

Transition Metal Complexes of 2-Hydroxy-N-(5-mercapto-1,3,4-thiadiazole-2-yl)benzilidine

معقدات العناصر الانتقالية للمشتق 2-هيدروكسي-N-(5-مركبتو-1,3,4-ثياديازول-2-يل)بنزيلدين

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الخلاصة : يتناول هذا البحث تحضير معقدات جديدة لعدد من العناصر الانتقالية، Cr^{+3} , Fe^{+3} , Co^{+2} , Ni^{+2} , Cu^{+2} , Pd^{+2} , Cd^{+2} , Pt^{+2} مع المشتق الجديد للمركب 2-امينو-5-مركبتو-1,3,4-ثياديازول من خلال مفاعله مع اورثو-هيدروكسي بنزالديهايد للحصول على 2-هيدروكسي-N-(5-مركبتو-1,3,4-ثياديازول-2-يل) بنزيلدين. شُخص ودرس هذا المركب باستخدام الطرق الطيفية والتحليلية أطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية-المرئية ومطيافية الامتصاص الذري، قياس الحساسية المغناطيسية والتوصيلية المولارية للمعقدات إضافة إلى حساب النسب المولية لتحديد الصيغ التركيبية المحتملة كما أجري فحص الرنين النووي المغناطيسي لليكاند المحضر. من خلال هذه الفحوص تبين إن المعقدات المحضرة تمتلك الأشكال الهندسية التالية.

$n=2,3,4$

1- شكل ثماني السطوح ذو الصيغة MLCl_n و ML_2Cl_n

2- بنية مربع مستوي ذو الصيغة ML_2Cl_2 , MLCl_2

3- بنية رباعي السطوح ذو الصيغة MLCl_2 , $\text{M}_2\text{L}_2\text{Cl}_2$

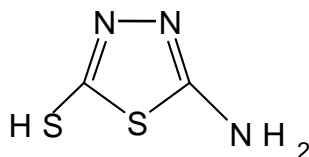
Abstract: This research concerning the preparation a new derivative of the compound 2-amino-5-mercapto-1,3,4-thiadiazole which reacted with o-hydroxy bezaldehyde to produce 2-hydroxy-N-(5-mercapto-1,3,4-thiadiazole-yl)benzilidine. The new ligand and it's complexes of the metal ions; Cr^{+3} , Fe^{+3} , Co^{+2} , Ni^{+2} , Cu^{+2} , Pd^{+2} , Cd^{+2} and Pt^{+4} were prepared and characterized by infra-red, FTIR and UV-visible spectroscopy ,atomic absorption, magnetic susceptibility and molar conductivity measurements .In addition the molar ratio measurements were used to identify the suspected molecular formula for the complexes and the nuclear magnetic resonance was carried out for the prepared ligand. These measurements suggest the following molecular formulas for the metal complexes:

1-Octahedral configuration with the formula; MLCl_n , ML_2Cl_n $n=2,3,4$

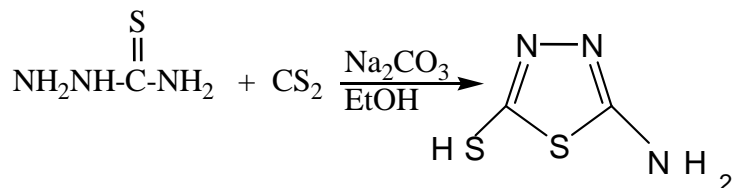
2-Square planer configuration with the formula; MLCl_2 , ML_2Cl_2

3-Tetrahedral configuration with the formula; MLCl_2 , $\text{M}_2\text{L}_2\text{Cl}_2$

Introduction: The compound 2-amino-5-mercapto-1,3,4-thiadiazole (1) was prepared first by Guha⁽¹⁾ at 1922 and since that time different method ,easy and simple were published to prepare this compound ⁽²⁻⁴⁾, and one of them by reaction of thiosemicarbazide with carbon disulfide in the presence of sodium carbonate as an activator, scheme (1). This compound was used as a starting material for the synthesis of many derivatives having 1,3,4-thiadiazole as a main nuclei.

