^{+2},Fe^{+3},Pd^{+4}).Complexes of 1-nitro5-azo-(4N(2`,4`-dichloro-6-yl-**δ**-triazine)-anilino acridineNADTAA are studied on the basis of their spectroscopic data. Structural information has been taken from spectroscopic. It has been found that the azo ligand behaves as neutral bidentate (N,N) ligand forming chelates with 1:2 (metal:ligand) stoichiometry Tetra hydral environment is suggested for metal complexes .

Keyword : 1-nitro5- azo- (4N(2`,4`-dichloro-6-yl-δ-triazine)-anilino) acridineNADTAA, complexes of Ag^{+} , Cr^{+2} , Pd^{+2} , Cu^{+2} , Co^{+2} , Cd^{+2} , Ni^{+2} , Zn^{+2} , Fe^{+3} , Pd^{+4} , spectroscopic data, stoichiometry suggested .

الخلاصة

في هذا البحث تم تحضير صبغة ازوية معقدة جديدة من باستخدام ثلاثة مركبات كيميائية مهمة الاكريدين و(2و 4 – ثنائي كلورو -6- يل – دلتا – ترايزين) –انلينو والايونات الفلزية (الاحادية و الثنائية والثلاثية والرباعية) . ومعقدات خلقت من هذه الصبغة اذ تم دراسة التركيب الكيميائي لكل من

الصبغة 1- نترو 5- ازو – (4 4 ,2) N – ثنائي كلورو -6- يل – دلتا – ترايزين) –انلينو) اكرايدين و معقداتها مع الايونات الفلزية وتمت الدراسة لهذه المركبات المعقدة المحضرة الجدبدة وتشخيصها بالطرق الطيفية للمركب 1- نترو 5- ازو – (4 4 ,2) N – ثنائي كلورو -6- يل – دلتا – ترايزين) –انلينو) اكرايدين و معقداتها مع ايونات الفضة (+1) والكروم (+2) والبلاديوم (+2) والنحاس (+2) والكوبلت (+2) والكادميوم (+2) والنيكل (+2) والخارصين (+2) والحديد (+3) والبلاديوم (+4) . ومن دراسة المعلومات الطيفية لقد وجدنا ان هذا المركب اللكيندي الازوي يتصرف كليكايند ثنائي السن (فلز :ليكايند) بنسبة 2:1 اي ليكايند كيليتي من خلال

ذرات النتروجين ومن هذه النسبة تم اقتراح الهيئة الفراغية لهذه المعقدات الايوينية.

1.Introduction

The development of natural and synthetic fiber production requires the study and implementation of new types of dyes with improved properties and superior results in terms of yield, resistance to light ,and resistance to dyeing of wool and polyamide fibers. For many years, the azo compounds have been the main class of dyes used in various applications such as textile fibers dyeing ,colouring of different materials and advanced organic synthesis. The synthesis and dyeing properties of azo compounds are described in many papers (1-6). Azo derivatives complex combinations have been widely used as dyes for synthetic polyamide supports and as" pigments".Complex combinations of particular

importance of Ag^+, Cu^{+2}, Pd^{+2} Fe^{3+} can be incorporated into different

classes of dyes, depending on the nature of the azo compounds used as ligand(7). Azo compounds containing a hetero ring are useful as the analytical reagent(8)because their complexing properties are often specific. Azo dyes are by far the most important and versatile class of dyes which have been studied and used more than any other class .They are water-soluble synthetic organic compounds possessing the characteristic(– N=N–), which links the chromophore and auxochrome to form coloured molecules of great structural diversity (9). Generally azo dyes contain between one and three azo linkages, linking phenyl and/or naphthyl rings that are usually substituted with some combination of functional groups including triazine amino, chloro, hydroxyl, methyl, nitro and sulphonate.Azo dyes exist in the trans form in which the bond angle is ca. 120°. The nitrogen atoms are sp2 hybridized .

