Synthesis and Characterization of Mn (П),Co(П), Ni(П) and Cu (П) Complexes With Mixed Ligands, Aceturic Acid and Urea

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Abstract:

The reaction of (aceturic acid) (a-a) and urea (U) in alkaline media with the following metal ions ($Mn^{(n)}$, $Co^{(n)}$, $Ni^{(n)}$ and $Cu^{(n)}$) in ethanolic medium with (1:2) (M:L) ratio yield series of neutral complexes of general formula [M (a-a)₂ U]. The prepared complexes were characterized by using FT.IR, UV-Vis spectroscopic and elemental microanalysis (C.H.N) as well as magnetic susceptibility and conductivity measurements.

Introduction:

1mmole). The mixture was stirred until change color and the precipitate was appeared. The solution mixture was filtered off and washed several time with DMF.

Results and Discussion:

The isolated complexes were crystalline solid soluble in some of common solvents such as ethanol, methanol and DMSO. They are relatively thermally stable. The conductivity measurement in ethanol (10^{-3}) indicated the non–electrolyte behavior [12].

The elemental analysis (C.H.N) and metal determination were found to be in agreement with calculated values which support the proposed formula of the complexes, Table (1), which includes the physical properties and elemental analysis. The IRspectra of ligand aceturic acid (a-a), Figure (1), exhibits a strong band at (3352) cm⁻¹ which indicated to v(NH) vibration [13] and very weak band for to v(CO) at (1581) cm⁻¹. The spectrum shows also sharp band at (1354) cm⁻¹ and strong band at (1716) cm⁻¹ were assigned to $v_s(COO) v_{as}(COO)$ and, respectively. On the other hand, the (I.R) spectrum of ligand urea(U) Figure (2), shows abroad band at (3441) cm⁻ ¹ and (3341) cm⁻¹ indicated to v(NH) and abroad band at (1678) cm⁻¹ assigned to v(CO) [14] on complexation, Mn and Co complexes shift with change in shape were observed from main band, the significant change in this band may be a result of coordination of the metal ion. These results are in good agreement with those reported previously for complexes octahedral [10]. The (I.R) spectra of the complexes showed two bands in the rang (3456-3329)cm⁻¹ and three bands at (3471-3414-3384)cm⁻¹ assigned to v(N-H) for urea and a ceturic acid.

Metal oxygen and metal nitrogen band further confirmed by the presence of the bands at (509-528) cm⁻¹ and (426-474) cm⁻¹ indicated to engagement of this group in coordination [15].

The spectrum of [Ni (a-a)₂ U], Figure (4), displays three band assigned to v(N-H) of two ligands. The broad band at (1597) cm⁻¹ is assigned to v(CO), which was shifted by (81) cm⁻¹ to a lower frequency compared to that of urea ligand, anew bands are also observed at (501) cm⁻¹ and (425) cm⁻¹ which assigned to v(M-O) and (M-N), respectively [16], Cu complex, shows similar spectrum to that of [Ni (a-a)₂ U] and similar assignment can be made to interpret [Cu(a-a)₂ U] spectrum but v(CO) shift by (51) cm⁻¹ compared The complexes with amino acids are very much investigated [1-3] for their polymer structure and because they represent simple models system for the study of magnetic interactions[4,5]. The antioxidants properties of some metal–protein, their cardio-protecting and neurons–modeling activity are a consequence of the implication in different biological functions which influenced the electronic transfer [6,7].

Previous work treat the potentiometric study of complexes compounds of zinc (π) [8,9] and copper (π) complexes on solution [10,11].

This paper reports synthesis and characterization of new complexes with mixed ligands (aceturic acid and urea) which may used as a (mimics) for biological molecules.

Experimental:

A- Materials:

All chemicals used were of reagent and used without further purification MnCl₂. 4H₂O, CoCl₂.6H₂O, NiCl₂.6H₂O and CuCl₂.2H₂O (Fluka), aceturic acid, urea (B.D.H).

B-Instrumentation :

IR-spectra kBr discs in the range (4000-400) cm⁻¹ in (Baghdad university–college of science) were obtained using (ashimadzu FT-IR-8400S) Fourier Transform Infrared spectrometer. Solution electronic spectra were records on (ashimadzu UV-160A) Ultra Violet – Visible spectrophotometer in (BaghdadUniversity–College of Science).

