

SYNTHESIS AND STUDY OF NEW METAL COMPLEXES DERIVED FROM 5-AMINO-3-[4'-PNITRO PHENYL-THIOSEMICARBAZIDO]-1,2,4-THIADIAZOLE

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Abstract

The new ligand 5-amino -3-[4'-P-nitrophenyl thiosemicarbazido]-1,2,4-Thiodiazole(L) was prepared along with its metal complexes with the selected ions Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The prepared complexes were elucidated by microelemental analysis (C.H.N.M), spectral methods (UV- visible) and (FT.IR), and other physical measurements (molar conductance in 10^{-3} M solution of (DMF), magnetic susceptibility for solid complexes and studied in solution using molar ratio(M:L) in ethanolic solution, Further more the stability of complexes in solutions were estimated via determination of stability constant Ks by spectrophotometric method.

Introduction

The insertion of functional groups into the ring of the heterocyclic compound 5-amino-1,2,4-thiadiazole -3-thione [1] was reported to produce some compounds of biological activity⁽¹⁻⁴⁾, as well as compounds of industrial uses such as antioxidants and polymer softeners^(5,6).

The efficiency of such derivatives might be increased or decreased on coordinating some of their donor atoms to a metal ion^(7,8).

Transition metal complexes of bivalent [M(II)] with derivatives of 1,2,4-thiadiazole ligands have been extensively investigated as catalysts for a number of organic redox reactions^(9,10).

In the present paper we prepared 3-[4'-P-nitro phenyl thiosemicarbazido]-1,2,4-Thiodiazole with some divalent transition metal ions.

Experimental

All the chemical, such as dithiobiuret[2], metal salts Cr(NO₃)₃.6H₂O, Mn(NO₃)₂.4H₂O, Co(NO₃)₂.6H₂O, Cu(NO₃)₂.6H₂O and Zn(NO₃)₂, solvents were purchased from fluka and used without purification the conductivities of (10^{-3}) M solution of the complexes were measured in (DMF) as solvent at (25 C°) using conductivity Hand-Held meter LF 330. The electronic spectra of the prepared complexes in UV-Vis. Region were recorded in absolute ethanol, and DMF solution using shimadzu model UV-Visible spectrophotometer. The IR. Spectra of the

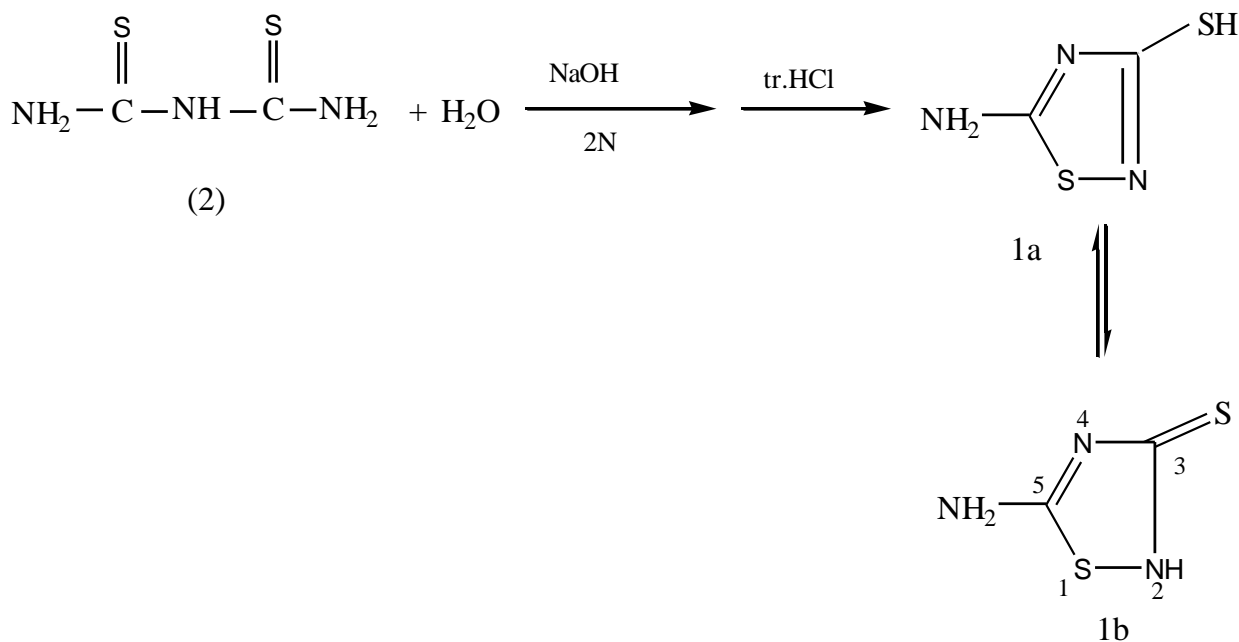
compounds were recorded with Shimadzu FTIR-3600 spectrophotometer.

