IBN AL- HAITHAM J. FOR PURE & APPL. SCI. VOL.19(4) 2006

Synthesis and Characterization of Some New Transition Metal Complexes of Amino Thiadiazole

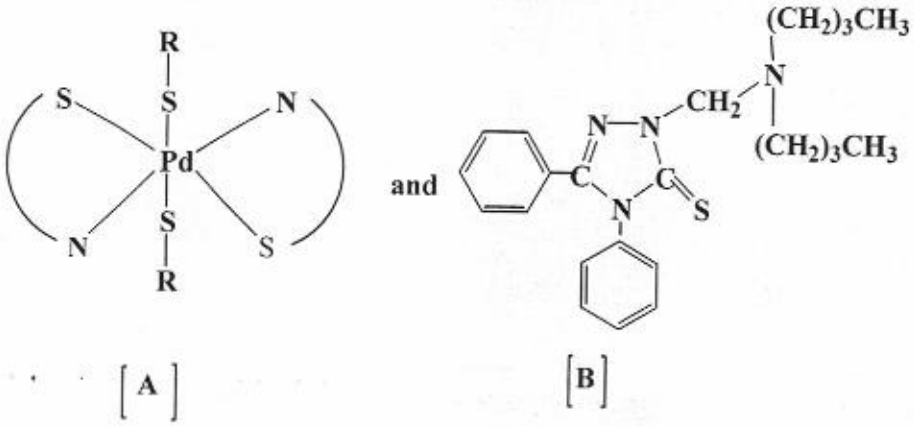
A.T.Numan,I.Kh.Jassim and I.O.Issa
Department of Chemistry, College of Education - Ibn-Al-Haitham , University of Baghdad

Abstract

New complexes of Cu (II),Ni(II) ,Co(II), and Zn(II) with 2-amino-5-*p*-Flouro Phenyl 1,3,4-Thiadiazole have been synthesized . The products were isolated , studied and characterized by physical measurements, i.e., (FT-IR) ,UV-Vis and the melting points were determined .The new Schiff base (L) has been used to prepare some complexes .The prepared complexes were identified and their structural geometry were suggested.

Introduction

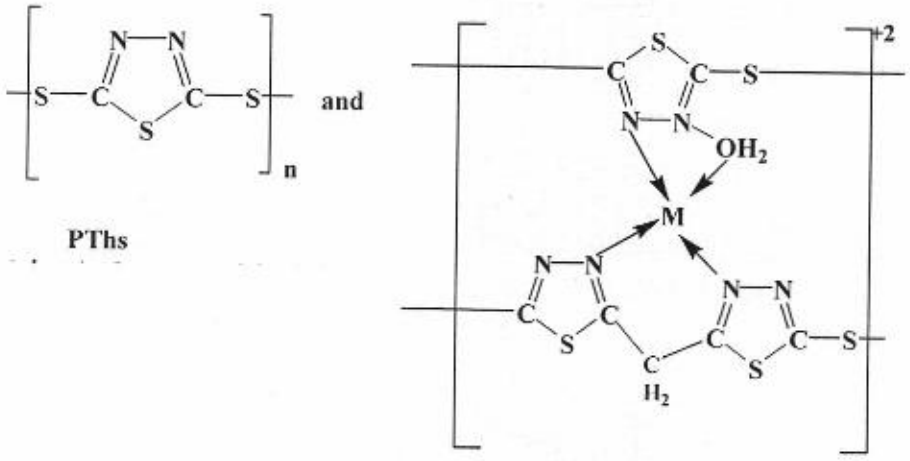
1,3,4-Thiadiazoles represent an important class of heterocyclic compounds that have many applications in our life (1-4) some of these are employed as herbicides (5) ,nervous system depressing (6) .Thus ,some of these heterocyclic compounds[A,B] used as a ligand to prepare biologically active compounds (7) .



[A] [B]

where R= oxadiazole

Ahmed et.al., (8) also used thiadiazole ligand to obtain some complexes as a polymer .



PThs

Other workers (9-10) used carbohydrate unit as a ligand to prepare some biologically active complexes .

