Synthesis and Complex Formation of Some Hydrochlorid Salts of Phenylaminoglyoxime

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Abstract: Carboxyphenylaminoglyoximes were synthesized by reacting *anti*-chloroglyoxime with 2-, 3- and 4-aminobenzoic acids. Their complexes with Ni(II), Co(II) and Cu(II) ions were isolated. The structures of these new compounds were proposed on the basis of elemental analysis, ^{1}H-NMR and IR data.

Key Words: Aminobenzoic acids, glyoxime ligands, glyoxime complexes

Bazı Fenilaminoglioksim Hidroklorür Tuzlarının ve Metal Komplekslerinin Sentezi

Özet: Bu çalışmada, *anti*-kloroglioksimin 2-, 3- ve 4-aminobenzoik asit ile reaksiyonundan 2-karboksifenilaminoglioksim (o-CPAGH$_2$), 3-karboksifenilaminoglioksim (m-CPAGH$_2$) ve 4-karboksifenilaminoglioksim (p-CPAGH$_2$) ligandları ve bu ligandların Ni(II), Co(II) ve Cu(II) iyonları ile kompleksleri sentezlenmiştir. Bu yeni bileşiklerin yapıları ^{1}H-NMR, IR ve elementel analiz teknikleri kullanılarak aydınlatılmıştır.

Anahtar Kelimeler: Aminobenzoik asitler, glioksim ligandları, glioksim kompleksleri

Introduction

Biological activities of both aminobenzoic acids and *vic*-dioximes have been investigated extensively [1,2]. Furthermore, transition metal complexes of this kind of compounds have been found to be of biological importance [3-6]. In the literature, the synthesis of *vic*-dioximes and their verious derivatives have been a subject of study for a long period of time. It is reported that *vic*-dioximes exist in the *anti*-, *amphi*-, and *syn*- geometric izomer forms, depending on the position of the OH groups in the molecule [9]. The *anti*- and *amphi*-forms of these isomers give two different coloured complexes with the some metal ions, but the *syn*-form does not form complexes [7].

The present work describes the synthesis of three new carboxyphenylaminoglyoximes (Figure 1). Some transition metal complexes of these compounds are reported and their structures are investigated (Figure 2).

Material and Method

All reagents were purchased from Merck or Fluka Company and are chemically pure. IR spectra were obtained by using a Pye-Unicom SP-1025 spectrophotometer in KBr pellets. ^{1}H-NMR spectra were recorded on a Varion T 100-A model spectrometer with DMSO-d$_6$ as solvent.

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Elemental analysis (Carlo-Erba 1106 Model) and melting point (Buchi SPM-20) were used to elucidate the structure of the ligands and their complexes.

anti-Chloroglyoxime was prepared according to the published methods.

Experimental

1. Preparation of Ligands

A solution of *anti*-chloroglyoxime (1.23 g, 1.00 mmol) in EtOH (10 mL) was added to dropwise into a solution of aminobenzoic acid (1.37 g, 1.00 mmol) in EtOH (15 mL) under constant stirring at 5^{o} C. After the addition of *anti*-chloroglyoxime, the solution was stirred for an additional 3 h and then left overnight at room temperature. After adjusting the pH of the mixture to 5.5 with 0.1 N $NaHCO_3$ solution, diethyleter (40 mL) was added to precipitate the ligand. The precipitate was filtered, washed with diethyleter and cold EtOH and dried in a vacuum oven.

These compounds are soluble in water, EtOH, pyridine, DMSO and DMF and insoluble in diethyleter.

The color, yield, melting point, elemental analysis, ^{1}H-NMR and IR data of these compounds are given in Table I, II and III.

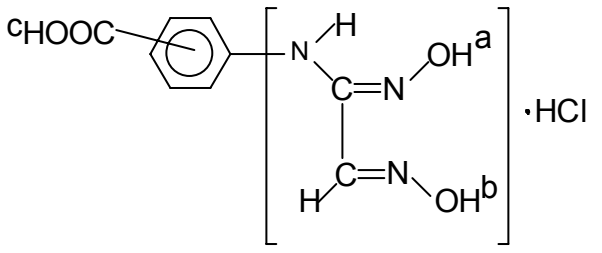
2. Preperation of Ni (II), Co (II) and Cu (II) Complexes of Ligands

An aqueous solution (15 mL) of the metal salt (1.00 mmol) was added to the solution of the ligand (2.00 mmol) in water (10 mL) under constant stirring at room temperature. The color of the mixture changed immediately and a sharp decrease in the pH of the mixture to about 3-3.5 was observed. The pH of the mixture was raised to 5-5.5 with a 0.1 N $NaHCO_3$ solution. Then, the mixture was stirred on a water bath at 60^{o} C for 0.5 h in order to complete the precipitation. The precipitated complex was filtered, washed with hot water and EtOH and dried in a vacuum oven. The color, yield, melting point, elemental analysis and IR data of the complexes are given in Table II and III.

These complexes are insoluble in DMSO, DMF and common solvents.

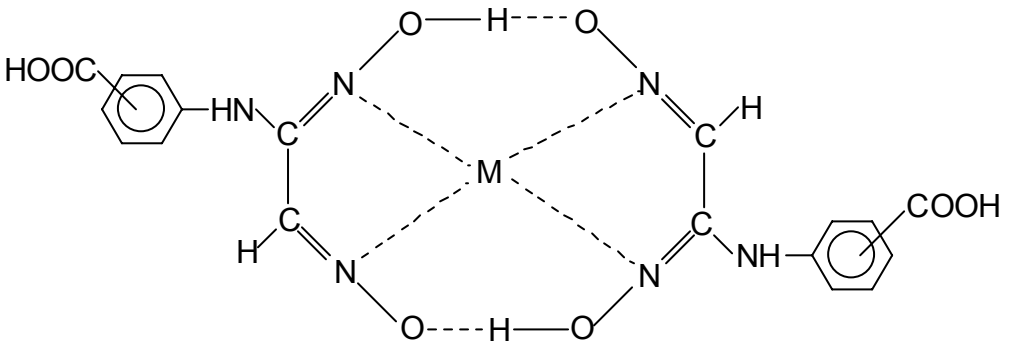
Results and Discussion

In this study, 2-carboxyphenylaminoglyoxime (o$CPAGH_2$), 3- carboxy-phenylaminoglyoxime (m$CPAGH_2$) and 4- carboxyphenylaminoglyoxime (p$CPAGH_2$) were synthesized by reacting *anti*-chloroglyoxime with o-, m- and p-aminobenzoic acid, respectively. The complexes of these ligands with Ni(II), Co(II) and Cu(II) ions were isolated (Fig. 1 and 2).



COOH = o-; m-; p-

Figure 1. General formulae of ligands.



COOH: o; m; p, M: Ni(II), Cu(II), Co(II) $(H_2O)_2$

Figure II. Octahedral and square-planar metal complexes of the ligands

The chemical shift values of –OH protons of these compounds are observed between 11.6-10.3 ppm for oxime groups and between 11.9-12.5 ppm for COOH groups [5,8,9]. The chemical shifts for –OH protons are the characteristic values for this type of *vic*-dioximes [7,10]. A broad singlet between 8.3-8.4 ppm belongs to N-H. Additional evidence for both O-H and N-H protons is also provided by the disappearance of these resonance on addition of one or two drops of D_2O. The resonance for the CH proton of the compounds is observed between 7.8-7.9 ppm and this value is in accordance with the values for other oximes [11,12]. Aromatic CH protons are observed at 6.5-7.7 ppm (Table I).

Table 1. ^{1}H-NMR Data for the Ligands in DMSO-d_6

Bileşikler	O-H^a oxime	O-H^b oxime	O-H^c acid	N-H	C-H alifatic	C-H aromatic
anti-oCPAGH$_2$	11.6	10.8	12.5	8.4	7.9	6.5-7.6
	(1H, s)	(1H, s)	(1H, s)	(1H, s)	(1H, s)	4H, m)
anti-mCPAGH$_2$	11.3	10.3	11.9	8.3	7.9	6.7-7.6
	(1H, s)	(1H, s)	(1H, s)	(1H, s)	(1H, s)	(4H, m)
anti-pCPAGH$_2$	11.5	10.3	12.0	8.5	7.8	6.8-7.7
	(1H, s)	(1H, s)	(1H, s)	(1H, s)	(1H, s)	(4H, m)

a; b; c; disappear on D_2O exchange, s: singlet, m: multiplet

In the IR spectra of the ligands (Tab. III), COOH and O-H bands exhibit a broad absorptionb between 2600-3400 cm^{-1}. Band due to C=O, C-O (carbonyl) and C=N, N-O (oxime) are at 1690-1660, 1400-1360 and 1650-1580, 1020-990 cm^{-1}, respectively [3,5,8,12-15]. Also all ligands show N^+-H peak around at 2750 cm^{-1} indicating that ligands are of salt form [16].

The Ni (II), Co(II) and Cu(II) complexes of the new ligands were prepared in water by addition of sufficient base (0.1 N $NaHCO_3$). The elemental analysis results and chracteristic IR absorptions are given in Tablo II and III. The metal ligand-ratio in all these complexes is 1:2, but Co(II) complexes have additional coordinated two water molecules for each complexes. As a result, an octohedral structure for Co(II) and square planar coordination for Ni(II) and Cu(II) compounds are proposed (Fig. 2). The shifts of C=N stretching frequency to lower frequency and vibration corresponding to the N-O band to higher frequency and the weak bending vibration of O—H…O bridges around 1700-1710 cm^{-1} indicate the formation of coordination band is between metal and the nitrogen atoms of the ligands [7,13,14,16]. In the case of the Co(II) complexes, the coordinated H_2O groups are identified by broad OH absorptions around 3450 cm^{-1} [16,17].