Magnetic Moments were determined on showed scientific Magnetic moment balance (Model No.MK₁) at room temperature (23C°) using Hg[Co(SCN)₄] as the calibrating agent⁽¹¹⁾ diamagnetic corrections were calculated from Pascal's constants.

The elemental analyses were conducted on a Corlo-Erba instrument. The percents of Metals in the complexes were estimated by flame atomic absorption – Shimadzu AA,670 with standard addition Method.

Preparation of 5-amino-1,2,4-thiadiazole-3-thione Shown below (1)

(I) Was prepared according to general published method (12) as described in Scheme (1).

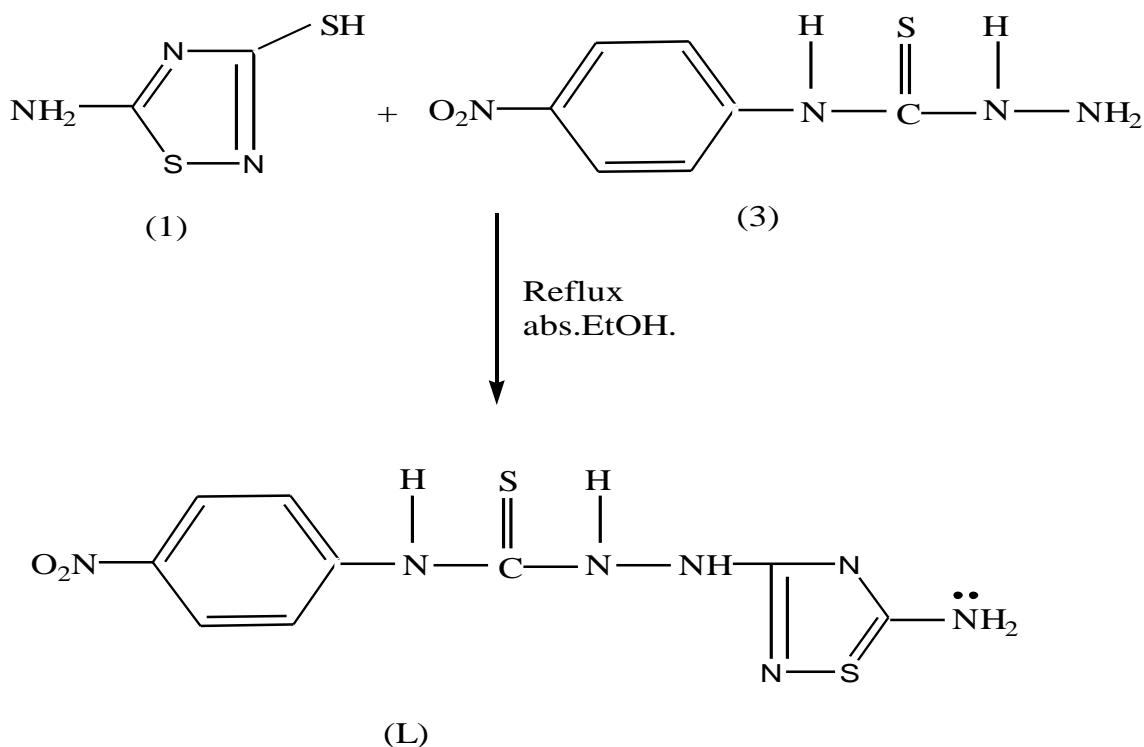


Scheme (1)

Preparation of 5-amino-3-[4'-P-nitro phenyl -Thiosemi- carbazide] -1,2,4-Thiadiazole

5-Amino -1,2,4-Thiadiazole 3-Thion [1] (0.01 mole, 1.33g) was dissolved in 20 ml absolute ethanol, and (0.01 mole, 1.80g) of 4-(P-nitro phenyl)-Thiosemicarbazide [3] in 20 ml absolute ethanol was added dropwise.

After the addition had been completed, the solution was refluxed with constant stirring for (6) hour, the mixture was filtered and the crude products was recrystallized from ethanol:distilled water in ratio (3:1 Vol) to afford 70% Yield Scheme(2).



Scheme (2)

Preparation of complexes (C₁-C₆)

A solution of metal nitrate in ethanol (20 mmole) was mixed with the ligand (L) in ethanol (40 mmole, 1.244g) in a 1:2 molar ratio except for Zn(II) 1:1. The contents were refluxed in (100 ml) absolute ethanol on an oil bath for two to three hours. The refluxed solution was then poured into ice cold water when a coloured solid separated out. The product was isolated by filtration, washed with ether,

recrystallized from dimethyl formamide and water, and dried over anhydrous CaCl₂ in Vacuum at room temperature.

The yields were (60-80)% in all complexes with respect to the ligand. They decompose at (295-320) °C and are most insoluble in common organic solvents such as ethanol, chlorobenzene, acetone, nitrobenzene, dichloromethane and chloroform. However, they are soluble in polar organic solvents (DMSO and DMF).