Micro analysis data (C.H.N) were collected using (Euro vector EA3000A) in (Jordan – university of Alal-Bayt). Solution electrical conductivities were measured using (Philips pw-Digital conductmeter) in (Al-NahrainUniversity – college of science). Magnetic properties were obtained using (Brucker B.M1.6) in (Al-Nahrain university–college of science). In addition Melting point was measured using (Stuart Melting Point Apparatus) in (Baghdad– Institute of Technology).

Synthesis of Complexes:

All of complexes were prepared by dissolving (0.254 g, 0.146 g, 0.163 g and 0.182 g) (1 mmole) of $(MnCl_2.4H_2O, CoCl_2.6H_2O, NiCl_2.6H_2O and CuCl_2.2H_2O$ respectively) in ethanol solution. The solution were added gradually with stirring to ethanolic KOH solution of aceturic acid (a-a). (0.25g, 2mmole), then added to urea solution (0.064g,

to $({}^{6}A_{1}g \rightarrow {}^{4}T_{2}g(n))$, $({}^{4}T_{1}g(f) \rightarrow {}^{4}A_{2}g(f))$, $[({}^{3}A_{2}g(f) \rightarrow {}^{3}T_{1}g(f))$, $({}^{3}A_{2}g(f) \rightarrow {}^{3}T_{2}g(f))]$ and $({}^{2}Eg \rightarrow {}^{2}T_{2}g)$ (d-d) electronic transitions respectively, suggesting octahedral structure about Mn^{π} , Co^{π} , Ni^{π} , and Cu^{π} ions .

Magnetic Moments:

Measuring magnetic susceptibility (μ eff) contributes to the determination of structure of the complexes and provides information about the number of unpaired electrons. The effective magnetic moments of complexes were measured according to spin only from the following equation [22]:

$$\mu s - o = 2\sqrt{2(s+1)}$$
 B.M

Where S = n / 2 (n=no. of unpaired electrons). The results obtained from this equation were compared with the experimental values obtained from magnetic measurements, Table (1).

These data can help to achieve the suggested structures of complexes supported by results from elemental analysis and (I.R) spectra.

The magnetic moment values for the complexes indicated octahedral structure about Mn π , Co $^{\pi}$, Ni $^{\pi}$, and Cu $^{\pi}$, metal ions.

According to the results obtained by chemical structure of the complexes may be suggested to octahedral.



Where $M = Mn^{\pi}$, Co^{π}, Ni^{π}, and Cu^{π}

to that of urea ligand [11], and other bands are listed in Table (2) .

Table (2) gives the absorption bands in infrared spectra of starting materials (ligands) and their complexes.

Electronic Spectra:

Ligand bands of maximum absorption and assignments related to the ligands,[17], and their complexes are listed in Table (3). The ligand (a-a) exhibited an absorption band, Figure (5), at wave number (36101.08) cm⁻¹ and (23255.81) cm⁻¹ were assigned to the moderate energy $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively and for (U) Figure (6) at wave number (35714.28) cm⁻¹ and (28985.50) were assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively.

The Spectra of Complexes:

[Mn(a-a)₂U]: the complex spectrum showed four absorptions at (35460.99) cm⁻¹related to charge transfer. The other three bands at (22222.22) cm⁻¹, (16949.15) cm⁻¹ and (12820.51) cm⁻¹ were caused by the electric transitions ${}^{6}A_{1}g \rightarrow {}^{4}T_{1}g(P) {}^{6}A_{1}g \rightarrow {}^{4}Eg(n)$ and ${}^{6}A_{1}g \rightarrow {}^{4}T_{2}g(n)$ respectively[8].

