

Sodium – N – (3-mercapto-1,2,4-thiadiazole) Dithiocarbamate as a Chelating ligand: complexes with Nickel(II), Paladium(II) and Platinum(IV).

تحضير ودراسة طيفية لمعقدات النيكل(II)، البلاتينيوم (II) والبلاتين (IV) مع صوديوم-N – (3-ميركابنتو-1,2,4-ثياديازول) ثايديازول) ثنائي كارباميت كليكاند مخلبي.

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Abstract:

Chelates of Ni (II), Pd (II) and Pt (IV) with potassium 3-amino-5-mercapto-1,2,4-thiodiazole -diethiocarbamate (TC⁻ K⁺) have been prepared. All these chelates have been characterized by thermal analysis (TG-DTA), Infra-red (IR), (UV/Vis) spectrum Magnetic sensitive and Conductivity measurement. Ni (II) and Pt (IV) chelates are found to have octahedral structures, while Pd (II) complex may have square planar symmetry.

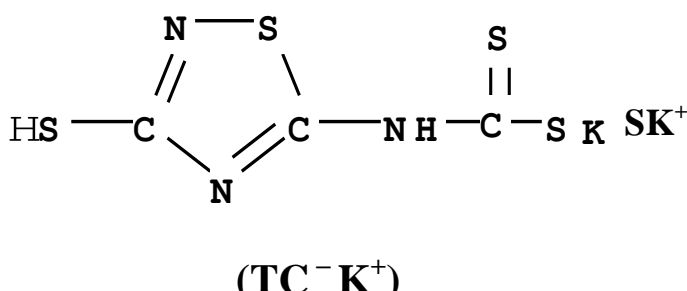
الخلاصة :

تم تحضير معقدات المخلبية لأيونات النيكل Ni(II) والبلاديوم Pd(II) والثنائية والبلاتين Pt(IV) الرباعي مع بوتاسيوم – 3-امينو – 5-ميركابنتو-1,2,4-ثياديازول- دايثايوكارباميت (TC⁻ K⁺). تم تشخيص المعقدات المخلبية بواسطة التحليل الحراري (TG-DTA) وأطياف الأشعة تحت الحمراء (IR), وأطياف الأشعة فوق البنفسجية والمرئية (UV./Vis.) وقياس الحساسية المغناطيسية وقياسات التوصيلية الكهربائية. ومن خلال الدراسات اقترح الشكل الثماني السطوح لمعقدات Ni (II), Pt(IV) فيما وجد ان معقد Pd (II) يمتلك الشكل المربع المستوي.

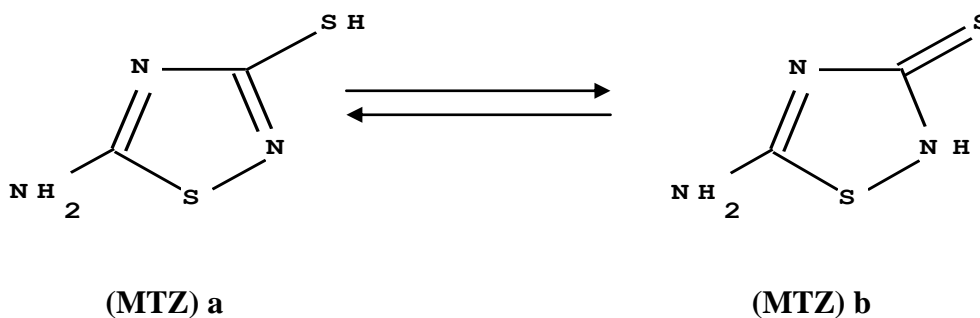
1. Introduction:

The insertion of functional groups into the ring of the hetero cyclic compound 3-amino-5-mercapto-1,2,4-thiadiazole (MTZ) was reported to produce many compounds of biological activity, i.e. drugs, fungicides^(1,2) as well as compounds of industrial uses such as antioxidants and polymer softeners^(3,4). The efficiency of such derivatives might be increased or decreased on coordinating of their donor atoms to a metal.

The synthesis of new thiocarbamate ligand (TC) derived from reaction of CS₂ with (MTZ)⁽⁵⁾ Anew ligand (TC) has more than potential donor sites or different coordinating abilities for binding with metal ion, therefore the linkage is the favorable to coordinate with Co(II), Ni(II), Cu(II) and Zn(II)^(6,7).



Scheme (1): (TC⁻ K⁺) Ligand



Scheme (2):(MTZ) Compound

2. Experimented:

All chemicals used of reagent grade.

In the preparation of metal chelates of Ni (II) , Pd (II) and Pt (IV), NiCl₂. 6H₂O, PdCl₂ , conc.HCl (36.5% v/v) and K₂PtCl₆ were used for chelation from Sigma and Fluka companies.