Table (1)
Suggested formulas, and Micro-elemental analysis of the Prepared complexes.

Comp.	Formula	Elemental analysis Calc.% (found)			
		C%	H%	N%	M%
L	C ₉ H ₉ N ₇ O ₂ S ₂	34.72 (33.91)	2.89 (2.50)	31.51 (30.88)	—
CrL	[Cr(C ₉ H ₉ N ₇ O ₂ S ₂) ₂ (NO ₃) ₂]	25.08 24.39	1.75 1.030	27.64 28.00	6.16 (6.01)
MnL	[Mn(C ₉ H ₉ N ₇ O ₂ S ₂) ₂ (NO ₃) ₂]	27.00 26.63	1.77 1.33	28.0 28.01	6.75 (6.43)
CoL	[Co(C ₉ H ₉ N ₇ O ₂ S ₂) ₂ (H ₂ O) ₂](NO ₃) ₂	25.77 24.89	2.14 2.01	26.73 26.65	6.68 (6.00)
NiL	[Ni(C ₉ H ₉ N ₇ O ₂ S ₂) ₂ (NO ₃) ₂]	26.86 (25.79)	1.74 (1.11)	27.86 28.00	6.96 (6.35)
CuL	[Cu(C ₉ H ₉ N ₇ O ₂ S ₂) ₂ (H ₂ O) ₂](NO ₃) ₂	25.54 25.22	2.12 (2.15)	26.49 (27.22)	7.51 (7.01)
ZnL	[Zn(C ₉ H ₉ N ₇ O ₂ S ₂)(NO ₃) ₂]	21.64 20.89	1.402 (1.22)	19.63 (20.11)	12.82 (12.78)

Table (2)
Characteristic stretching vibrational frequencies (cm⁻¹) located in I.R. spectra of ligand(L) and its metal complexes.

Comp.	IR absorption ν (cm ⁻¹)									
	νNH ₂	νN-S	νC=N	νN-N	νC=S	νNO ₃	M-N	M-O	νO-H	δ-OH
La,lb	3350(m) 1350	1350	1595(s)	—	1050(s)	—	—	—	—	—
L	3410(m) 1345(m)	1345(m)	(1605(s))	950(m)	1010(s)	1450(s)	—	—	—	—
CrL	3250(br.) 1362(s)	1362(s)	1580(s)	930(m)	990	1430(m)	590	590	—	—
MnL	3180(br.) 1358(m)	1358(m)	1587(s)	940(m)	980	1420	398(m)	—	—	—
CoL	3200(br.) 1360(m)	1360(m)	1605(s)	925(m)	980	1415(m)	410(w)	410(w)	3610*(br.)	1615(s)
NiL	3180(m) 1349(m)	1349(m)	1579(s)	930(m)	1000(s)	1405(s)	418(w)	—	—	—
CuL	3210(m) 1356(m)	1359	1592(s)	940	995	1440	405(w)	405(w)	3450*(br.)	1605(s)
ZnL	3300(m) 1355(m)	1355(m)	1567(s)	950(m)	968(m)	1430(s)	410	—	—	—

S=strong, m=medium, w=weak, br=broad * = referred to asymmetrical vibrational modes of (O-H) for water molecular, and rocking(O-H) for Co(II) and Cu(II) complexes.

Table (3)
Elementic spectra Data ,Conductance in (DMF) Magnetic Moments(B.M)and stability constants of metal complexes.

Comp.	Magnetic moment μ_{eff} (B.M)	Molar conductance Λ_m (DMF)	Stability constant $K(\text{L.mol}^{-1})$	UV-Visible Peak λ_{max} (nm)			
				$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	d-d trans.	Charge transfer
L				220	315	—	—
CrL	3.50	80	5×10^3	230	295	615 ^a 415	
MnL	5.50	145	2.5×10^3	218	310	495	390 ^b
CoL	2.95	180	3.5×10^4	240	320	715 ^a 590	
NiL	0.0	210	4.5×10^4	235	332	515	380 ^b
CuL	1.30	195	9.5×10^4	260	350	520 ^a	
ZnL	0.0	190	7.5×10^3	242	313		365 ^b

a = extinction coefficient (ϵ_{max}) for d-d transition.

b = extinction coefficients(ϵ_{max}) for charge transfer $M \rightarrow L$ or $L \rightarrow M(\text{ZnL})$.

Result and Discussion

The stoichiometrics of the ligand and its complexes confirmed by their elemental analyses.

Elemental analyses (C.H.N.M)forward to be in good agreement with the general formula given for the complexes.

Conductivity Measurement

The observed conductivity measurements of the complexes in DMF solution (10^{-3}M) indicated the electrolytic behaviour in (1:2) ⁽¹³⁾ ratio for all complexes except for CrL which was (1:1) .

