Synthesis and Characterization of some new complexes of Co(II),Ni(II) and Cu(II) ions with Schiff base ligand Benzilidinedimalonyl hydrazide

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Abstract

In this paper the synthesis and characterization of some binuclear complexes of cobalt (II), nickel(II) and cupper(II) ions have been reported. These complexes have been prepared by the reaction of metal nitrate or chloride of the above transition metals with Schiff base ligand derived from benzil and malonyl hydrazide the prepared complexes have the general formula : $[M_2(BDMH_4)X_4]$ and $[M_2(BDM)]$ for neutral and basic mediums respectively. Where M:Co(II), Ni(II) and Cu(II) ions, BDMH_4:hydrazide ligand, and X: NO₃⁻ or Cl⁻ ions. The ligand and its complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, electronic and infrared spectroscopy. The ligand acts as an octadentate to form neutral complexes with the metal ions under investigation the measurements showed that some of these prepared complexes have an octahedral geometry (neutral medium) and the prepared complexes were in tetrahedral or squar planner environment(basic medium). Powder x-ray diffraction technique was applied for two of the prepared complexes, whereas crystal structural information's were obtained crystal symmetry, space group, unit cell, axis, unit cell volume...etc .

Introduction

Schiff base ⁽¹⁾ ligands were considered to be one of the most important used ligands in coordination chemistry so many complexes were prepared from these ligands because of their simple and reliable coordination with transition and non-transition metals. Those complexes were reported to be applied in large extent in medical ⁽²⁾, industrial ⁽³⁾ and agriculture ⁽⁴⁾ fields. It was shown that Schiff bases have the ability to form colored complexes with several metal ions, so that they were applied in qualitative and quantitative determination of such ions in analytical chemistry ⁽⁵⁾.

It's of our interest to continue studying the preparation and characterization of new complexes with Schiff base ligand of benzilidinedimalonyl hydrazide.

Experimental

Materials and methods

All chemicals used in the preparation of the coordination compounds under investigation were purchased from BDH and Fluka Ltd. Company, the prepared compounds were characterized using several instrumental analysis included :

CHN (Allba't uni-Jordan), IR, Atomic absorption measurements, Molar conductivity, Magnetic measurement, Electronic spectrophotometry, Powder x-ray diffraction (Ind. Equinox 1000 X-ray Diffractmeter). Preparation of ligand benzilidinedimalonyl hydrazide ligand was prepared⁽⁶⁾ by addition of a solution of 2.64g (0.02M) of malonyl dihydrazide in 40ml hot ethanol to a solution of 2.1g (0.01M) of benzil in 25ml hot ethanol. The mixture was then reflexed for 6 hrs. after that the mixture was left to cool down to room temperature, The yellow precipitate thus formed was filtered off and washed with cold ethanol. Recrystallization from ethanol and drying at 50°C.

Preparation of complexes for Co(II), Ni(II) and Cu(II) ions were prepared in both neutral and basic mediums according to the following procedures :-

i- Type (1) in neutral medium these complexes were prepared by adding an alcoholic solution of the metal salts(0.02 mol.) to a hot solution of alcoholic ligand(0.01 mol.) the mixture was refluxed for 3hr. after that cooled down to afford the product, it was washed with cold ethanol and left to dry in air at room temperature.

ii- Type (2) in basic medium these complexes were prepared by adding an alcoholic solution of potassium hydroxide (1M) until the PH= 9-10 to hot solution of the ligand (0.01mol.) to this solution an alcoholic solution (10ml.) of the metal salts (0.02mol.) were added the mixture was refluxed for 3hr. after that cooled down to afford the product, it was washed with cold ethanol and left to dry in air at room temperature Table(1).

Complexes	Formula Complexes	medium	Wt. of	Wt. of	type of metal
No.			ligand(g)	metal salts(g)	salts
1	[Co ₂ (BDMH ₄)Cl ₄]	neutral	0.438	0.476	CoCl ₂ .6H ₂ O
2	[Co ₂ (BDMH ₄)(NO ₃) ₄]	neutral	0.438	0.582	Co(NO ₃) ₂ .6H ₂ O
3	[Co ₂ (BDM)]	basic	0.438	0.476	CoCl ₂ .6H ₂ O
			0.438	0.582	Co(NO ₃) ₂ .6H ₂ O
4	[Ni ₂ (BDMH ₄)Cl ₄]	neutral	0.438	0.476	NiCl ₂ .6H ₂ O
5	[Ni ₂ (BDMH ₄)(NO ₃) ₄]	neutral	0.438	0.582	Ni(NO ₃) ₂ .6H ₂ O
6	[Ni ₂ (BDM)]	basic	0.438	0.476	NiCl ₂ .6H ₂ O
			0.438	0.582	Ni(NO ₃) ₂ .6H ₂ O
7	[Cu ₂ (BDMH ₄)Cl ₄]	neutral	0.438	0.341	CuCl ₂ .2H ₂ O
8	[Cu ₂ (BDMH ₄)(NO ₃) ₄]	neutral	0.438	0.483	Cu(NO ₃) ₂ .3H ₂ O
9	[Cu ₂ (BDM)]	basic	0.438	0.341	CuCl ₂ .2H ₂ O
	1997 (1998) 1997 (1997)		0.438	0.483	Cu(NO ₃) ₂ .3H ₂ O

