New Coordination Polymers of Nickel and Cobalt with Thiolactic and Thioglycolic Ligands

Akram A. Mohammed , Nabil H. Buttrus , Mohammed J. Issa
Chemistry Department ,College of Science , Mosul University , Mosul , Iraq

(Received: 2 / 12 / 2012---- Accepted: 19 / 5 /2013)

Abstract

This work involves the preparation and investigation of new coordination complexes of Ni (II) and Co(II) with the ligands thiolactic (L_1) and thioglycolic (L_2) acids. The analysis of the purified products with UV, IR and magnetic measurements shows square-planer environment of the complexes having the formula: $[M(L_1)_2]$ and $[M(L_2)_2]$ where M is the transition metal ions. The prepared complexes were converted to macromolecules through the addition of ethylene diamine (en) and diethylene triamine (dien) . The new products show the hexa-coordination configuration when investigated by using the prementioned techniques. The limiting viscosity measurements show that the new products possess high molecular weight when compared with the original complexes. This observation reveals that the terminal and intermediate amine groups are playing an important role in connecting neighbor molecules or ions and converting them to macromolecules. Thermal stability thermograms show the high stability of the new complexes if compared with the original one. Also, the stability increased directly with the amount of the amine added.

Key words: Coordination Polymers, Thiolactic and Thioglycolic acids, Nickel and Cobalt.

Introduction

Coordination polymers of rare earth and transition metals have received significant attention in recent years because of their potential optical, magnetic and porous properties, especially for the carboxylates [1-6]. The nature of binding between metal ions and ligands continues to be a focal point of research in coordination chemistry. The search for new ligands with enhanced affinity for metal ions such as Co^{+2} , Ni^{+2} , Pt^{+2} , Pd^{+2} and Hg^{+2} has attracted much interest . Different studies have led to grafted or encapsulated ligand inorganic polymers, and sol-gel for toxic metal separation and environmental application [7-10]. Mercapto ligands RSH are major class of ligands with high affinity for M^{+2} ions are have successfully used to remove Hg^{+2} ions from aqueous solutions. A series of new 2-phenyl pyridine Au (III) complexes [Au(PPy)X] with various thiolate ligands has been synthesized and characterized where X=(SCN), (NCS) (1), TLC (thiolactate) (2), TSC (thiosalicylate) (3), DMP (2,3-dimercapto-1-propanol) (4), DMS (2,3-dimercaptosuccinic acid) (5). The crystal structure of Au (PPy) (SCN) (NCS) (1) shows the two soft carbanion and sulfer donor mutually cis to each other [11] .

The reaction between $InCl_3$ with sodium mercapto acetic acid $NaSCH_2COOH$ in 4-methyl pyridine affords $[Cl\ In(SCH_2COO)_2]\ [4Me\ Py\ H]_2$, X-ray of the complex show a distorted square pyramidal geometry with the $^-SCH_2COO^-$ ligands in the trans conformations [12].

Metal complexes with difunctional ligands are very interesting and in continuation of our studies [13-15], we are presenting here the preparation and characterization of new coordination polymers of Co^{+2} and Ni^{+2} with thiolatic and thioglycolic ligands.

Experimental

Materials

Thiolactic acid (L_1), Thioglycolic acid (L_2), Ethylene diamine (en), Diethylene triamine (diene), Nickel acetate (hydrated) and Cobalt acetate (hydrated) were reagent grade (Fluka). Solvents: Ethanol , Ether and DMSO commercially available were used without further purification .

Preparation of complexes

1-Thiolactic acid complexes $[M(L_1)_2]$

Nickel salt (0.01 M, 2.49 gm) and cobalt salt (0.01 M, 2.49 gm) were dissolved in 10 ml ethanol respectively. Thiolactic acid (0.02 M, 2.12 gm) dissolved in 10 ml ethanol was as added to each solution . The mixtures was refluxed for 3 hrs in 100 ml round flask. After cooling the precipitate was separated, washed with ether then dried under vacuum.