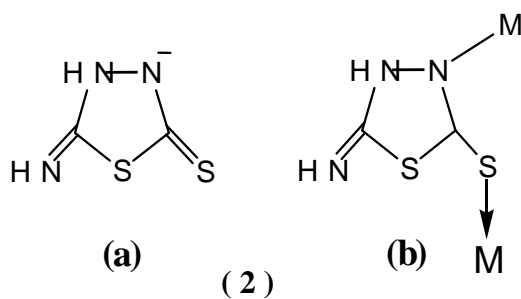


(1)



Scheme -1-

Metal complexes of (1) was prepared and investigated with several transition metal ions⁽⁵⁻⁸⁾. Schiff base derived from (1) with the metal complexes of the ions; Co^{+2} , Ni^{+2} , Cu^{+2} and Mn^{+2} were reported⁽⁹⁾. These complexes suggest the coordination occurs through the nitrogen atom of the thiadiazole ring, and thiol group (SH)⁽¹⁰⁻¹³⁾ (2).



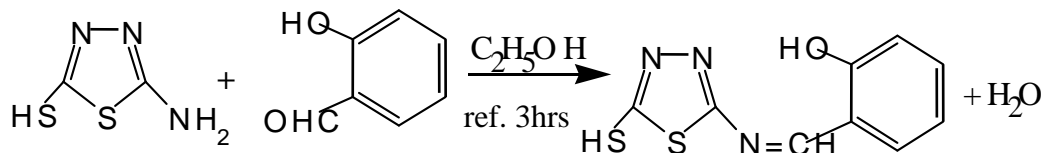
The new ligand 2-Hydroxy-N-(2-mercapto-1,3,4-thiadiazole-5-yl)benzelidine and the complexes of the metal ions: Cr^{+3} , Fe^{+3} , Co^{+2} , Ni^{+2} , Cu^{+2} , Pd^{+2} , Cd^{+2} and Pt^{+4} were prepared and investigated in this research.

Physical measurements: The following analytical and physical measurement were used for the prepared ligand and complexes:

- 1- To identify the metal percentage in the complexes by using Shimadzu flame atomic absorption Model;6809.
- 2- Melting points were measured by Stuart scientific melting points apparatus.
- 3- UV-visible spectra were carried out (200-1000nm) with Hitachi UV-2000 spectrophotometer.
- 4- Infra - red spectra were carried out with Pye-Unicom SP3-100 spectrophotometer ($4000-600\text{cm}^{-1}$) and Test scan Shimadzu FTIR 8000 series spectrophotometer ($4000-200\text{cm}^{-1}$) by using KBr and CsI disk.
- 5- Molar conductivity for the ligand and complexes with the concentration 10^{-3}M and DMF as a solvent were measured by Inolad conductivity 740 WTW Statten model LF91 D812.
- 6- Magnetic susceptibility for the complexes were conducted using faraday method with Balance-Magnetic susceptibility Model MSB-MK-I apparatus.
- 7- Nuclear magnetic Resonance (H^1 -NMR) for the prepared ligand was carried out using H^1 NMR-Unter suchunges auftrag AVS-400 in Germany with CD_3OD as a solvent.

Experimental:

1-Preperation of the ligand : The ligand was prepared as reported in the reference⁽¹⁴⁾ with some modification ; 0.001 mole (0.133g) of (1) and 0.001 mole (0.122g) of o-hydroxy benzaldehyde were dissolved in anhydrous ethanol (20ml), then refluxed for three hours and cooled. The precipitate was filtered and recrystallized from ethanol-benzen(1/1) to afford a bright yellow precipitate ,Scheme (2).