Table (1): Conditions for the preparation of complexes in neutral and basic medium

Results and Discussion

Benzilidinedimalonyl hydrazide

Ligand (BDMH₄) was prepared according to the following equation :



The chemical and physical properties for (BDMH₄) listed below. m.p. = 223-225°C, Yellow, M.Wt. =438, Chemical

Formula(C20H22N8O4) CHN analysis: theoretical

%C=54.79, %H=5.06, %N=25.56

Experimental %C=54.53, %H=5.15, %N=25.32 Two types of the complexes with (BDMH₄) were prepared according to the following equations :





(basic medium complexes)

All the prepared complexes in this study are colored and stable at room temperature. shows some physical and chemical properties of the prepared complexes. The molar conductivity for the prepared complexes were measured using DMF at 10^{-3} M the results obtained table (2), indicate that the complexes have molar conductance values of (10-22) Ω^{-1} mol⁻¹cm² indicating that all the complexes are non-electrolytes.

Complexes	Complexes Formula	color	m.p.	л(10 ⁻³ М)	Element analysis calc.(Found)%			
No.			°C	DMF Ω^{-}	М	С	H	N
				¹ mol ⁻¹ cm ²				
1	[Co ₂ (BDMH ₄)Cl ₄]	Brown	273-	12	16.88	34.41	3.18	16.05
			275		(16.79)	(34.54)	(3.25)	(16.13)
2	[Co ₂ (BDMH ₄)(NO ₃) ₄]	dark	249-	21	14.65			
		Brown	251		(14.71)			
3	[Co ₂ (BDM)]	Brown	258-	18	21.34	43.50	3.29	20.29
			260		(21.28)	(43.37)	(3.42)	(20.36)
4	[Ni ₂ (BDMH ₄)Cl ₄]	Green	278-	15	16.83			
			280		(16.72)			
5	[Ni ₂ (BDMH ₄)(NO ₃) ₄]	Brown	259-	10	14.60	29.88	2.76	20.91
			261		(14.74)	(29.68)	(2.84)	(20.84)
6	[Ni ₂ (BDM)]	Light	261-	12	21.27	43.53	3.29	21.27
		green	263		(21.18)	(43.44)	(3.36)	(21.33)
7	[Cu ₂ (BDMH ₄)Cl ₄]	green	242-	22	17.97	33.96	3.13	15.84
			244		(17.82)	(33.84)	(3.20)	(15.88)
8	[Cu ₂ (BDMH ₄)(NO ₃) ₄]	green	254-	12	15.62			
			256		(15.77)			
9	[Cu ₂ (BDM)]	green	268-	11	22.63	1		
		-	270		(22.71)			

Table (2): Physical and chemical properties of the prepared complexes

IR Spectra

IR spectra of the prepared ligand showed that stretching band of free azomethine group (1620cm⁻¹) was shifted to lower value by (12-40cm⁻¹) on complex formation which indicates that coordination occurred between nitrogen of this group and the metal ions⁽⁷⁾. IR data also showed band at (1650cm⁻¹) related to carbonyl group of the ligand, which was shifted to a lower value by (10-35cm⁻¹) in the spectra of complexes formed in neutral medium, such results demonstrated that coordination occurred through oxygen of the carbonyl group⁽⁸⁾.

It seems that data in case of the prepared complexes in basic medium proved the elimination of the hydrogen of (OH) group after tutomerisim process and formation of chromofore group(C=N-N=C)which give identical band in the range of (1560-

1580cm⁻¹)⁽⁹⁾. Stretching band of the free NH₂ group in the ligand appear, at (3300cm⁻¹), which is shifted to a lower values (15-25cm⁻¹) the metal ions are coordination through nitrogen atom ⁽¹⁰⁾. Table (3) show new bands in the ranges of (425-465cm⁻¹) and (450-510cm⁻¹) which are related to M-N and M-O bands respectively (11,12). Finally, and in order to confirm the results obtained in conductivity measurements, it is important to note whether the nitrate group coordinated to the metal ions or act as a free ion outside the coordination sphere, this can be performed by looking at IR data of (NO₃) group which is showed three bands in the ranges (1000-1015cm⁻¹), (1370-1390cm⁻¹) and (1500-1515cm⁻¹) and this is indicated that NO3 coordinated with metal ions in neutral medium and act as a monodentate ligand⁽¹³⁾.