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Table II. The Colors, melting points, yields and elemental analytical of the ligands and complexes

Compound	Structure	Color	m.p. ° C	Yield %	Calculated (Found) %				
					C	H	N	M	Cl
o-CPAGH$_2$	$C_9H_9N_3O_4$	Pale Green	215	65	41.62 (41.12)	3.85 (3.34)	16.18 (15.66)	-	13.68 (14.23)
m-CPAGH$_2$	$C_9H_9N_3O_4$	White	195	60	41.62 (41.69)	3.85 (3.55)	16.18 (16.45)	-	13.68 (14.14)
p-CPAGH$_2$	$C_9H_9N_3O_4$	white	198	45	41.62 (41.33)	3.85 (3.97)	16.18 (15.87)	-	13.68 (14.01)
[o-CPAGH]$_2$Ni	$C_{18}H_{16}N_6O_8Ni$	Red	>300	80	42.94 (42.61)	3.18 (2.76)	16.70 (16.45)	11.73 (11.45)	-
[o-CPAGH]$_2$Co.2H$_2$O	$C_{18}H_{20}N_6O_{10}Co$	Dark brown	>300	80	40.07 (40.67)	3.71 (3.34)	15.58 (15.10)	10.95 (11.34)	-
[o-CPAGH]$_2$Cu	$C_{18}H_{16}N_6O_8Cu$	Dark green	>300	75	42.56 (42.50)	3.53 (3.98)	16.55 (16.87)	12.51 (12.91)	-
[m-CPAGH]$_2$Ni	$C_{18}H_{16}N_6O_8Ni$	Red	>300	80	42.94 (42.85)	3.18 (2.71)	16.70 (16.54)	11.73 (12.01)	-
[m-CPAGH]$_2$Co.2H$_2$O	$C_{18}H_{20}N_6O_{10}Co$	Brown	>300	85	40.07 (39.87)	3.71 (3.45)	15.58 (16.02)	10.95 (11.34)	-
[m-CPAGH]$_2$Cu	$C_{18}H_{16}N_6O_8Cu$	Dark green	>300	80	42.56 (42.33)	3.53 (3.23)	16.55 (16.09)	12.51 (12.69)	-
[p-CPAGH]$_2$Ni	$C_{18}H_{16}N_6O_8Ni$	Red	>300	85	42.94 (42.88)	3.18 (2.91)	16.70 (16.53)	11.73 (11.64)	-
[p-CPAGH]$_2$Co.2H$_2$O	$C_{18}H_{20}N_6O_{10}Co$	Dark brown	>300	75	40.07 (40.43)	3.71 (3.84)	15.58 (15.97)	10.95 (11.45)	-
[p-CPAGH]$_2$Cu	$C_{18}H_{16}N_6O_8Cu$	Green	>300	85	42.56 (42.33)	3.53 (3.98)	16.55 (16.89)	12.51 (12.20)	-

Table III. Characteristic IR. Bands of The Ligands and Their Complexes (KBr-pellets, cm^{-1})

Compound	H_2O	O-H oxime	O-H Acid	N^+-H	N-H	O-H..O	C=N	C=C Arom.	C=O	C-O	*N-O*
$OCPAGH_2$	-	3340	3400-2600	2750	-	-	1650	1560	1690	1390	1020
$MCPAGH_2$	-	3350	3400-2600	2750	-	-	1640	1560	1680	1380	1010
$PCPAGH_2$	-	3340	3400-2600	2760	-	-	1640	1560	1680	1380	1020
$[oCPAGH]_2Ni$	-	-	3400-2600	-	3390	1730	1630	1550	1660	1380	1000
$[oCPAGH]_2Co$	3450	3280	3400-2600	-	3370	1720	1600	1540	1680	1390	1000
$[oCPAGH]_2Cu$	-	-	3400-2600	-	3380	1720	1590	1500	1670	1400	1000
$[oCPAGH]_2Ni$	-	-	3400-2600	-	3400	1700	1610	1520	1660	1370	990
$[oCPAGH]_2Co$	3450	3270	3400-2600	-	3350	1710	1590	1520	1670	1360	990
$[oCPAGH]_2Cu$	-	-	3400-2600	-	3360	1710	1580	1490	1660	1380	1010
$[oCPAGH]_2Ni$	-	-	3400-2600	-	3340	1710	1580	1530	1680	1370	1000
$[oCPAGH]_2Co$	3450	3580	3400-2600	-	3380	1720	1590	1530	1690	1390	1000
$[oCPAGH]_2Cu$	-	-	3400-2600	-	3370	1710	1600	1520	1670	1380	990