Scheme-2-

2-Preperation of the complexes:

a-Metal complexes of Fe^{+3} , Ni^{+2} , Cu^{+2} , Cd^{+2} and Pt^{+4} ; 0.005 mole (0.118g) of the ligand dissolved in hot abs.ethanol (20ml) was mixed with 0.005 mole of the metal chloride dissolved in hot abs.ethanol (10ml).The mixture stirred and refluxed for ½ hour, the resulting precipitate was filtered and dried ,Table(1).

b- Metal complexes of Cr^{+3} and Co^{+2} ; same procedure as above except the mixture refluxed for three hours and to precipitate the metal complexes the pH of the solution modified by using Sodium carbonate solution (5%) to pH 6.9 in case of Co^{+2} and 7.7 in case of Fe^{+2} .

c- Metal complex of Pd^{+2} ; 0.001 mole (0.177g) of PdCl_2 and 0.002 mole (0.117) of NaCl were dissolved in dist. water (10ml), the mixture was stirred until a clear brown solution formed. 0.001 mole of the ligand dissolved in abs. ethanol (20ml) was added and the resulting mixture was refluxed for one hour, cooled and filtered. Recrystallization from hot abs. ethanol afford a red brownish precipitate

Table(1) Physical properties of the ligand and metal complexes

Seq.	Formula	Color	m.p °C	Yield%
1	$\text{C}_9\text{H}_7\text{N}_3\text{S}_2\text{O}$	bright yellow	198	63
2	$[\text{Cu}_2(\text{L})_2\text{Cl}_2]\text{Cl}_2$	brown	222	31
3	$[\text{Ni}(\text{L})]\text{Cl}_2$	light brown	>300	44
4	$[\text{Co}(\text{L})\text{Cl}_2]$	deep brown	274	18
5	$[\text{Cd}(\text{L})\text{Cl}_2]$	white	275	89
6	$[\text{Pd}(\text{L})\text{Cl}_2]$	reddish brown	290	83
7	$[\text{Cr}(\text{L})_2]\text{Cl}_3$	green	>300	31
8	$[\text{Fe}(\text{L})_2]\text{Cl}_3$	deep brown	208	45

9	[Pt(L)Cl ₄]	black red	272	33
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Results and discussion :

- 1- **H¹-NMR:** The proton nuclear resonance spectrum for the ligand was carried out using CD₃OD as a solvent and the following peaks were detected, Fig.(1):
 - a- Single peak at δ 13.3ppm for SH>
 - b- Tetra peak at δ 4.6-5.1ppm for CH adjacent to four proton of the aromatic ring.
 - c- Multiple peak at δ 6.9-7.7ppm for 4H of the disubstitute aromatic ring.
 - d- Single peak at δ 8.8ppm for CH of the Schiff base.
- 2- **Infra-red spectra:** A new stretching band of (C=N) appeared at 1610cm⁻¹ in the prepared ligand instead of the two stretching bands at 3140 and 3260cm⁻¹ of (NH₂) in the original compound (1) indicate occurrence of the reaction and a Schiff base been formed . Other stretching bands for SH group at 2390cm⁻¹ , 3074cm⁻¹ of OH group and 1064cm⁻¹ of (N-N) group of the diazole ring were also detected. In the metal complexes down load shifting for SH and N-N stretching bands indicate the coordination of the metal ion occurred through N and S atoms. New stretching bands of M-N, M-Cl and M-S recorded at lower region (200-600cm⁻¹), while an additional band detected in Cu⁺² complex for bridge (Cl-M-Cl) at 279cm⁻¹ which it was lower than them terminal (M-Cl)⁽¹⁵⁾, Table(2)
- 3-

Table(2) Major Infra-red absorption bands (cm⁻¹) of the ligand and complexes

Seq.	ν SH	δ NH+ ν C=N thioamide	ν OH	ν C=N Schiff	ν C-S	ν M-OH Solvent	ν M-N	ν M-S	ν M-O	ν M-X
1	2380	1571, 1527	3074	1610	759	—	—	—	—	—
2	2335	1569, 1500	3085	1612	748	3300, 1126	528	385	—	327, 291
3	2368	1571, 1520	3176	1624	756	—	464	—	—	385, 314
4	2368	1575, 1519	3200	1608	729	3371, 1150	424	376	—	352, 293
5	2335	1554, 1510	3176	1606	750	3298	538	383	—	318, 293 277
6	2366	1560, 1514	3103	1606	790	3382	563	464	—	383, 312
7	2375	1554, 1487	3121	1609	768	—	518	422	352	
8	2335	1560, 1519	3190	1614	—	—	460	329	291	239, 277
9	2381	1555, 1519	3193	1614	702	3305	475	370	—	339, 291