Experimental

Reagents were purchased from Fluka and Redial –Dehenge chemical Co., .IR spectra were recorded as (CsI) discs using a

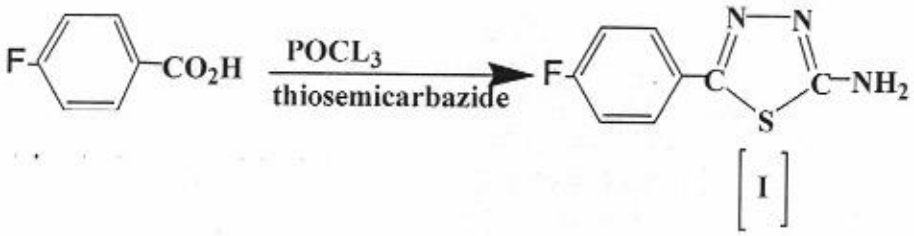
shimadzou 8300-FT-IR Spectrophotometer in the range (4000-200) cm^{-1} .

Electronic spectra of the prepared compounds were measured in the region (200-400) nm for 10^{-3} M solution in DMF at 25 ^{0}C using a shimadzu ,160 spectrophotometer with (1.00 cm^{-1}) matched quartz cell .Elemental microanalyses were performed on a (C.H.N) analyzer ,model 1106 (carlo-Erba),while metal contents of the complexes were determined by atomic absorption (A-A) technique using a shimadzu AA688G atomic absorption spectrophotometer . Electrical conductivity measurements of the complexes were recorded at 25 ^{0}C for 10^{-3}M solutions of the samples in DMF using a PW 4526 digital conductivity meter , magnetic measurements were recordcd on a Bruker BM 6 instrument at 298 k following the Faradys method. Chloride contains for complexes were determined by using potentiometeric titration method on (686-Titro processor - 665.Dosimat-metrohn Swiss).

Preparation of [2-amino-5-*p*-Flourophenyl 1,3,4-thiadiazole]:

An equimolar of p-flouro benzoic acid (0.02 mole) and thiosemicarbazide (0.02 mole) in (10ml) of phosphorous oxy chloride were refluxed for (4)hours .On cooling to room temperature ,the mixture was diluted with water and refluxed for (1hour) and filtered

The filtrate was neutralized with potassium hydroxide to precipitate the product ,y ield (0.2g) (75%),M.P>250 ^{0}C.



[I]

Preparation of Schiff base ligand [HL]

To a hot ethanolic solution of [I] (0.01 mole) ,a solution of salcialdehyde (0.01mole) in(10ml)ethanol was added with (1-3) drops of glacial acetic acid ,the reaction mixture was refluxed for (3hours)

,on cooling the separated solid brown was filtered and re-crystallized from ethanol to yield (0.2g) (65%). M.P (145^{0}C).

Synthesis of the complexes

-Synthesis of [Ni(L) Cl_2]

Ligand (L)(0.334mmole) and KOH (0.0189g) (0.334 m mole) were suspended in dry methanol .The mixture was heated under reflux ,during which time the suspended solution became clear .A solution of (0.079g),0.332 m mole) $NiCl_2.6H_2O$ in (10 ml) MeOH] was added to the above mixture .The reaction was allowed to reflux for (1hour).The solution was allowed for a slow evaporation and a red-brown precipitate was formed ,(yield 0.1g, 70%),M.P(245^0)Dec.

Synthesis of [Co(L)Cl_2]

In (50ml) round bottom flask (0.055g,0.23m mole)of (CoCl2.$6H_2O$) was dissolved in (10ml)methanol .A solution of (0.079g,0.26m mole) of (HL) in(10ml) ethanol and KOH(0.0189G,0.334m mole) was added to the above mixture .The reaction was allowed to reflux for (2hrs) The precipitate red blue which was formed upon standing was collected ,washed with (2ml) ether and dried to give (0.07g,71%) of the title compound , m.p(285^{0}C) dec.

Synthesis of [Cu(L)Cl_2]

The method used to prepare [Cu(L)Cl_2] was analogous to that in(2-a) with $CuCl_2.6H_2O$(0.055g,0.23m mole) .The quantities of the other reagents were adjusted accordingly and the identical work –up procedure gave a green precipitate (0.075) (75%) ,m.p(253-255)^{0}C.dec.

