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Synthesis, Spectroscopic and Thermal Behaviour of Salicylaldimine Complexes

I.S. Ahmed, T.Y. Mohammed[*] and M.M. Moustafa
Chemistry Department, Faculty of Science, Benha University, Benha,Egypt.

THE COMPLEXES of N-salicylaldimine 2-urea (L_1) and N-salicylaldimine-2-thiourea (L_2) with Fe(III), Co(II), Ni(II) and Cu(II) are formed in the molar ratios (1:1) as well as (1:2) (M:L) and characterized by elemental analysis, IR, electronic spectra, thermogravimetric analysis and magnetic measurements. The stoichiometry, proton-reagent stability constant, conditional formation constant of the complexes and the conductance are determined by using potentiometric and conductometric measurements. The study revealed that the ligands behave as monobasic bidentates, electronic spectra and magnetic measurements indicate that the metal chelates have octahedral or square-planar arrangements. Also, the TG analysis indicates the presence of hydrated and coordinated water molecules. The electrolytic and nonelectrolytic nature of the complexes were assigned based on molar conductance measurements.

Schiff bases are known for their biological, industrial and analytical importance [1,2]. There are reports on the synthesis of transition and inner-transition metal complexes of Schiff bases involving salicylaldehyde and amines, amino acids and aminophenols [3,4]. The Schiff bases are of great importance in the complexometric titration [5] . The aim of the present investigation is to study the stoichiometry and structure of the complexes formed when Fe(III), Co(II) , Ni (II) and Cu(II) salts are allowed to react with salicylaldimine ligand . Also, thermogravimetric analysis of the metal chelates were discussed .

Experimental

Materials

All chemicals used were of pure grade (BDH) or Aldrich. The preparation of Schiff base compounds were prepared as reported [6]. After recyrstallization from ethanolic solution their purities were confirmed by elemental analysis as well as confirmed by IR and ^{1}H-NMR spectra . The chemical structure of this is shown in Fig .1 .

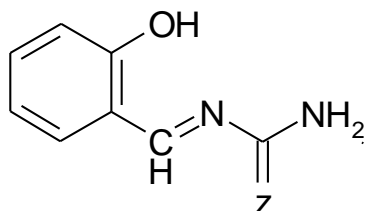
[*]E- mail : Dr_talaat2003@yahoo.com

Fig.1. Structure of salicylaldimine derivatives Z = O; L_1 (Urea) and Z=S ; L_2 (Thiourea)

Synthesis of metal chelates

The metal chelates of the compounds under investigation were synthesized by mixing 20 ml of hot methanolic solutions of N-salicylaldimine-2-urea (L_1) and N-salicylaldimine-2-thiourea (L_2) (0.02 mol) and 20 ml of a methanolic solution of metal salt (0.02 mol) of Fe(III), Co(II), Ni(II) and Cu(II) chloride. The mixture was left to stand on steam bath for 4hr. In some cases, the metal chelates did not separate on standing and few drops of ammonia solution were added slowly with stirring to adjust the pH to 6-8 which resulted in precipitation. The formed metal chelates were then filtered and washed several times with bidistilled water and methanol until the filtrate become colorless, then the chelates were dried over anhydrous $CaCl_2$.

Apparatus and procedure

Elemental analysis were performed in the Microanalytical Center of Cairo University. The metal content of the chelates was determined after wet decomposition as previously described [7] followed by EDTA titration [8,9] (Table 1) .

Conductometric titrations of 50 ml 5 x 10^{-3} M ligand solution of ethanol-water (75 %v/v) were carried out with 5 x 10^{-4} M of Fe(III), Co(II), Ni(II) and Cu(II) ions. Also, the conductivity measurement on solid chelates in DMF were carried out using a YSI model 32 conductance meter.

The infrared spectra of the ligands as well as of the chelates were obtained by applying the KBr disc technique using Perkin-Elmer 1430 infrared spectrometer. The visible spectra of free ligand and their chelates were measured by applying Nujol mull and DMF technique using Jascow 530 spectrophotometer with 10 mm matched Quartz Cell.

Thermogravimetric analysis of chelates were achieved using Schimadzu thermal analyzer. The weight loss was measured from ambient temperature up to 700°C ramped at 10°C/min in air atmosphere. The magnetic susceptibility was measured with a Gouy's set up at room temperature using $Hg[Co(NCS)_4]$ as calibrating agent and calculations were made using computed values of Pascal's constants.