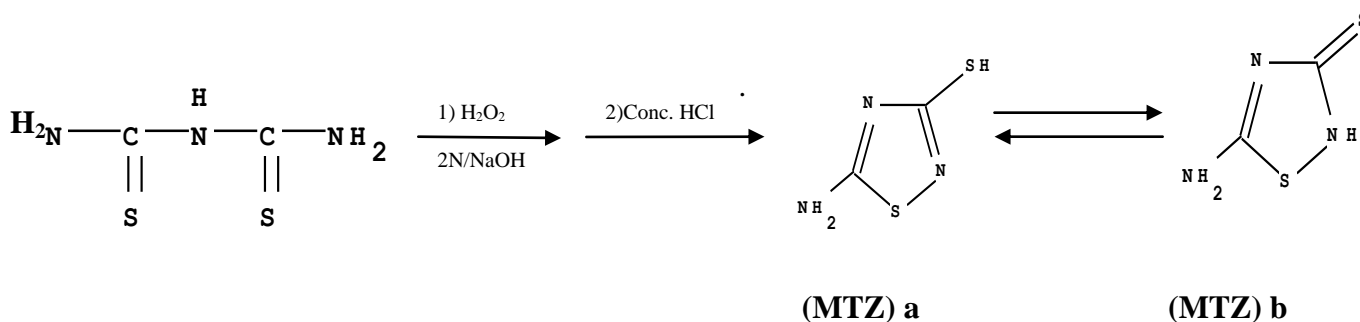
F.T.IR were recorded on F.T.IR – 8300 Shimadzu in the range (400-4000) cm⁻¹ at Al-Nahrain University.

The u.v. – visible spectrum of compounds were done on u.v. 1650 pc Shimadzu spectrophotometer. Magnetic susceptibiliyies (xg) were carried out at 20C° by Farady, method using mercury tetrathiocyaneto Cobalt (II) as calibrant . metal estimations were carried out spectrophotometrically using atomic absorption Schimadzu AA-670 spectrophotometer at Ibn-Sina Centre.

Conductivity measurements were obtained using Philips pw-digital meter.

Preparation of 3-amino-5-mercapto-1,2,4-thiodiazole (MTZ):

Was carried out according to the method reported in literature ⁽⁸⁾ .

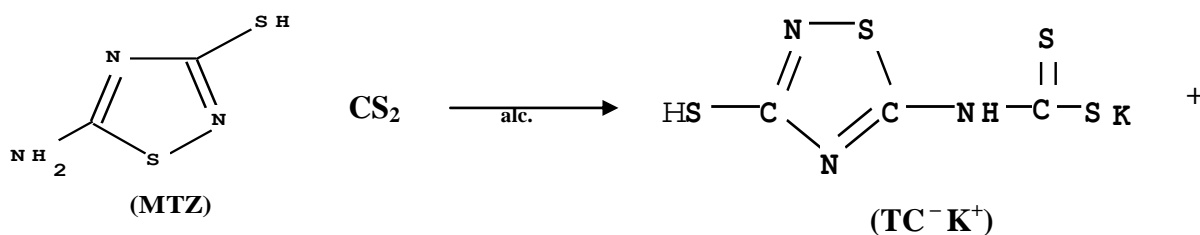


Scheme (3)

Preparation of (TC⁻K⁺) ligan

A

solution (MTZ) of (2gm) in 50ml of ethanol was added to (0.56,10 mmole) of KOH with stirring . The solution was cooled to (10c⁰) and add (1.1 ml) of carbondisulfiede . Stirring was continued at 10c⁰ for 3hrs .A pal-yallow precipitate was formed the product was filtered off , crystallized from, ethanol and dried under vacuum .



Scheme (4)

Preparation of complexes (C₁):

(0.494 gm , 2mmol) from (TC⁻ K⁺) ligand was dissolved in (15 ml) absolute ethanol , the solution add to mixture formed (2mmole,0.117gm of NaCl +1mmol,0.237gm NiCl₂.6H₂O) dissolved in 25ml of absolute ethanol. The resulted mixture was allowed to reflux about 1.5hrs., the dark brown complex in color precipitated on adding 15%NH₃ as buffering agent. The isolated complex was filtered off washed several times with ethanol and finally dried in vacuum over anhydrous calcium chloride .

Preparation of C₂ – C₃ complexes :

TC⁻ K⁺ (0.494gm, 2mmol) in (15ml) absolute ethanol was added to the solution containing (1mmole,0.278gm of PdCl₂) Or (1mmol,0.486gm of K₂PtCl₆) and the mixture was refluxed for 2 hours, the orange color complex precipitates after the PH of solution adjusted between the rang (5 - 5.5), yielded the titled compound in (85%C₂, 95%C₃).

Physical measurements:

The analyses of the metals were carried out by the standard methods⁽⁹⁾ magnetic moments were obtained at room temperature (25°C) by Gouy balance using Hg{Co(NCS)₄} as the calibrating agent at Al-Mosul University. Infrared spectra were recorded in KBr and CsI. Discs on a pye Unicomp SP 2000 spectrophotometer (4000-200cm⁻¹), electronic spectra were recorded in D.M.F. on a perkin Elmer 330 spectrophotometer at AL-Mustansiriya University.

The electrical conductance measurements were carried out in 0.001M solutions of D.M.F. with the help of a Toshniwal conductivity bridge (type C101 – 02A) and a dip type cell calibrated with potassium chloride solution.

Nickel was estimated gravimetrically as bis (dimethylglyoximato) Nickel(II)⁽¹⁰⁾. Thermal analysis were carried out for paladium and nickel complexes by NETZCH STA 409 PG/PC using heating rate of 35C/min., temperature range of thermolysis was (25°C-500°C) in nitrogen atmosphere.

Table (1): physical properties, elemental analysis (M%), and magnetic susceptibility for the prepared compounds.

