Synthesis And Characterization Of Some New Metal Complexes Of Ethyl Cyano (2-Methyl Carboxylate Phenyl Azo Acetate)

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Abstract

Complexes of (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}) with the ligand Ethyl cyano (2-methyl carboxylate phenyl azo acetate) (ECA) have been prepared and characterized by FTIR, (UV-Visible), Atomic absorption spectroscopy, Molar conductivity measurements and magnetic moments measurements. The following general formula has been suggested for the prepared complexes $[M(ECA)_2]Cl_2$ where M = (Co^{2+}, Ni^{2+}, Cu^{2+} ,Zn^{2+}, Cd^{2+}, Hg^{2+}) and the geometry is octahedral.

Key words: Ethyl cyano (2-methyl carboxylate) phenyl azo acetate, complexes.

Introduction

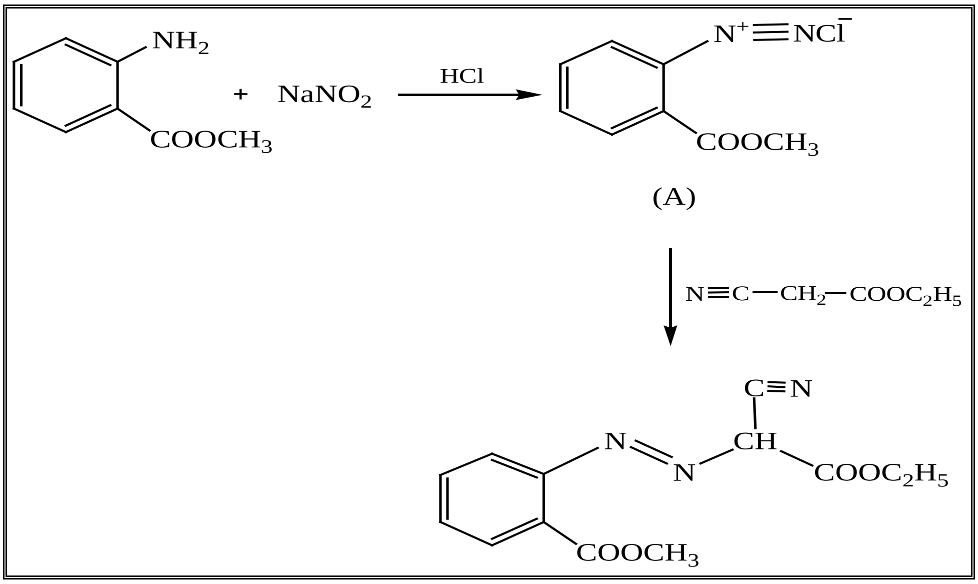
Azo compounds are very important class of chemical compounds receiving attention in scientific research, they are highly colored and have been used as dyes and pigments for along times[1,2]. Transition metal azo complexes have played an important role in the development of coordination chemistry and have wide application in industry and biological systems[3-8]. Rafid[9] prepared the azo dye 2-(2-pyridal azo)1,8-dihydroxy naphthalene and their complexes with some transition metals. A series of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of azo-compounds containing hydroxyl quinoline moiety have been synthesized and characterized by elemental analysis, molar conductance, magnetic moments, IR, electronic and ESR spectral studies. The thermal analysis of the complexes was also used to confirm the structures of the complexes[10]. In this paper, we described the preparation and characterization of some new metal ions complexes with Ethyl cyano (2-methyl carboxylate phenyl azo acetate) (ECA).

Experimental

All chemical used were of reagent grade (supplied by either Merck or Fluka) and used as supplied. ^{1}HNMR spectrum was recorded using Ultra Shield 300 MHz, Bruker, Switzerland, at University of Al al-Bayt, Jordan. The FTIR spectra in the (4000-400) range cm^{-1} were recorded as KBr disc on Shimadzu FT infrared spectrophotometer. (UV-Vis) spectra were recorded using (Shimadzu UV-Vis. 160A) (UV-Vis) spectrophotometer in ethanol solution (10^{-3} M), Metal contents of the complexes were determined by atomic absorption technique using Shimadzu AA680G Atomic absorption spectrophotometer. Magnetic moments (μ_{eff} B.M) were measured employing Faraday method using balance magnetic susceptibility model, MSBMKT, melting points were determined by using Stuart-melting point apparatus. Conductivity measurements were carried out using Philips PW. Digital conductivity meter.