2-Thioglycolic acid complexes $[M(L_2)_2]$

To similar solutions of nickel and cobalt mentioned in (1), (0.02 M, 1.84 gm) of thioglycolic acids dissolved in 10 ml ethanol was added. The procedure then continued as mentioned in clause (1).

3- Ethylene diamine (en) complexes

a- $[M(L_1)_2en]$ and $[M(L_2)_2en]$ complexes :

Ethylene diamine (0.01 M, 0.6 gm) dissolved in 10 ml ethanol was added to the complexes $[M\ (L_1)_2]$ (0.01 M, 2.66 gm) Co and (0.01 M, 2.66 gm) Ni, dissolved in 10 ml ethanol. The mixtures was refluxed for 3 hrs then precipitated by cooling. The precipitate washed with ether then dried under vacuum.

b- $[M(L_1)_2(en)_2]$ and $[M(L_2)_2(en)_2]$ complexes :

Ethylene diamine (0.02 M, 1.2 gm) dissolved in 10 ml ethanol was added to the complexes prepared in (1) according to the following weights after dissolving in 10 ml ethanol, (0.01 M, 2.66 gm)Co complex and (0.01 M, 2.66 gm) Ni complex. The procedure then continued as (3a)

4- Diethylene triamine (dien) complexes

a- $[M(L_1)_2$ dien] and $[M(L_2)_2$ dien] complexes :

Diethylene triamine (0.01 M, 1.03 gm) dissolved in 10 ml ethanol was added to the complexes of Ni and

تحضير ودراسة بوليمرات تناسقية جديدة للنيكل والكوبلت مع ليكاندات الثايولاكتيك والثايوكلايكولك

اكرم عزيز محمد ، نبيل هادي بطرس ، محمد جاسم

قسم الكيمياء ، كلية العلوم ، جامعة الموصل ، الموصل ، العراق

(تاريخ الاستلام: 2 / 12 /2012 ---- تاريخ القبول: 19 / 5 /2013)

الملخص

تضمن البحث تحضير معقدات تناسقية جديدة لاملاح النيكل والكوبلت مع كل من حامض الثايولاكتيك (L_1) والثايوكلايكولك (L_2) . شخصت المعقدات الناتجة باستخدام الأطياف الالكترونية والأشعة تحت الحمراء والمغناطيسية وتم الاستنتاج ان المعقدات الناتجة هي بشكل المربع المستوي وتمتلك التراكيب الآتية : $[M(L_1)_2]$ او $[M(L_2)_2]$ حيث ان M تمثل ايون العنصر الانتقالي . وفي خطوة لاحقة تم تحويل هذه المعقدات الى جزيئات بوليمرية بإضافة القاعدتين اثلين ثنائي امين (en) وثنائي اثلين ثلاثي امين (dien) بنسب مختلفة الى المعقدات حيث حصلنا على معقدات جديدة ذات بنية ثمانية السطوح . وتم التأكد من هذه التراكيب باستخدام طرق التشخيص المذكورة أنفا. وأشارت دراسة الوزن الجزيئي للمر كبات المحضرة من خلال قياسات اللزوجة الذاتية إن هذه المركبات امتلكت أوزانا جزيئية اعلى من نظائرها في المعقدات الاولى بعد اضافة القاعدتين (en) و(dien) . وتزداد هذه الاوزان الجزيئية مع زيادة نسبة القاعدة المضافة مما يدل على ان مجاميع الامين الوسطية والطرفية تؤدي دورا مهما في الترابط مع الجزيئات المجاورة مما يؤدي الى زيادة الوزن الجزيئي للمركب . ودلت دراسة الاستقرارية الحرارية ان المركبات الجديدة تمتلك استقرارا حراريا اعلى من المعقدات الاوليه المكونة لها . ويزداد الثبات الحراري طرديا مع زيادة نسبة القاعدة المضافة .

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Viscosity measurements

The molecular weight of polymers was determined viscometrically. Intrinsic viscosity [η] was used as an approximate measure for molecular weight changes according to Mark-Hauwink-Sakurada equation [43] :

$[\eta] = K (M_v)^a$

Where, M_v = viscosity average molecular weight .