Synthesis of [Zn(L) Cl_2]

A similar procedure to that described for [Cu(L)Cl_2] but with ($ZnCl_2$-$2H_2$ O)(0.039g) (0.22 m mole) with (0.07 g)(0.023 m mole)(HL) to give a white precipitate ,which was washed with (2ml) of ethylether to give (0.078g)m.p(225^{0}C) dec.

Results and Discussion

Synthesis of the ligand

The new ligand type (NO) was prepared according to the general method scheme (1).

Complexes

The complexes are stable at room temperature , non hygroscopic , insoluble in non polar solvent but soluble in (DMF) and (DMSO) .

The analytical and physical data (table 1) and spectral data (table 2and 3) are compatible with the suggested structures scheme 1.

Elemental analysis indicate that the complexes of (HL) with Ni(II) ,Co(II) ,Cu(II) and Zn(II) can be formulated as [M(L) Cl_2] where M= Ni ,Co ,Cu and Zn .

I.R spectral data:

The IR spectra of the ligand and its metal complexes are presented in (table 2) .The disappearance of the (OH) band of the free ligand in the IR of the metal complexes indicates that the (OH) group is de protonated and coordinated to the metal ion as (-O^-) (11) , on the other hand , the (C=N) stretching moietie shifted to a higher frequency by about (13)cm^{-1},compared to the free ligand table (2) (figure 1), it has been noticed that (-C-S-) did not changes .These (I.R) results indicate that the ligand is coordinated to Ni(II),Co(II),Cu(II),Zn(II) via both (N and O) .The new (IR) bands appearing at (450-462) cm^{-1} and (553-559)cm^{-1} and (295-362) cm^{-1} are assigned to υ(M-O) , υ (M-N) and υ(M-Cl) vibrations ,respectively (figure1- a,b,c) (12). The bands at (840cm^{-1}) (740 cm^{-1}) don't change values that's mean the sulfer atom not coordinated to metal (13).

Electronic spectra:

The electron spectra of the ligand and its metal complexes in(DMF) are summarized in table (3) (figure 2).

(HL) ligand in DMF shows three bands at (215,304,381)nm, the band in the (215)nm region is ascribed to a(π -π^*) transition due to molecular orbitals originating in the (-N-C-) moiety ,in the ligand .The band appearing in (304,381)nm is assigned to the azomethane chromophore (n-π^*) transitions (14) .The (uv-vis) spectra of the complexes displayed absorbtion at (300-316) nm to the ligand field .The (uv-vis) spectrum of [Ni(L)Cl_2].The band at (490)nm was attributed to (d-d) transition of type ($^1B_{1g} \leftrightarrow {}^1A_{1g}$) (15) , suggesting a square planar structure about (Ni) ion .

The [Co(L)Cl_2] complex (figure 2a).The band at (733)nm was attributed to (d-d) transition of type ($^4T_{2F} \leftrightarrow {}^4A_2$) (16).

[Cu(L)Cl_2] exhibit two bands at (406,737)nm which can be assigned to [$^2B_1 \leftrightarrow {}^2A_1$] and [$^2B_1 \leftrightarrow {}^2E$] transitions .

The band at (380) nm in the spectrum of $[Zn(L)Cl_2]$ assigned for charge transform , since (Zn) (II) (figure (2b) is (d^{10}) systems ,suggesting a tetrahedral structure about Co(II),Cu(II) and Zn(II)[17] .

Conductivity measurements :

The molar conductance of the complexes in (DMF) lie in the (3-6)s.cm^2.mol^{-1} range table (3),indicating their non- electrolytic nature with neutral ratio (18).

Magnetic moment :

The magnetic moments for some complexes are shown in table (3) The Ni (II) (0.64 B.M)complex has a square planar geometry however, the Co(II) (4.15 B.M) has a distorted tetrahedral geometry .