Compound symbol	Formula	M.P. (°C)	Color	Yield %	M% calc(found)	μ _{eff} (BM)	Λ _m (Ω ⁻¹ .mol ⁻¹ .cm ²)
L	C ₃ H ₂ N ₃ S ⁻ ₄ K ⁺	195-197	Pale yellow	95	-	-	-
C ₁	Na ₂ [Ni(L) ₂ Cl ₂]	225-227	Dark Brown	80	9.16 (8.69)	3.5	180
C ₂	[Pd(L) ₂].2H ₂ O	265 ^d	Orange	85	11.37(10.91)	0	45
C ₃	[Pt(L) ₂ Cl ₂]	272 ^d	Orange	95	10.16 (9.5)	1.35	20

d = decomposed

Table (2): Infrared spectra and electronic transitions for the T c Na⁺ ligand and it's metal complexes.

compound	I.R bands (cm ⁻¹)					U.V – Vis. Peaks
	γ _{C=N}	γ _{N-S}	ν _{C-S}	ν _{M-N}	(ν _{M-S} , ν _{M-Cl})	λ _{max} (nm), ε _{max}
L	1610(s)	1385(m)	735(m)1230(s)	-	-	250,320(3500)
C ₁	1580	1390	725 1220(s)	420(m)	360 330(m)	260,295,580*
C ₂	1560	1395	715 1200(s)	430(m)	415	245,315,380*(30.000)
C ₃	1600	1390	1225(s)	415(m)	390 250 (w)	260,305,520*(80)

s = strong , w = weak , m = medium

* = referred to d-d spectra

c = referred to charge transfer transitions.

3. Results & Discussion:

3-1 Physical data and elemental analysis:

Table (1) describes color, melting points and elemental analytical data of the ligand (I) and its metal complexes.

The analytical data table (1) indicates all the complexes are insoluble in water and common none – coordinating solvents but are soluble in coordinating solvents like D.M.F. and DMSO. C₁ and C₃ complexes were weak electrolytes in D.M.F solution . The magnetic moment values of Ni complex are 3.5B.M respectively at room temperature and show that the complexes are of low spin type with pseudo octahedral environment around the metal ion⁽¹⁰⁾.The mole ratio method was used to determine the ratio of metal and ligand , the study shows the ligand Coordinated to metal in 1:2 ratio.

3-2 Infra-Red Spectra:

The characteristic stretching vibration modes concerning ligand and its metal complexes are described in table (2). Infra-red spectrum of the free ligand exhibited strong high intensity bands due to $\nu_{C=S}$, $\nu_{C=N}$ and ν_{N-S} ⁽¹¹⁾ at 1230, 1610 and 1385cm⁻¹ respectively.

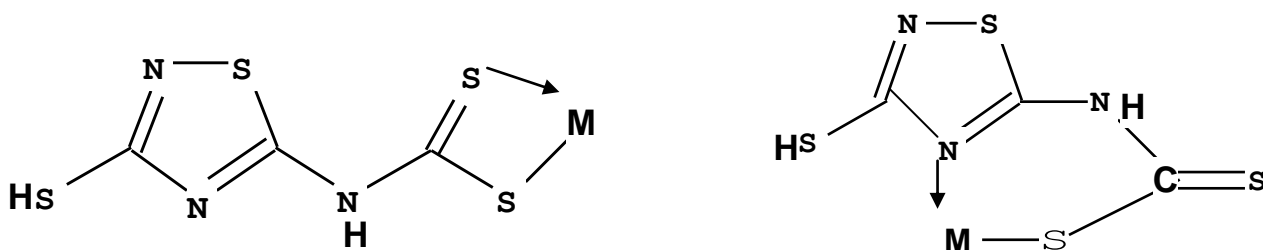
The ligand (L) exhibit different types of coordination patterns as shown by infra-red spectral changes upon complication. The bands due to ($\nu_{C=S}$) & were shifted to lower frequencies by (30 - 45cm⁻¹) range⁽¹²⁾ for all the prepare complexes this suggest the impairment of thin carbomate group and nit thioamide in participation in coordination with the metal ion. As well as the absorption band of ($\nu_{C=S}$) is shifted to higher frequencies by (5-10)cm⁻¹ which is due to strain of thiadiazole ring via formation of six-member ring⁽¹³⁾ as shown in figure (1) ,figure(2) and figure(3) .

Two new bands appear around 500 and 300cm⁻¹ in the finger print region of complexes which could be assigned to coupled vibration having contribution from ν_{M-L} and ν_{M-S} ⁽¹⁴⁾ .

3-3 Electronic Spectra:

The Ni(II) complex exhibits two electronic spectral bands at 9000 and 18000 cm⁻¹ in the visible region due to the $A_2^3g \longrightarrow T_2^3g$ & $A_2^3g \longrightarrow T_1^3g$ transitions respectively in an octahedral field. The electronic spectral parameter of the complex as follow : $^{15}Dq = 9500cm^{-1}$, $\beta = 0.5$, $B = 600$ & $B^0 = 30.49$. the reduction of the Raccah parameter from the free ion value of 800cm⁻¹ and B of 28% testify to the presence of strong M-L covalent⁽¹⁶⁾ bonding in the complexes.

However the absorption spectrum of Pd(II) complex showed one high intensity band at 19230cm⁻¹ and was assigned to $dxy \longrightarrow eg^*$ transition of square planer complex⁽¹⁷⁾. Further more the Pt(IV) complex showed charge transfer electronic transitions at 25420cm⁻¹ and 23600cm⁻¹ respectively which are attributed to ($Pt^{+4} \longrightarrow Cl^-$) or ($Pt^{+4} \longrightarrow L$) transition high intensity⁽¹⁸⁾ as shown in figure(4),figure(5) ,figure(6) and figure(7) .