Synthesis of the ligand ethyl cyano (2-methyl carboxylate phenyl azo acetate) (ECA)

A solution of methyl-2-amino benzoate (1.3ml, 0.01mole) in concentrated HCl (3ml) was cooled to (0-5˚C), a cooled solution of sodium nitrite (1.5g in 10ml of water) was added dropwise during 10 minutes, then the reaction mixture was stirred for 30 minutes at the same temperature. The mixture was added to an ice-cold mixture of ethyl cyano acetate (0.01mole) and sodium acetate (4.1g, 0.05mole) in ethanol (30ml) dropwise with stirring over 15 minutes. Afterwards the stirring was continued for 30 minutes and the reaction mixture then left to stand at room temperature for 2 hours. The solid product formed was collected and recrystallized from ethanol to give the orange crystals (ECA), m.p (142-144˚C), yield (75%) scheme (1).



Scheme (1): Synthesis route for ligand (ECA)

Synthesis of complexes

A solution of metal chloride contains (0.11g, 0.11g, 0.076g, 0.061g, 0.091g and 0.122g) (1mmole) of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2.H_2O$ and $HgCl_2$) respectively in ethanol was added to a solution of the ligand (ECA) (0.25g, 2mmole) in ethanol (5ml).

After stirring for 3 hours colored precipitate was formed at room temperature, the rustling solids was filtered off, recrystalized from ethanol and dried at 50˚C.

Results and discussion

The isolated complexes were crystalline solids soluble in common solvents like ethanol, dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO), the conductivity measurements in ethanol indicated electrolytic behavior. The molar ratio method was followed to know the ratio of metal ion to ligand in complexes. Ethanol was used as a solvent, the (M:L) ratio was found to be (1:2). Table (1) includes the physical properties; the magnetic measurements (μ_{eff} B.M) for the complexes.

Spectra studies

The ^{1}HNMR spectrum of the ligand (ECA) was recorded in DMSO, Fig (1), showed the following signals: singlet (s) at δ(2.50) ppm for (DMSO), triplet (t) at δ(1.35) ppm for (3H, CH_3), singlet (s) at δ(3.9) ppm for (3H, OCH_3), quartet (q) at δ(4.34) ppm for (2H, OCH_2) and multiplet (m) at δ(7.2-8.0) ppm for (4H, Ar-H).

Infrared spectra

The infrared spectra of ligand (ECA) and its complexes are given in Table (2). The strong absorption bands at the (1701) cm^{-1} and (2222) cm^{-1} in the free ligand, Fig (2) are due to υ(C=O) ester and υ(C≡N) [11,12], in the complexes spectral, Fig (3) for cobalt complex, the bands have been found in the range between (1637-1508) cm^{-1} shifted to lower frequencies by (64-193) cm^{-1} which indicates the coordination of the oxygen atom at the υ(C=O) group in methyl ester [13] and band of υ(C≡N) was absent which indicates the coordination through the nitrogen atom of υ(C≡N). The ligand spectrum showed a band at (1454) cm^{-1} due to υ(N=N)[14], the spectra of complexes show this band about (1436-1373) cm^{-1} shifted to lower frequencies by (81-18) cm^{-1} which indicates the coordination of the ligand (ECA) through the nitrogen atom of the azo nitrogen[15,16] and new bands appeared in the spectra of metal complexes at (530-510) cm^{-1} and (462-415) cm^{-1} attributed to the (M-O) and (M-N) respectively[17].

Electronic spectra

The absorptions and assignments related to the ligand and its complexes are listed in Table (3), the ligand (ECA), Fig (4) exhibited an absorption bands at (253) nm (39525) cm^{-1} and (361) nm (27710) cm^{-1} which may be attributed to ($\pi \longrightarrow \pi^*$) and ($n \longrightarrow \pi^*$) transitions[18].