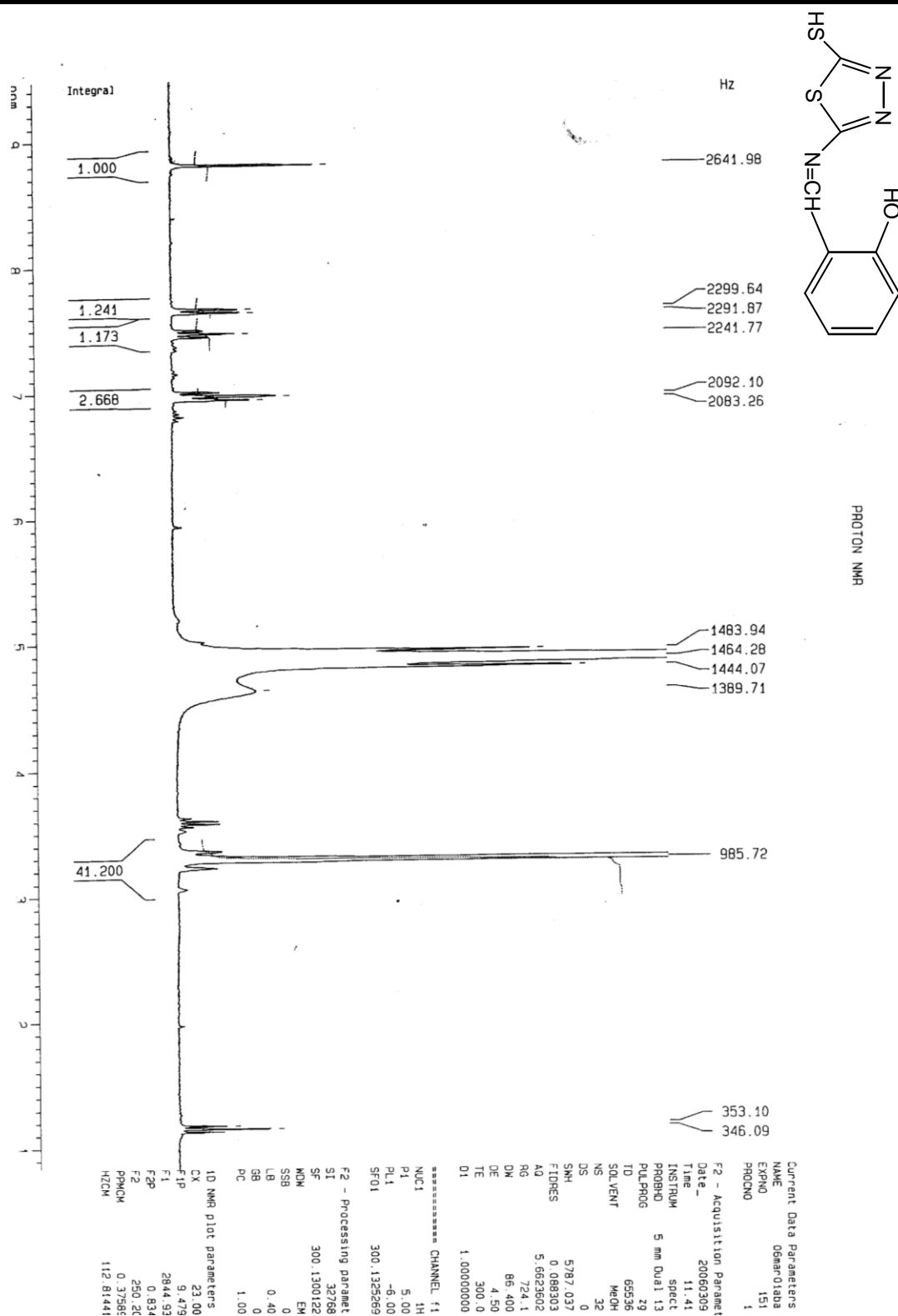


Fig. (1) ^1H NMR of the prepared ligand

3- Electronic spectra: For the prepared ligand, three absorption bands were detected, first one located at 314nm for ($n \rightarrow \pi^*$) of the Schiff base group ($C=N$), while the second was at 252nm for ($n \rightarrow \pi^*$) of the two interact ($C=C$) group of aromatic and thiadiazole ring⁽¹⁶⁾ and the third one located at 219nm for ($n \rightarrow \sigma^*$) of hydroxyl group(OH).

For the spectra of metal complexes the following results were obtained :

a- Cu^{+2} complex showed a broad band at around 650nm due to ($B_{1g} \rightarrow ^2E_g$) transition and with the infra red spectra, obtained magnetic susceptibility and molar conductivity, would suggest a non ionic square planner with dimmer formula^(17,18).

b- Ni^{+2} complex, two bands were observed, the first one was a broad band located at 723nm attributed to ($^3A_{2g} \rightarrow ^3T_{1g}$) and [$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$] transition and the second one at 657nm due to ($^1A_{1g} \rightarrow ^1B_{1g}$) and ($^1A_{1g} \rightarrow ^1E_g$) transition and this results go with square planner complex⁽¹⁹⁾.

c- Co^{+2} complex showed a three bands at 656nm and 610nm attributed to [$^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$] and [$^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$] respectively while the third one detected at 575nm due to charge transfer transition. These results with the value (4.8B.M) of magnetic moment suggest a high spin octahedral geometry^(20,21).