K and a = constant depending on polymer, solvent and temperature .The determined [η] values listed in table 1 show low values for the primary complexes (A,B,C,D) if compared with the rest complexes . This phenomenon may be explained by the high steric hindrance of the coordination monomers which prevents high degree of polymerization . This result agrees with charles findings [44] , where he got an oligomeric compound on polymerization of $[Cu(CH_3CO_2)_2CH:CH(CH_3CO_2)_2]$. Such behavior was explained by the intermolecular chain termination caused by the transfer of an electron from the coordination metal to the centre of the chain (chain-transfer to monomer) and the transfer of the metal ion (MII) to its oxidized state (MIII) . Kluiber and lewis [45] mentioned that the main reason for the low molecular weight of the bidentate chelated polymers is due to the insolubility of certain parts of the chain in the medium , which prevents the growth of the polymeric chain .

Investigation of [η] values of the rest complexes show that the addition of (en) and (dien) ligands to the complexes leads to high [η] values which reveals the formation of high molecular weight compounds . The terminal ($-NH_2$) and intermediate (-NH-) groups in (en) and (dien) ligands may form H-bands with the neighboring carbonyl groups. As well as , complexes chelated with two (en) or (dien) molecules show higher viscosities than complexes chelated with one (en) or (dien) molecules . Moreover , viscosities of (dien) and $(dien)_2$ complexes are higher than the similar (en) and $(en)_2$ complexes . One the other hand , differences in ligand length affects the complexes molecular weight ; so [η] show high values when L_1 ligand (thiolactic acid) is used than L_2 ligand (thioglycolic acid) .

Thermal stability

Thermograrimetric analysis (TGA) at variable temperatures in air of Co and Ni polymer complexes are shown figures 1 and 2 respectively . Investigation of these thermograms show three distinguishable weight depression : firstly at 100-120 °C , the second after 160 °C and the last after 320 °C .

These changes in weight are explained as a result of the gradual decomposition of the compounds at these temperatures . The comparison of thermal stability of the original complexes with their polymeric (en) and (dien) polymers show high thermal stability of the latter compounds. This effect may be due to the many coordination established from different amine groups which, in turn increases the molecular weight and thermal stability of he polymeric complexes. In general it was found that thermal stability of cobalt and nickel complexes with (en) and (dien) ligands decreased in the following order : $(dien)_2 > (en)_2 >$ dien > en > original

This observation shows that increasing amino groups leads to more stable complexes due to large number of H-bonds formed .

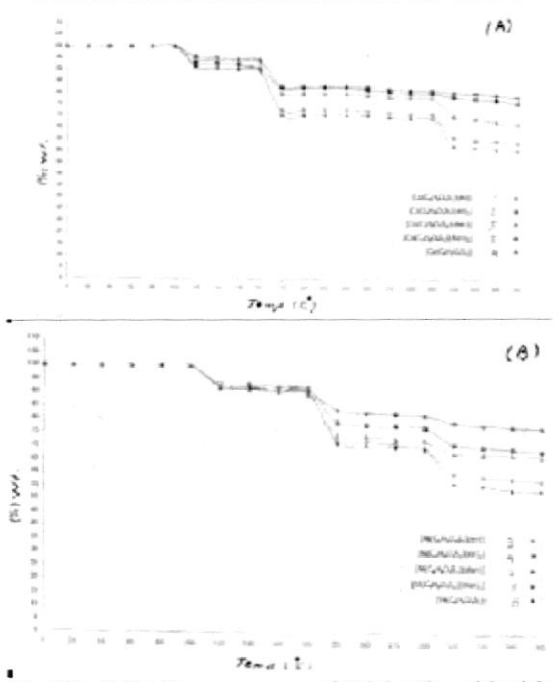


Fig (1) : TGA thermograms of thiolactic acid with cobalt (A) and nickel (B)