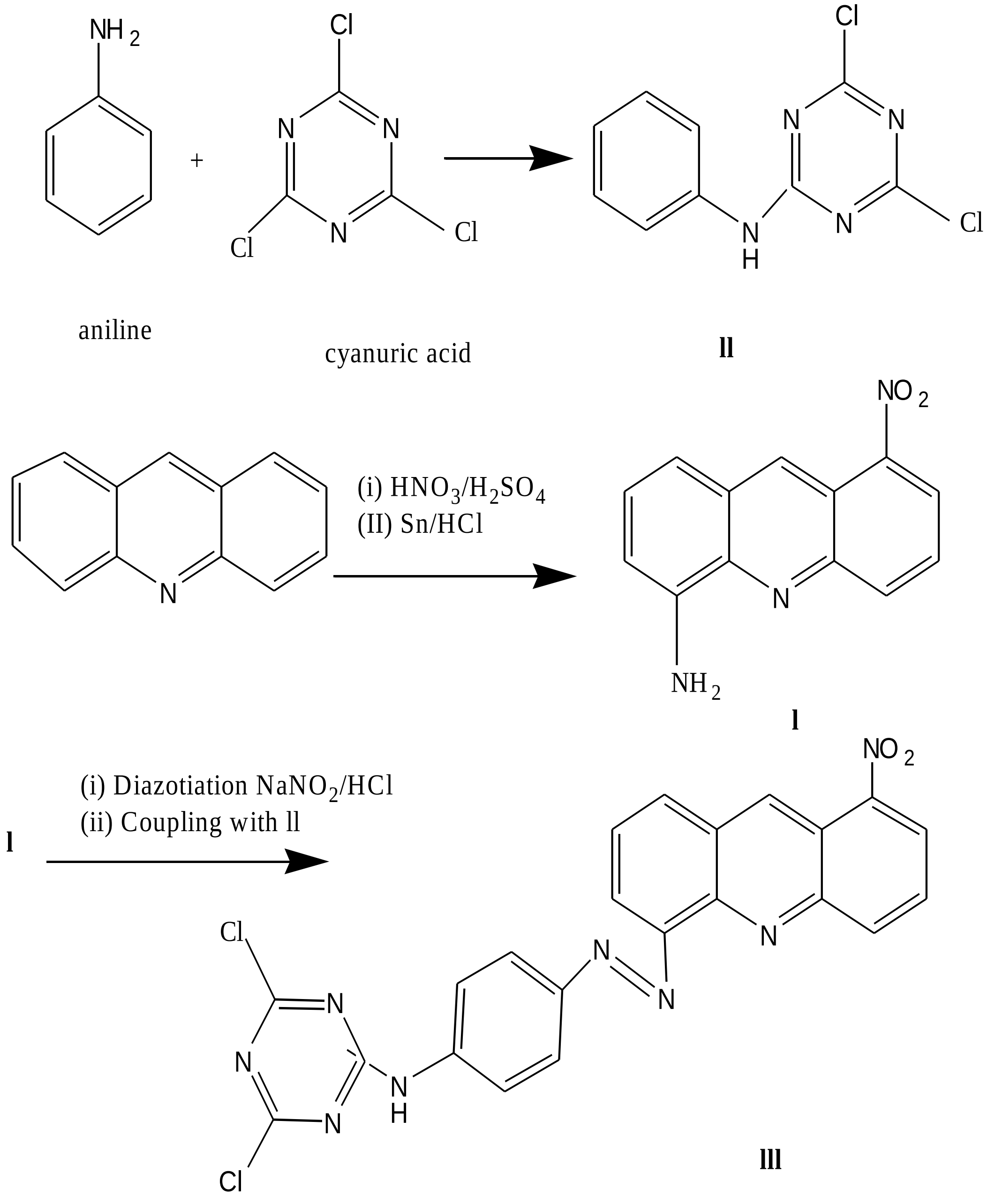
2.Experimental

Double distilled water and chemicals of highest purity were in all experimental, which supplied by fluka , BDH and Merck.

2.1 Experimental Procedure

Synthesis of ligand 1-nitro5- azo- (4N(2`,4`-dichloro-6-yl-δ-triazine)-anilino) acridine HL NADTAA(III) was prepared according to the following general procedure(10,11)Show the Scheme1.

1-nitro-5-amino acridine (II) was diazotized by adding 1.2ml of 30% HCl and 4ml water to a solution of 0.209g, 1mmol of (I)in aqueous $NaNO_2$1mmol at (0-5)^oC. On completion of diazotization (1-2) hr, the diazoniun mixture was added dropwise to a solution of1mmol of (2,4-Dichloro-6-yl-δ-triazine)-anilino (II) in 10% NaOH. On completion of coupling (1-5) hr the precipitate(III) was filtered off and washed with a hot chloroform and acetone recrystallized from ethanol mp= 130-132, 70% yield.



Scheme1. Synthesis ligand(HL)NADTAA(III)

Synthesis ofazo complex(12) .

Dissolving 1mmol of azo dyes (HL)NADTAA(III)) in 50ml of ethanol which then added dropwise with vigorous stirred to 0.5mmol of salts

(M=CO(∏) ,Ni(∏) , Cu(∏) ,Zn(∏) ,Cd(∏) ,Fe(ш) , Pd(∏) ,Cr(∏) ,Pd(Iv), Ag(I) dissolve in 10ml hot distilled water . This mix heated 50 ^{o} for 30 mint left over night . Sold complex formed washed 5ml hot ethanol and dried stored in desicator two week gives colored complexes .

3. Results and discussion

3.1 UV-Visble Spectra .

The prepared 1-nitro5-azo- (4N(2`,4`-dichloro-6-yl-δ-triazine)-anilino) acridineNADTAA (HL) and complexes compounds have been studied by using UV-Visible spectra and measured in Ethanol with concentration (1×10-4)M , in the range 200-650 nm , 1cm cell of guartz . The electronic absorption data of the investigated compounds are shown in Table1while the spectra of prepared (HL) and complexes compounds are shown in Figures 1 to 5 . The spectra of 1-nitro5-azo- (4N(2`,4`-dichloro-6-yl-δ-triazine)-anilino) acridineNADTAA (HL) are characterized by three bands , the first strong band , of the longest wave length (λmax) is at the (240-320 nm , ε =15620 L.mol^{-1}.cm^{-1}) respectively which are attributed to the(π →π*) transitions of - N=N- group(13) , the second band is at (200-230 nm, ε =12330 L.mol^{-1}.cm^{-1}) respectively and could be attributed to the(π →π*) transitions of the aromatic system , while the third band is at the (320-380 nm , ε =3360 L.mol^{-1}.cm^{-1}) , which attributed to (π →π*) transitions of the acridine ring system of molecular(14) . By comparing the spectra of NADTAA (HL) and complexes compounds. For Metal (Ag^{+}, Cr^{+2} , Pd^{+2} , Cu^{+2} , Co^{+2} , Cd^{+2} , Ni^{+2} , Zn^{+2} , Fe^{+3} , Pd^{+4}). We observed

that the bands attributed to the - N=N- group . In the UV region too high intensity transitions in the UV region are due the transitions involving predominantly ligand oribitals.On the other hand , in the case of Cd^{+2}, Ni^{+2}, Zn^{+2} ,Cr^{+2} and Ag^{+}complexes , the transitions of azo group remained in the same wave length (λnm) . This can be interpreted that nitrogen atom of acridine ring is not involved in complexes with these, that this band acquires an appreciable shift towards lower energy (red shift) . The red shift can be explained by the principle that the excited states of these compounds are less polar than the ground states , respectively . On can see that the absorptions shift as the result of red shift resulting from the increased conjugation .

Table 1. UV-Vis Spectra of NADTAA (HL)and complexes compounds .

Sym.	**λ_{nm} azo group** **($\pi \rightarrow \pi^*$)**	**ε . L.mol^{-1}.cm^{-1}**
HL	252	15620
$Ag^{+}L_2$	250	10300
$Zn^{+2}L_2$	250	15620
$Pd^{+2}L_2$	285	19990
$Cu^{+2}L_2$	265	10400
$Co^{+2}L_2$	260	4370
$Cd^{+2}L_2$	252	3540
$Ni^{+2}L_2$	250	2780
$Cr^{+2}L_2$	250	15620