Complex No.	υ(C=O)	υ (C=N)	υ azine	υ (NH ₂)	υ (NO ₃)	v(M-O)	υ (M-N)
			(-C=N-N=C-)				
BDMH ₄	1650	1620	-	3300	-	-	-
1	1630	1598	-	3275	-	450	435
2	1635	1580	-	3284	1000,1380,1515	470	425
3*	-	1593	1560	3285	-	495	430
4	1615	1608	-	3278	-	510	465
5	1640	1585	-	3285	1015,1390,1510	484	445
6*	-	1600	1575	3276	-	485	430
7	1638	1595	-	3280	-	468	434
8	1637	1582	-	3277	1010,1370,1500	505	430
9*	-	1605	1585	3280	-	485	455

Table (3): IR data (cm⁻¹) of the ligand and it's complexes in neutral and basic media

* Complexes in basic medium

• Magnetic susceptibility

Magnetic susceptibility data are presented in table (4) which showed that Co(II) complexes have values within $(3.91-4.6BM)^{(14,15)}$ range. Which indicate that such complexes have high spin tetrahedral and octahedral geometry. Similarly, it seems that Ni(II) complexes have the same geometry with values within (2.95-3.45BM) ^(16,17) range . For Cu(II) complexes in addition to their octahedral geometry and square planar^(18,19) with magnetic value within (1.78-2.2BM) range were shown.

Electronic spectra

Electronic spectra of Co(II) complexes, table (4), which have been prepared in neutral medium, shows three transitions related to high spin octahedral geometry⁽¹⁵⁾ which are:

 $v_1 9316 - 10922 \text{ cm}^{-1} {}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$ ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F) v_2 14230 - 15854 \text{ cm}^{-1}$ ${}^{4}T_{1}g(F) \rightarrow {}^{4}T_{1}g(P) v_{3} 18155 - 20774 \text{ cm}^{-1}$

While the Co(II)complex prepared in basic medium showed one electronic absorption band at (13240cm⁻¹) which is attributed to tetrahedral geometry⁽¹⁴⁾.On the other hands, the electronic spectra for Ni(II) complexes were showed three bands attributed to octahedral geometry and these transitions are⁽¹⁷⁾:

v₁ 9422 - 10835 cm⁻¹ ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{2}g(F)$ v₂ 13350 - 16648 cm⁻¹ ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(F)$ v₃ 21585 - 22320 cm⁻¹ ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(P)$

The Ni(II)complex prepared in a basic medium show one electronic absorption band at (14133cm⁻¹)which is attributed to tetrahedral geometry⁽¹⁶⁾. Cu(II) complexes appeared to have octahedral(14578 and 14650cm⁻¹) and square planar(15853cm⁻¹) geometry for both neutral and basic medium respectively^(19,20).

Table (4): Magnetic susceptibility data and Electronic spectral values (cm ⁻¹) for	the prepared complexes in
neutral and basic mediums	

Complex No.	Complexes Formula	v ₁	v ₂	v ₃	μ _{eff} (B.M.)	Geometry
1	[Co ₂ (BDMH ₄)Cl ₄]	9316	14230	18155	3.91	Oh
2	[Co ₂ (BDMH ₄)(NO ₃) ₄]	10922	15854	20774	3.97	Oh
3	[Co ₂ (BDM)]	-	1 . 3.	13240	4.60	Td
4	[Ni ₂ (BDMH ₄)Cl ₄]	9422	13350	21580	2.95	Oh
5	[Ni ₂ (BDMH ₄)(NO ₃) ₄]	10835	16648	22320	3.10	Oh
6	[Ni ₂ (BDM)]	-	-	14133	3.45	Td
7	[Cu ₂ (BDMH ₄)Cl ₄]	-	-	14650	1.78	Oh
8	[Cu ₂ (BDMH ₄)(NO ₃) ₄]	-	-	14578	1.85	Oh
9	[Cu ₂ (BDM)]	-	-	15853	2.20	Sq.pl.

Powder x-ray diffraction (PXRD)results

In our work also powder x-ray diffraction (PXRD) technique has been applied for two complexes using wave length (Co-K α 1.788970A⁰) to give information about the crystal symmetry, space group, unit cell, axis, unit cell volume...etc. The results were analyzed

by Match program ⁽²¹⁾ and presented in Figures(1,2) and table(5). According to these results we can prove that coordination between ligand and metal(II) ions took place and a new coordination compounds were formed



Fig. (1) Pattern PXRD for [Co₂(BDMH₄)(NO₃)₄]



Fig. (2) Pattern PXRD for [Ni₂(BDMH₄)(NO₃)₄]