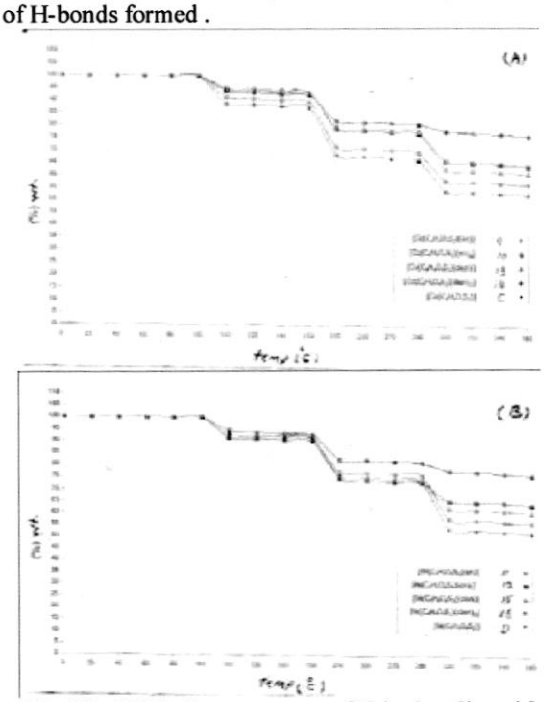
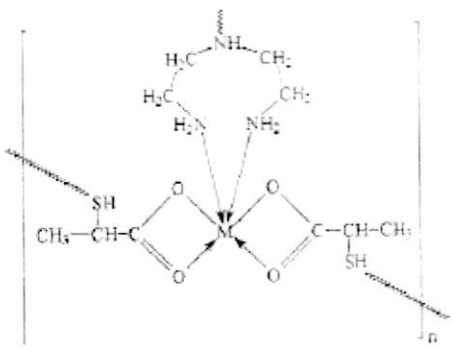
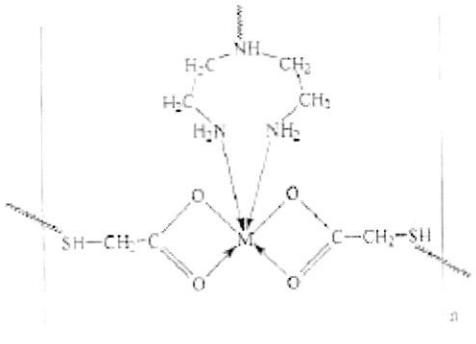


Fig (2) : TGA thermograms of thioglycolic acid with cobalt (A) and nickel (B)



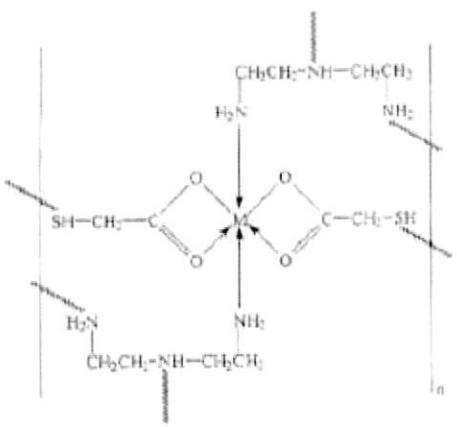
(11,10)



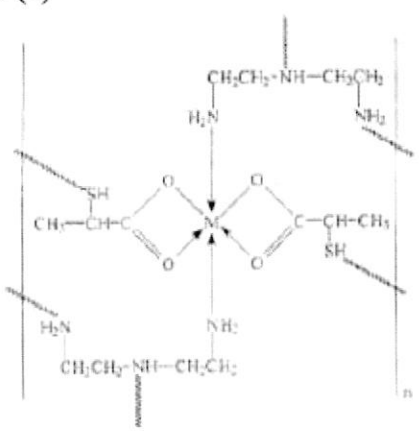
(11,9)

M=Co(II) , Ni (II)

Scheme (4)