$Fe^{+3}L_2$	290	17500
$Pd^{+4}L_2$	300	11000

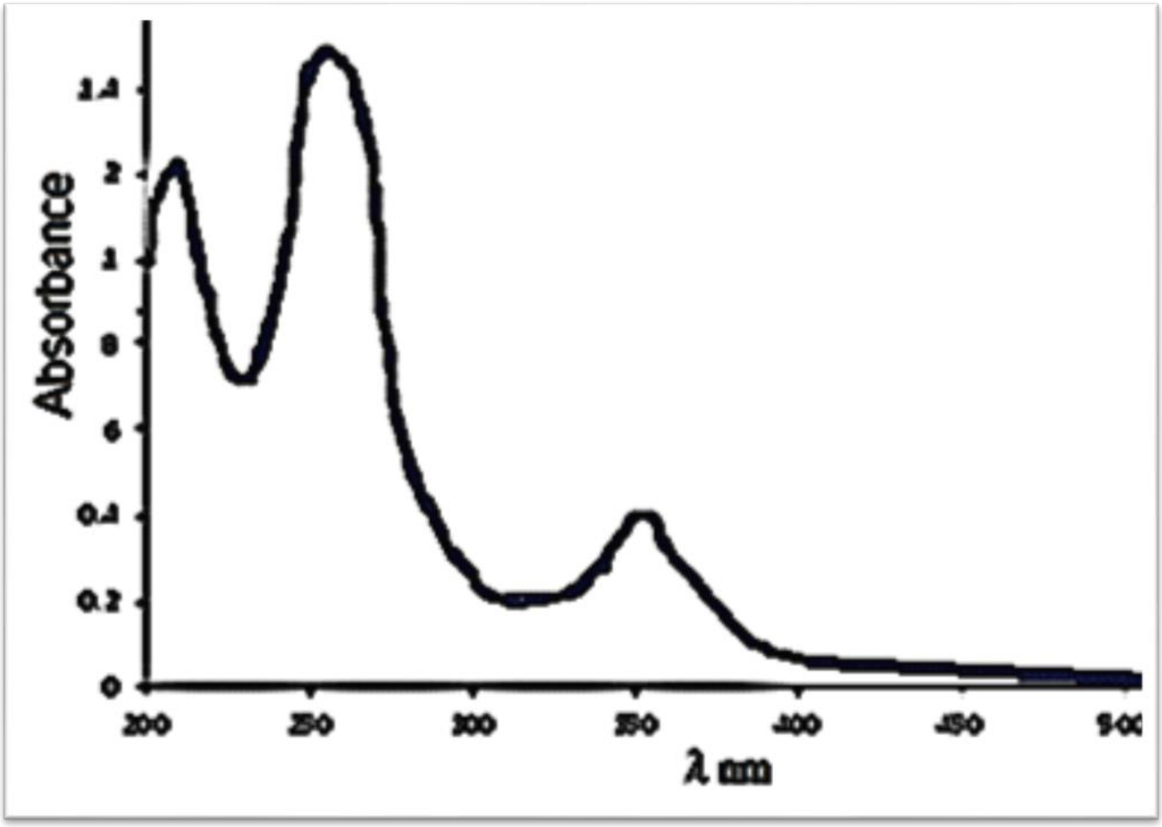


Figure 1 UV- Vis spectra of NADTAA (HL) compound .

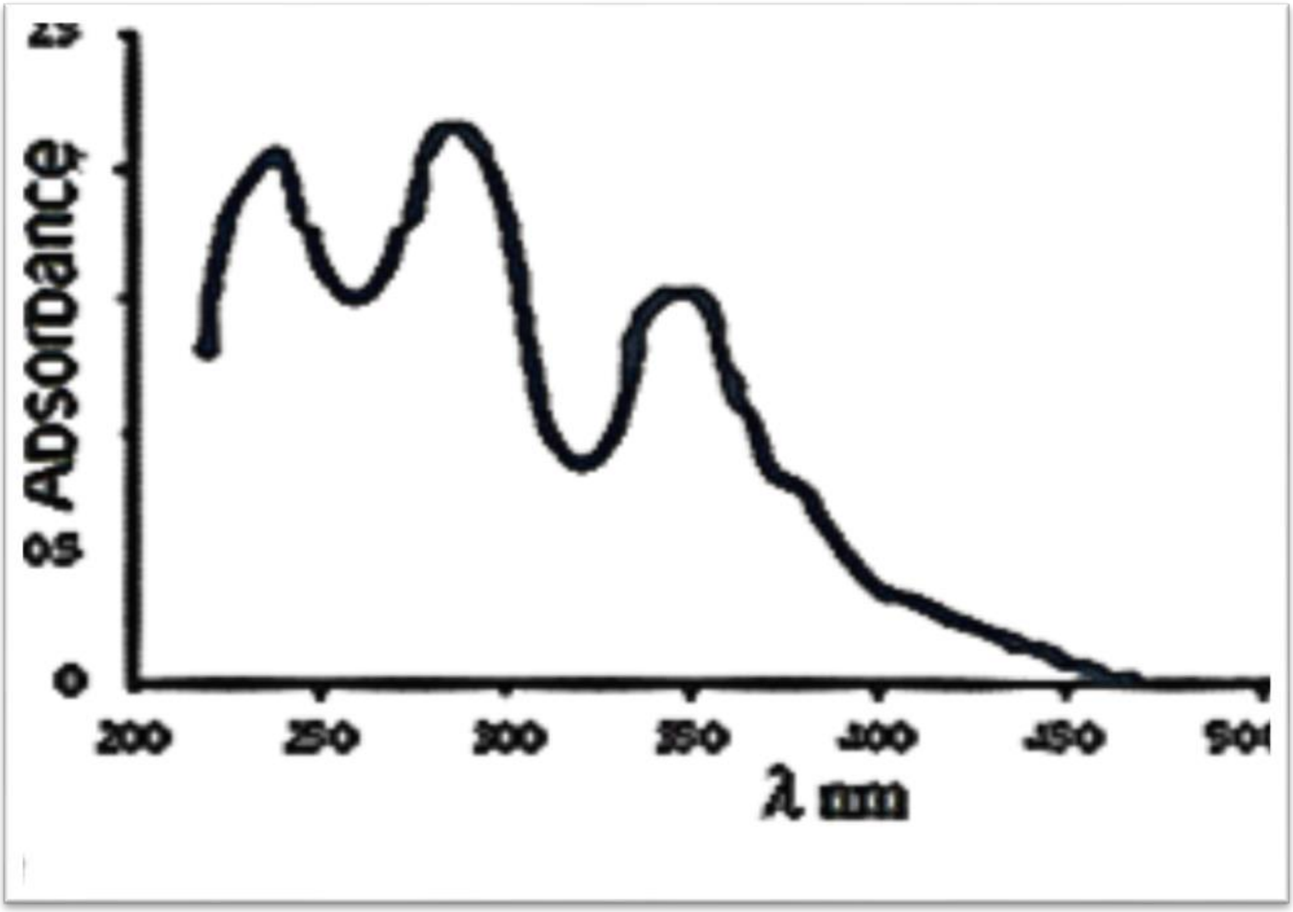


Figure 2. UV- Vis spectra of $Pd^{+2}L_2$ complex compound .