- 1. [Co(a-a)₂U]: The complex, Figure (7), gave absorption at (36101.08) cm⁻¹ assigned to charge transfer. Another two band at (19607.84) cm⁻¹ and (12091.89) cm⁻¹ were found to be caused by electronic transitions ${}^{4}T_{1}g(f) \rightarrow {}^{4}T_{1}g(P)$ and ${}^{4}T_{1}g(f) \rightarrow {}^{4}A_{2}g(f)$ respectively[18].
- 2. [Ni (a-a)₂U]: The complex spectra revealed the following absorption band,.(35587.18) cm⁻¹ attributed to the charge transfer[19], two absorption at (25316.45)cm⁻¹ and (13605.44) cm⁻¹ were due to the electronic transitions ${}^{3}A_{2}g(f) \rightarrow {}^{3}T_{1}g(f)$ and ${}^{3}A_{2}g(f) \rightarrow {}^{3}T_{2}g(f)$.
- 3. [Cu(a-a)₂U]: The complex gave band, Figure (8), at wave number (36231.88) cm⁻¹ caused by charge transfer and only one absorption band at (12515.64) cm⁻¹ due to electronic transition ${}^{2}\text{Eg} \rightarrow {}^{2}\text{T}_{2}\text{g}$. This result is in a good agreement with the previous work of copper(π) complexes of octahedral geometry [20,21].

The peaks at [780,827,(395,735) and 799nm] in the spectra of Mn, Co, Ni and Cu complexes are assigned

No.	Compound	Color	M.P.C°	M% Calc (found)	Analysis calc.(found)			Conductivity δ cm ² .mole ⁻¹	μ _{EFF} (BM)
					С%	H%	N%	in CH ₃ OH	,
1-	Aceturic acid (a-a)	white	207		41.02	5.97	11.96		
					(40.97)	(3.83)	(11.79)		
2		1.4	00		20.00	6.66	46.68		
2-	Urea (U)	white	90		(19.85)	(6.61)	(46.20)		
3-	[Mn (a-a), I]]	Brown	142dec	15.83	31.15	4.61	16.14	14.3	5.80
5-	[iiiii (u u) ₂ 0]	BIOWI	142000.	(15.22)	(31.02)	(4.01)	(16.05)		
4	[Co (a-a) ₂ U]	Deep-green	120	16.79	30.79	4.55	15.96	13.5	3.26
4-				(16.21)	(30.25)	(3.85)	(15.91)		5.20
5-	[Ni (a-a) ₂ U]	Green	140	16.57	30.88	4.57	16.00	10.2	2.2
				(16.05)	(30.71)	(3.99)	(15.91)		2.5
6-	[Cu (a-a) ₂ U]	[Cu (a-a) ₂ U] Pale-green	250	17.85	30.36	4.49	15.73	18.4	1.62
				(16.84)	(30.22)	(4.11)	(15.09)		1.02

Table (1) ;- Physical properties and elemental analysis of the complexes .

dec=decomposed calc.=calculated

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No.	Compound	ν(NH) urea +ν(NH) Aceturic acid	υ(COO) asym	υ(COO) sym	υ(CO)	υ(M-O)	υ(M-N)
1-	Aceturic acid (a-a)	3352 (s)	1716 S	1354 (sh)	1581 (vw)		
2-	Urea (U)	3441(b) 3344(b)			1678(b)		
3-	[Mn (a-a) ₂ U]	3456(s) 3329(s)	1662(s)	1465(sh)	1616(b)	509(s)	426(s)
4-	[Co (a-a) ₂ U]	3471(w) 3414(vw) 3348(vw)	1639(vw)	1356(s)	1597(s)	528(s)	474(s)
5-	[Ni (a-a) ₂ U]	3482(vw) 3410(vw) 3379(vw)	1654(vw)	1369(sh)	1597(b)	501(s)	425(s)
6-	[Cu (a-a) ₂ U]	3456(s) 3402(sh) 3342(s)	1654(b)	1431(sh)	1627(b)	532(s)	420 (s)

Table (2) ;- The absorption bands in infrared spectra o	f starting materials
(Ligands) and their complexes(cm ⁻¹)).

Where:- sh=sharp , vw=very weak , s=strong , b=broad .

Table (3) ;- The electronic spectra for the ligands and their complexes .