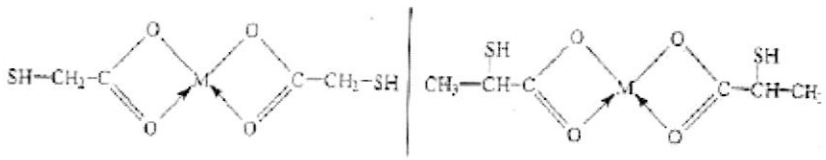
(16,14)



(15,13)

M=Co(II) , Ni (II)

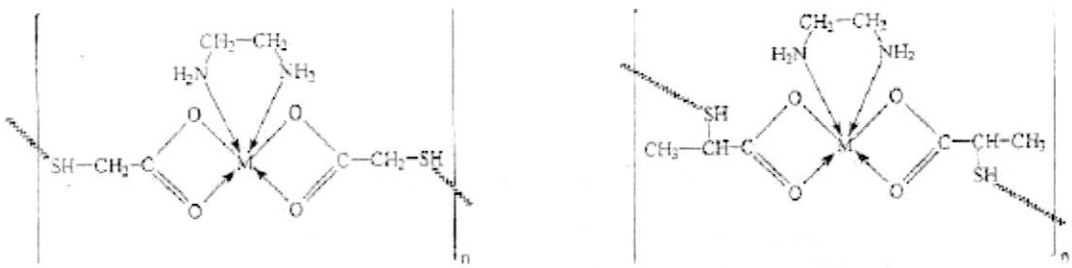
Scheme (5)



(C,D) (B,A)

M=Co(II) , Ni (II)

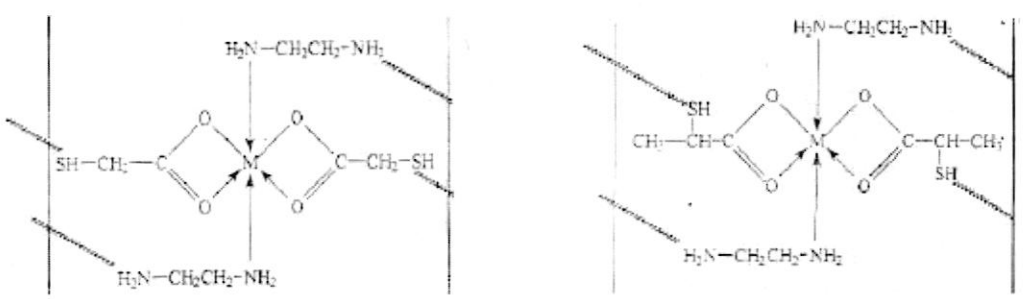
Scheme (1)



(7,5) (3,1)

M=Co(II) , Ni (II)

Scheme (2)



(8,6) (4,2)

M=Co(II) , Ni (II)

Scheme (3)

cm^{-1} shifted to lower frequency assigned coordination with neighbor metal ions [39,40] . The IR spectra of (SH) show absorption bands in the region 2370-2560 cm^{-1} shifted some what to higher frequencies which assigned no coordination with the original metal ion but coordination with the neighbor metal ion [41,42] .

Table 3 : Infrared spectral data of the free ligands and their Co(II) and Ni(II) complexes