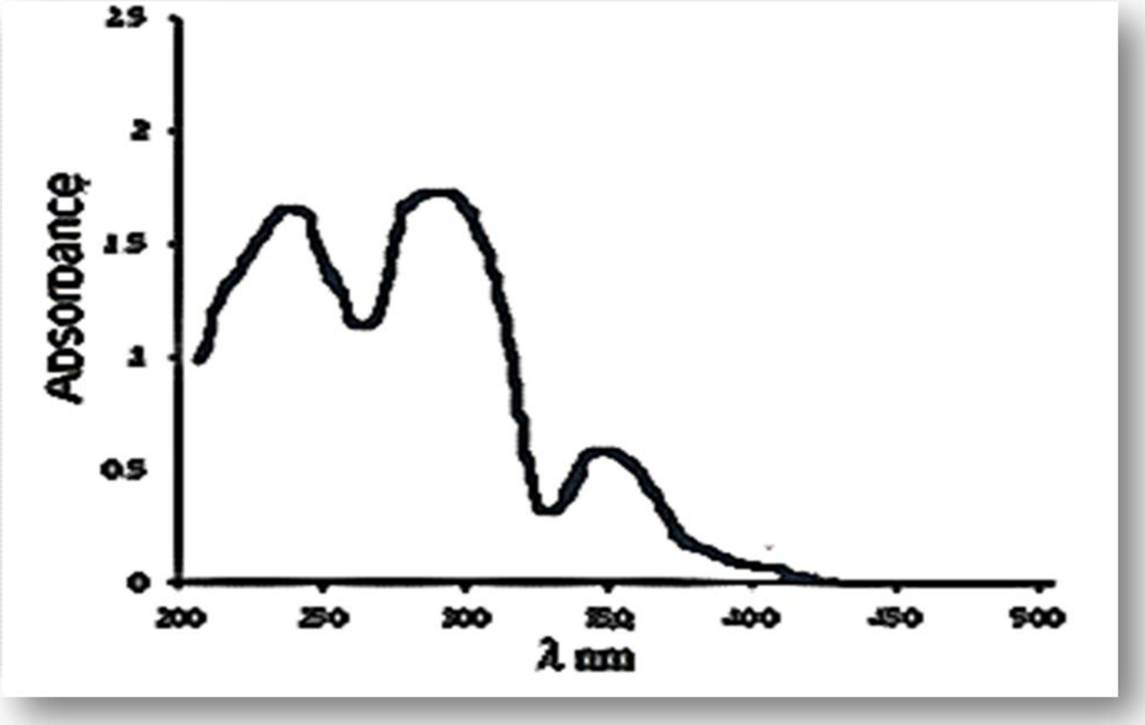


Figure 3.UV- Vis spectra of $Pd^{+4}L_2$complex compound .

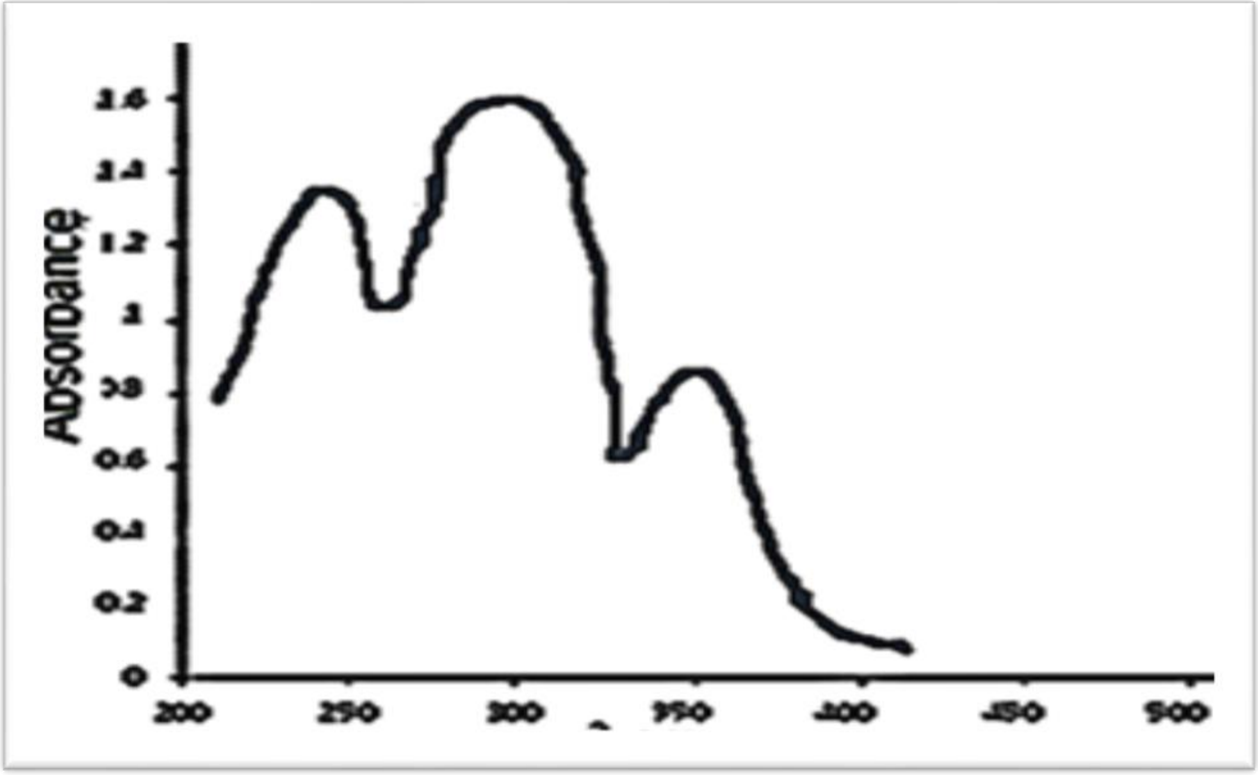


Figure 4.UV- Vis spectra of $Fe^{+3}L_2$ complex compound .