d- Cd^{+2} complex did not shoe any electronic transition due to d^{10} configuration, so the suggested geometry will depend on the physical measurements.

e- Most of Pd^{+2} complexes will prefer the square planner geometry^(22,23) due to the position of this element in the second round with increasing of ligand field, Table(3).

f- Cr^{+3} complex shoed two bands at 710nm of [$^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$] and 640nm of [$^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$] and that goes with an octahedral geometry^(24,25).

g- Fe^{+3} complex , three bands were observed at 757nm, 725nm and 304nm attributed to $^4A_{1g} \rightarrow ^4T_{1g}(G)$, $^4A_{1g} \rightarrow ^4E_g$, $^4A_{1g}(G)$ and $^4A_{1g} \rightarrow ^4T_{1g}(P)$ transitions respectively. These bands suggest low spin octahedral geometry⁽²⁶⁻²⁸⁾ and that agree with the value of magnetic moment (1.77B.M.).

h- Pt^{+4} complex showed two bands at 561nm of $^3A_{1g} \rightarrow ^3T_{1g}$ and 412nm of $^3A_{1g} \rightarrow ^3T_{2g}$ transitions, while the third band did not appear because it needs high energy²². These results with (0.0B.M.) suggest a low spin octahedral geometry^(29,30).

Table(3) Electronic spectra absorption bands(nm) of ligand and complexes

Seq.	Band I		Band II		Band III		Geometry
	λ_{max} nm	$\nu_{cm^{-1}}$	λ_{max} nm	$\nu_{cm^{-1}}$	λ_{max} nm	$\nu_{cm^{-1}}$	
1	314	31847	252	39682	—	—	—
2	650	15389					Tetrahedral
3	723	13869	657	15267	391	17391	Square planer
4	656	12300	610	16393	575		Octahedral
5					—	—	Tetrahedral
6	703	14224	736	13586	301	33222	Square planer
7	703	14224	606	16501	—	—	Octahedral
8	757	13210	725	13793	304	32894	Octahedral
9	561	17825	421	23752	341	29325	Octahedral