Scheme. (5): Patterns of coordination sites by L-ligand

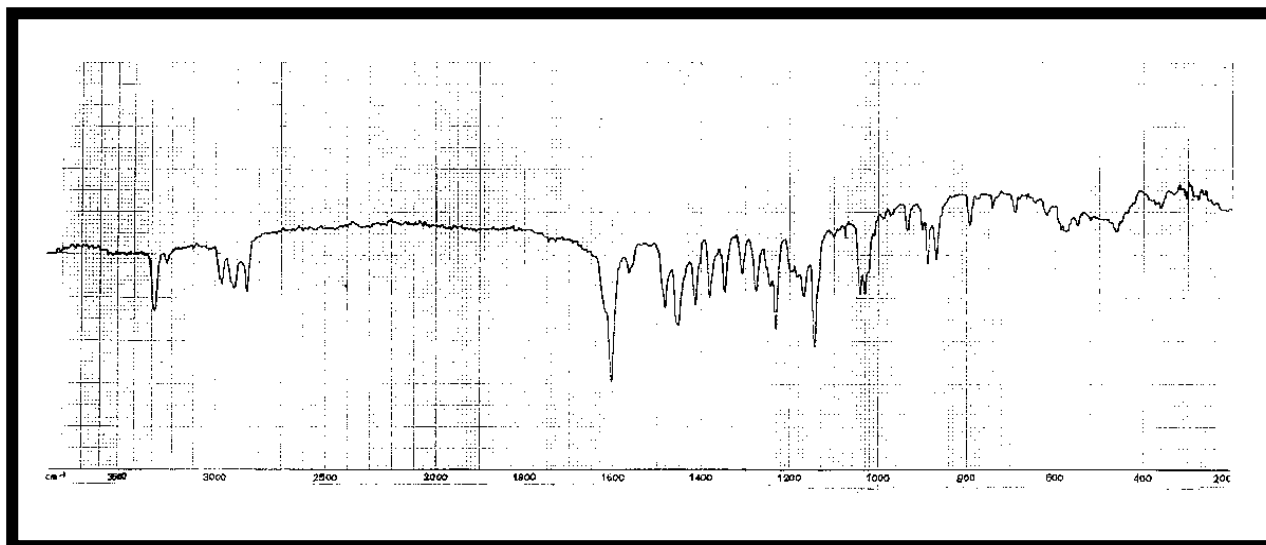


Fig. (1): I.R. spectrum of ligand KBr disk

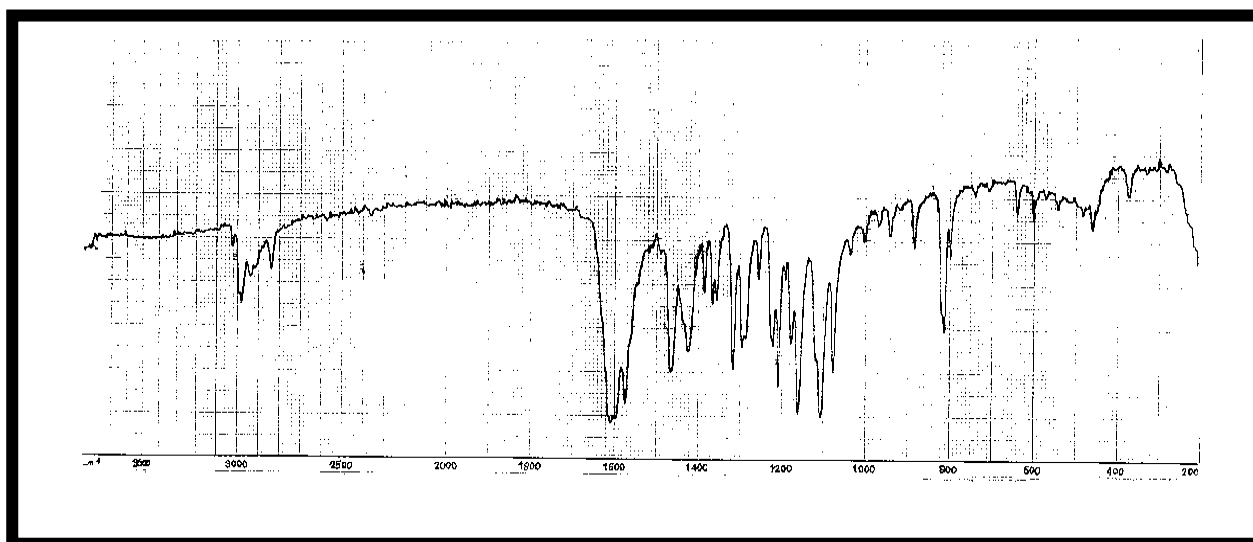