Spectral studies

Infrared spectra :-The diagnostic band of the infra-red spectra and their assignment for the free ligand and its complexes are gives in Table(2).

The bands observed at 3350cm^{-1} , $1595,1050$ and 1350cm^{-1} in the spectrum of starting material (la,lb) are assigned to $\text{NH}_2, \text{C}=\text{N}, \text{C}=\text{S}$ and ⁽¹⁴⁾ bands. upon substitution of thiol group of (la) with 4-P-nitrophenyl thiosemicarbazide.

The new ligand (L) shows new bands at $950,1450$ and cm^{-1} which may be attributed to N-N,N=O and bending of 1,4-disubstituted benzene ring⁽¹⁵⁾ .

A comparison of the infrared spectra of the free ligand and metal complexes reveals that all Table (2), coordination of metal to nitrogen of amino group in position (5) and nitrogen number (4) of the ring to form five-membered ring system due to the negative shift in stretching amino (νNH_2) by range (200-160) cm^{-1} and red shift of (C=N) by range (10-25) cm^{-1} metal nitrogen band is further confirmed by the presence of bands around(410-510) cm^{-1} ⁽¹⁶⁾ .

Finally the presence of water molecule coordinated to metal was explained by diagnostic bands at (3610-3450) cm^{-1} (-OH) and (1605-1615) cm^{-1} (rocking $\delta\text{O-H}$)bands ⁽¹⁷⁾ .

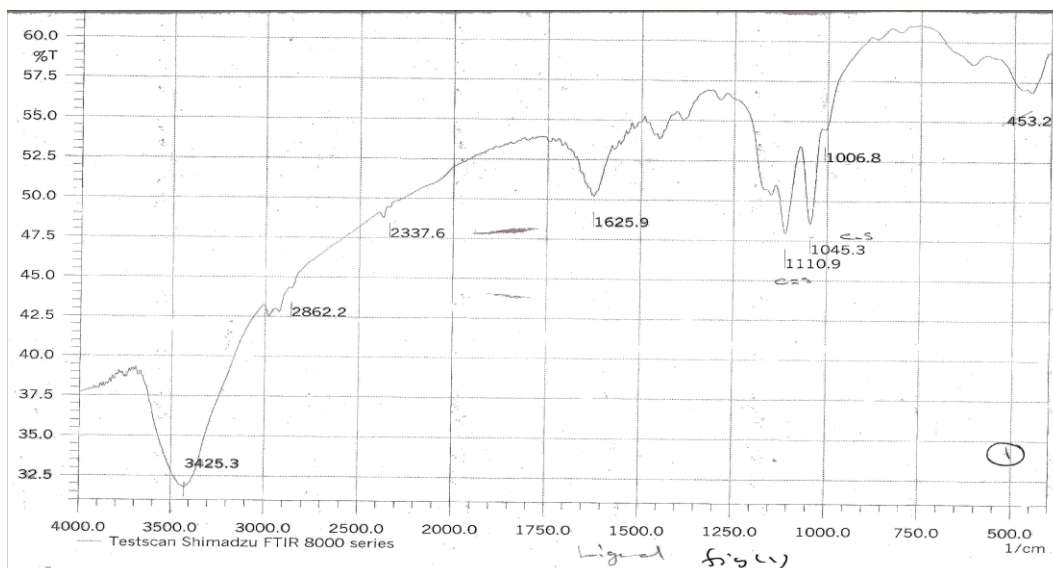


Fig.(1) : FT.IR.Spectrum of L. ligands.