TABLE 1. Data of elemental analysis and molar conductance of metal chelates with salicylaldimine derivatives.

Compd. No.		Ratio (M:L)	%C		%H		%N		%M		%Cl		A_m (ohm^{-1} cm^2 mol^{-1})
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
I	$[Fe.L_1.4H_2O]2Cl.2H_2O$	1:1	24.13	24.10	1.76	1.59	7.04	6.88	14.04	13.95	17.86	17.75	98.60
II	$[Fe.2L_1.2H_2O]Cl.2H_2O$	1:2	39.24	39.15	2.86	2.75	11.44	11.40	11.41	11.30	7.26	7.15	86.30
III	$[Fe.L_2.4H_2O]2Cl.2H_2O$	1:1	23.20	23.10	1.69	1.65	6.77	6.70	13.49	13.35	17.16	17.10	90.50
IV	$[Fe.2L_2.2H_2O]Cl.2H_2O$	1:2	36.83	36.80	2.69	2.60	10.72	10.60	10.71	10.65	16.81	6.70	85.60
V	$[Co.L_1.4H_2O]Cl.2H_2O$	1:1	26.27	26.25	1.92	1.90	7.66	7.61	6.13	16.10	9.71	9.65	105.50
VI	$[Co.2L_1.2H_2O]2H_2O$	1:2	42.02	41.98	3.06	2.95	12.26	12.20	12.89	12.70	-	-	7.10
VII	$[Co.L_2.4H_2O]Cl.4H_2O$	1:1	23.00	22.95	1.68	1.55	6.71	6.65	14.11	14.08	8.50	8.45	99.40
VIII	$[Co.2L_2.2H_2O]4H_2O$	1:2	36.58	36.50	2.67	2.60	10.67	10.55	11.22	11.15	-	-	8.50
IX	$[Ni.L_1.4H_2O]Cl.2H_2O$	1:1	26.29	26.25	1.92	1.80	7.67	7.60	16.07	15.95	9.72	9.65	110.11
X	$[Ni.2L_1.4H_2O]2H_2O$	1:2	42.04	42.03	3.07	3.02	12.26	12.20	12.85	12.78	-	-	7.70
XI	$[Ni.2L_2.4H_2O]Cl.2H_2O$	1:1	25.18	25.15	1.84	1.74	7.35	7.50	15.40	15.35	9.31	9.28	92.30
XII	$[Ni.2L_2.4H_2O]HH_2O$	1:2	36.59	36.60	2.68	2.60	10.67	10.55	11.19	11.15	-	-	5.50
XIII	$[Cu.L_1.2H_2O]Cl.2H_2O$	1:1	25.95	25.90	1.89	1.78	7.57	7.45	17.16	17.12	9.59	9.40	85.70
XIV	$[Cu.2L_1]4H_2O$	1:2	41.60	41.55	3.03	2.90	12.13	12.08	13.76	13.70	-	-	6.60
XV	$[Cu.L_2.2H_2O]Cl.4H_2O$	1:1	24.87	24.80	1.81	1.70	7.25	7.20	16.45	16.30	9.20	9.10	80.21
XVI	$[Cu.2L_2]4H_2O$	1:2	38.91	38.85	2.84	2.80	11.35	11.25	12.87	12.25	-	-	7.10

Results and Discussion

The conductometric titration curves of the ligands under investigation with Fe(III), Co(II), Ni(II) and Cu(II) ions exhibit two inflection at molar ratios of 0.5 and 1.0 indicates the formation of (1:1) and (1:2)   (M:L) complexes species in solution.