Table (5): Crystal data for two of the prepared complexes and metal salt used for their preparation						
PXRD information	Complexes No.2	Complexes No. 5	Metal Salt			
Molecular Formula	$Co_2C_{20}H_{22}N_{12}O_{16}$	Ni ₂ C ₂₀ H ₂₂ N ₁₂ O ₁₆	Co(NO ₃) ₂ .6H ₂ O			
Molecular weight	804	803.8	291			
Crystal system	monoclinic	monoclinic	monoclinic			
Space group	P2/m(10)	P2/m(10)	C2/c(15)			
Unit cell parameters	a=8.95,b=11.43,	a=12.62,b=9.75,	a=14.69,b=6.112,			
$(\mathbf{A}^{\circ 3})$	c=12.66,β=108.62	c=10.53,β=112.15	c=12.632,β=118.45			
Cell volume(A°)	1227.3	1197	997.2			
Z(no.of molecules or	4	4	4			
atoms/ cell unit)						
θ range(deg)	1.98-114.73	2.04-114.58	13.71-74.76			
Index ranges	$0 \le h \le 5$	$-2 \le h \le 2$	$-10 \le h \le 9$			
	$0 \le k \le 4$	$0 \le k \le 7$	$0 \le k \le 4$			
	$-3 \le 1 \le 3$	0≤1≤5	$0 \le l \le 9$			

Conclusion

According to the above results obtained for the prepared complexes, It can be concluded that the ligand coordinated with Co(II), Ni(II) and Cu(II) ions in neutral medium to form complexes with an

octahedral geometry, Figure (3) . Meanwhile, in case of basic medium, it seems that complexes with tetrahedral geometry were obtained for Co (II) and Ni(II)ions Figure(4) and square planer for Cu (II) ion Figure (5).



M = Co (II), Ni (II), Cu (II). $X = CI', NO_3$

Fig. (3) Octahedral geometry for the complexes prepared in neutral medium



M = Co (II), Ni (II)

Fig.(4) Tetrahedral geometry for the complexes prepared in basic medium



Fig.(5) Square planer geometry for the complexes prepared in basic medium

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تحضير وتشخيص عدد من المعقدات الجديدة للكوبلت (II) والنيكل(II) والنحاس(II) مع ليكاند قاعدة

شيف بنزليدين ثنائى مالونيل هيدرازيد

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الملخص

في هذا البحث تم تحضير عدد من المعقدات ثنائية النوى لأيونات الكوبلت (II) والنيكل (II) والنحاس (II) وذلك بمفاعله كلوريدات او نترات هذه الفزات مع ليكاند قاعدة شيف بنزليدين ثنائي مالونيل هيدرازيد ، وللمعقدات المحضرة الصيغتين العامتين :[M2(BDMH4)X4] و [M2(BDM] و [M2(BDM]) و [M2(BDM] للوسطين المتعادل والقاعدي على التوالي ، حيث يمثل M: ايونات الكوبلت (II) والنيكل (II) والنحاس (II) ويمثل BDMH4 الليكاند المتعادل و اللوسطين المتعادل والقاعدي على التوالي ، حيث يمثل M: ايونات الكوبلت (II) والنيكل (II) والنحاس (II) ويمثل BDMH4 الليكاند المتعادل و الليكاند المتعادل و الليكاند المشحون بشحنة سالبة (في الوسط القاعدي) بينما يمثل X الكلور او ايونات النترات. شد خص الليكاند ومعقداته بالطرائق التحليلية والطيفية والمغناطيسية وبينت نتائج هذه الدراسات ان الليكاند يسلك في هذه المعقدات سلوك ثماني النتاسق ليعطي معقدات متعادلة لها بنية ثماني والطيفية والمغناطيسية وبينت نتائج هذه الدراسات ان الليكاند يسلك في هذه المعقدات سلوك ثماني النتاسق ليعطي معقدات متعادلة لها بنية ثماني السطوح في الوسط المتعادل وينية ربين متائج هذه الدراسات ان الليكاند يسلك في هذه المعقدات سلوك ثماني النتاسق ليعطي معقدات متعادلة لها بنية ثماني السطوح في الوسط المتعادي و المعادي يسلك في هذه المعقدات سلوك ثماني النتاسق ليعطي معقدات متعادلة لها بنية أماني والطيفية والمينا والمعامي وبينت نتائج هذه الدراسات ان الليكاند يسلك في هذه المعقدات سلوك ثماني النتاسق ليعطي معقدات متعادلة لها بنية ثماني والطيفية والمعناطيسية وبينت زراعي السطوح او المربع المستوي في الوسط القاعدي . وتم قياس طيف الاشعة المسينية للمسحوق لمعقدين من الصطوح في الوسط القاحدي . وتم قياس طيف الاشعة المينية المسحوق المعقدين من من محضرة ورما من خلال هذا القياس على أنواع الأنظمة البلورية ومجموعة النقطة ومعاملات وحدة الخلية (المعقدات المعقدين .