

## ***Synthesis and Characterization of Fe(II),Cd(II),Hg(II) and Ag(I) complexes with 2-Thiotolylurea Ligand.***

**تحضير وتشخيص معقدات الحديد (II) والكادميوم (II) والزنبق (II) والفضة (I) مع ليكاند 2- ثايوتوليل يوريا**

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### **Abstract**

Complexes reaction of  $Fe^{+2}$ ,  $Cd^{+2}$ ,  $Hg^{+2}$  and  $Ag^{+}$  with the 2-thiotolylurea were prepared in ethanolic medium with the (1:1) M:L ratio yielded a series of neutral complexes. The prepared complexes were characterized using flame atomic absorption, microelemental analysis (C.H.N), chloride content (Mohr Method) , FT.IR and UV-Vis spectroscopic, as well as magnetic susceptibility and conductivity measurement. From the above data, the proposed molecular structure for  $Fe^{+2}$ ,  $Cd^{+2}$  and  $Hg^{+2}$  complexes are tetrahedral geometry while  $Ag^{+}$  complex is trigonal structure.

### **الخلاصة**

يتضمن هذا البحث تحضير معقدات  $Fe^{+2}$ ,  $Cd^{+2}$ ,  $Hg^{+2}$ ,  $Ag^{+}$  مع ليكاند 2- ثايوتوليل يوريا في وسط الإيثانول وبنسبة مولية (2:1) فلز : ليكاند مع الايونات ثنائية الشحنة وبنسبة (1 : 1) مع أيون الفضة الاحادي . شخّصت المعقدات المحضرة بوساطة تقنية الامتصاص الذري , أطيف الاشعة تحت الحمراء والاشعة فوق البنفسجية – المرئية والتحليل الدقيق للعناصر (C.H.N) فضلاً عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية، كما تم تقدير محتوى الكلور باستخدام طريقة مور . ومن النتائج المحصول عليها فان الشكل الفراغي المقترح لمعقدات الحديد (II) والكادميوم (II) والزنبق (II) هو هرم رباعي السطوح بينما اتخذ معقد الفضة (I) هيئة مثلث مستوي

### **Introduction**

N,N-Disubstituted urea and thiourea possesses a remarkable capacity for coordination with transition metals giving rise to highly colored chelate compounds<sup>(1,2)</sup>. The complexation capacity of urea derivatives has been reported in several studies<sup>(3,4)</sup>. Complexes of urea, thiourea and derivatives with transition and rare earth metals are receiving great attention since these complexes have shown antitumor ,antiviral, bacteriostatic and antioxidative activity.<sup>(5,6)</sup> It is well established that many transition metals<sup>(7,8)</sup> and rare earth metals<sup>(9)</sup> . In recent years , there has been increasing interest in the electrochemical behavior of thiourea and substituted thiourea at different metal electrodes due to their various structures and applications as additives for metal electrodeposition and its ability the corrosion process<sup>(10)</sup>. In view of above and in continuation of our previous investigations devoted to the development of antimicrobials<sup>(11-15)</sup>. In this paper reports the synthesis and identification of new complexes with 2-thiotolylurea.

### **Experimental**

**a- Materials:-** All chemicals used were of reagent grade and were used without further purification  $FeCl_2.9H_2O$ ,  $CdCl_2.H_2O$ ,  $HgCl_2$ ,  $AgNO_3$  (Fluka) 2-thiotolyl urea (B.D.H).

**b- Instrumentation:-** I.R-spectra with CsI discs in the range  $(4000-200) cm^{-1}$  were obtained using (a Shimadzu FT.IR - 8400 S) Fourier Transform Infrared Spectrophotometer. Electronic

spectra were recorded on (a Shimadzu U.V-160A) Ultra Violet-Visible Spectrophotometer. Atomic absorption were obtained using (a Shimadzu A.A-160A) Atomic Absorption / Flame Emission Spectrophotometer. Conductivity measurements were carried out in DMF using (Philips Pw-Digital Conductmeter). Magnetic properties were obtained using (Balance Magnetic Susceptibility, Model MSI-MKI). In addition melting points were measured using (Stuart Melting Point Apparatus).

### **Synthesis of Metal Complexes (general method)**

All complexes were prepared by dissolving 0.39g, 0.27g, 0.37g and 0.23g (1mmole) of  $\text{FeCl}_2 \cdot 9\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HgCl}_2$  and  $\text{AgNO}_3$  respectively in the aqueous solution was added gradually with stirring to the ethanolic ligand solution (0.25g, 1mmole) using stoichiometric amounts (1:1) metal : ligand molar ratio, crystalline precipitate observed. The resulting precipitate was filtered off, recrystallized from ethanol and dried at 50 °C.