The formation constants of the complexes were also studied as a function of the ionic radii of the metal ions (Fig.2) . The relation between   the stability constants of the respective complexes and ionic radii of transition metal ions shows that the Fe^{3+} -complexes have the highest stability compared to the other complexes (Table 2).
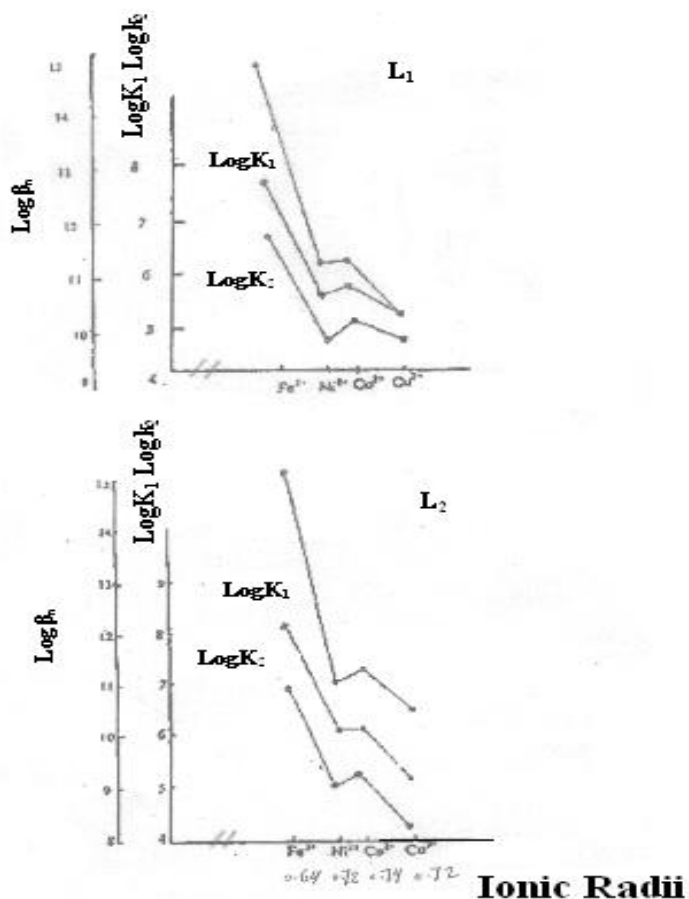

Fig. 2. The stability of the complexes as a function of the ionic radii of the metal ion.

TABLE 2. Potentiometric data of the ligands and its complexes with transition metal ions.

Compd	Ionic radii Å	Potentiometric data					
		Log K_a^H	-ΔG*	Log K_1	Log K_2	Log $β_n$	-ΔG* Cal/mole
L_1	-	8.2	11.14	-	-	-	-
Fe^{3+}	0.64	-	-	8.11	6.90	15.01	20.40
Co^{2+}	0.74	-	-	6.01	5.23	11.24	15.27
Ni^{2+}	0.72	-	-	5.98	5.01	10.99	14.93
Cu^{2+}	0.72	-	-	6.23	4.23	10.45	14.21
L_2	-	10.2	13.86				
Fe^{3+}	0.64	-	-	8.14	7.10	15.24	20.71
Co^{2+}	0.74	-	-	6.12	5.48	11.60	15.76
Ni^{2+}	0.72	-	-	6.46	5.12	11.58	15.74
Cu^{2+}	0.72	-	-	5.48	5.10	10.58	14.38

IR-spectra

The mode of bonding of the Schiff base to the transition metal ions was elucidated by investigating the IR spectra of the chelates (1:1) and (1:2) (M:L) as compared to those of the free ligands (Fig. 3) . The broad bands observed at 3302 and 3170 cm^{-1}, assigned to ν(OH) in the spectra of the free ligands 1 and 2 , respectively ; their position is shifted to higher wavenumbers 10-20 cm^{-1} in their complexes. This behaviour may be attributed to the participation of the phenolic OH group of the Schiff base in chelation with the metal ion. The bending δ(OH) bands at 1353 and 1363 cm^{-1} of the free ligands exhibit a shift to 5-10 cm^{-1} to lower wavenumber values on complexation. This behaviour is due to the liberation of the proton from phenolic OH group of the ligand through chelation with metal ions. The ν(C=O) band at 1656 cm^{-1} for ligand 1 and ν(C=S) at 1353 cm^{-1} for ligand 2 , exhibit no shift of the wavenumbers on complexation which may not be taken as evidence for participation of C=O or C=S group in coordination. The ν(C=N) bands at 1622 and 1615 cm^{-1} for ligand 1 and 2, respectively [10] exhibit a shift of 10-20 cm^{-1} to lower or higher wavenumbers on complexation which may be taken as evidence for the participation of azomethine nitrogen in chelate formation. The new bands appearing in the range of 530-500 cm^{-1} are assigned to ν(M-N); ν(M-O) and ν(M-Cl), respectively [11, 12] . The band at 3000-3300 cm^{-1} in the spectra of chelates may be due to the νOH vibration of coordinate water molecules [13] .
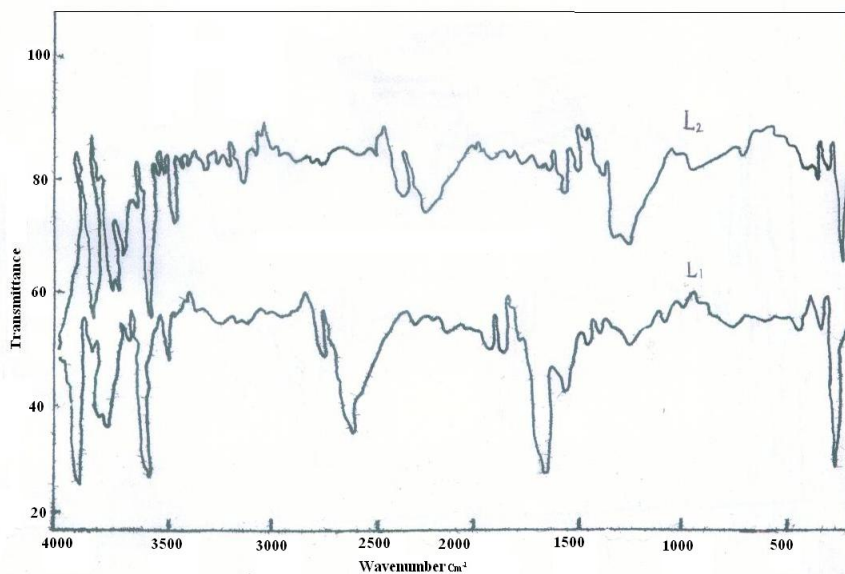
Fig. 3. IR spectra of N- salicylaldimine-2- urea (L$_1$) and N- salicylaldimine-2-thiourea (L$_2$) .

The electronic spectra and magnetic measurements

The electronic absorption spectra of the free ligands and their complexes under investigation were performed in dimethyl formamide as solvent. The electronic spectra of the free ligands (1 and 2) display three bands, the first one at 38610-39216 cm^{-1} which attributed to transition within the phenyl moiety, the second band at 35714-37037 cm^{-1} which may be due to the n-π^* transition of C=O and C=S group, the later band at 30488-31250 cm^{-1} which attributed to the charge transfer within the ligand molecules.

The electronic spectra of the chelates Fe(III), Co(II) and Ni(II) with the ligands (1 and 2) (1:1) (M:L) as well as (1:2) (M:L), respectively, show bands at 20739-24101 cm^{-1}, which can be assigned to $^2A_{1g} \rightarrow {}^2T_{2g}$ transition for Fe(III), $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ for Co(II) and $^3A_{2g} (F) \rightarrow {}^3T_{1g} (P)$ for Ni(II) chelates.

The high intesnity of the band and the paramagnetic nature support the distortion of octahedral geometry for these chelates [14, 15] . On the other hand, the Cu(II) chelates with the ligands (1 and 2) (1:1) or (1:2) (M:L), respectively show a broad band at 21281 cm^{-1} with the maxima at 21200 cm^{-1} which has been assigned to $^2B_{1g} \rightarrow {}^2E_g$ transition, the intensity of the bands and the magnetic moment values support square-planar geomtry for these chelates [16,17] (Table 3).

TABLE 3. Data of thermogravimetric analysis and magnetic moment of the metal chelates with salicylaldimine derivatives.

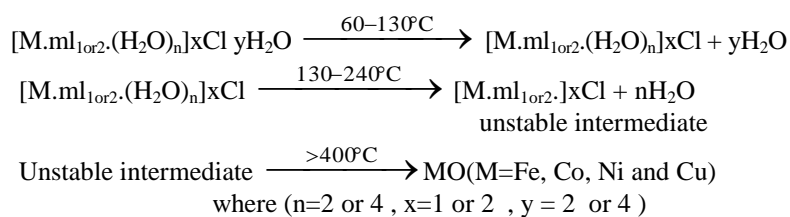| Compd. No.	Chelate	(M:L)	Water of hydration Weight loss%		No. of H$_2$O molecules	Temp. (°C)	Water of coordination Weight loss %		No. of H$_2$O molecules	Temp. (°C)	* Metal oxide residue %		μ$_{eff}$ B.M
			Found	Calc.			Found	Calc.			Found	Calc.	
I	[Fe.L$_1$.4H$_2$O]2Cl.2H$_2$O	1:1	9.03	9.05	2	130	18.07	18.10	4	240	17.66	18.06	1.80
IV	[Fe.2L$_2$.2H$_2$O]Cl.2H$_2$O	1:2	6.83	6.91	2	120	6.83	6.91	2	240	13.50	13.78	1.70
V	[Co.L$_1$.4H$_2$O]Cl.2H$_2$O	1:1	9.80	9.85	2	120	19.60	19.70	4	230	20.01	20.51	3.90
X	[Ni.2L$_1$.2H$_2$O]2H$_2$O	1:2	7.85	7.8	2	125	7.85	7.88	2	220	16.05	16.36	3.11
XII	[Ni.2L$_2$.2H$_2$O]4H$_2$O	1:2	13.50	13.72	4	125	6.80	6.86	2	230	13.80	14.24	2.89
XIII	[Cu.L$_1$.2H$_2$O]Cl.4H$_2$O	1:1	19.35	19.46	4	130	9.65	9.73	2	225	20.50	21.50	1.89
XIV	[Cu2L$_1$]4H$_2$O	1:2	15.50	15.60	4	120	-	-	-	220	17.10	17.23	1.72
XVI	[Cu2L$_2$]4H$_2$O	1:2	14.45	14.59	4	125	-	-	-	220	15.80	16.11	1.68

