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Synthesis, Characterization and Antimicrobial Studies of Co(II) and Ni(II) Complexes Using 1,2 Cyclohexane Dione Dioxime as Ligand

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Abstract: *Cyclohexanedione dioxime and its Co(II) and Ni(II) complexes with some amino acids were synthesized and characterized by elemental analysis, infrared and conductivity. The results showed that the 1,2 cyclohexanedione dioxime reacted with the Co(II) or Ni(II) chloride in 1:1:1 (metal: Hcyclo: AA or Ampy) molar ratio where AA = Glycine, Histidine, Ampy = Aminopyridine and Hcyclo = 1,2 Cyclohexanedionedioxime. The infrared spectra revealed that the V(C=N) in the free Hcyclo ligand occurred at 1458cm^{-1}, in the complexes, this band was shifted to lower frequencies. This indicates coordination of the metal ions to nitrogen of the ligand. The synthesized complexes were tested against some pathogenic bacteria (Escherichia coli, Staphylococcus aureus, Streptococcus pyogene and Klebsiella pneumoniea). The results indicates that the complexes were not potent against the screened bacteria.*

Keywords: *Complexes, bioinorganic, synthesis, antimicrobial*

I. Introduction

Model complexes of the first row transition metals with dioximes have been widely studied. Much attention has been devoted by bioinorganic as well as medicinal chemists to the relationship between the metal ion and their complexes as antitumour and antibacterial agents (Zahid *et al., 2001*). According to Sekhon and Leena (2006), Pharmaceutical industries, which have been dominated by organic drugs are now focussing much attention on inorganic drugs because: many of the metal ions in biology have stimulated the development of metal-base therapeutics and inorganics drugs are likely to be transferred in the body by oxidation and ligand subtitution reactions.

This work is related to the synthesis, characterization and antimicrobial studies of Co(II) and Ni(II) complexes using 1,2 cyclohexane dione dioxime as primary ligand and histidine, glycine and 2-amino pyridine as secondary ligands. Antimicrobial activities of the complexes were screened against different strains of bacterial such as *Escherichia coli, staphylococcus aureus, klepsiella pneumoniea* and *streptococcus pyogene*. The baterial activities of the complexes were determined by the filter paper disc agar diffusion method. (Taura *et al., 2004*).

II. Experimental

Materials and Methods

All chemicals and solvents used in the synthesis are of analytical grade. All metal(II) salts were used as chlorides.

Preparation of the metal complexes

The complexes were prepared in 1:1:1 mole ratio of metal(II) : Hyclo : Amino acid or 1:2:1 mole ratio of metal(II) : Hyclo : Amino pyridine following the method of (Adkhis *et al*., 2003). The complexes were prepared by dissolving 1,2 cyclo (0.003 mmol, 0.4265 g) in 30 ml of 50% H_2O/EtOH.This was brought to boiling for a few minutes and (0.003 mmol, 0.7131g) of metal(II) salt ($NiCl_2{\cdot}6H_2O$) was dissolved in 30 ml of 50% H_2O/EtOH which was slowly added. The mixture was stirred magnetically under reflux for 1 hour after which (0.003 mmol, 0.4655 g) of amino acid (histidine) dissolved in 30 ml of 50% H_2O/EtOH was added with stirring and then refluxed for another 1 hour. The mixture was carefully poured into a beaker and then covered with a filter paper and allowed to stand at room temperature for 24 hours. The precipitate obtained was filtered and washed with (3 x 5) ml portions of ethanol. The products were dried in a desiccator over $CaCl_2$. The same procedure was repeated for the other compounds.