References

1-Rahm,V.and Pandey ,H.N. (1974). Chem.Pharm.Bull.22,2778

2.Parmar,S.S.;Chaudhary,S.K.;Kumar,S. Spiro,H.R.(1977)J.Pharm.Sci (7): 66,971

3-Mohan, J. (1983),.Indian J.Chem., 22B,270

4-Maxwell ,R.; Wasdahl, D. A.;Wolfson, A.C.; Stenberg,V. I. (1984).J. Med. Chem. ,27,1567

5-Abdul –Rahman, S. (2005),Engineering Journal e Islamic University of Gaza. (1):13 p35-95

6-Uzoe –Y,Yagi-K;Nakamura-M; Akamatsu-M,Miyake-T and Matsumura-F ,(2000),Pesticide Biochemistry and Physiology, 66,Iss 2,pp 92-104.

7-Rehab, A.M.;Ayad, H.Jassim and Mouayed, Q.Al-Abachi (2003),National Journal of Chemistry, 9,115-125

8-Ahmed,S. H;Modher,Y. M. and Salwa,A.Jabar (1999), Iraqi J. Sci.,.40 A,No.3,

9-Simon, R.B.; Cara, L. F. (2004). J.Adam,and Chris Orvig Bioconjiugate Chem., 15, 923-926

10-Adriano, Duatti; Andrea, Marchi; Luciano, Magon; Edward Deutsch;Valerio, Bertolasi and Gastone, Gilli. (1987). Inorg. Chem. 26, 2182-2186

11-Xishi, Tai ;Xianhoug, Yin ;Qiang; Chen. and Miny, Utan, (2003).Molecules,8,439-443.

12-Dakhyl,A.B.(2001).Spectral study of some sciff base.,Salah Aldeen Univ. College of Education tikrit iraq.

13-Sonmez,M. and Sekerci ,M .(2002). Polish –J-Chem.,76,907-914

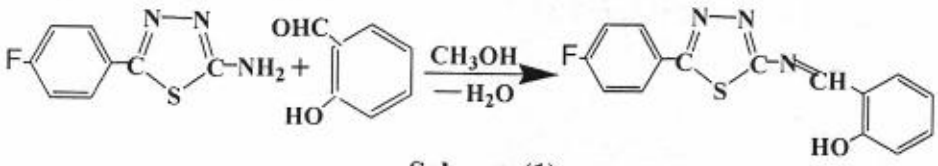
14- Gill, N.S. and kingdom, H.J. (1966). ,Aust-J-Chem.19,2197

15.Silverstein,R.M.;Bassler,C.G.andMorrill,T.C.(1974).Spectrometric identification of organic compounds .3rd eidition,Wiley and Sons USA-,247-254-189 (1974).

16-David,N.(1964). Complexes and first row transition element . translated by Wissam ,I.A., mosl Univ Iraq;127,134,137

17-Dunm ,T.M.(1960) .The visible and ultraviolet spectra of complex compound in modern coordination chemistry . New YOrk ;Inter Science.

18-Ravichandran,N.S and Thangaraja ,C.(2004). J-Chem .Sci;4;215-219.



Scheme (1)

Table: (1) Analytical and physical data of the ligand and their complexes

Complexes formula	colour	M.P.° C	Yield %	Found, (calc.%)				
				C	H	N	Metal	Cl
$C_{15}H_{10}N_3OFS$	Brown	145	65	59.32 (60.19)	4.32 (3.37)	15.23 (14.04)	–	–
Ni(L) Cl_2	Red brown	295 (dec.)	80	41.23 (42.10)	3.21 (2.12)	8.95 (9.82)	12.25 (13.72)	17.23 (16.75)
Co(L) Cl_2	Red blue	285 (dec.)	78	43.21 (42.08)	1.92 (2.12)	8.23 (9.64)	14.95 (12.63)	15.72 (16.57)
Cu(L) Cl_2	Green	255(dec.)	73	42.31 (41.63)	1.89 (2.10)	8.76 (9.71)	16.23 (14.83)	14.23 (16.28)
Zn(L) Cl_2	White	225(dec.)	83	39.23 (41.45)	3.23 (2.90)	7.32 (9.67)	12.31 (15.05)	15.82 (16.23)