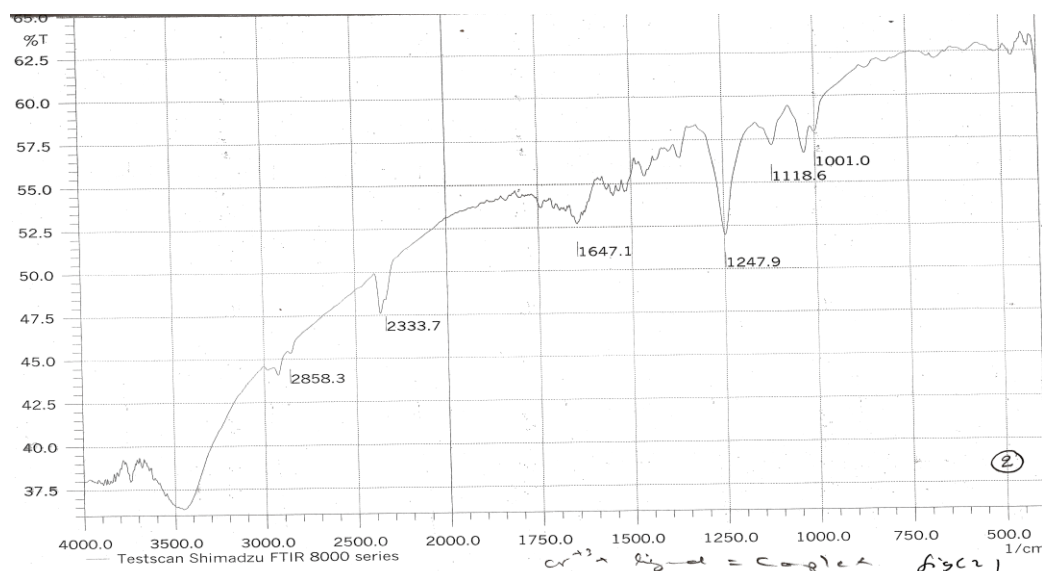


Fig.(2) : FT.IR.Spectrum of Cr.

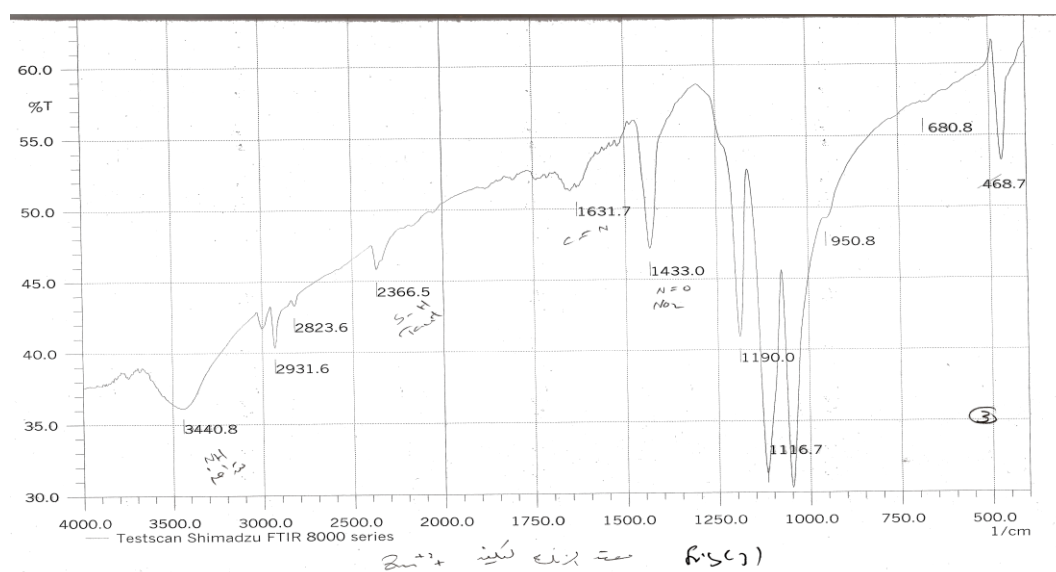


Fig.(3) : FT.IR.Spectrum of Mn.

Electronic Spectra

The important electronic spectral data of the ligand and metal complexes are described in Table (2). The spectrum of ligand solution in absolute ethanol shows two peaks at 220 and 315 nm which are assigned to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions⁽¹⁸⁾. Fig. (4).

The green solution of CrL complexes exhibits two weak transition in visible (415&615) nm which are forbidden spin transition of (${}^4A_{2g} \rightarrow {}^4T_{2g}$) ($10Dq$) and (${}^4A_{2g} \rightarrow {}^4T_{1g}$) (F)⁽¹⁹⁾ respectively, this supports the octahedral geometry complexes Fig.(5).

The (MnL) complex was more soluble in DMF giving a deep red colour, this reveals the presence of vacant coordination site on the metal ion which led to formation an octahedral complex with solvent molecules⁽²⁰⁾ only one absorption band was observed in the visible region of 495nm and was assigned to the forbidden transition (${}^6A_{2g} \rightarrow {}^4E_g, {}^4A_{1g}(G)$)⁽²¹⁾, the magnetic moment in the solid state ($\mu_{\text{eff}}=5.5\text{B.M}$) indicated which spin-tetrahedral complex⁽²¹⁾.

The spectrum of Co(II) complex exhibited a multiple bands at (715)nm and (590)nm

bands are characteristic octahedral Cobalt (II) complexes assigned to (${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$) and (${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$) transitions⁽²²⁾.

The NiL complex gave a yellow orange colour in DMF which refers to the presence of vacant coordination sites on the metal ion. The solid was found diamagnetic, indicating a square planar geometry⁽²³⁾. The new weak bands in the visible region of Ni(II) complex at (380 and 515)nm are assigned to charge transfer ($dxy \rightarrow \pi^*$)(T_{2g}) and (${}^1A_{2g} \rightarrow {}^1A_{2g}$) respectively⁽²³⁾.

The blue complex of Cu(II) gave deep green colour in DMF and shown broad band at 520nm of Spin transition (${}^2E_g \rightarrow {}^2T_{2g}$)⁽²³⁾.

The presence of one unpaired electron was investigated upon the magnetic moment value ($\mu_{\text{eff}} = 1.05\text{B.M}$) of distorted octahedral⁽²⁴⁾.

The yellow solution of Zn(II) complex in DMF, shown-high intensity peak at 365nm which are attributed to (M→L) charge transfer transition⁽²⁵⁾. The solid was found diamagnetic and the suggested structure is a tetrahedral complex.

Fig.(4): UV-Visible spectrum of ligand (10^{-3}M) in Ethanol.

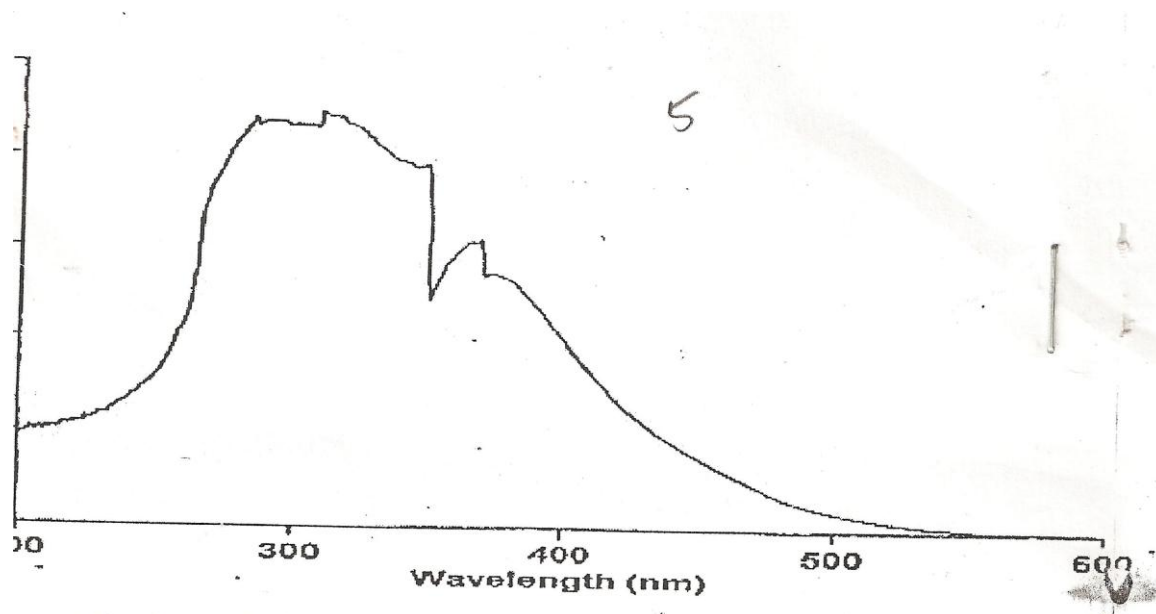
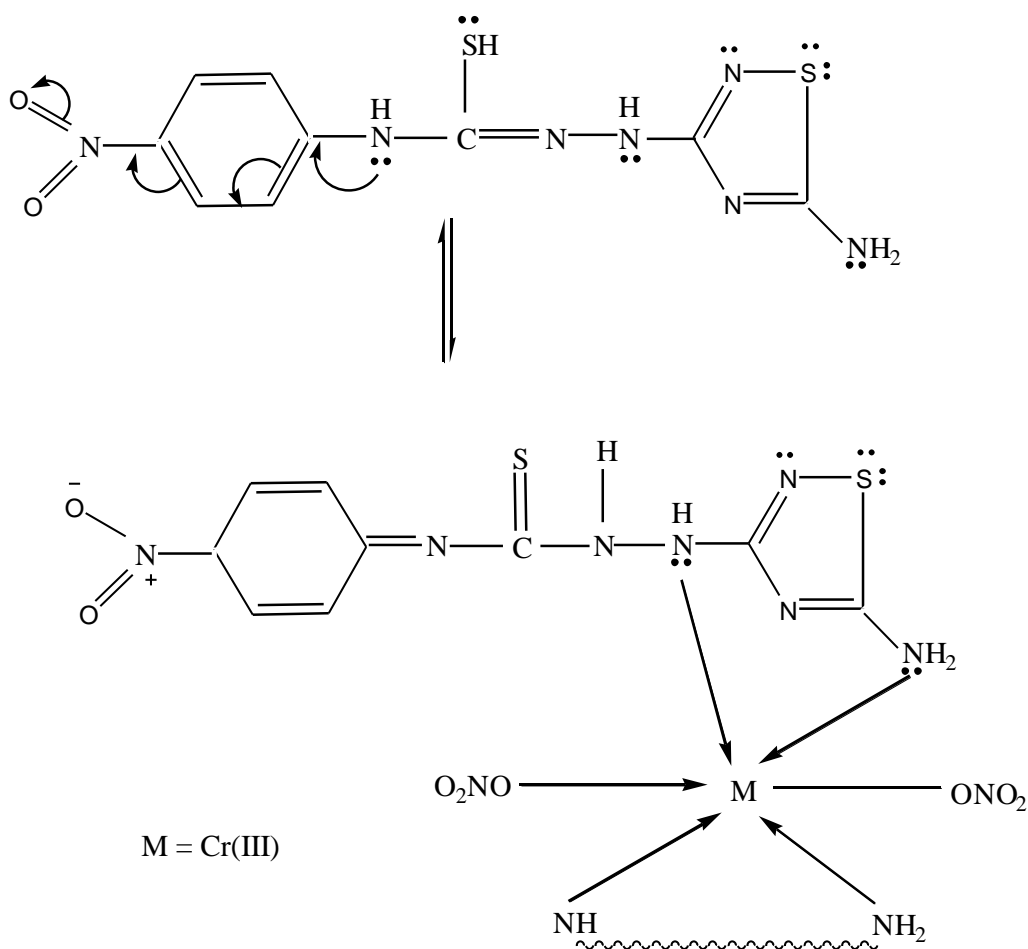


Fig.(5) : UV-Visible spectrum of Cr(III) complex in DMF.

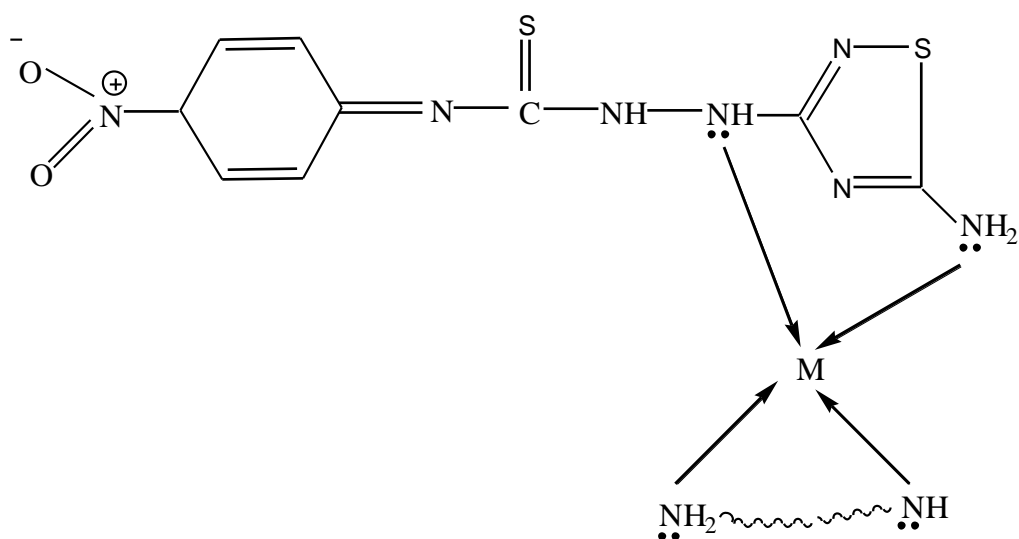
Suggested stereochemical structures:

According to the results obtained for elemental and spectral analyses, the suggested

structures of the above mentioned complexes, can be illustrated as follows :

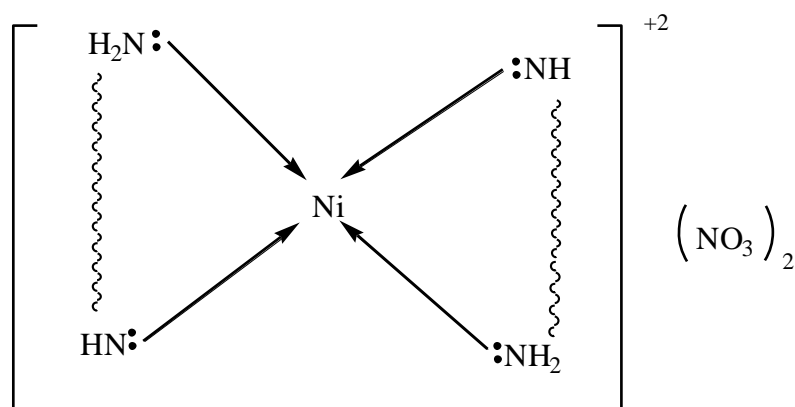


Structure (I) octahedral of C_1 complex.