The spectra of complexes

- [Co(ECA)$_2$]Cl$_2$ complex

The spectrum of deep green complex of Co(II) exhibited the following bands at (40000) cm^{-1}, (27472) cm^{-1}, (15037) cm^{-1} and (12285) cm^{-1} which have been assigned to (C.T), $^4T_{1g(F)} \longrightarrow {}^4T_{1g(P)}$, $^4T_{1g} \longrightarrow {}^4A_{2g}$ and $^4T_{1g} \longrightarrow {}^4T_{2g}$ respectively[19]. The ($\acute{B}$) found to be (376.93) cm^{-1} and $\beta = \acute{B} / B_{\circ}$ comes out to be (0.388) which indicates the presence of covalent bond in the complex. The magnetic moment value for cobalt(II) complex is (4.34) B.M in the range of octahedral.

- [Ni(ECA)$_2$]Cl$_2$ complex

The spectrum of red complex, Fig (5) exhibited the following absorptions at (39840) cm^{-1}, (27777) cm^{-1}, (19920) cm^{-1} and (13071) cm^{-1} which have been assigned to (C.T), $3A2g \longrightarrow {}^3T_{1g(P)}$, $^3A_{2g} \longrightarrow {}^3T_{1g(F)}$ and $^3A_{2g} \longrightarrow {}^3T_{2g}$ respectively[20]. The ($\acute{B}$) was found to be (565.6) cm^{-1} and $\beta = \acute{B} / B_{\circ}$ comes out to be (0.543) which indicates the presence of covalent bond in the complex. The magnetic moment is (3.29) B.M confirmed the fore mention geometry.

- [Cu(ECA)$_2$]Cl$_2$ complex

The spectrum of deep red showed absorptions bands at (39370) cm^{-1} and (27548) cm^{-1} which were assigned to charge transfer transitions (C.T) and only one absorption band was observed at (19231) cm^{-1} which was assigned to $^2Eg \longrightarrow {}^2T_{2g}$ transition[21,22]. The magnetic moment value for copper(II) complex is (1.75) B.M in the range of octahedral.

- [Zn(ECA)$_2$]Cl$_2$, [Cd(ECA)$_2$]Cl$_2$ and [Hg(ECA)$_2$]Cl$_2$

The orange complexes of Zn(II), Cd(II) and Hg(II) showed only charge transfer of $M \longrightarrow L$ in the range (40000-27322) cm^{-1} because the electronic configuration of Zn(II), Cd(II) and Hg(II) which confirm the absence of any (d-d) transition[23].

According to spectral data as well as those obtained from elemental analysis, the chemical structure of the complexes suggested the octahedral, Fig (6).

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Zinc(II) with glycine, N-acetyl and N-benzoyl-1-glycine anions in aqueous and ethanolic solution by polarographic method, J. Inorg. Nucl. Chem., 37: 2344.

Table (1): Physical properties of ligand and its metal complexes

Formula	Molecular weight	Colour	M.p°C or dec.	Metal % Found (Calc.)	Molar conductivity (S.cm^{2}mole^{-1}) in Ethanol (10^{-3} M)	μ_{eff} (B.M)
$C_{13}H_{13}O_4N_3$ [ECA]	275	Orange	142-144°C	-	2.4	-
$[Co(ECA)_2]Cl_2$	679.93	Deep green	95(dec.)	8.50 (8.66)	80	4.34
$[Ni(ECA)_2]Cl_2$	679.69	Red	100(dec.)	7.46 (8.64)	75	3.29
$[Cu(ECA)_2]Cl_2$	684.54	Deep red	98(dec.)	10.07 (9.28)	81	1.75
$[Zn(ECA)_2]Cl_2$	686.39	Orange	120(dec.)	9.56 (9.53)	82	0.00
$[Cd(ECA)_2]Cl_2$	733.4	Orange	130(dec.)	14.72 (15.33)	76	0.00
$[Hg(ECA)_2]Cl_2$	821.6	Orange	118(dec.)	23.84 (24.42)	72	0.00

Table (2): Characteristic infrared bands of the ligand (ECA) and its metal complexes

Compound	υ(N=N)	υ(C=O) Ester	υ(C≡N)	M-N	M-O
$C_{13}H_{13}O_4N_3$ [ECA]	1454	1701(s)	2222(s)	-	-
$[Co(ECA)_2]Cl_2$	1435(m)	1627(s)	-	420(w)	526(w)
$[Ni(ECA)_2]Cl_2$	1436(m)	1637(s)	-	424(w)	530(w)
$[Cu(ECA)_2]Cl_2$	1404(w)	1620(s)	-	418(m)	520(w)
$[Zn(ECA)_2]Cl_2$	1435(m)	1508(s)	-	418(m)	518(w)
$[Cd(ECA)_2]Cl_2$	1373(m)	1624(m)	-	415(m)	516(m)
$[Hg(ECA)_2]Cl_2$	1435(m)	1612(s)	-	462(m)	510(w)