General equations for the formation of all the metal(II) complexes are shown below:

$MCl_2.nH_2O$ + Lp + Ls -------MLpLs (Cl) + H_2O

Where M = , Co(II), Ni(II),

Lp = primary ligand (1,2 cyclohexane dione dioxime)

Ls = secondary ligand

n = 1, 2, 3, 4, or 5

III. Physical Measurements

The infrared (IR) spectra were recorded on FTIR – 84005 model in the range 4000 – 350 cm^{-1} for the ligands and complexes. Microanalysis was performed on a Perkin Elmer model 2400 series II CHNS/O elemental analyzer. Molar conductivity was determined for complexes that are soluble in methanol only. A 10^{-3} M solution was used. The conductivity of the complexes were determined at room temperature (30^0C) using exstick (R) series model EC 500/conductivity and temperature meter. Antimicrobial activities of the metal(II) complexes were screened against different strains of bacteria, (*Escherichia coli, Staphylococcus aureus, Streptococcus pyogene and Klebsiella pneumoniea*). Nutrient agar was used as bacteriological media. Tetracycline was used as a control drug. The antibacterial activities of the complexes were determined by the filter paper disc agar diffusion method. (Abdul, 2008).

IV. Results And Discussion

The analytical data of the complexes and some physical properties are summarized in table 1. The complexes exhibit various shades of colours ranging from dark-brown to rose-red. They all decomposed before melting. The complexes are air-stable and also soluble in certain solvents such as methanol and ethanol. The low molar conductance values of the complexes revealed that they are non-electrolytes (Muhammad *et al*; 2007).

Table 1: Physical Properties of the Complexes

	Compound	Molecular formula (molar mass)	Color	Yield g(%)	M.P/D.T	Scm^2mol^{-1}	Found %M (cald)
A_1	$[CoCl(1,2\ cyclo)(His).H_2O]$	$Co(C_{12}H_{18}N_5O_5)Cl)$ (406.4)	Dark Brown	1.212 (65)	290(d)		14.50 (14.26)
A_2	$[CoCl(1,2\ cyclo)(gly).H_2O]$	$Co(C_8H_{14}N_3O_5)Cl)$ (326.4)	Dark Brown	0.988 (69)	310(d)	9.30	18.05 (17.83)
A_3	$[CoCl(1,2cyclo)_2(2\text{-}ampy).H_2O]$	$Co(C_{17}H_{27}N_6O_5)Cl)$ (489.4)	Dark Brown	1.468 (55)	320(d)	10.00	12.04 (11.95)
B_1	$[NiCl(1,2\ cyclo)(His).H_2O]$	$Ni(C_{12}H_{17}N_5O_4)$ (353.7)	Blood-red	1.219 (72)	280(d)	-	16.59 (16.30)
B_2	$[NiCl(1,2\ cyclo)(gly).H_2O]$	$Ni(C_8H_{13}N_3O_4)$ (273.7)	Blood-red	1.282 (60)	290(d)	-	21.44 (20.90)
B_3	$[NiCl(1,2cyclo)_2(2ampy).H_2O]$	$Ni(C_{17}H_{27}N_6O_5)Cl)$ (489.2)	Blood-red	1.468 (55)	300(d)	-	12.00 (12.12)