### **Results and Discussion**

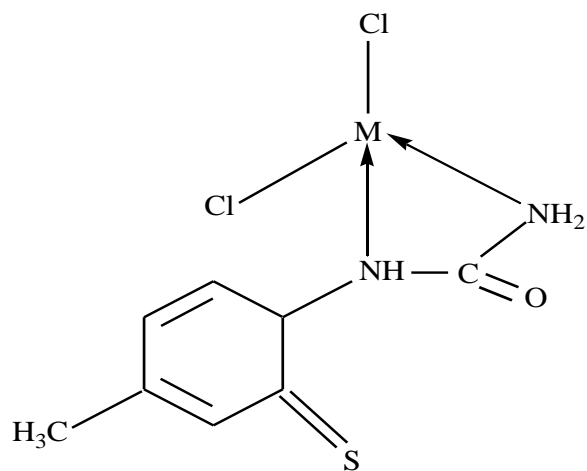
The complexes have been prepared by direct reaction of ethanolic solution of the ligand with aqueous solution of metal ions at (1:1) metal to ligand molar ratio. The complex combinations of  $\text{Fe}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Hg}^{+2}$  and  $\text{Ag}^+$  with the 2-tiotolylurea appeared as powders with high melting points. The (C.H.N) and chloride analysis with metal contents were found to be in agreements with calculated values (Table-1) includes the physical properties and elemental analysis. The observed molar conductance in DMF ( $10^{-3}\text{M}$ ) fall in the range (8.06-19.21  $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ ). These values of the molar conductance (Table-2) are well within the expected range for non-electrolytes<sup>(16)</sup>. The effective magnetic moment (Table-2) of  $\text{Fe}^{+2}$  complex at (4.24 B.M). This value refer to a paramagnetic (high spin) for tetrahedral geometry. In the case of  $\text{Cd}^{+2}$ ,  $\text{Hg}^{+2}$  and  $\text{Ag}^+$  complexes because of filled -d orbital of these complexes, therefore the magnetic moment ( $\mu=0$ ) are diamagnetic<sup>(17)</sup>. The UV-Vis spectra data for the free ligand and all metal complexes are listed in (Table-2). The UV-Vis spectrum of the ligand (Fig-1) shows two peaks at 257nm and 30 nm assigned to ( $\pi$ -  $\pi^*$ ) and ( $n$ -  $\pi^*$ ) electronic transitions<sup>(18,19)</sup>. The electronic spectrum of  $\text{Fe}^{+2}$  complex gave absorption at 268 nm due to charge transfer (C.T). Other peak at 420 nm was found to be caused by (d-d) electronic transition<sup>(20)</sup> type  $^5\text{E} \rightarrow ^5\text{T}_2$ .

The spectra of  $\text{Cd}^{+2}$ ,  $\text{Hg}^{+2}$  and  $\text{Ag}^+$  complexes appeared peaks at 265 nm in the spectrum of  $\text{Cd}^{+2}$  (Fig-2), 291 nm in the spectrum of  $\text{Hg}^{+2}$  (Fig-3), and 284 nm in the spectrum of  $\text{Ag}^+$  complex were assigned to charge transfer<sup>(21)</sup>. The spectra of these complexes appearance a great bathochromic shift in the visible region (452-440 nm). The high shift gave a good indication for complex formation.

The I.R spectrum of the ligand (Fig-4) exhibited two bands at 3371  $\text{cm}^{-1}$  and 3263  $\text{cm}^{-1}$  indicated to  $\nu(\text{NH}_2)$  and  $\nu(\text{NH})$  respectively<sup>(22,23)</sup>, on complexation (Fig-5) a shiften with change in shape were observed from these bands, while increasing in intensity were noticed, the significant may be a result of coordination with the metal ion. Very strong band was observed at 1620  $\text{cm}^{-1}$  due to stretching vibration of  $\nu(\text{C}=\text{O})$ <sup>(24)</sup>. Since no significant change in this band was noticed, the possibility that coordination occurs via the (C=O) group. The characteristic band in the ligand spectrum at 1450  $\text{cm}^{-1}$  which was assigned to the  $\nu(\text{C}-\text{N})$  stretching<sup>(25)</sup>, suffered a great change to higher frequency was also observed on complexation with metal ion. A new group of bands were also observed in the I.R spectrum of  $\text{Ag}^+$  complex at 1357, 1041 and 817  $\text{cm}^{-1}$ . These bands were also assigned to the presence of the monodentate  $\text{NO}_3^-$  group. Two new stretching bands were noticed around (447-440)  $\text{cm}^{-1}$  which were assignable to the  $\nu(\text{M}-\text{N})$  of the primary and secondary amine<sup>(26,27)</sup>. Another weak band was also appeared around (293-270)  $\text{cm}^{-1}$  which attributed to the  $\nu(\text{M}-\text{Cl})$  mode. (Table-3) gives the characteristic absorption for the free ligand and its complexes.