Where: s = strong, m = medium, w = weak

Table (3): Electronic spectra data of ligand (ECA) and its complexes in ethanol solvent

Compound	λ_{max} nm	Wave number cm^{-1}	ε_{max} Molar^{-1}cm^{-1}	Assignment
Ligand [ECA]	253	39525	567	$\pi \longrightarrow \pi^*$
	361	27710	1207	$n \longrightarrow \pi^*$
$[Co(ECA)_2]Cl_2$	250	40000	428	C.T
	364	27472	870	$^4T_{1g(F)} \longrightarrow {}^4T_{1g(P)}$
	665	15037	10	$^4T_{1g} \longrightarrow {}^4A_{2g}$
	814	12285	8	$^4T_{1g} \longrightarrow {}^4T_{2g}$
$[Ni(ECA)_2]Cl_2$	251	39840	365	C.T
	360	27777	869	$^3A_{2g} \longrightarrow {}^3T_{1g(P)}$
	502	19920	12	$^3A_{2g} \longrightarrow {}^3T_{1g(F)}$
	765	13071	8	$^3A_{2g} \longrightarrow {}^3T_{2g}$
$[Cu(ECA)_2]Cl_2$	254	39370	1178	C.T
	363	27548	1497	C.T
	520	19231	143	$^2E_g \longrightarrow {}^2T_{2g}$
$[Zn(ECA)_2]Cl_2$	253	39525	422	ILCT
	366	27322	915	ILCT
$[Cd(ECA)_2]Cl_2$	254	39370	421	ILCT
	361	27472	989	ILCT
$[Hg(ECA)_2]Cl_2$	250	40000	323	ILCT
	362	27624	720	ILCT

ILCT: Internal Ligand Charge Transfer

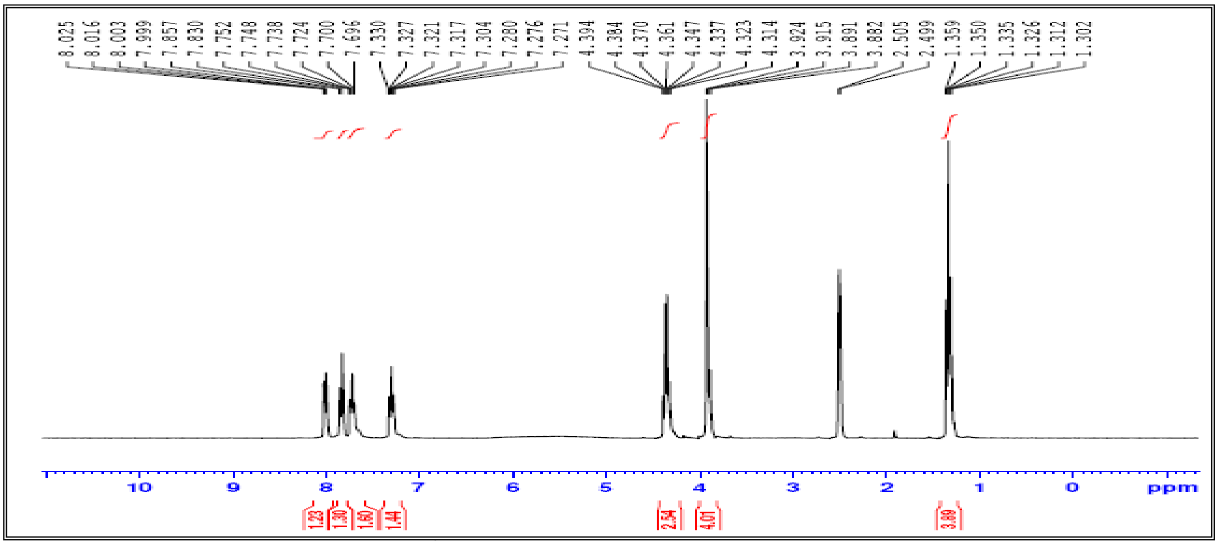

Fig. (1): ^{1}HNMR spectrum of ligand (ECA)