Fig. (2): I.R. spectrum of C₃ – complex CsI

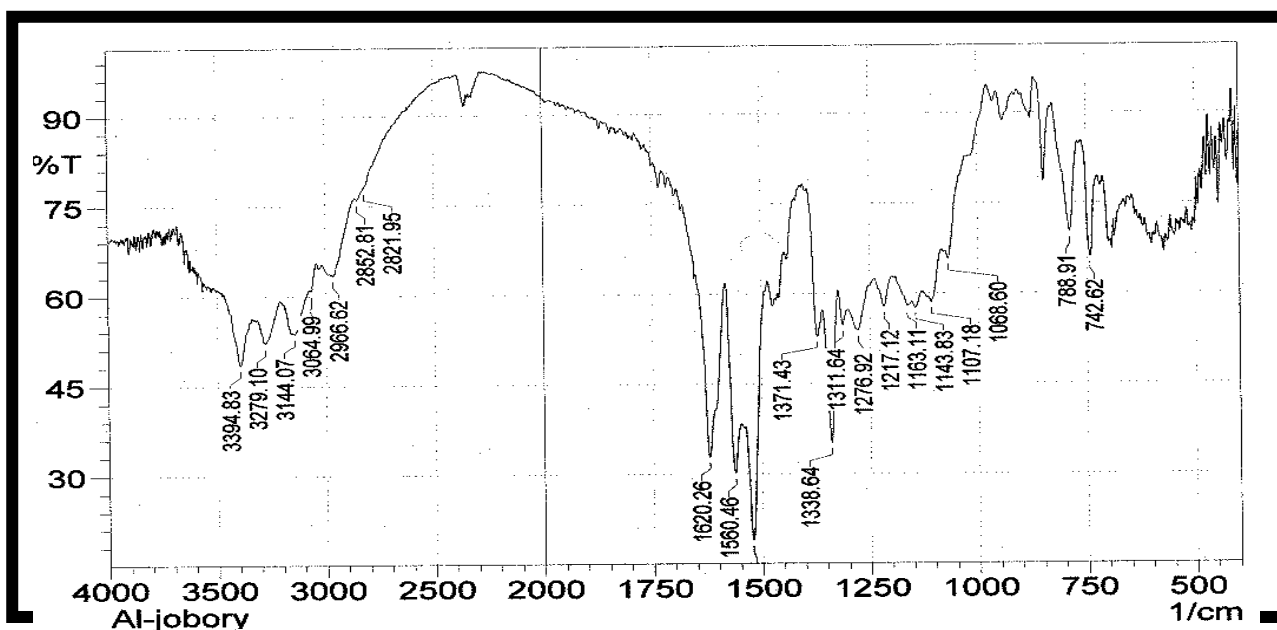
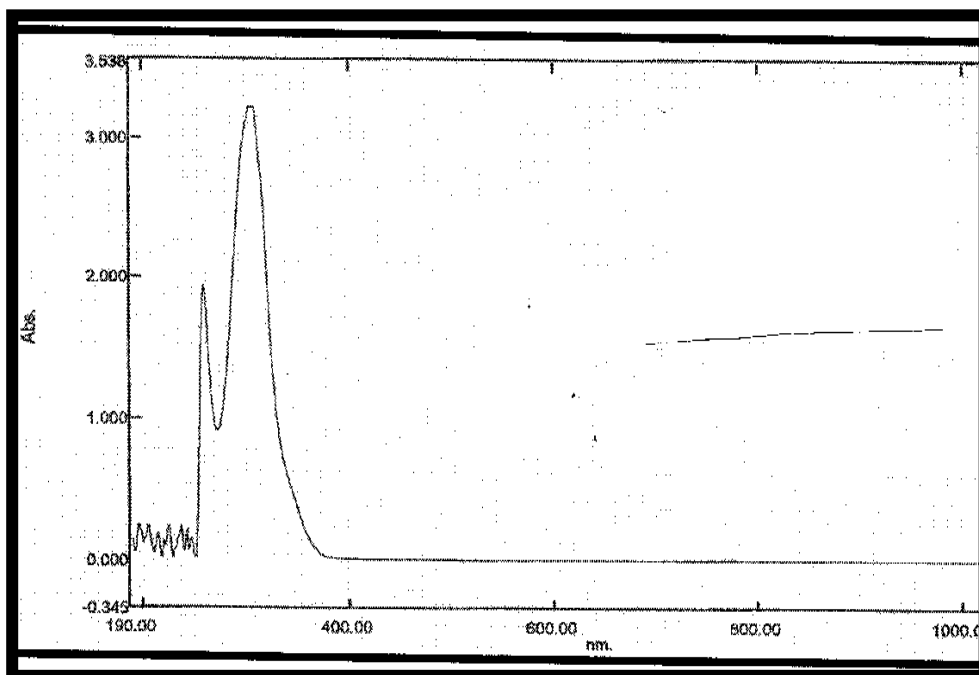
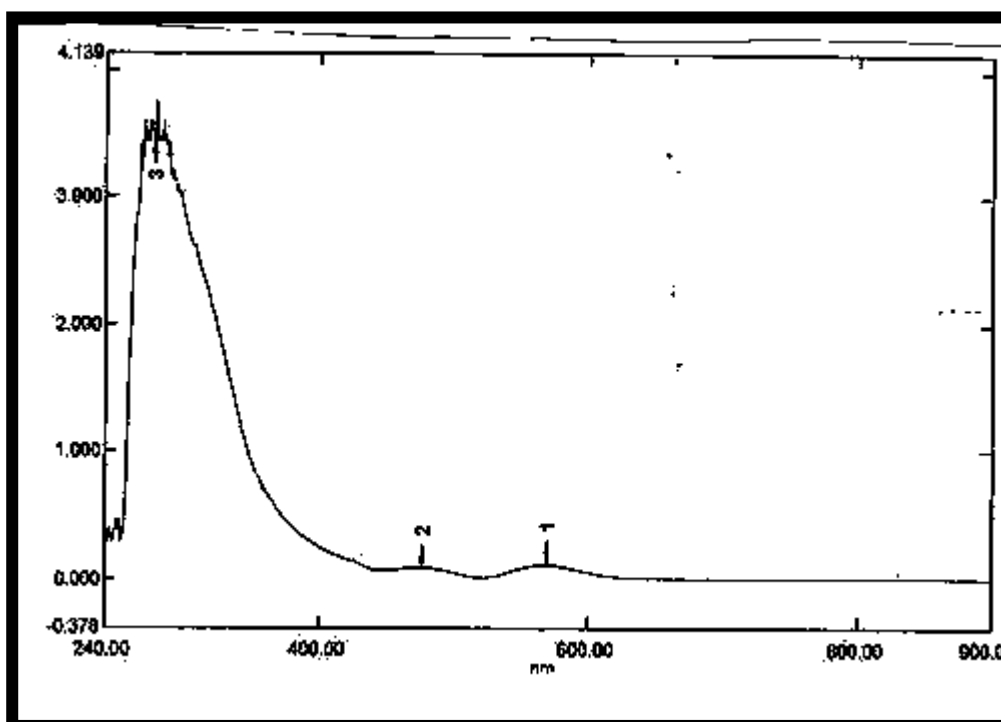