No.	υ_{coo}		$\Delta\upsilon$	υ_{M-O}	υ_{M-N}	υ_{NH2}	υ_{SH}
	υ_{asym}	υ_{sym}					
A	1578(s)	1326(s)	192	460(s)	_	_	2360(m)
B	1586(s)	1396(s)	190	500(w)	_	_	2365(m)
C	1596(s)	1395(s)	201	491(m)	_	_	2450(m)
D	1595(s)	1395(s)	200	510(s)	_	_	2360(m)
1	1581(s)	1384(s)	197	460(s)	410(m)	3266(m)	2500(m)
2	1578(s)	1383(s)	195	480(s)	400(m)	3270(m) 3358(m)	2500(m)
3	1593(s)	1385(s)	208	470(w)	418(s)	3290(m)	2530(m)
4	1593(s)	1386(s)	197	466(m)	405(s)	3275(w) 3370(w)	2435(m)
5	1575(s)	1364(s)	211	463(m)	420(s)	3260(m)	2560(m)
6	1611(s)	1401(s)	210	475(s)	420(s)	3275(w) 3360(w)	2500(m)
7	1580(s)	1384(s)	196	465(s)	400(m)	3275(m)	2530(m)
8	1589(s)	1385(s)	204	475(w)	416(s)	3280(w) 3380(w)	2490(m)
9	1580(s)	1370(s)	210	510(s)	425(s)	3265(m)	2515(m)
10	1585(s)	1380(s)	205	522(s)	430(m)	3270(w) 3380(w)	2520(m)
11	1642(s)	1432(s)	210	478(s)	466(m)	3275(w)	2500(m)
12	1640(s)	1435(s)	205	521(s)	465(m)	3270(w) 3275(w)	2480(m)
13	1580(s)	1384(s)	196	468(m)	442(s)	3265(m)	2370(m)
14	1599(s)	1408(s)	191	492(m)	440(s)	3270(w) 3400(w)	2500(m)
15	1627(s)	1430(s)	197	530(m)	415(m)	3270(m)	2510(m)
16	1582(s)	1389(s)	193	530(m)	462(m)	3265(w) 3395(w)	2560(m)

(s)=strong (m)=medium (w)=weak (M)=metal ion

Complex structures

From the listed information's it may be concluded that the suggested chemical structures of the prepared coordination polymers are as follows :

a/The complexes A-D have the square planer geometry (Scheme 1) .

b/Addition (en) and $(en)_2$ ligands to the complexes (1-8) gives an octahedral polymer units (Schemes 2,3) .

c/Addition (dien) and $(dien)_2$ ligands to the complexes (9-16) leads to polymeric octahedral units (Schemes 4,5) .

^4T_1g (F) ⟶ ^4T_1g (P) (υ_3) .

While low spin tetra- coordinated Co (II) complexes (A and C) show absorptions 18023-18348 cm^{-1} which assigned to the electronic transition (^4A_1g ^4E_1g) which suggest the square-planer structure of these complexes [19-20] .

Nickel complexes

The hexa-coordinated Ni (II) complexes (3,4,7,8,11,12,15,16) show magnetic moments values in the range 3.26-3.48 B.M. Table (1), which agrees with the high spin octahedral structures [25,26], while tetra- coordinated Ni (II) complexes (B and D) show magnetic moments properties which points the square-planer structure [27,28] .

The electronic spectra of the same complexes exhibit three transitions in the ranges 7000-11000 cm^{-1} , 12000-20000 cm^{-1} and 21000-28000 cm^{-1} , which belongs to the transitions [29-30] :

^4A_2g (F) ⟶ ^3T_2g (F) (υ_1) .

^4A_2g (F) ⟶ ^3T_1g (F) (υ_2) .

^4A_2g (F) ⟶ ^3T_1g (P) (υ_3) .

While the tetra- coordinated Ni(II) complexes (B and D) show exhibit two absorption bands at 15384-16525 cm^{-1} which belongs to the transition ^1A_1g ⟶ ^1B_1g (υ_2) . The position of these transitions agrees with square-planer Ni(II) structure .

Table 2: Electronic spectra of Co(II) and Ni(II) complexes in DMSO solvent

Co complexes	Electronic Transmissions (cm^{-1})		
	$^4T_1g(F) \longrightarrow {}^4T_2g(F)$	$^4T_1g(F) \longrightarrow {}^4A_2g(F)$	$^4T_1g(F) \longrightarrow {}^4T_1g(P)$
1	10101	13262	20000
2	10204	13132	20000
5	10141	16666	25641
6	10204	16339	24390
9	10893	16341	22222
10	10186	16393	23809
13	10121	13595	22324
14	10111	14300	22224
	$^2A_{1g} \longrightarrow {}^2E_g$		
A	18348		
C	18023		
Ni Complexes	$A_2g(F) \longrightarrow {}^3T_2g(F)$	$^1T_1g(F) \longrightarrow {}^1T_2g(F)$	$^1T_1g(F) \longrightarrow {}^1T_2g(F)$
3	10204	12345	25000
4	10893	18516	25125
7	11764	16077	26315
8	11627	15348	25641
11	10438	17600	25974
12	11261	16949	22421
15	10183	12723	27543
16	10869	13623	22727
	$^1A_1g \longrightarrow {}^1A_2g$	$^1A_1g \longrightarrow {}^1B_1g$	
B	15384	23529	
D	16525	24390	