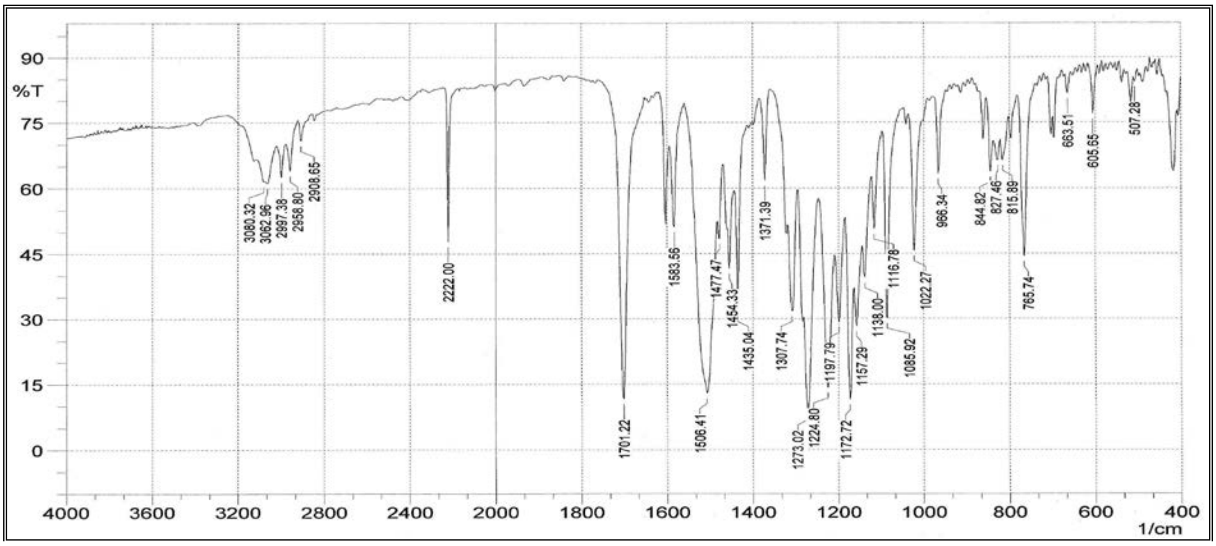

Fig. (2): Infrared spectrum of ligand (ECA)