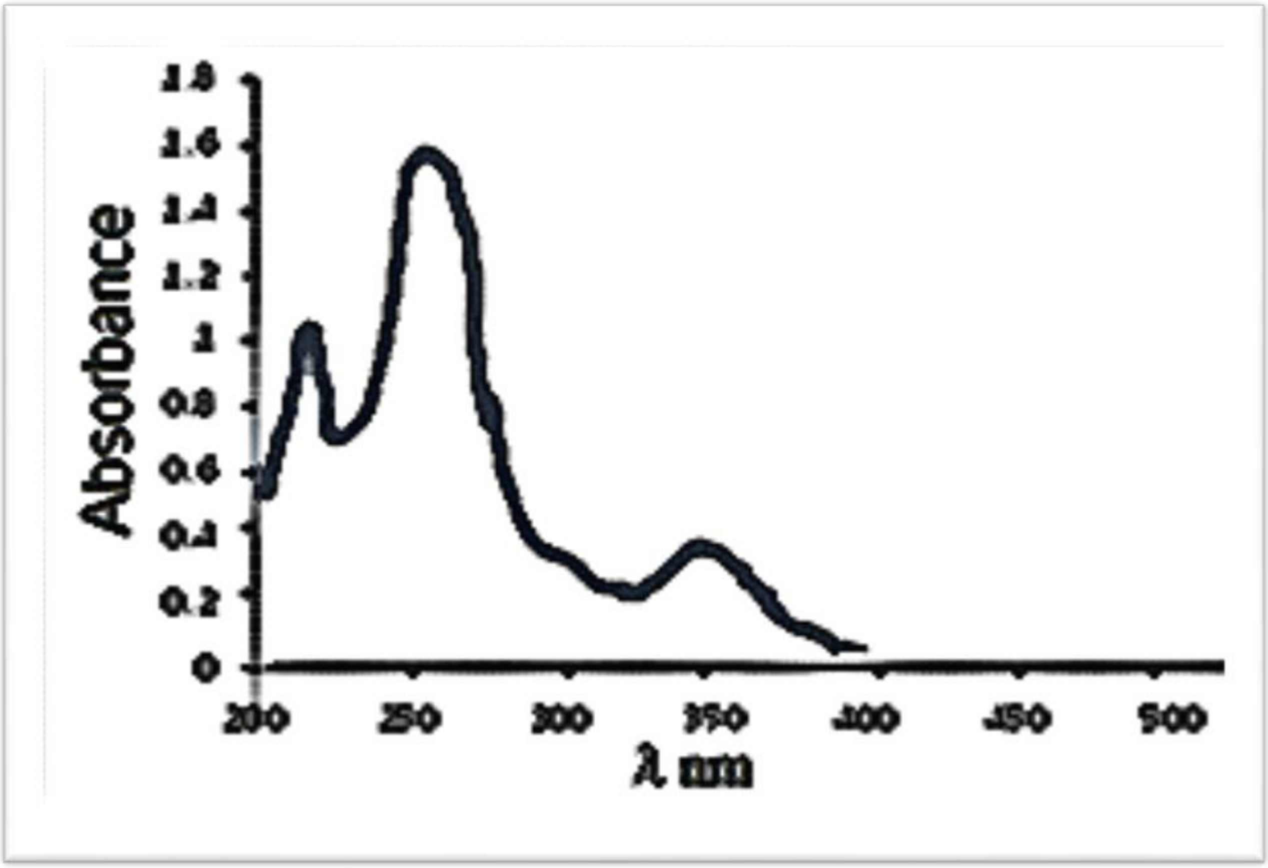


Figure 5.UV- Vis spectra of $Ag^{+}L_{2}$ complex compound .

3.2 Suggested Geometries

Metal complexes of suitable hypodentate ligands viz. ,NADTAA (HL) in which fewer than the maximum number of donor atoms are involved in interaction with metal centers are important in the context of design and syntheses of heteropolymetallic systems(15 .The NADTAA (HL) ligand offers several alternatives to coordination to metal. The 1:2 stoichiometry (Metal:Ligand) as shown Figure 6 indicated that NADTAA (HL) ligand is indeed mono anionic . We chose the some metal ions ,vis. , Co(∏), Ni(∏), Fe(∏).These metal ions are known to form stable coordinatively saturated octahedral complexes (16), while metal ions,viz. ,Pd(∏) ,Pd(1V). These metal ions are known to form stable coordinatively saturated tetrahedral complexes ,as shown Figure 7 ,thereare three potential sites to produce circles represent possible chelation sites . Thus , in principle , we expect that the trans-isomer of NADTAA (HL) is right one to produce coordination to metal and possible is the only one formed in ligand›s synthetic process , due to steric hindrance of the aniline triazine moieties , as shown Figure 8 . If these assumptions are founded , only three chelating positions would be possible , those named 1,2,3 in Figure 7 , the 3 site should be the preferred one , on the other hand , using the information given from Table2. IR bands for the ligands NADTAA (HL) and their metal complexes viz., $Fe^{+3}L_2$, the complexes are suggested geometries , as shown Figure 9 IR spectrum of the complex can be used to indicate the donor atom ofligands for bonding with metal ions by the decreasing of wave number due to the decreasing of the bond order of the donor atom . The results from the infrared-spectra of NADTAA (HL) and $Fe^{+3}L_2$ complex are shown in Figure10.Table 2.The IR spectrum of the ligand shows a broad band at 3462.22cm^{-1} , which could be attributed to

(N-H) of the anilino group with minor shift, this band remains in the same region in free and complexed NADTAA (HL).Thus,this(N-H)group remains intact in solid complex , indicating its non-involvement in coordination of the ligand to the metal ion(16).The (N=N) stretching vibration is shifted to lower frequencies or even disappears , hidden under other frequencies when the spectrum of free ligand is compared with its complex.This indicatedes the involvement of the azo group in coordination to metal ions(17) ,also IR spectrum of ligand revealed a band at 1697.36cm^{-1} due to (C=N) of the acridine ring . This band decreased in intensity in the case of the Fe (ш) complex indicating that it has been affected upon coordination to the metal ion . In the far IR spectra of the complex , there is new band observed in the region 586.36cm^{-1} which is absent in the spectrum of the free ligand .Therfor ,the band observed at 586.36cm^{-1} (M-N) provide conclusive evidence concerning the bonding of nitrogen and azo group to the metal ion.Thus the a bove IR spectra data lead to suggest that the ligand behaves as a bidentate" chelating agent" and the coordination sites are the nitrogen atom of azo group nearest to phenyl ring and nitrogen atom of acridine ring , to give six-membered chelat ring . as shown in Figure 9.

Table 2 Selected IR data (4000-200)cm^{-1} for NADTAA (HL) ligand and its complex of Fe(III) ion.