Fig. (3) : FT-IR spectrum of complex (C₂)-CsI

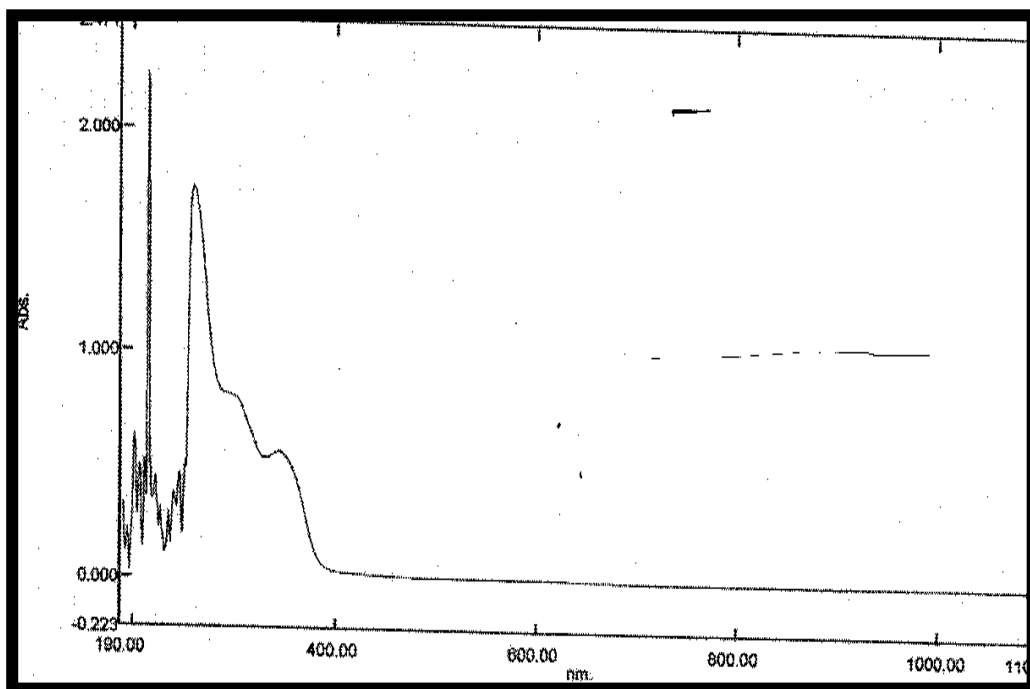
Peak	Area	Area	Area	Area	Area	Area
742.62	395					
788.91	464					
1068.6	0.243					
1107.18	0.313	65.722	3.233	1074.39	1028.09	5.88
1143.83	0.139	58.581	2.778	1114.89	1084.03	6.397
1163.11	0.239	57.632	1.57	1151.54	1130.32	4.923
1217.12	0.622	58.017	1.697	1190.12	1153.47	8.225
1276.92	0.951	57.788	4.808	1238.34	1199.76	8.473
1311.64	0.348	53.87	5.269	1298.14	1251.84	11.437
		54.744	4.186	1321.28	1300.07	5.266



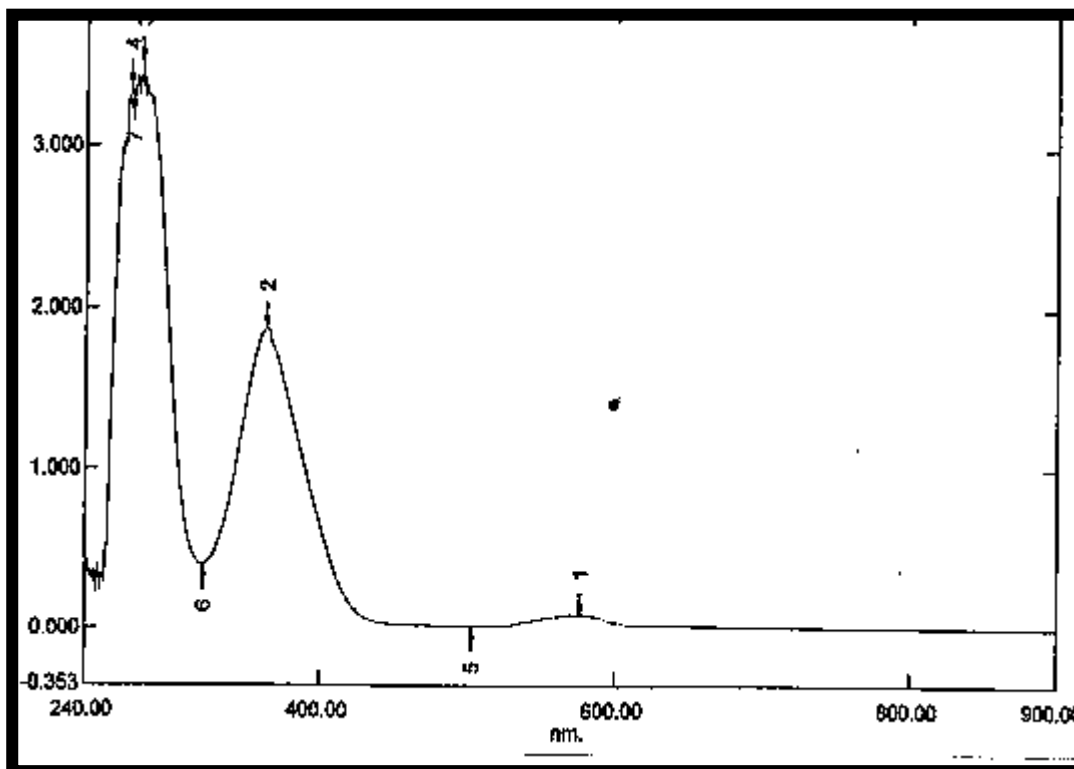
Fig(4): (UV./Vis.) spectrum of (L)