(calc.) = calculated , (dec.) = decomposed

Table: (2) The I.R. spectral data of the ligand and their complexes

Complexes formula	υ(C=N) imine	υ(C-N=C)	υ(N-N)	υ(C-H) aromtic	υ(C=C)	υ(C-O)	υ(C-F)	υ(C-S)	υ(O-H)	υ(M-O)	υ(M-N)	υ(M-Cl)
$C_{15}H_{10}N_3OFS$	1595	1560	1200	3006	1508	1149	1232	840 750	3320	-	-	-
Ni(L) Cl_2	1608	1519	1060	3100	1443	1158	1234	840 763	-	522	462	295
Co(L) Cl_2	1606	1519	1031	2929	1473	1151	1236	839 761	-	592	505	273
Cu(L) Cl_2	1602	1523	1043	2921	1487	1153	1237	840 758	-	586	468	376
Zn(L) Cl_2	1614	1519	1060	2881	1485	1140	1238	844 760	-	520	457	260

Table: (3) Electronic spctral data, conductance measurements and magnetic moments of ligand and their complexes

Complexes formula	λ max (nm)	εmax (molar^{-2}cm^{-1})	Λ (Ω^{-1}cm^{2}mole^{-1})	Solvent	Magnetic moments (B.M)
$C_{15}H_{10}N_3OFS$	215 304 381	1355 1217 1014	–	DMF	-
Ni(L) Cl_2	300 490	2210 120	23	DMF	0.64
Co(L) Cl_2	304 733	1624 51	6	DMF	4.15
Cu(L) Cl_2	316 406 737	1532 725 56	32	DMF	-
Zn(L) Cl_2	301 387	1711 1020	22	DMF	-

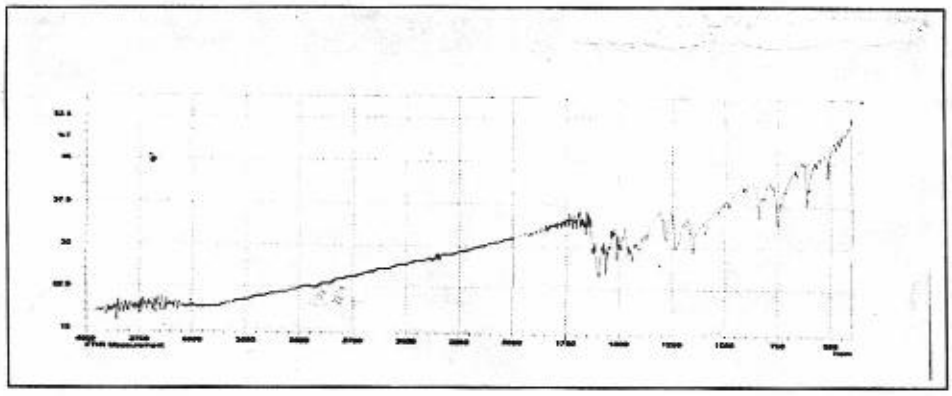


Fig. (1) The I.R. spectrum of the ligand (HL)