V. Infrared Spectra

The relevant IR frequencies for the complexes are reported in Table 2: In the IR spectrum of 1,2 cyclohexanedionedioxime, a band occurring at 1458 cm^{-1} is assigned to the *V* (C = N) vibration. A low intensity band appearing at 1156 cm^{-1} is probably due to the *V* (N – O) vibration band. The broad band at 743 cm^{-1} is attributed to δ(NOH) of the oxime part of the molecule (Hamrit *et al;* 2000).The *V* (C=N) frequency at 1458 cm^{-1} in free Hcyclo is observed at around 1410 – 1464 cm^{-1} in the spectra of Co(II) complexes and 1415 – 1459 cm^{-1} in the spectra of Ni(II) complexes. This suggests that the ligand is coordinated to the metal ion through the nitrogen of the oxime. The medium intensity at 1156 cm^{-1} is assigned to *V* (NO). This band shifted to a low intensity at 1140 cm^{-1} in the spectra of Co(II) complexes and 1157 cm^{-1} in Ni(II) complexes. The band occurring at 743 cm^{-1}, assigned to δ(NOH) in free ligand, shifted to 721 cm^{-1} in both the spectra of Co(II) and Ni(II) complexes. In free amino acids the band of medium intensity occurring at around 3114 cm^{-1} in histidine and 3162 cm^{-1} in glycine were shifted to 3160 cm^{-1} in the spectra of Co(II) complexes and 3165 cm^{-1} in the spectra of Ni(II) complexes respectively. The two absorption bands occurring near 1581 and 1412 cm^{-1} in amino acids corresponding to the asymmetric and symmetric stretching vibration bands of carbonyl, in the complexes are shifted to 1555 cm^{-1} and 1459 cm^{-1} as weak bands. In the spectra of the complexes the bands around 3190 – 3393 cm^{-1} region indicates the presence of *V* (OH). Some new bands are observed in the region 460 – 490 cm^{-1} and 410 – 450 cm^{-1}. This indicates the formation of *V* (M – O) and *V* (M –N) bonds respectively (Nakamato, 1963; Hamrit *et al;* 2000., Karwecka and Pajdowski, 1979., Cotton and Wilkihson, 1986).

Table 2: Relevant infrared frequencies (cm^{-1}) for the complexes

	Compound	$V(NH_3^+)$	$\delta(NH_3^+)$	$Vas(COO^-)$	$Vsy(COO^-)$	V(C=N)	V(NO)	δ (NOH)	V(OH)	V(M-O)	V(M-N)
	1,2 cyclo					1458s	1156m	743b	3382m		
	Histidime	3114b	1631s	1581m	1412m				3114b		
	Glycine	3162m	1608b	1560b	1456s				3162b		
	2-Amino Pyridine	3182s	1607s						3382b		
A_1	$[CoCl(1,2cyclo)(His)\ .H_2O]$	3160w	1630w		1459w	1420s	1125w	759s	3350b	490b	450b
A_2	$[CoCl(1,2\ cyclo)(gly)\ .H_2O]$	3159w	1650w	1555w	1459w	1430s	1120w	721m	3393b	464b	410b
A_3	$[CoCl(1,2cyclo)_2(2\text{-}ampy)\ .H_2O]$	3160w	1640w			1464s	1155m	721m	3350b	470b	450b
B_1	$[NiCl(1,2\ cyclo)(His)\ .H_2O]$	3160w	1640w	1570m	1459w	1410s	1155m	721m	3350b	470b	450b
B_2	$[NiCl(1,2\ cyclo)(gly)\ .H_2O]$	3165w	1630w	1571s	1462w	1415s	1157s	721m	3190b	480b	430b
B_3	$NiCl(1,2cyclo)_2(2\text{-}ampy).H_2O$	3160w	1645w			1459s	1157s	721m	3250b	490b	450b

S=sharp, m=medium w=weak b=broad

Table 3: Microanalysis of representative complexes

	Compounds	Molecular formula (molar mass)	Found (calculated)% C	H	N	M found (cald)
B_1	[NiCl(1,2Cyclo)(His) .H_2O]	Ni($C_{12}H_{17}N_5O_4$) (353.71)	41.87 (40.71)	5.28 (4.80)	15.90 (19.70)	16.59 (16.30)
B_2	[NiCl(1,2Cyclo)(gly) .H_2O]	Ni($C_8H_{13}N_3O_4$) (273.71)	41.81 (35.07)	5.21 (4.74)	15.68 (15.34)	21.44 (20.10)
B_3	`[NiCl(1,2Cyclo)$_2$(2-ampy) .H_2O]	Ni($C_{17}H_{27}N_6O_6$)Cl (489.2)	41.57 (41.69)	5.19 (5.52)	15.66 (17.17)	12.00 (12.12)

Microanalysis suggests the proposed structures of the complexes as shown below. Based on the analysis there is one chloride atom attached to the metal ion.