4- Magnetic measurements: Magnetic susceptibility for all the metal complexes were measured except Cd^{+2} complex due to the electronic configuration¹⁰ and the Pd^{+2} and Pt^{+4} complexes gave a diamagnetic properties ($\mu_{\text{eff}} = 0.0$ B.M.) because of location of these two elements in second and third round (low spin). The other metal complexes showed the following values of magnetic moments, Table(4).

a- Cu^{+2} complex gave a value of ($\mu_{\text{eff}} = 0.0$ B.M.) because it is dimmer and interact between the two electrons of the two ions occurs to produce a diamagnetic properties⁽³¹⁾.

b- Ni^{+2} complex observed a magnetic moment of ($\mu_{\text{eff}} = 1.4$ B.M.), $\text{eg}^4 \text{t}_{2\text{g}}^4$ which it was less than the theoretical one of the ion alone and that suggest a square planner geometry^(19,32,33),

c- Co^{+2} complex showed an effective magnetic moment ($\mu_{\text{eff}} = 4.8$ B.M.) which expected for ground state term(T) of high spin($\text{t}_{2\text{g}}^5 \text{eg}^2$) octahedral geometry⁽³²⁾.

d- Cr^{+3} complex gave a little higher value ($\mu_{\text{eff}} = 4.0$ B.M.) than the theoretical one ($\mu_{\text{eff}} = 3.87$ B.M.) which suggest a high spin octahedral geometry($\text{t}_{2\text{g}}^3 \text{eg}^0$)⁽³⁴⁾.

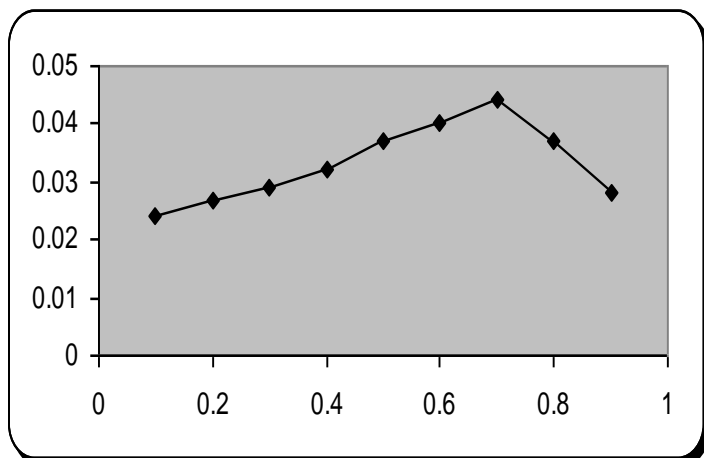
e- Fe^{+3} complex evaluate a magnetic moment of ($\mu_{\text{eff}} = 1.7$ B.M.) which suggest a low spin octahedral geometry($\text{t}_{2\text{g}}^5 \text{eg}^0$)⁽³³⁾.

5- Molar conductivity Measurements: The molar conductivity were measured for all complexes using dimethyl formamide(DMF) as a solvent with the concentration of 10^{-3} M at room temperature. Most complexes showed no or very weak conductance which means non ionic nature, while the other appeared to be good electrolyte with ionic nature, table (4), and that was approved by using a solution of silver nitrate and a white colloidal precipitate of silver chloride was obtained. These results go with the suggested formulas.

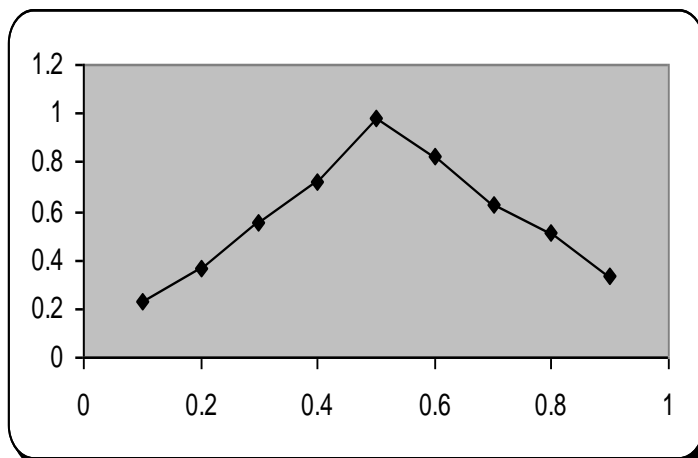
Table(4) Magnetic and Molar Conductivity Measurements of Complexes