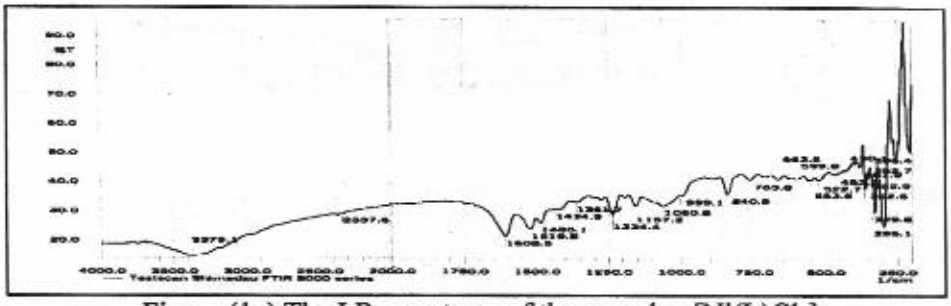


Fig. (1a) The I.R. spectrum of the complex $[Ni(L)Cl_2]$

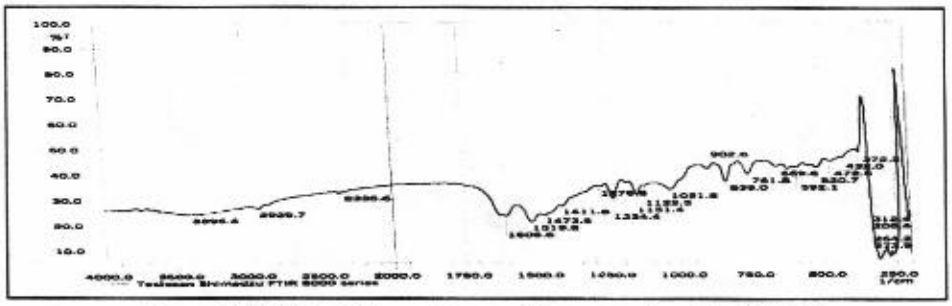


Fig. (1b) The I.R. spectrum of the complex $[Co(L)Cl_2]$

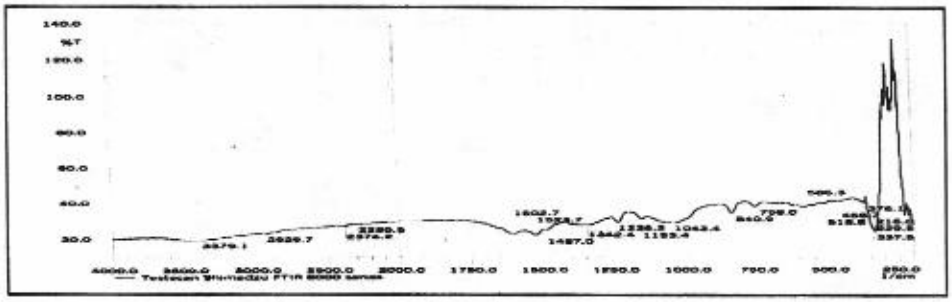


Fig. (1c) The I.R. spectrum of the complex $[Cu(L)Cl_2]$

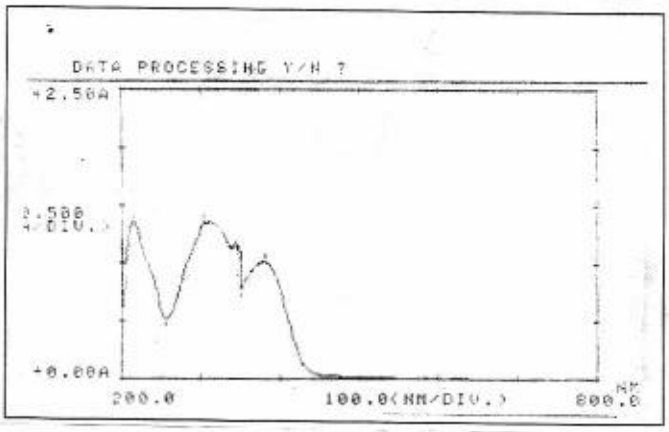


Fig. (2) The UV-Vis spectrum of the ligand (HL)

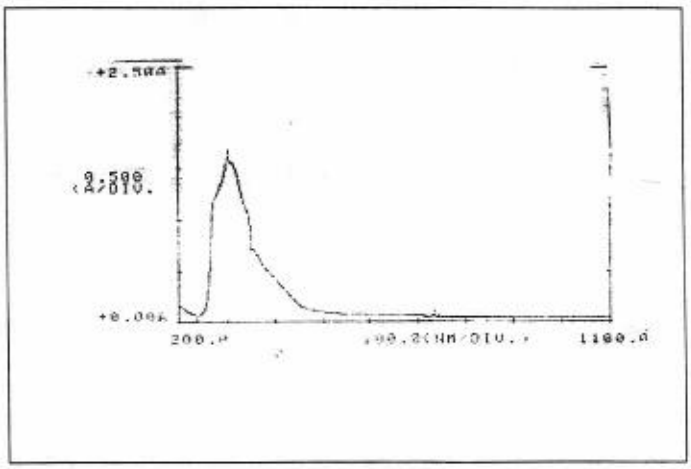


Fig. (2a) The UV-Vis spectrum of the complex $[Co(L)Cl_2]$

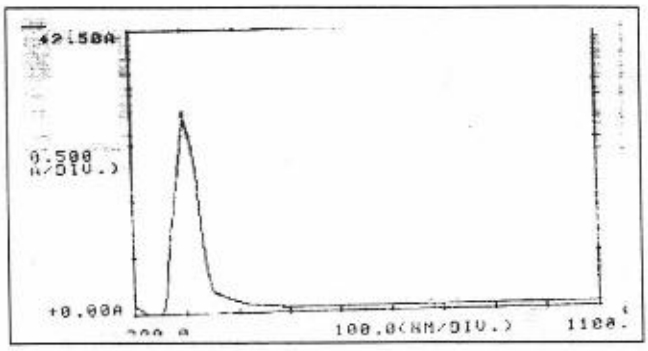


Fig. (2b) The UV-Vis spectrum of the complex $[Zn(L)Cl_2]$

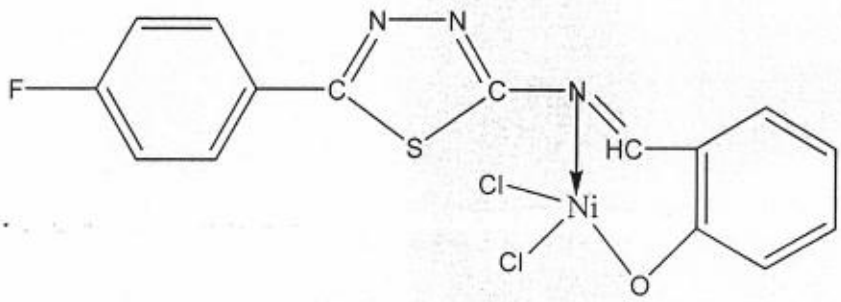
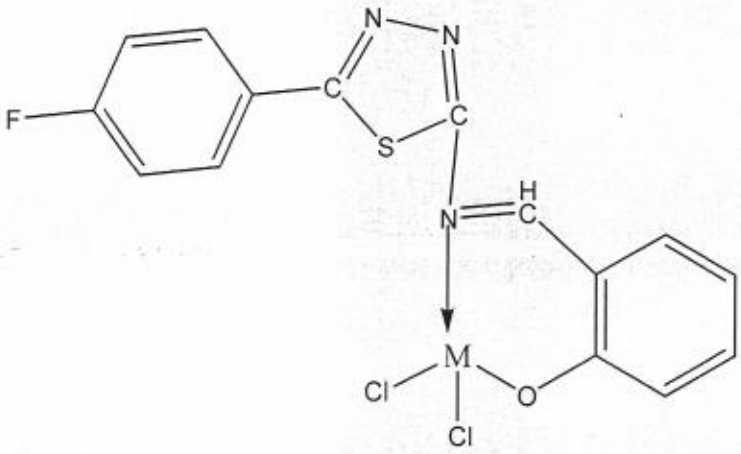


Fig. (3) The proposed structure of the Ni complex



M= Cu, Co, Zn

Fig.(4) The proposed structure of the complexes

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد 19 (4) 2006

تحضير وتشخيص لبعض معقدات العناصر الانتقاليه لامينو ثايا دايازول

أحمد ثابت نعمان ، ابتسام خليفه جاسم و عيسى عمران عيسى
قسم الكيمياء ،كلية التربيه أبن الهيثم، جامعة بغداد

الخلاصة

تم تحضير عدد من المعقدات الجديدة لبعض العناصر الانتقالية مثل Zn (II), Cu (II), Ni (II) ,Co (II) مع المركب 2-أمينو-5-بارا فلورو فنيل 1، 3، 4-ثايادايازول بعد مفاعلته مع السالسالديهايد كقاعدة شف حيث تم استخدامها كاليكاند (L) لتحضير عدد من المعقدات الجديدة .

شخصت المركبات الناتجة من خلال تعيين درجات انصهارها واطياف الاشعة تحت الحمراء (FT-IR) ،الاشعة المرئية/ فوق البنفسجية (UV-Vis) ، وقياسات التوصيلية فضلا عن طيف الكتلة للمادة الاساسية وقد تم اقتراح الشكل الهندسي للحالة الصلبة باستخدام تقنية الامتصاص الذري اللهبي للعناصر وقياس الحساسية المغناطيسية لبعض العناصر .