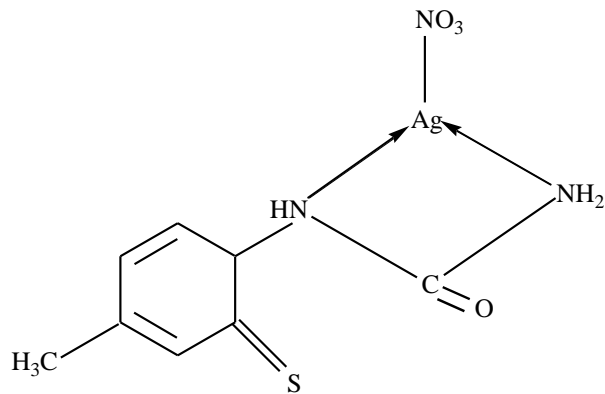
According to the results obtained and spectral analysis, the chemical structures of the complexes may be suggested.

a- Tetrahedral for the  $\text{Fe}^{+2}$ ,  $\text{Cd}^{+2}$ , and  $\text{Hg}^{+2}$  complexes



$\text{M}^{+2} = \text{Fe} , \text{Cd} , \text{Hg}$

b- Trigonal for the  $\text{Ag}^{+}$  complex.



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**Table (1):- Physical Properties and Elemental Analysis for the Complexes.**

Compounds	Color	M.P °C	Yield %	Analysis Calc.(Found)				
				Cl%	M%	C%	H%	N%
Ligand (2-TTU)	White	159	-	-	-	-	-	-
[Fe(2-TTU)Cl <sub>2</sub> ]	Brownish Yellow	235	68	23.05 (22.51)	18.12 (17.87)	31.16 (30.88)	2.92 (2.53)	9.09 (8.65)
[Cd(2-TTU)Cl <sub>2</sub> ]	White	210	72	19.50 (19.02)	30.68 (30.07)	26.37 (26.01)	2.47 (2.13)	7.69 (6.95)
[Hg(2-TTU)Cl <sub>2</sub> ]	White	282	65	15.67 (14.57)	44.27 (43.55)	21.19 (20.93)	1.98 (1.61)	6.18 (5.87)
[Ag(2-TTU)NO <sub>3</sub> ]	White	227	66	19.72 (18.73)	30.68 (28.98)	26.66 (26.24)	2.50 (2.08)	7.77 (7.05)

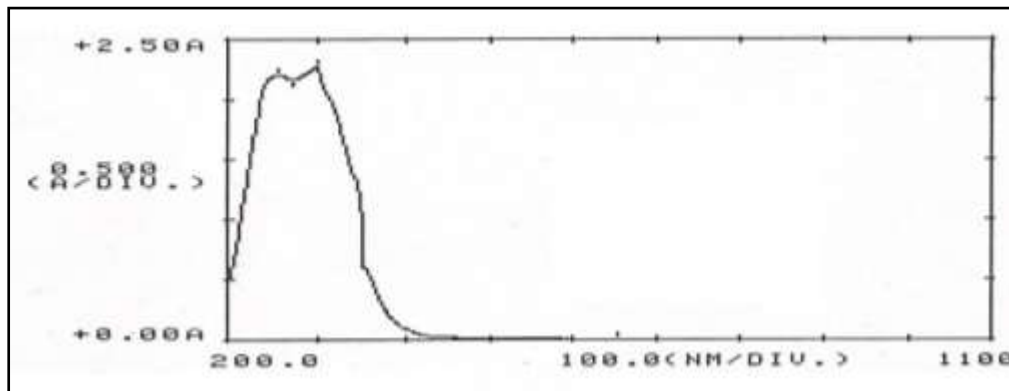
**Table (2):- The Electronic Spectra for the Ligand and Its Complexes.**