Seq.	Molecular Formula	Molar Conduc. Λ_m ($\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$)	μ_{eff} (B.M)	M;L ratio	$K_f \times 10^3$	Geom.
1	$[\text{Cu}_2(\text{L})_2\text{Cl}_2]\text{Cl}_2$	165	Diamag.	2:2	3.81	Tet.
2	$[\text{Ni}(\text{L})\text{Cl}_2]$	46	Diamag.	1:1	1.17	S.P.
3	$[\text{Co}(\text{L})_2\text{Cl}_2]$	47	4.8	1:2	0.96	O.h.
4	$[\text{Cd}(\text{L})\text{Cl}_2]$	34	Diamag.	1:1	0.64	Tet.
5	$[\text{Pd}(\text{L})\text{Cl}_2]$	26	Diamag.	1:1	0.53	S.P.
6	$[\text{Cr}(\text{L})_2]\text{Cl}_3$	223	4.1	1:2	0.86	O.h.
7	$[\text{Fe}(\text{L})_2]\text{Cl}_3$	230	1.7	1:2	0.78	O.h.
8	$[\text{Pt}(\text{L})\text{Cl}_4]$	35	Diamag.	1:1	0.43	O.h.

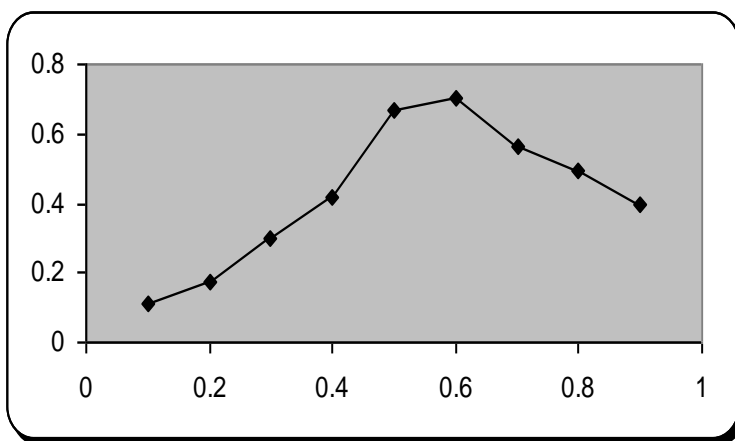
6- Molecular Formula Determination: A continuous variation method (Job method) was used to obtain the molecular formula and formation constant of the complexes, table(4). The measurements obtained showed 1:1 ratio of metal:ligand for Ni, Cd, Pd and Pt complexes while it is 1:2 ratio for Cr, Fe and Co complexes and 2:2 ratio for Cu complex, Fig.(2,3 and 4).



$V_L / V_L + V_M$ ($\lambda_{max} = 721\text{nm}$)
Fig.(2) Continuous variation of L:Ni



$V_L / V_L + V_M$ ($\lambda_{max} = 813\text{nm}$)
Fig. (3) Continuous variation of L:Co



$V_L / V_L + V_M$ ($\lambda_{max} = 773\text{nm}$)
Fig. (4) Continuous variation of L:Cu

Suggested Formulas: After combining all the physical measurements, the following molecular formulas for the complexes can be evaluated:

- a-** Octahedral configuration for Co, Cr, Fe and Pt, Fig. (5 and 6)
- b-** Dimmer tetrahedral for Cu, Fig.(7)
- c-** Square planner for Ni and Pd, Fig.(8)
- d-** Tetrahedral for Cd, Fig.(9)