Fig(5): (UV./Vis.)Spectrum of (C1)complex



Fig(6): (UV./Vis.)Spectrum of (C2) complex



Fig(7):(UV./Vis.)Spectrum of (C3) Complex

3-4 Thermal analysis:

Steps of thermolysis of the ligand and its metal complexes for C1 & C3 complexes in table (4). Results of weight loss were quite agreeable with the theoretical values as well as confirmed those obtained from atomic absorption. Both the complexes C1 & C3 were found to give metal sulfides as final residues which refers to the stability of these sulfides^(19,20). Figure (8) shows that the elimination of chloride ion in the coordination sphere for C1 complex took place at lower temperature, while the atoms of ligand related to thiadiazole ring left the metal at temperature higher than 300°C which indicates the participation of C=N group of the ring in coordination with the metal ion⁽²¹⁻²²⁾.

According to the above mentioned results from elemental, spectral and thermal analysis as well as magnetic susceptibility, the suggested structures of the prepared metal complexes may be illustrated as follows:

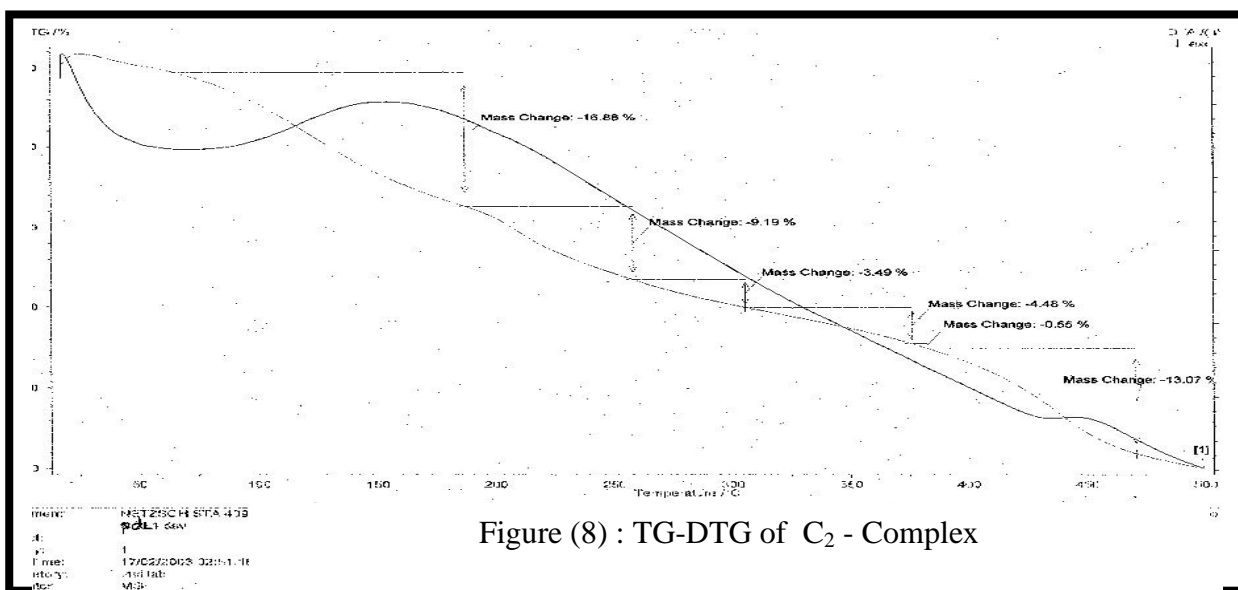


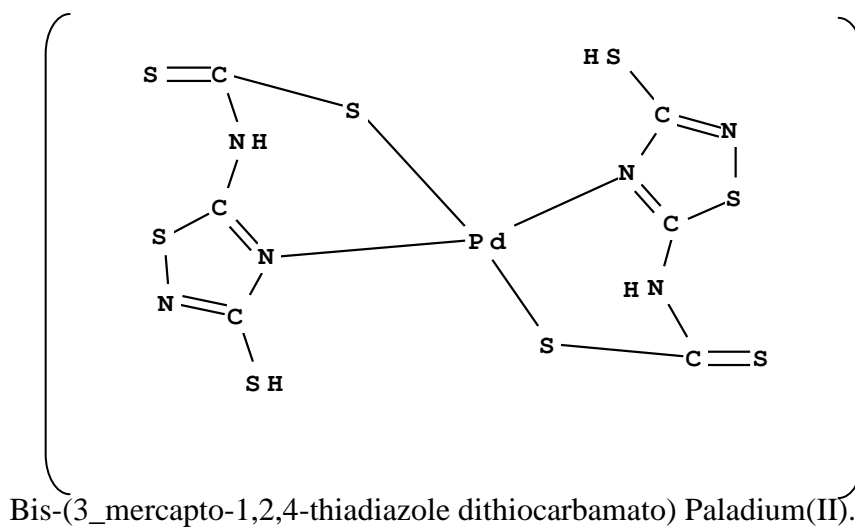
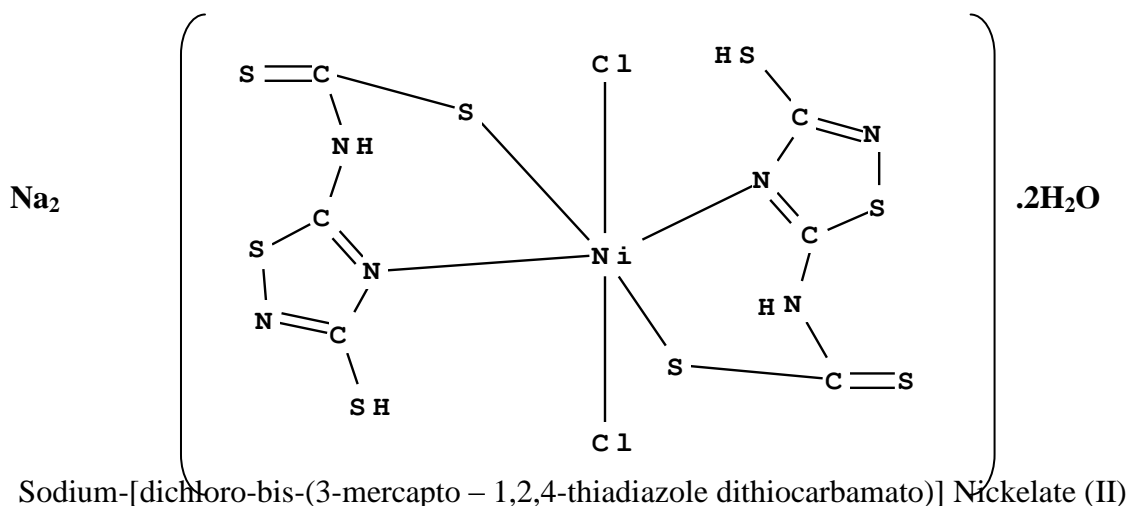
Figure (8) : TG-DTG of C₂ - Complex

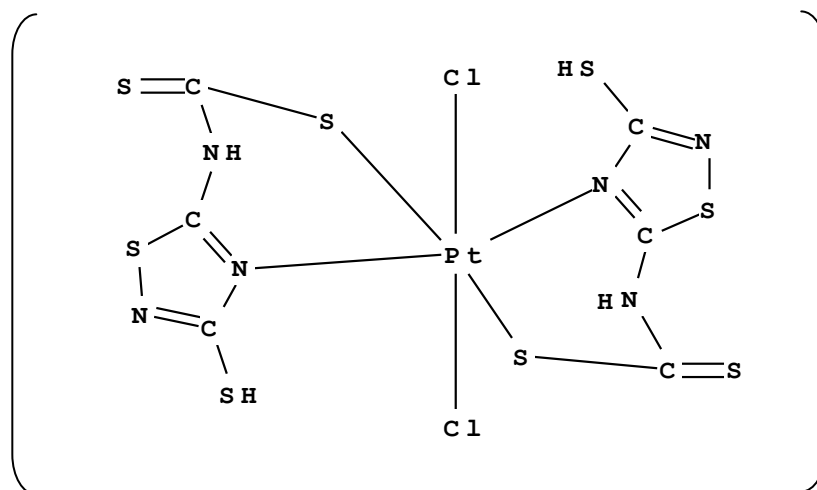
Table (3): TG-DTA – Analysis for C₁-Complex

Stable Phase	Temperature Range	Loose of weight calc.(found)
Na ₂ [Ni(C ₃ H ₂ N ₃ S ₄) ₂ Cl ₂]		
-Cl	-	-
Na[Ni(C ₃ H ₂ N ₃ S ₂) ₂ Cl]	50 – 170	5.39(5.01)
-SH		
Na[Ni(C ₆ H ₂ N ₃ S ₃)Cl]	170 – 190	2.31(2.44)
-Cl		
Na[Ni(C ₆ H ₂ N ₃ S ₃)]	190 – 210	1.5(1.030)
-2HCN		
Na[Ni(C ₄ HNS ₃)]	210 – 260	2.99(3.15)
-C ₄ HN		
NiS + Na ₂ S	260 – 400	60.91(61.61)

Table (4): TG-DTA – Analysis for C₂-Complex

Stable Phase	Temperature Range	Loose of weight calc.(found)
[Pd(C ₃ H ₂ N ₃ S ₄) ₂]	-	-
↓ -HCN		
[Pd(C ₃ H ₂ N ₃ S ₄) ₂]	65 – 190	16.88(17.1)
↓ -2SH		
[Pd(C ₃ HN ₃ S ₃) ₂]	190 – 235	9.19(8.99)
↓ -(HNSC ₂) ₂		
[Pd(CNS) ₂]	235 – 263	4.98(5.2)
↓ -CS ₂		
1/2 PdS + 1/2 PdN ₄	263 – 400	13.07(2.99)





Dichloro-bis-(3-mercapto-1,2,4-thiadiazole-dithiocarbamato) Platinum(IV).

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