* Metal oxide residue % : At temperature ranges from 400 to 700 ^{0}c .
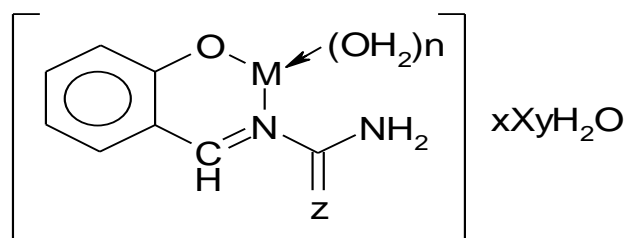
Thermogravimetric analysis

The thermal analyses were performed for the chelates of [Fe.L_1.4H$_2$O] 2Cl.2H$_2$O(I), [Fe.2L_2.2H$_2$O] Cl.2H$_2$O (IV), [Co.L_1. 4H$_2$O] Cl.2H$_2$O(V), [Ni.2L_1,.2H$_2$O] 2H$_2$O(X), [Ni.2L_2.2H$_2$O] 4H$_2$O (XII), [Cu.L_1.2H$_2$O] Cl.4H$_2$O(XIII), [Cu.2L_1,] 4H$_2$O(XIV) and [Cu.2L_2] 4H$_2$O(XVI), respectively. From TG curves, the weight losses were calculated for the different steps and compared with those theoretically calculated for the suggested formulas based on the results of the elemental analyses as shown in Table 1. The first weight loss at temperature up to 130 °C is attributed to the loss of hydrated water molecules for all complexes. Whereas, the second step of the weight loss within the temperature range 130-240 °C which is assignable to coordinated water molecules in the inner sphere of the metal chelates. For the (1:1) (M:L) chelates of Fe(III), Co(II) and Cu(II) with the ligand (L_1) and (1:2) (M:L) chelates of Fe(III), Ni(II) and Cu(II) with the ligand L_2 or L_1, the weight losses are about 9.03, 9.80 and 19.35 % for (1:1) (M:L), respectively and this can be attributed to the loss of two water molecules. That is eliminated at temperature up to 130 °C; 18.07, 19.6 and 9.56 % weight (loss is assignable to four water coordinated molecules for complexes (I,III and V) and to two water coordinated for complex (XIII), respectively), within the temperature range 130-240 °C.

On the other hand, for (1:2) (M:L) chelates of Fe(III), Ni(II) and Cu(II) with ligands L_2 and L_1 periodically, the weight losses are 6.83, 7.85, 13.5, 15.50 and 14.45 %, respectively; which are attributed to the removal of two hydrated water molecules of complexes (IV and X) and four hydrated water molecules of complexes XII, XIV and XVI, respectively. The weight losses are about 6.83, 7.85 and 6.80 % for the complexes (IV, X and XII), respectively, attributed also to the removal of two coordinated water molecules in these chelates of Fe(III) and Ni(II), but for chelates of Cu(II) no participation of coordinated water molecules within the complexes XIV and XVI, respectively.