Compounds	$\lambda_{max}$ (nm)	ABS	$\epsilon_{max}$ (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	$\Lambda_m$ (S.cm <sup>2</sup> .mol <sup>-1</sup> ) in DMF (10 <sup>-3</sup> M)	$\mu_{eff}$ (B.M)
Ligand (2-TTU)	257	2.201	2201	-	-
	300	2.276	2276		
[Fe(2-TTU)Cl <sub>2</sub> ]	268	0.944	944	13.09	4.24
	420	1.317	1317		
[Cd(2-TTU)Cl <sub>2</sub> ]	256	0.682	682	8.06	-
	452	0.994	994		
[Hg(2-TTU)Cl <sub>2</sub> ]	291	0.326	326	19.21	-
	440	0.387	387		
[Ag(2-TTU) NO <sub>3</sub> ]	284	1.203	1203	17.97	-
	435	0.735	735		

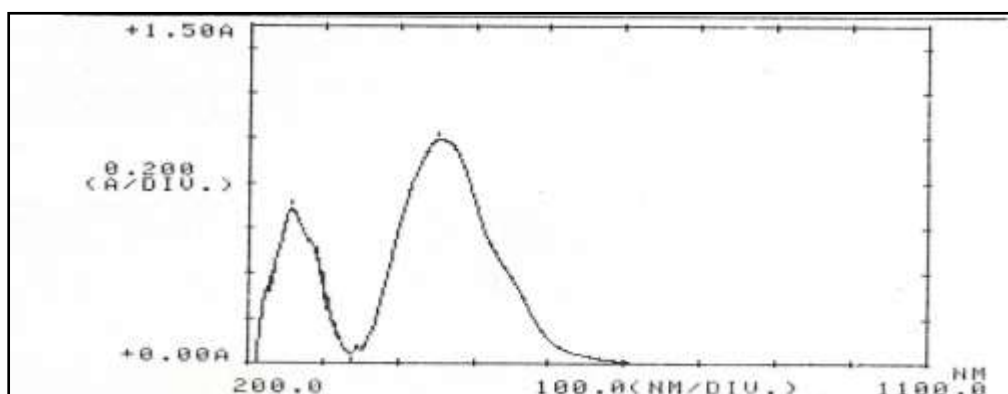
**Table (3):- The Main Frequencies of the Ligand and Their Complexes (cm<sup>-1</sup>)**

Compounds	$\nu$ (NH <sub>2</sub> )	$\nu$ (NH)	$\nu$ (C=O)	$\nu$ (C-N)	$\nu$ (M-N)	$\nu$ (M-Cl)	$\nu$ (NO <sub>3</sub> )
Ligand (2-TTU)	3371 S.	3263 S.	1620 Sh.	1450 S.	-	-	-
[Fe(2-TTU)Cl <sub>2</sub> ]	3255 S.	3417 S.	1620 S.	1527M.	447 W.	293 W.	-
[Cd(2-TTU)Cl <sub>2</sub> ]	3294 S.	3201 S.	1620 Sh.	1527 Sh.	440 W.	285 W.	
[Hg(2-TTU)Cl <sub>2</sub> ]	3278 S.	3400 S.	1620 M.	1535 M.	443 W.	270 W.	
[Ag(2-TTU) NO <sub>3</sub> ]	3262 br.	3294 br.	1620 M.	1535 M.	447 W.	-	1357 Sh. 1041 S. 817 S.

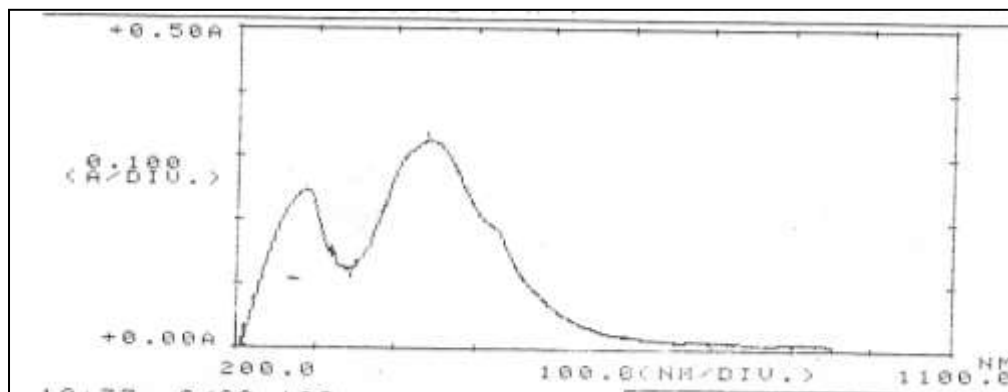
s = strong , sh = sharp , br = brood , m = medium , w = week.