Infrared spectra

Table (3) shows the more characteristic infrared spectral bands of the free ligands and their complexes. The most significant information on the geometry of these complexes comes from the analysis of the stretching frequencies of the functional groups which are closely related to the way in which they are coordinated to the metal ion [31] . The IR spectra of the complexes show in the carbonyl stretching region, broad and intense bands ranging between 1540-1642 cm^{-1} and 1395-1430 cm^{-1} assigned for asym. υ_{COO} an sym. υ_{COO} respectively. Table (3) lists the magnitude of $\Delta\upsilon$ ($\Delta\upsilon = \upsilon_{asym} - \upsilon_{sym}$) values. When $\Delta\upsilon$ is between 150-180 cm^{-1} , it suggests the presence of monodentate bonding of carbonyl group to metal ion, and suggests a bidentate attachment when $\Delta\upsilon$ is between 190-295 cm^{-1} [32,33] . In some cases , when $\Delta\upsilon > 200$, it means that the only way in which all carboxylate groups are bound to the metal atom is through polymeric structure [34,35] . The M-O absorption bands appear generally at 450-550 cm^{-1} [36] . Our results show absorption bands at 460-530 cm^{-1} which coincides with the previously mentioned results [37,38]. Moreover , the IR spectra show absorption bands in the region 400-466 cm^{-1} , which are assigned to M-N , this result agrees with the literature where M-N absorption appears generally 360-500 cm^{-1} [36] . The absorption due to υ_{NH2} group for all complexes contain (en) and (dien) ligands except (A,B,C,D) appears at 3260-3282 cm^{-1} . This band generally appears at 3400 cm^{-1} , but because of coordination , it is shifted to lower frequency , that means it is shared in coordination . As well as , frequencies of (NH_2) absorption band at 3850-3400

Co prepared in (1) according to the weights (0.01 M, 2.66 gm) Ni and (0.01 M, 2.66 gm) Co dissolved in 10 ml ethanol .

b-$[M(L_1)_2$ (dien)$_2]$ and $[M(L_2)_2$ (dien)$_2]$ complexes : Diethylene triamine (0.02 M, 2.06 gm) dissolved in 10 ml ethanol was added to the same complexes of Ni and Co prepared in (4a). The procedure then continued as mentioned before .

Physical measurements

The IR spectra was recorded on Tensor 27Co . Brucker (FT-IR) spectrophotometer in the region (250-4000 cm^{-1}) using CsI pellets. Electronic spectra were recorded on Shimadzu (UV-Vis) solutions of complexes in DMSO at 25 °C using 1 cm quartz cell. Magnetic measurements was operated using solid state Faraday's method by using Brucker BM.6 balance at 25 °C . Intrinsic viscosity was determined by using Ubbelohde viscometer at 30 °C in DMSO solvent. Thermogravimetric analysis (TGA) was obtained by using the method mentioned in ref [16] .

Results and Discussion

1- preparation of Co and Ni complexes

Co and Ni complexes with thiolactic and thioglycolic acids are prepared by the reaction of these acids with hydrated acetate salts of these metals :

$$M(CH_3CO_2)_2.4H_2O + 2\ CH_3.CH(SH)CO_2H \xrightarrow[\triangle\ 3h]{\text{ethanol}} [M(C_6H_{10}O_4S_2)] + 2\ CH_3CO_2H + 4H_2O$$

$$M(CH_3CO_2)_2.4H_2O + 2\ HS.CH_2.CO_2H \xrightarrow[\triangle\ 3h]{\text{ethanol}} [M(C_4H_6O_4S_2)] + 2\ CH_3CO_2H + 4H_2O$$

M=Ni or Co.