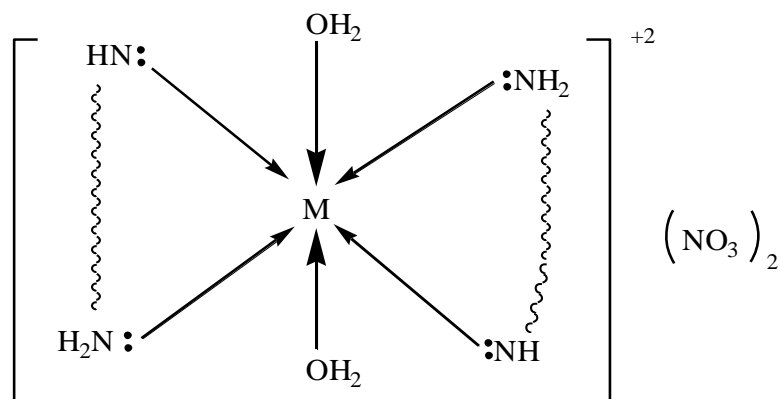


M = Mn(II)

Structure (II) Tetrahedral Suggested stereochemical structure of the C_2 complex.

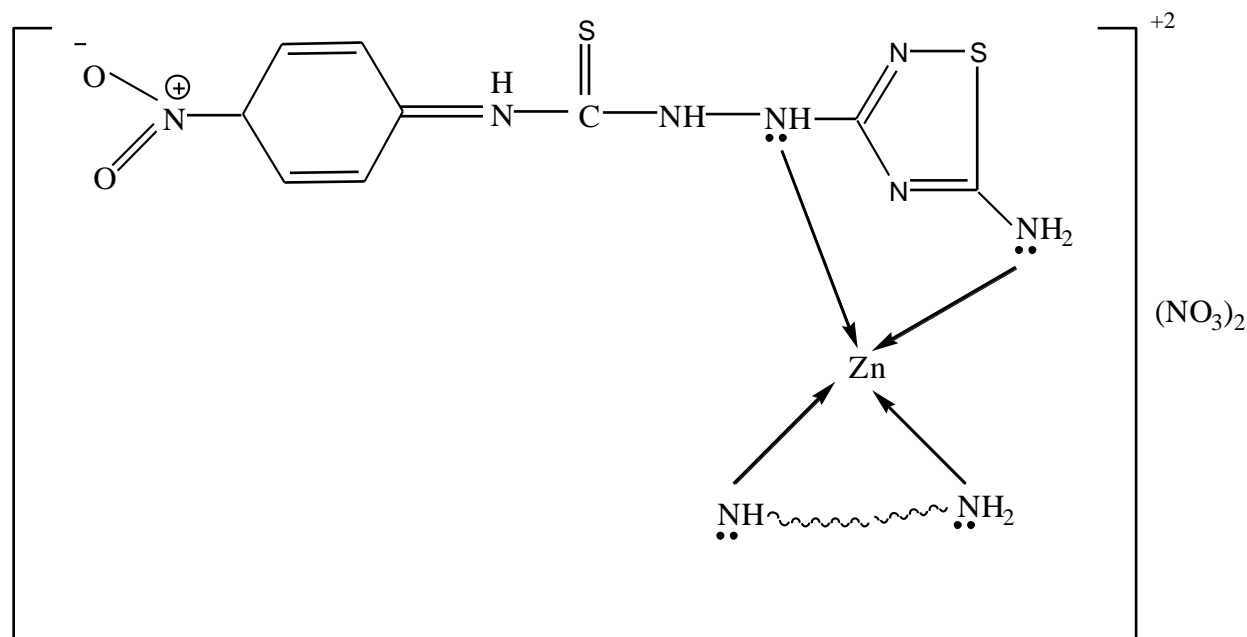


Structure (III) Square planar Symmetry of C_4 complex.



M = Co(II) and Cu(II)

Structure (IV) Octahedral Symmetry of C_3 and complex C_5 complex.



M = Zn (II)

Structure (V) Tetrahedral symmetry of C₆ complex.

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الخلاصة

تم في هذا البحث تحضير ليكاند جديد (٥-امينو -٣-
 ٤'-بارانترو فنيل ثايو سيمي كاريازيدو) (١,٢,٤- ثايداديازول
 مع مجموعة من معقدات مع بعض الايونات المنتقاة (الكروم
 الثلاثي ، المنغنيز ، الكوبلت ، النيكل ، النحاس ، الزنك
 الثنائية) . درستُ وشخصت المعقدات بالتحليل الدقيق
 للعناصر (كاربون - هيدروجين، نتروجين -فلز) والطرق
 الطيفية المعروفة (طيف الاشعة تحت الحمراء المعززة
 بتحويلات فورير وطيف الاشعة فوق البنفسجية - المرئية)
 فضلاً عن قياس الحساسية المغناطيسية للمعقدات في الحالة
 الصلبة ، قياس التوصيل المولاري لمحاليلها بطريقة النسب
 المولية في محلول (10^{-3}) مولاري لمذيب (N-N- ثنائي
 مثيل فورماميد) تم تعيين قياس نسبة الليكاند : فلز في
 محلول الايثانول . علاوة على ذلك تم دراسة استقرارية
 المعقدات في محاليلها من خلال تعيين ثوابت الاستقرارية .