No.	Compound	λ_{nm}	ABS	wave number (cm ⁻¹)	€ _{max} (molar ⁻¹ .cm ⁻¹)
1	A acturia said (s. s)	277	0.205	36101.08	205
1-	Aceturic actu (a-a)	430	0.085	23255.81	85
2-	Urea (U)	280	0.116	35714.28	116
		345	0.075	28985.50	750
	[Mn (a-a) ₂ U]	282	0.158	35460.99	158
2		450	0.085	22222.22	85
3-		590	0.079	16949.15	79
		780	0.050	12820.51	50
	[Co (a-a) ₂ U]	277	0.197	36101.08	197
4-		510	0.054	19607.84	54
		827	0.022	12091.89	22
	[Ni (a-a) ₂ U]	281	0.521	35587.18	521
5-		395	0.375	25316.45	375
		735	0.185	13605.44	185
6-	$[C_{\rm H}(a,a)]$ [1]	276	0.812	36231.88	812
	$[Cu (a-a)_2 U]$	799	0.171	12515.64	171



Fig. (1) FT-IR Spectrum of the ligand (aceturic acid)



Fig. (2) FT-IR Spectrum of the ligand (urea)



Fig. (3) FT-IR Spectrum of the [Mn $(a-a)_2U$] Complex



Fig. (4) FT-IR Spectrum of the [Ni (a-a)₂U] Complex





References:

- Nakamato K., [[Infrared Spectra of Inorganic and Coordination Compounds]], New York, (1998).
- 14- Karczynki F., Kes Z., Mat Z., J.inorg. Nucl. Chem, 37(1975)PP.2344.
- 15- Place C., Zimmermann E.M., Gulliot G., Bois C., J.Inorg. chem., 37(1998)PP.4030.
- 16- Korenev V.I and Kardapol A.A., coordination compounds, 33(2007)PP.1754.
- 17- Al-Janabi M.Y., [[The Physical Methods in Inorganic Chemistry]], (1983).
- Antolin L., Marrcotrigiano G., Menabue L., Pellacani G.C., Salladini M., Ssola M., Inorgchem, 42(1985)PP.3621-3626.
- 19- Green wood N.N. and Earnshow A.,[[Chemistry of the Elements]],Ed. Wiley J. and Sons inc. New York (1998).
- 20- Kemp W., [[Organic spectroscopy]], 2nd edition, 8 (1987)PP.144.
- 21- Calvo R., Steren C.A., Piro.O.E, Zuniga F.J., Castellano E., Inorg.chem., 32 (1993) PP. 6016 -6022.
- 22- Barrrow G.M.[[Physical Chemistry]], 3rd ed. Graw Hill Kogakusha, Tokyo (1973).

- 1- Chen Y., pasquinelh R., shepherd R., lnorg. chem., 39(2000):PP.1180-1182.
- 2- Manunson A., Frapart I, Abrahamsson M., Horner O., Akermark B., sun L.C.,J. of Amer. chem. Soc., 121 (1999) PP.89-92.
- Lin H.L., zhu Z.X., Chen Y.T., polyhedron, 15 (1996) PP.3241-3245.
- 4- Bunting J.W.and.Thong, K.M , Can.J. chem., 48 (1970) PP.1654-1658.
- 5- Okishi Y., Lmai Y and Aida K., J. Inorg. Nucl. chem., 35(1973)PP.101.
- 6- Szabo T., Rockenbauer A., Korecz L., Polyhedron, 18(1999) PP.1969-1972.
- 7- Formicka G., Kozlowski H., Jezowka B., Inorg. chem. Acta, 1(1997)PP.24-25.
- 8- Prasad R.N.,Mithlesh A., J.chem. soc., 48 (2003) PP.95.
- 9- Hallman P.S., Perrin D.D and Watt A., J.Bio chem., 121(1997) PP.549-555.
- 10- Pop V.,David L.,.Simut C.,Filip S.,Oragan M.,J. physical unio, 35(2003) PP.851-853.
- 11- Battaglia L.P and Bonamartini A., Act acryst, 12 (1977) PP.3625-3636.
- 12- Geary W.J, Coord. Rev., 7(1971) PP.81.

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الملخص

حضرت معقدات ((Μn(π)، ^(Π)، Co^(Π) و Ni^(Π)) مع ليكاندات مختلطة من ((a-a) (a-a) و ((Urea (U)) في وسط قاعدي وبوجود الايثانول بنسبة (1:2) (ليكاند : فلز) للحصول على المعقدات المتعادلة ذات الصيغة العامة [M (a-a)₂ U] . شخصت جميع المعقدات المحضرة باستخدام اطياف الاشعة تحت الحمراء والاشعة فوق البنفسجية والمرئية والتحليل الكمي الدقيق للعناصر فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهريائية.