

Some Metal Complexes of Benzoinlidene aminophenol and Benzoinlidene benzoic acid with Co(II), Ni(II) and Cu(II) Chlorides Analogous to The Active Site of Carboxypeptidas

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المخلص

تم في هذا البحث تحضير عدد من المركبات المعقدة وذلك بتفاعل كلوريدات الكوبلت والنيكل والنحاس مع ليكاندين من نوع قواعد شيف تم الحصول عليها من تفاعل البنزوين مع كل من اورثو-امينو حامض البنزويك والامينو-فينول وقد اتضح بأن الليكاندين يعملان بشكل ثلاثي السن. وقد حصلنا على معقدات أيونية بنسبة 1:1 واقترحنا لها الصيغ العامة $[MLH_2X]X$ و $K[MLCl]$ (حيث يمثل LH_2 و L الليكاندين -benzoinlidene m-aminophenol and benziolidene o-aminobenzoic acid - في حالة التعادل وفي حالة الأيون السالب ثنائي القاعدة على التوالي) الناتجة عن الوسطين المتعادل والقاعدي على التوالي. لقد اتضح من دراسة التحليل الدقيق للعناصر والأشعة تحت الحمراء والأطياف اللايكترونية والحساسية المغناطيسية، أن المعقدات المتكونة في الوسطين المتعادل والقاعدي رباعية التناسق حيث يعمل الليكاندان بشكل ثلاثي السن متعادل وثلاثي السن ثنائي القاعدة على التوالي. كما تشغل الجهة التناسقية الرابعة بأيون الكلوريد.

Abstract

Several complexes of general formula $[MH_2LCl]Cl$ and $K[MLCl]$ (where $M=Co, Ni, Cu$; H_2L and L the neutral and dibasic forms of the Schiff base ligands the benzoinlidene-*m*-aminophenol (BAP) and benzoilidene-*o*-aminobenzoic acid (BAB) were prepared by the reaction of the metal chloride with the ligands in both neutral and basic media, respectively.

The ligands were obtained by the condensation of benzoin with *m*-aminophenol or *o*-aminobenzoic acid. The complexes were studied by means of chemical, physical and spectral methods. These studies were revealed that the ligands act as neutral tridentate and dibasic tridentate in neutral and basic medium respectively. All complexes were found ionic of 1:1 with tetrahedral structure.

Introduction

Metal complexes provide the active sites of many enzymes, such as the heme-iron containing group in catalase, peroxidase and cytochrome oxidase, vitamin B_{12} which contains cobalt in dozen enzymes [1,2] and zinc containing group in carboxypeptidase A [3-6]. In this enzyme the metal is coordinated approximately tetrahedrally to two nitrogen atoms and an oxygen atom from three amino acids in the protein chain [7]. The fourth coordination site is free or is probably a loosely bound water molecule at this position when the enzyme is not engaged in active catalysis.

In continuation with previous work on metal complexes with BAP ligand [8] in which 1:2 metal to ligand ratio was obtained with an octahedral geometry such complexes lack the mobile ligand such as Cl^- ion or H_2O molecule which is very important in the reaction of the active

site of the enzyme. So in the present work we choose metal ions other than $Zn(II)$ which are $Co(II)$, $Ni(II)$ and $Cu(II)$ with another ligand BAB in addition to BAP to obtain tridentate ligands of N, O, O, donor atoms which provide three coordination sites, whereas the fourth site is occupied by chloride ion. Spectral and magnetic studies were performed for such complexes.

Experimental

The ligands were prepared by condensation of an equimolar quantities of benzoin with *m*-aminophenol [8] and *o*-aminobenzoic acid in ethanolic medium. The mixture was refluxed for about two hours and on cooling the ligands were precipitated then filtered off, washed with cold ethanol and dried.

Preparation of the complexes

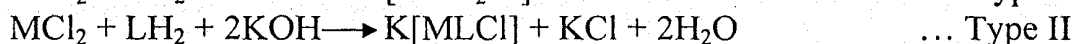
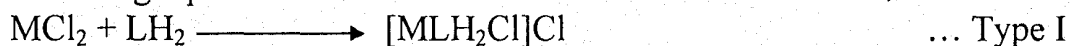
Two procedures were adopted for preparation of the complexes. In the first one an excess amount of the ligand dissolved in minimum amount of the ethanol was added slowly to an ethanolic solution of the metal salt (always 0.01 mol dissolved in 25 ml of ethanol was used). The mixture was then refluxed for about 3-4 hours and then cooled. The precipitated complexes were filtered off washed with ethanol and dried. In the second method 0.1N potassium hydroxide solution was added to the mixture of the metal salt and the ligand until complete precipitation at pH 8.5-9. The separated complexes were filtered off washed with ethanol and dried.

Physical and spectral measurements

The ligands and their complexes were analyzed for carbon hydrogen and nitrogen using 1106 CE microanalyser. Molar conductances were carried out for 10^{-3} M solution in dimethylsulfoxide (DMSO) using an electric conductivity measuring device model LF-42. Magnetic susceptibility measurements were performed on Burker BM6 instrument. The infrared absorption spectra were recorded on Perkin-Elmer SP.1100 spectrophotometer using KBr disc techniques in the range ($200-4000\text{ cm}^{-1}$). The electronic spectra of the complexes in 10^{-3} M DMSO solution were recorded Shimadzu Uv-160 spectrophotometer.

Results and Discussion

Two types of cobalt (II), nickel (II) and copper (II) complexes were prepared by the reaction of their chloride salts with the Schiff base ligands the benzoinlidene-*m*-aminophenol and the benzoinelidine *o*-aminobenzoic acid in both neutral and alkaline media according to the following equations.



As indicated in the above equations cationic (Type I) and anionic (Type II) species were obtained from neutral and alkaline solutions respectively. The analytical data of the ligands and their complexes (Table 1) are in a good agreement with the given formulae indicating that the all complexes contain 1:1 metal to ligand ratio. The complexes are air stable at room temperature but some of them decompose between 100-199°. Both types of the complexes are soluble in dimethylsulfoxide and their molar conductance in this solvent indicate 1:1 for both types I and II (Table 1).

The coordination sites of the ligand were suggested as a result of the comparison of the infrared absorption spectra of the ligand and its complexes (Table II).

For the complexes formed in neutral medium showed bands due to stretching vibration of OH groups at $3280-3320\text{ cm}^{-1}$ indicate coordination through phenolic hydroxide without deprotonation, since these bands located in the free ligands at 3356 and 3362 cm^{-1} , which is supported with the blue shift at $\nu(\text{C-O})$ at $1299-1326$ in complexes compared with those in at $1282, 1292$ for BAB and BAP free ligands respectively [9]. In addition for the complexes obtained of BAB ligand, the band due to carbonyl group located in the free ligand at about 1680 cm^{-1} shifted to lower frequency in complexes by about 30 cm^{-1} . As well as the azomethine band showed negative shift which located between $1610-1630\text{ cm}^{-1}$ compared with the same band at the ligands at 1635 and 1629 for BAB and BAP respectively. On the other hand for the complexes formed in basic medium, deprotonation was observed for phenolic groups and for carboxylic group, since the ir bands for the former groups disappeared from the spectra of the complexes, while the carboxylate anion COO^- band appeared at about $1420-1430\text{ cm}^{-1}$ [10]. In these complexes similar shift (as above) was observed in the azomethine band, thus, in basic medium the ligands acted as dibasic tridentate. In the ir spectra of both types of complexes two new bands were observed at $350-452\text{ cm}^{-1}$ and attributed to $\nu(\text{M-N})$, $\nu(\text{M-O})$ and $\nu(\text{M-Cl})$ stretching vibration, respectively. This represent a further evidence for the coordination of the ligands through both azomethine nitrogen and oxygen atoms [11].

The magnetic susceptibility for the complexes indicating that they are paramagnetic and their magnetic moments (Table 1) were related to tetrahedral structure [12], which confirmed by the electronic spectra of the complexes which gave bands (Table 1) that assigned to tetrahedral

geometry for cobalt (II) complexes since ν_1 and ν_2 bands were not observed for these complexes, while three bands were appeared for nickel complexes indicating the formation of an octahedral nickel (II), complexes, due the coordination of two molecules of dimethylsulfoxide while in solid state gives the value of tetrahedral geometry [13]. On the other hand tetrahedral structure was suggested for copper (II) complexes, since it is the most probable one as indicated from the band positions. [14]

From the above discussion, it was indicated that the ligands form two types of complexes cationic and anionic in neutral and alkaline media respectively, as well as 1:1 metal to ligand ratio was obtained, in addition to that a mobile ligand (Cl^- ion) is protected which is very important in the reaction of the complexes.

Table 1. Some physical and spectral data of the complexes

Compound	Colour	M.P.	%	Analysis % found (cal)			μ_{eff} B.M	λ_{max} DMSO cm^{-1}	Electronic spectra of the complexes (cm^{-1})		
				C	H	N			ν_1	ν_2	ν_3
BAP*	Pale yellow	89	72.5	79.4 (79.2)	5.29 (5.15)	4.63 (4.49)					
BAB**	Pale yellow	102	60.9	79.3 (76.2)	4.84 (4.69)	4.24 (4.16)					
[Co(BAP)Cl]Cl	Brown	169***	44.2	55.5 (55.6)	3.70 (3.62)	3.24 (3.19)	4.00	32.5		12400	
[Co(BAB)Cl]Cl	Chocolate	161	50.5	54.7 (54.6)	3.47 (3.36)	3.04 (3.01)	3.94	28.5		12360	
[Ni(BAP)Cl]Cl	Gray	121	79.1	55.5 (55.3)	3.70 (3.66)	3.24 (3.19)	4.10	35.6			
[Ni(BAB)Cl]Cl	Gray	150	60.5	54.8 (54.7)	3.48 (3.46)	3.04 (3.02)	4.09	38.3	10580	13875	22010
[Cu(BAP)Cl]Cl	Dark brown	132	30.2	54.9 (54.7)	3.66 (3.65)	3.20 (3.10)	1.97	30.9		14000	
[Cu(BAB)Cl]Cl	Dark brown	182***	25.1	54.2 (54.0)	3.44 (3.42)	3.01 (2.99)	2.03	36.2		1552	
K[Co(BAP)Cl]	Brown	175	31.5	55.3 (55.0)	3.23 (3.26)	3.23 (3.21)	4.08	34.7			
K[Co(BAB)Cl]	Blue	142	60.0	54.6 (54.3)	3.03 (3.00)	3.03 (3.05)	3.95	33.0		13297	
K[Ni(BAP)Cl]	Green	199***	42.2	55.4 (55.6)	3.23 (3.20)	3.23 (3.13)	4.17	32.0		12690	
K[Ni(BAB)Cl]	Green	110***	52.0	54.6 (54.8)	3.03 (3.05)	3.03 (3.01)	4.20	42.2		15527	
K[Cu(BAP)Cl]	Petroleum	120	62.6	54.7 (54.3)	3.19 (3.16)	3.19 (3.21)	1.90	40.2		14653	
K[Cu(BAB)Cl]	Green	162	27.9	54.0 (53.8)	3.00 (2.98)	3.00 (3.20)	1.86	37.2			

* BAP = Schiff base derived from *m*-aminophenol
 ** BAB = Schiff base derived from *o*-aminobenzoic acid
 *** Decomposition

Table (II): Important IR spectral bands (cm^{-1}) for BAP and BAB ligands and their complexes of neutral and alkaline mediums

Compound	$\nu(\text{O-H})$	$\nu(\text{C-O})$	$\nu(\text{C=N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-Cl})$	$\nu(\text{C=O})$
BAP	3356	1292	1629				
BAB	3362	1282	1635				1680
[Co(BAP)Cl]Cl	3315	1310	1620	410	450	350	
[Co(BAB)Cl]Cl	3320	1300	1625	420	452	360	1652
[Ni(BAP)Cl]Cl	3310	1299	1610	430	440		
[Ni(BAB)Cl]Cl	3280	1320	1630	425	450	370	1650
[Cu(BAP)Cl]Cl	3300	1326	1620	410	435		
[Cu(BAB)Cl]Cl	3295	1300	1610	425	450	380	1655
K[Co(BAP)Cl]	-	1320	1615	420	452	385	
K[Co(BAB)Cl]	-	1315	1620	430	445	390	1425
K[Ni(BAP)Cl]	-	1322	1615	410	450	370	
K[Ni(BAB)Cl]	-	1310	1610	430	450	380	1430
K[Cu(BAP)Cl]	-	1299	1610	420	452	370	
K[Cu(BAB)Cl]	-	1300	1620	421	445	350	1420

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الأشكال المتوقعة

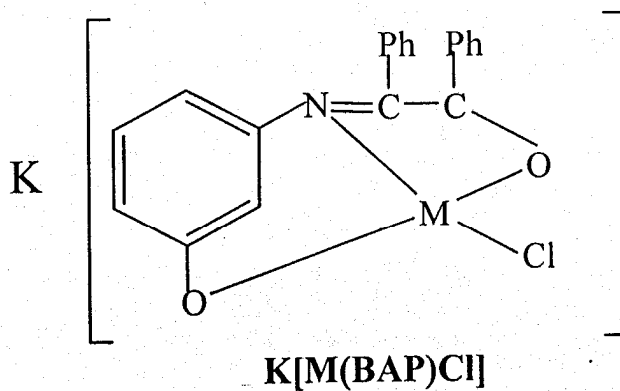
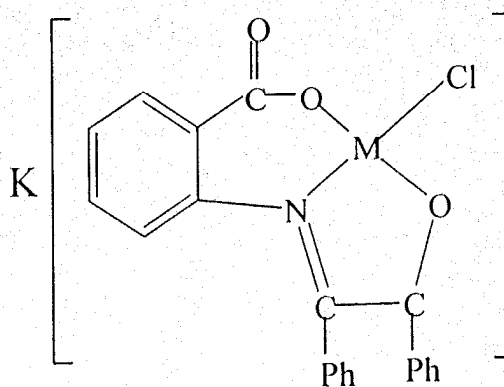
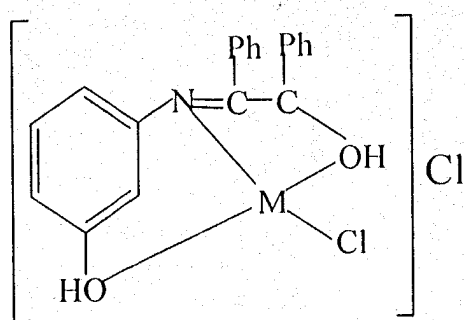
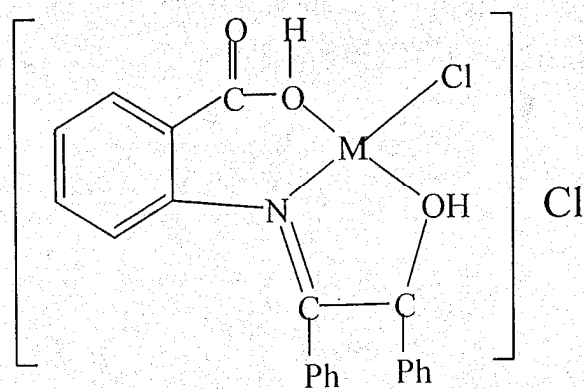


Fig. 1. The most probable structure of the complexes