Sym.Compound	V(N-H)	V(C=N)	V(N=N)	V(C-N-C)
ligand NADTAA (HL) ligand	3462.22	1697.36	1544.99	1382.96
$Fe(L)_2Cl_2.2H_2O$	3460.03	1643.35	a	1228.66

a : These bands have disappeared

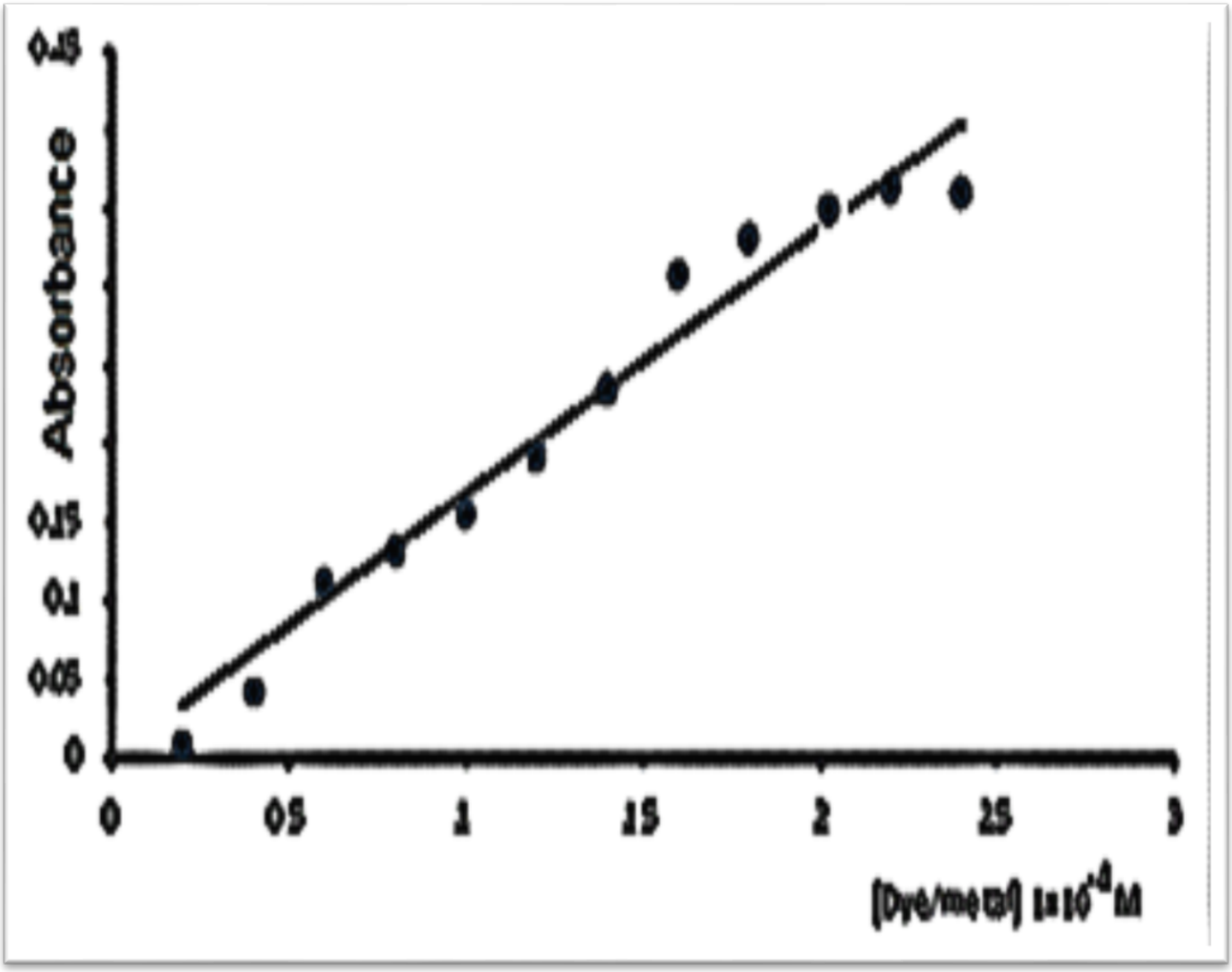


Figure 6.Composition of $Fe^{+3}L_2$ complex compound by mole ratio method .

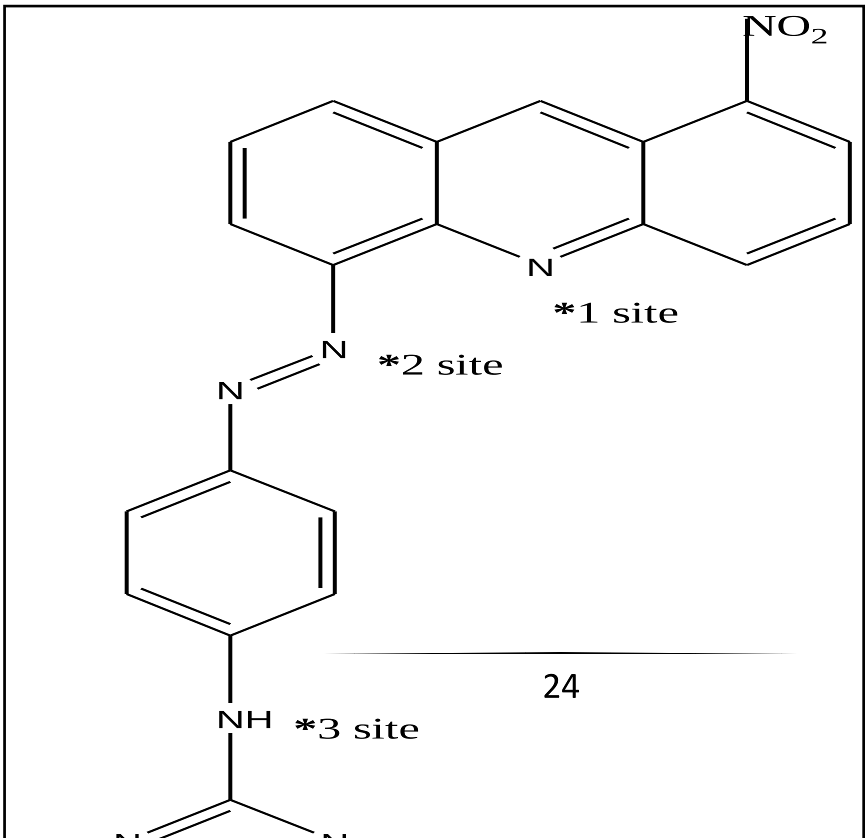
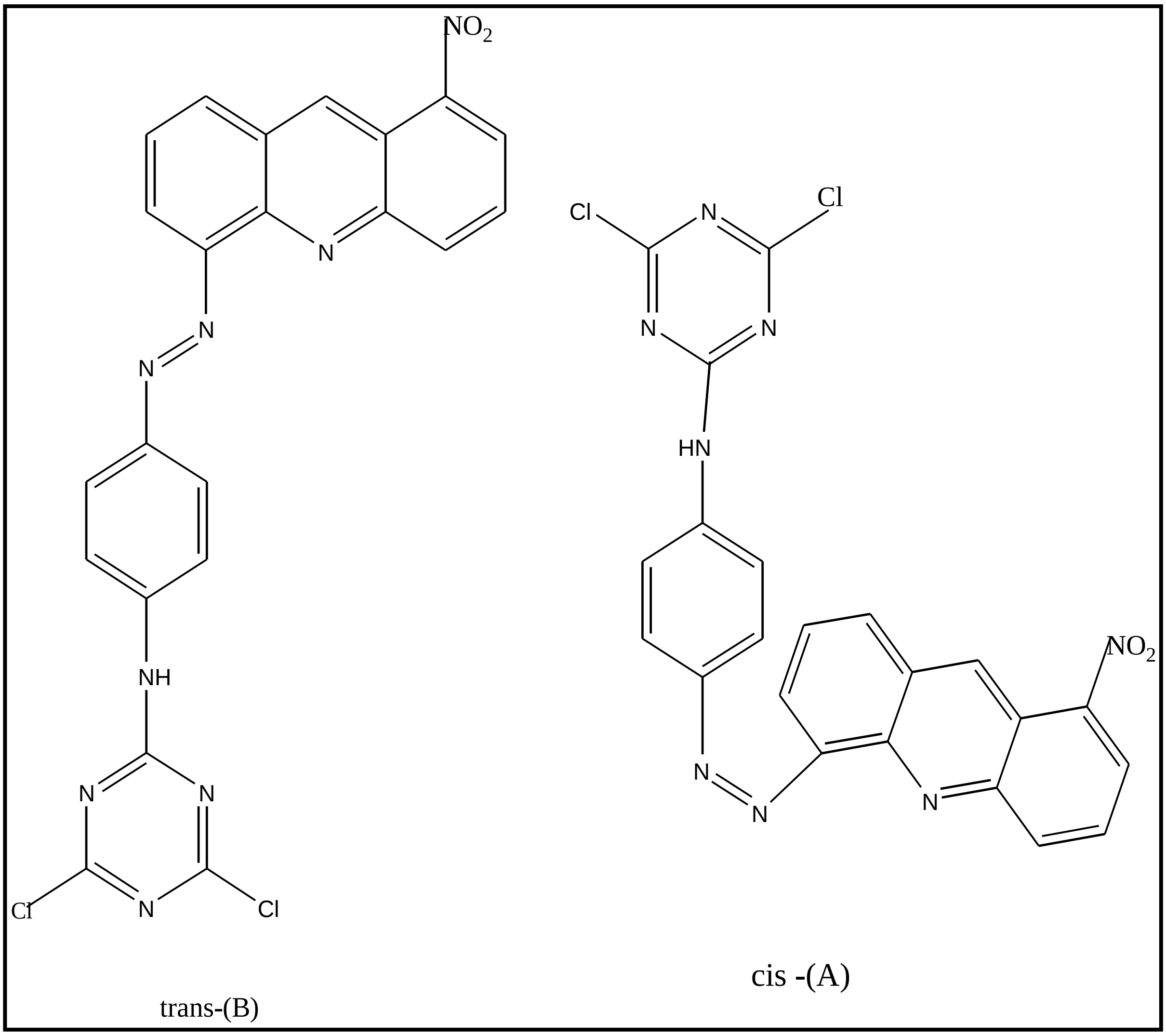


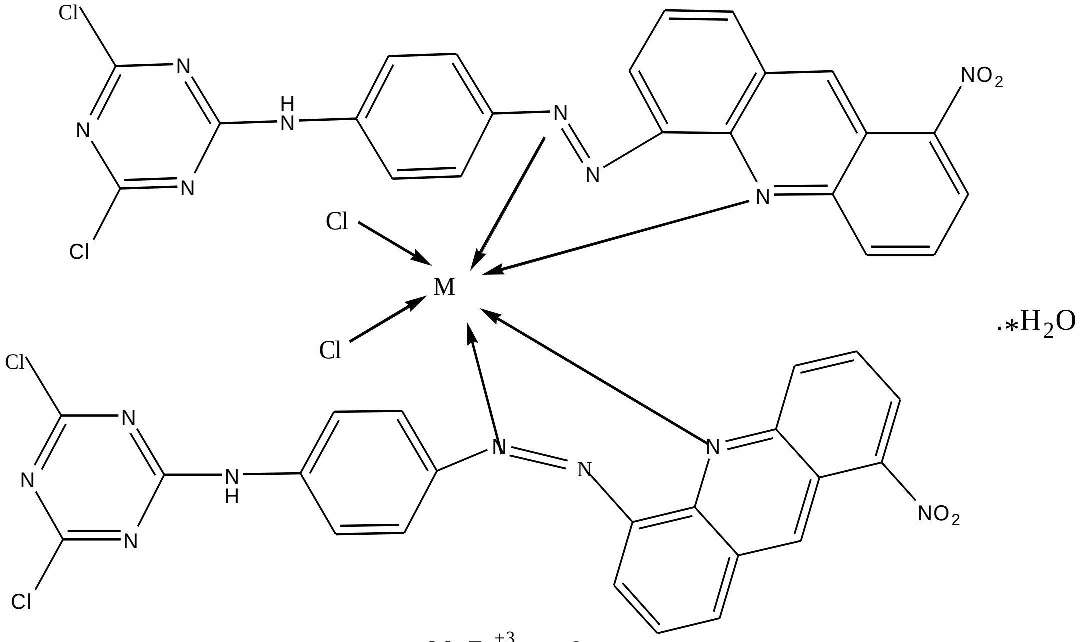
Figure 7. Possible coordination sites in NADTAA (HL) ligand