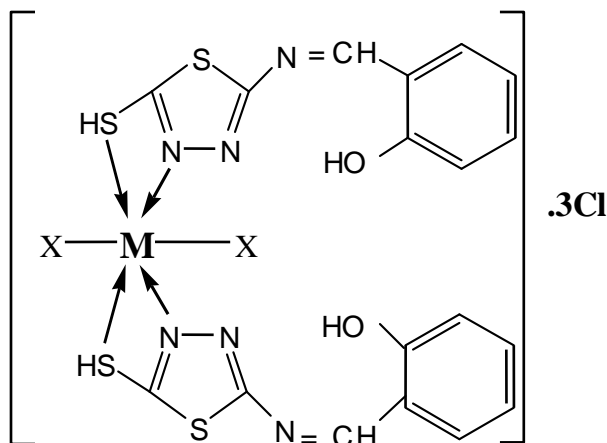


Fig.(5) suggested formula for Co, Cr and Fe complexes
X= Cl for Co, ethanol for Cr and Fe

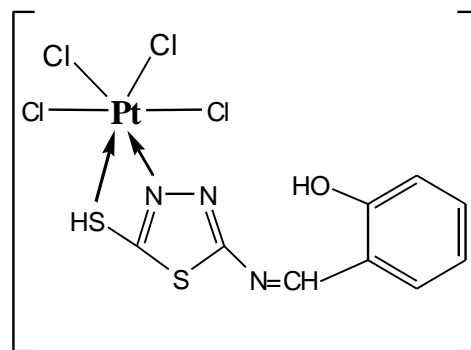


Fig. (6) suggested formula for Pt complex

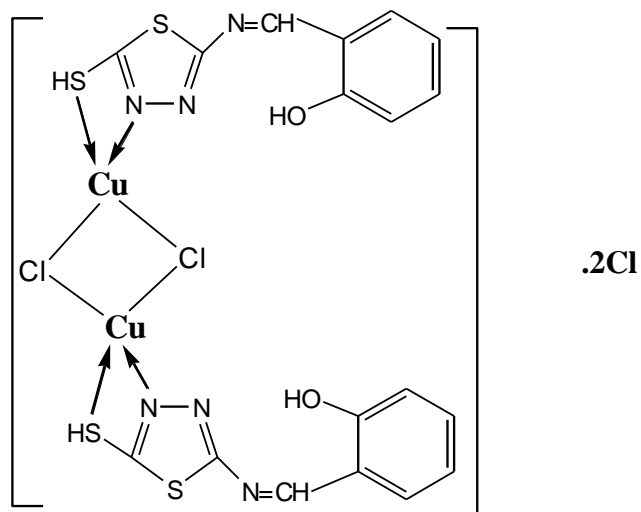


Fig.(7) suggested formula for Cu complex

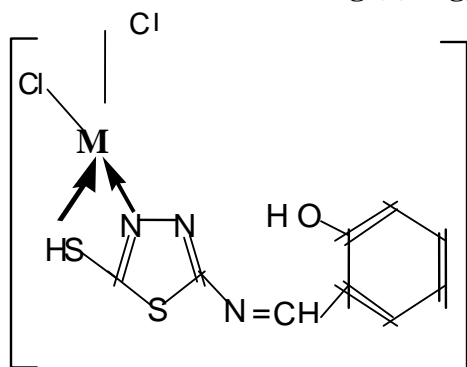


Fig.(8) suggested formula for Ni

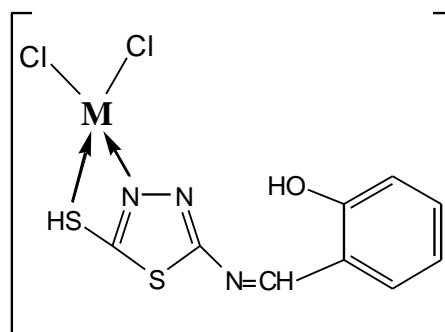


Fig.(9) suggested formula for Co complex

and Pd complexes

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