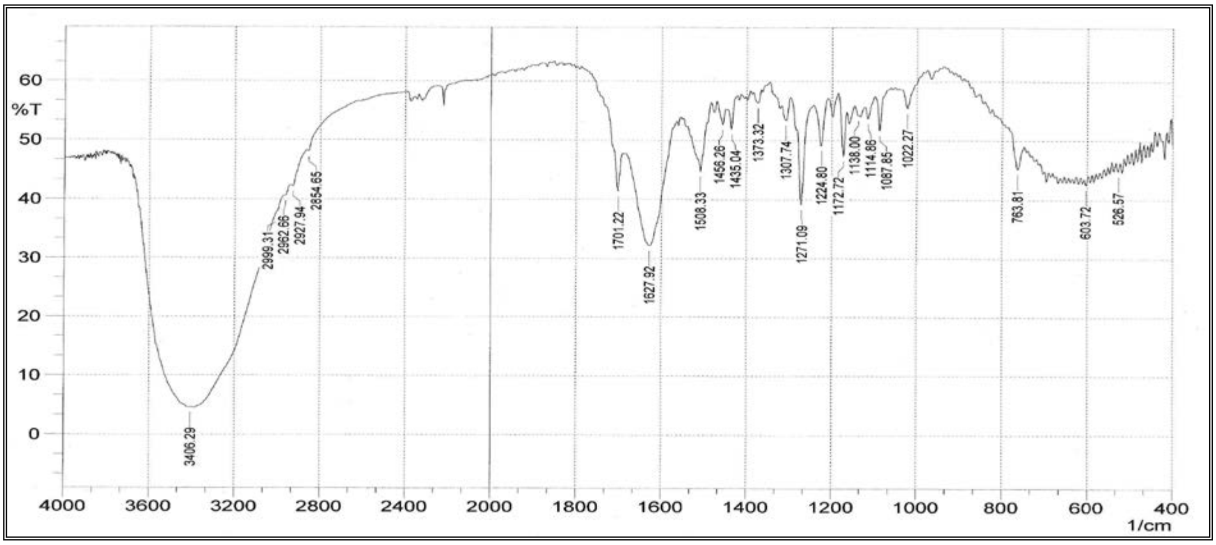

Fig. (3): Infrared spectrum of $[Co(ECA)_2]Cl_2$

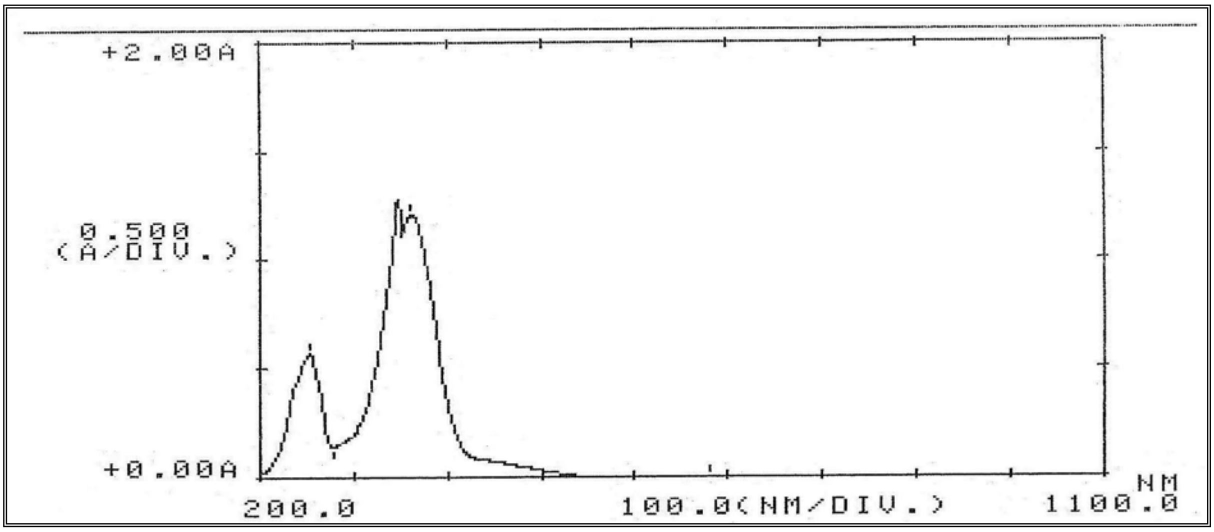

Fig. (4): Electronic spectrum of ligand (ECA)