The percentage of metal oxide was found experimentally as the end product from TG-curves at temperature range from 400-700°C, the metal oxide residue amounted to 17.66, 20.01 and 20.50% for (1:1) (M:L) complexes (I, V and XIII), respectively, and the corresponding calculated values are 18.06, 20.51 and 21.50 %, respectively. The metal oxide percentage of the (1:2) (M:L) complexes (IV, X, XII, XIV and XVI), respectively was found to be 13.50, 16.05, 13.80, 17.10 and 15.80%, respectively, which are in good agreement with calculated ones for the suggested formula in Table 3. The following scheme, may be suggested for the thermal degradation of the chelates with Fe(III), Co(II), Ni(II) and Cu(II), respectively.

$$[M.ml_{1or2}.(H_2O)_n]xCl\ yH_2O \xrightarrow{60-130^{\circ}C} [M.ml_{1or2}.(H_2O)_n]xCl + yH_2O$$

$$[M.ml_{1or2}.(H_2O)_n]xCl \xrightarrow{130-240^{\circ}C} [M.ml_{1or2}.]xCl + nH_2O$$
$$\text{unstable intermediate}$$

$$\text{Unstable intermediate} \xrightarrow{>400^{\circ}C} MO(M=Fe, Co, Ni\ and\ Cu)$$
$$\text{where } (n=2 \text{ or } 4,\ x=1 \text{ or } 2,\ y=2 \text{ or } 4)$$

Scheme 1 .

n = 2 or 4, x = 1 or 2, y = 2 or 4, X = Cl, Z = O or S and
a- M; Fe(III), Co(II), Ni(II) and Cu(II) (I:I) (M:L)
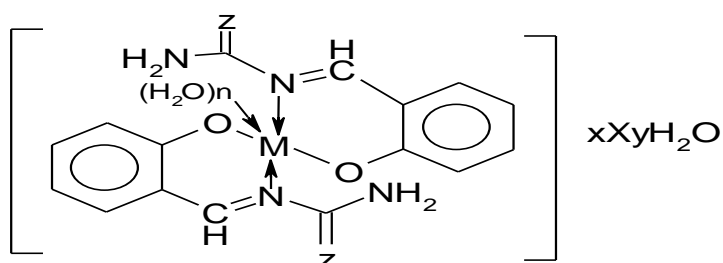
n = 0 or 2, x = 1; y = 4, X = Cl,
b- M; Fe(III), Co(II), Ni(II) and Cu(II) (I:2) (M:L)
Fig. 4 (a ,b) : Suggested structural formula of complexes.

Conclusions

Based on the elemental analysis; potentiometric and conductometric measurements; spectral, thermogravimetric analysis and magnetic moments measurements of the metal ions complexes of salicylaldimine derivatives, the following conclusions are supported:

i-The salicylaldimine derivatives with Fe(III), Co(II), Ni(II) and Cu(Il) ions are formed in ratios (1:1) and (1:2) (M:L) in solution as well as in the solid state.

ii-The electronic spectra data and magnetic moment value of the Fe(lII), Co(II), and Ni(II) chelates with salicylaldimine derivatives show octahedral arrangement; but in case of Cu(Il) chelate show square-planar arrangement (Fig. 4- a,b)

iii-The most important conclusion drawn from the above investigation is that the mono basic bidentate ligands is coordinated to the metal ions through the O and N as donor atoms in (1:1) as well as (1:2) (M:L) chelates. Also, the structure of chelates is constructed.

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تشييد بعض مركبات السالسيلديمين ٢- يوريا ، والسالسيلديمين
٢- ثيويوريا ووصف التحليل الحرارى والطيفى لهذة المركبات

ابراهيم السيد أحمد ، طلعت يونس محمد و مصطفى محمود مصطفى
قسم الكيمياء - كلية العلوم – جامعة بنها – بنها – مصر .

تم استخدام مركبات السالسيلديمين ٢- يوريا ، والسالسيلديمين ٢- ثيويوريا
كمركبات مخلبية لتكوين متراكبات مع العناصر الانتقالية مثل الحديد . والكوبلت
والنيكل والنحاس بنسب مولارية (١:١) وايضا ٢:١ عنصر : ليجاند .

تم توصيف هذه المتراكبات باستخدام التحليل للعناصر ، والاشعة تحت
الحمراء ، والانتقال الطيفى والتحليل الحرارى والمغناطيسى. ثم حساب ثابت
التكوين لتلك المتراكبات باستخدام التوصيلية وايضا باستخدام القياسات الجهدية .
ومن خلال تلك النتائج توصلنا الى ان هذه المركبات لليوريا ، والثيويوريا ثنائية
الاعطاء واوضحت الدراسات ان شكل المتراكبات إما سداسى أو رباعى الشكل ،
ومن خلال قياسات التوصيل المولارى أوضحت ان أغلب المتراكبات أيونية
وذلك يدل على وجود أيونات الكلوريد أو النتات فى المتراكب .