2- preparation of polymeric complexes

These complexes are prepared by the addition of the binding bases, ethylene diamine (en) and diethylene triamine (dien) in two ratios 1:1 and 1:2 (complex: base).

The formula structures, yield (%), colors and decomposition temperatures are shown in Table (1).

Table 1 : Formula structures , yield(%) with some physical properties of the prepared complexes with Nickel and Cobalt

No.	Formula Structure	Yield (%)	Color	Decomp. Temp(C°)	μ_{eff}(B.M)	[η] ($ml.gm^{-1}$)
A	$[Co(C_6H_{10}O_4S_2)]$	86	brown	204	2.32	0.151
B	$[Ni(C_6H_{10}O_4S_2)]$	84	green	220	Dia	0.138
C	$[Co(C_4H_6O_4S_2)]$	78	brown	206	2.51	0.113
D	$[Ni(C_4H_6O_4S_2)]$	90	green	210	Dia	0.091
1	$[Co(C_6H_{10}O_4S_2)(en)]$	87	black	>350	4.80	0.220
2	$[Co(C_6H_{10}O_4S_2)(en)_2]$	85	brown	>350	4.87	0.450
3	$[Ni(C_6H_{10}O_4S_2)(en)]$	80	Green	>350	4.33	0.207
4	$[Ni(C_6H_{10}O_4S_2)(en)_2]$	82	Purple	>350	3.31	0.425
5	$[Co(C_4H_6O_4S_2)(en)]$	76	Brown	>350	4.72	0.191
6	$[Co(C_4H_6O_4S_2)(en)_2]$	75	Brown	>350	4.82	0.315
7	$[Ni(C_4H_6O_4S_2)(en)]$	72	Dark-green	>350	3.44	0.175
8	$[Ni(C_4H_6O_4S_2)(en)_2]$	70	Dark-green	>350	3.32	0.300
9	$[Co(C_6H_{10}O_4S_2)(dien)]$	86	brown	>350	4.85	0.394
10	$[Co(C_6H_{10}O_4S_2)(dien)_2]$	86	brown	>350	4.96	0.666
11	$[Ni(C_6H_{10}O_4S_2)(dien)]$	77	green	>350	3.26	0.372
12	$[Ni(C_6H_{10}O_4S_2)(dien)_2]$	76	green	>350	3.40	0.625
13	$[Co(C_4H_6O_4S_2)(dien)]$	75	brown	>350	4.86	0.240
14	$[Co(C_4H_6O_4S_2)(dien)_2]$	80	brown	>350	4.96	0.588
15	$[Ni(C_4H_6O_4S_2)(dien)]$	83	green	>350	3.35	0.237
16	$[Ni(C_4H_6O_4S_2)(dien)_2]$	80	Dark-green	>350	3.48	0.540

Characterisation of complexes

The coordination complexes of thiolactic and thioglycolic acids with Co(II) and Ni(II) and their polymeric forms with (en) and (dien) are characterized as shown below :

Magnetic moments and Electronic spectra

Cobalt complexes

The hexa-coordinated Co (II) complexes (1,2,5,6,9, 10,13,14) show magnetic moments values in the range 4.72-4.96 B.M. Table (1) , which agrees with the high spin octahedral structures, while tetra-coordinated Co (II) complexes (A and C) show magnetic moments ranged between 2.32-2.51 B.M. which agrees with square-planer Co (II) structures[17,18] .

The electronic spectra of high spin hexa-coordinated Co (II) complexes Table (2) exhibit three transitions in the regions 7000-10000 cm^{-1} , 12000-16000 cm^{-1} and 17000-22000 cm^{-1} , belonging to the transitions [17-20] :

$^4T_1g\ (F) \longrightarrow {}^4T_2g\ (F)\ (\upsilon_1)$.

$^4T_1g\ (F) \longrightarrow {}^4A_2g\ (F)\ (\upsilon_2)$.