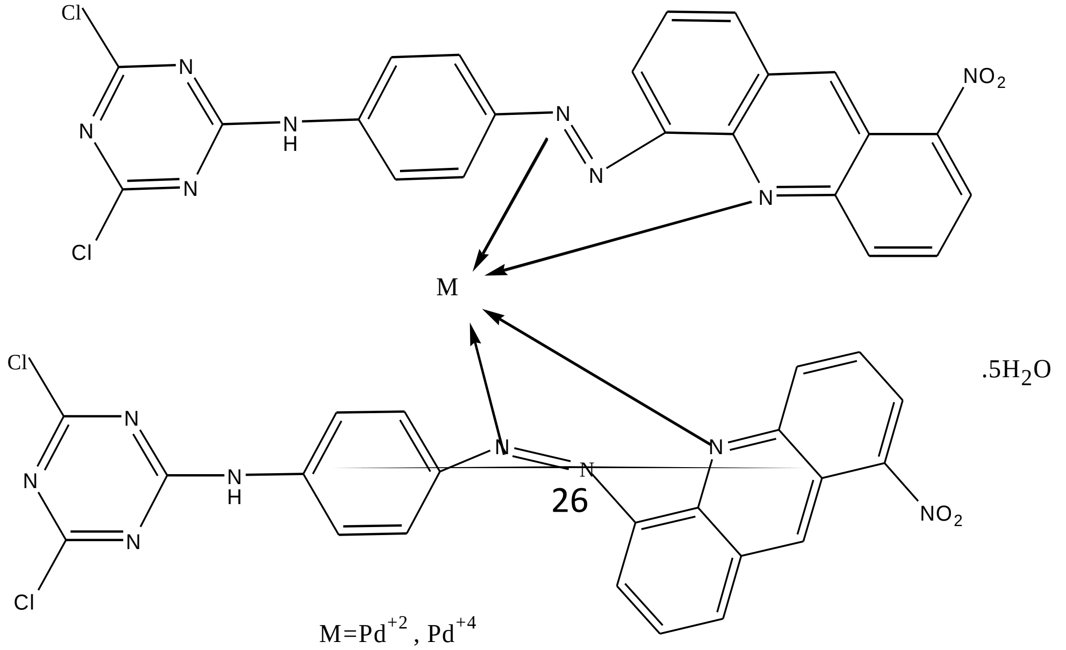
trans-(B)

cis -(A)

Figure 8 Structure of possible isomers of theNADTAA (HL) ligand .



M=Fe^{+3} , $*$=2



M=Pd^{+2}, Pd^{+4}

Figure 9. Proposed structural formula of NADTAA (HL)-metal complexes .

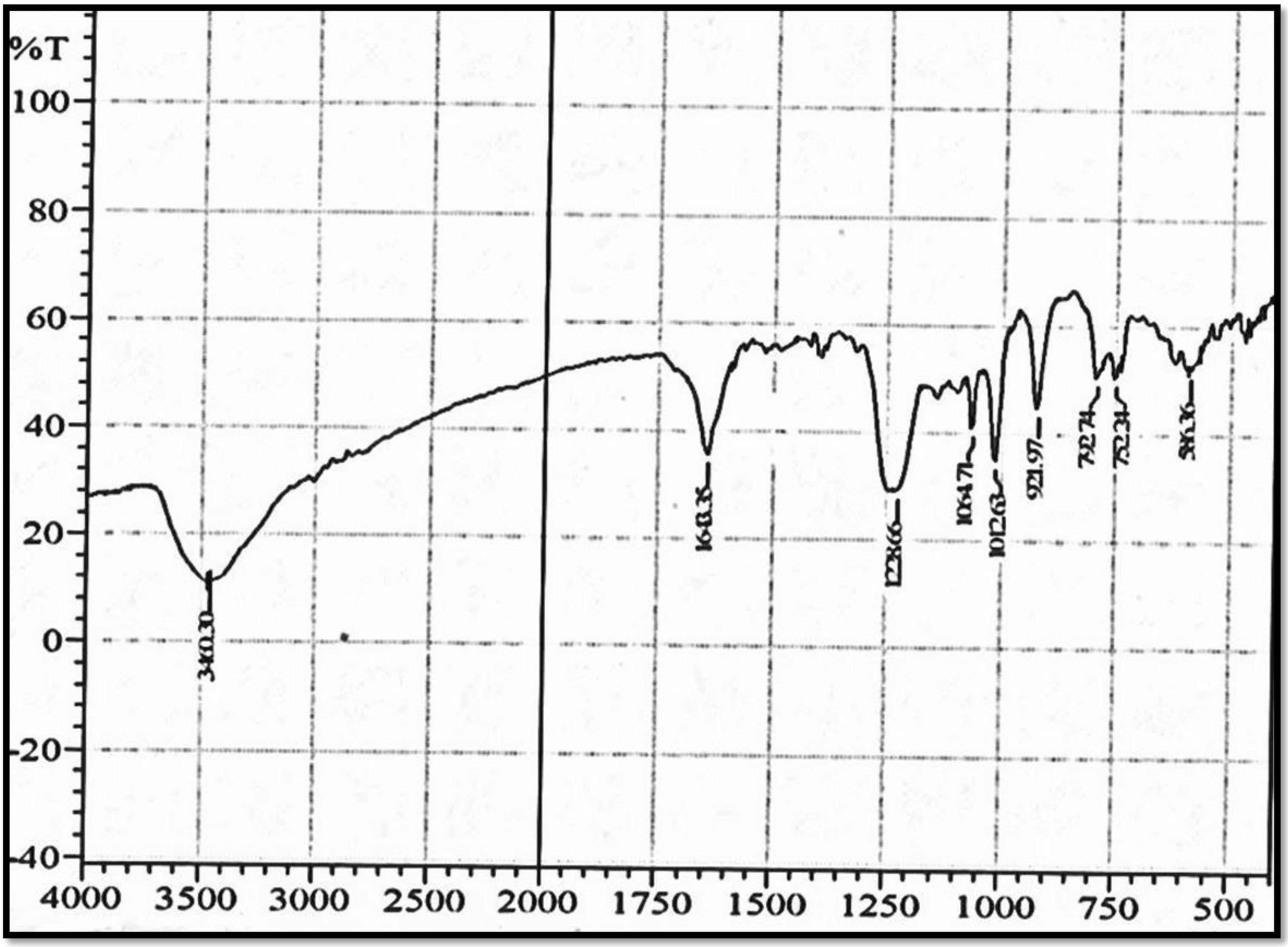


Figure 10 .IR spectra of azo complex of acridine NADTAA (HL) with Fe .

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