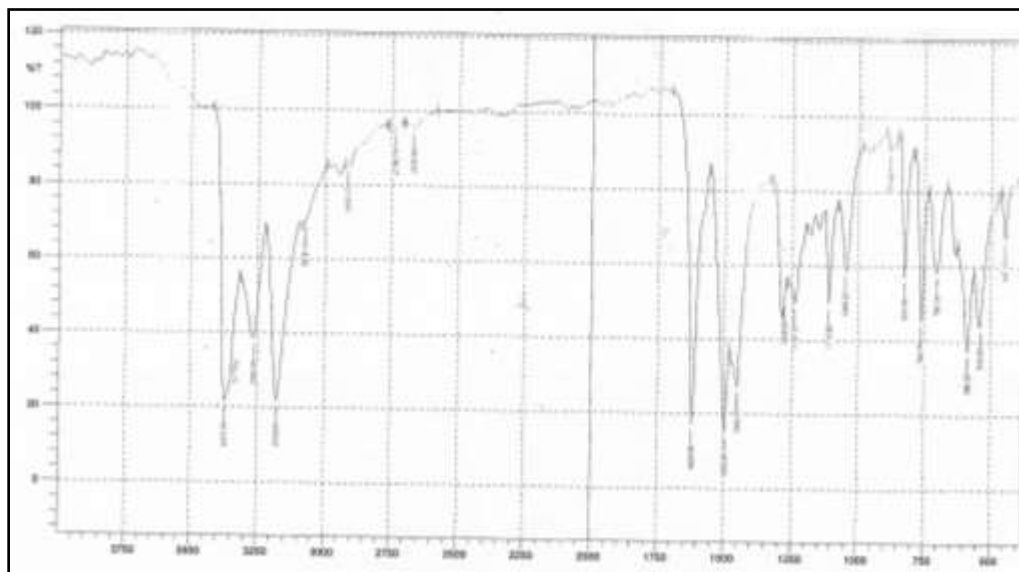
**Fig.(1):- The UV-Vis Spectrum of the Ligand.**



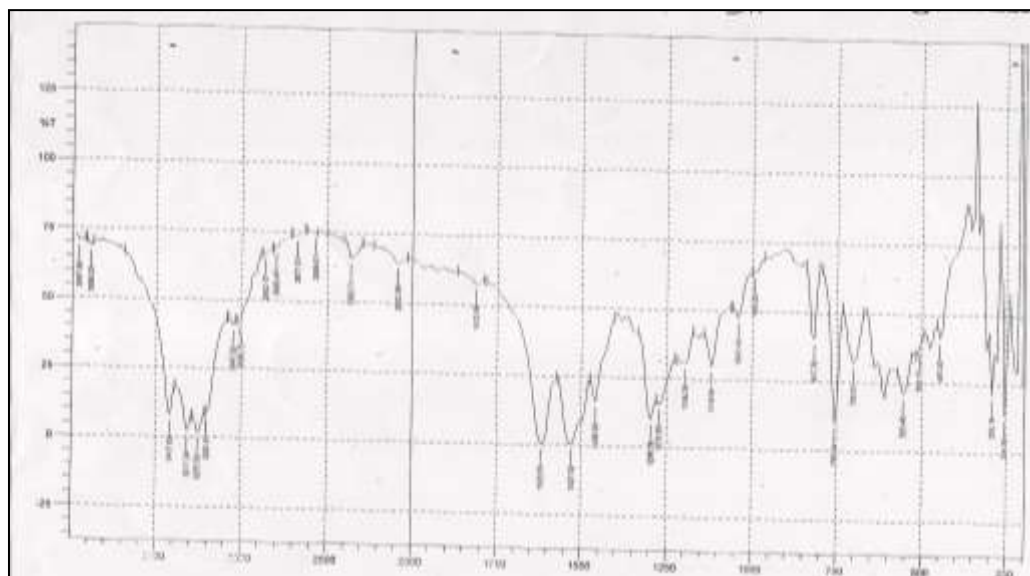
**Fig.(2):- The UV-Vis Spectrum of the [Cd (2-TTU)Cl<sub>2</sub>] Complex.**



**Fig.(3):- The UV-Vis Spectrum of the [Hg (2-TTU)Cl<sub>2</sub>] Complex**



**Fig.(4):- The FT.IR Spectrum of the Ligand**



**Fig.(5):- The FT.IR Spectrum of the [ Fe (2-TTU)Cl₂ ] Complex.**