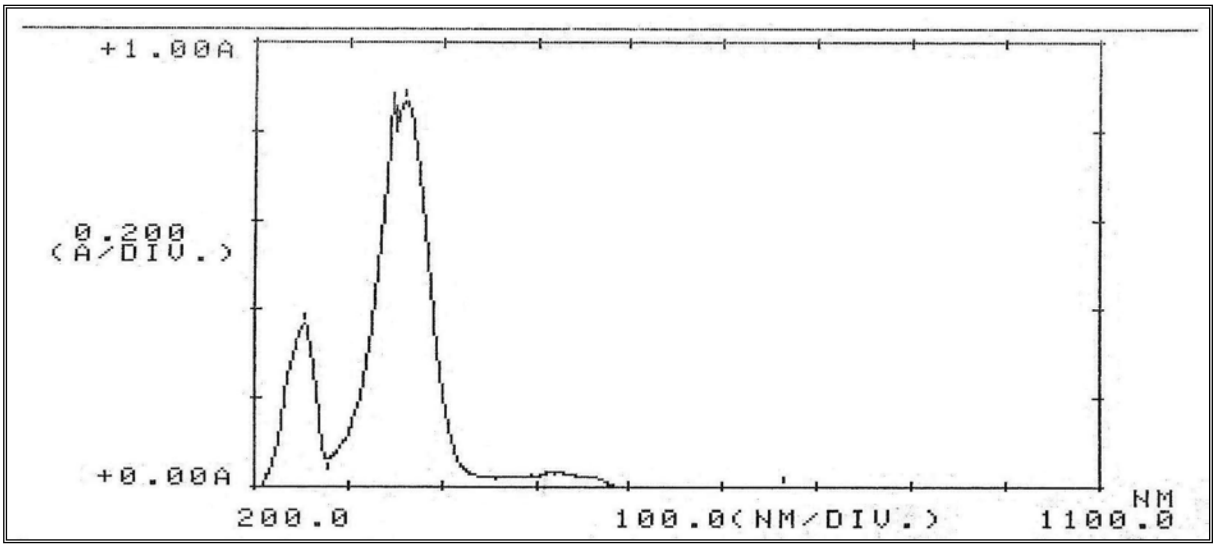

Fig. (5): Electronic spectrum of $[Ni(ECA)_2]Cl_2$

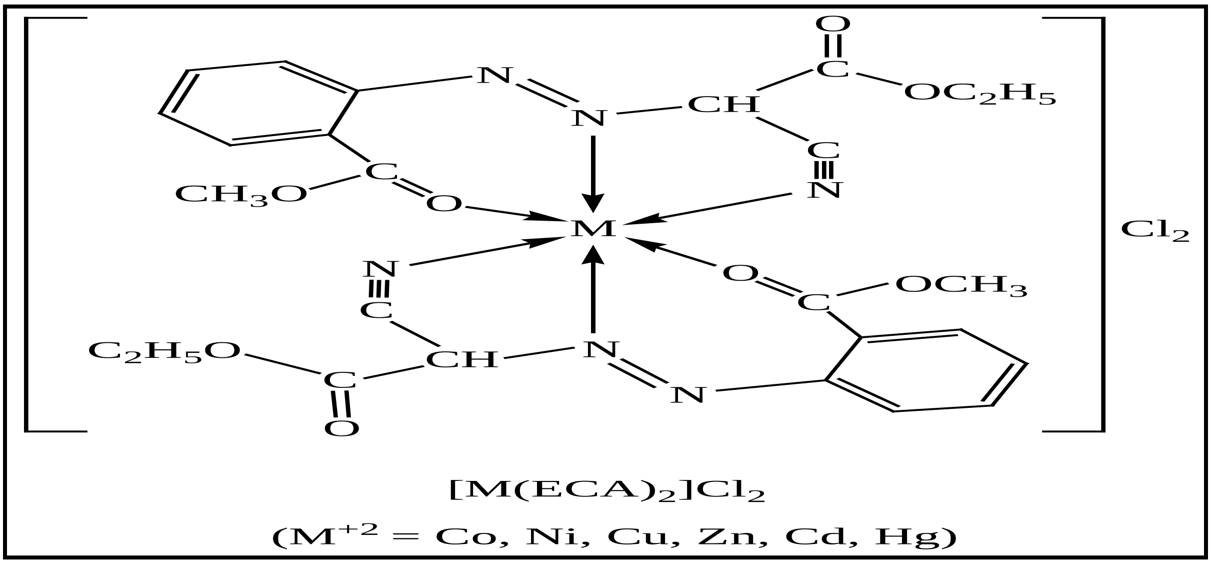

Fig .(6): The proposed structural formula of the complexes

تحضير وتشخيص بعض المعقدات الفلزية الجديدة مع الليكاند اثيل سيانو (2- مثيل كاربوكسليت فنيل ازو خلات)

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استلم البحث في : 17 نيسان 2012 ، قبل البحث في : 20 تشرين الثاني 2012

الخلاصة

حضرت بعض المعقدات الفلزية الجديدة مع الليكاند اثيل سيانو(2- مثيل كاربوكسليت فنيل ازو خلات) مع ايونات (Co(II) ، Ni(II) ، Cu(II) ، Zn(II) ، Cd(II) وHg(II)) وشخصت بالطرائق الطيفية وهي طيف الاشعة تحت الحمراء، وطيف الاشعة فوق البنفسجية والمرئية فضلا" عن تعيين نسبة الفلز في المعقدات بوساطة طيف الامتصاص الذري، وقياس التوصيلية المولارية لمحاليل المعقدات في مذيب الايثانول، وتحديد النسبة المولية لليكاند الى الفلز، وقياس العزم المغناطيسي للمعقدات المحضرة. وفي ضوء التشخيصات اعلاه اقترح الشكل الثماني السطوح لهذه المعقدات.

الكلمات المفتاحية: اثيل سيانو(2- مثيل كاربوكسليت فنيل ازو خلات)، معقدات.