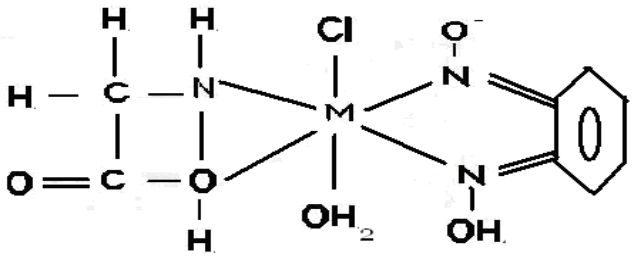

Fig. 1 Proposed structure of [MCl(Hcyclo)AA.H_2O]

AA = Glycine M = Ni(II), Co(II)

Antimicrobial studies

The antimicrobial activity of the ligand and the complexes were tested on gram positive *staphylococcus aureus, streptococcus pyogene* and gram negative *Escherichia coli and klebsiella pneumoniae.* This was done by measuring the inhibition zone in (mm) around the tested material.

The synthesised metal complexes in comparism to the uncomplexed ligands were screened for antimicrobial activity against bacterial species and paper disc diffusion method was adopted for the determination of antimicrobial activity {Cheesbrough 2004). Tetracycline (250mg) was used as a control drug.

Table 4: Antimicrobial activity of the ligands and their metal(II) complexes.

	Concentration (mg/ml)												
	Ligand/Complex	E.C			S.A			S.P			K.P		
		600	400	200	600	400	200	600	400	200	600	400	200
	Lp	++	++	+	+++	+++	++	+++	+++	+++	+++	++	++
	Ls	-	-	-	-	-	-	-	-	-	-	-	-
A_1	[CoCl(1,2 cyclo)(His).H_2O]												
A_2	[CoCl(1,2 cyclo)(gly).H_2O]	-	-	-	-	-	-	-	-	-	-	-	-
A_3	[CoCl(1,2cyclo)$_2$(2-ampy) .H_2O]	-	-	-	-	-	-	-	-	-	-	-	-
B_1	[NiCl(1,2 cyclo)(His).H_2O]	-	-	-	-	-	-	-	-	-	-	-	-
B_2	[NiCl(1,2 cyclo)(gly).H_2O]	-	-	-	-	-	-	-	-	-	-	-	-
B_3	[NiCl(1,2cyclo)$_2$(2ampy).H_2O]	-	-	-	-	-	-	-	-	-	-	-	-

E.C= Escherichia coli, S.A= Staphylococcus aureus, S.P= Streptococcus pyogene, K.P= Klebsiella pneomoniae.

1,2 cyclohexanedionedioxime showed varying degrees of inhibition on the growth of microorganisms. At 600-200 mg it showed a moderate activity against *Escherichia coli*. The ligand was highly active against *Staphylococcus aureus* at 600-400 mg, at 200 mg it was moderately active. Also the ligand showed activity against *Streptococcus pyogene* at all concentrations. It also shows activity against *Klebsiella pneumonia*. At 600 mg the activity was high but at 400-200 mg it was moderately active. In the complexes there are no activities at all. And this suggest that the complexes are not potent against the screened bacterials.

VI. Conclusion

The complexes are formed in moderate yields (55 – 72%) and have different shades of colours ranging from dark brown to rose-red. The complexes also show varying degrees of solubilities in protic solvents like methanol and ethanol. The molar conductance of the compounds that dissolved in methanol were in the range 9.3 – 10.0 $Scm^2\ mol^{-1}$ indicating that they are non-electrolytes, since a value in the range 75 – 90 $Scm^2\ mol^{-1}$ is expected for a 1:1 electrolyte (Fabretti and Peyronel, 1978). The invitro antimicrobial screening of the complexes showed that the primary ligand is potential antimicrobial agent against the tested microorganisms.

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