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Synthesis and Characterization of Cr(III), Fe(III) and Ni(II) Complexes of α-Amino, Imidazolepropanoic Acid

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Histidine (α-amino, imidazolepropanoic acid) complexes with Fe^{3+}, Ni^{2+} and Cr^{3+} were prepared and characterized by thermal analysis as well as different spectroscopic techniques *i.e*., ultraviolet spectroscopy, fourier transform infrared spectroscopy and atomic absorption spectroscopy. The antimicrobial activity of the complexes was observed against three strains of bacteria (*Escherichia coli*, *S. aureus* and *Pseudomonas*). The data gathered showed the coordination behaviour of the ligand with the metal ions.

Key Words: Thermal analysis, Ultraviolet, Fourier Transform Infrared, Atomic absorption spectroscopy.

INTRODUCTION

Histidine (α-amino, imidazolepropanoic acid) (Fig. 1) is a basic, genetically coded amino acid. It is essential for human development ("semi-essential")[1]. Histidine is also a precursor of histamine, a compound released by immune system cells during an allergic reaction. It is needed for growth and for the repair of tissue, as well as the maintenance of the myelin sheaths that act as protector for nerve cells. It is further required for the manufacture of both red and white blood cells and helps to protect the body from damage caused by radiation and in removing heavy metals from the body. In the stomach, histidine is also helpful in producing gastric juices and people with a shortage of gastric juices or suffering from indigestion, may also benefit from this nutrient. People suffering from schizophrenia or bipolar (manic) depression should not take a histidine supplement without the approval of their medical professional. Dairy, meat, poultry and fish are good sources of histidine as well as rice, wheat and rye[2]. Histidine is, like many other amino acids, important for growth and general tissue repair[3]. Histidine is essential in forming many metal bearing enzymes and compounds, examples being the anti-oxidant super oxide dismutase, the iron storage protein ferritin, the iron uptake regulation protein-FUR, the copper storage and iron metabolism cofactor cerulplasmin, red blood cell hemoglobin, the toxic metal storage protein metallothionein and the cysteine regulating enzyme, cysteine dioxygenase[4]. The interaction of metal ions with proteins and other biological

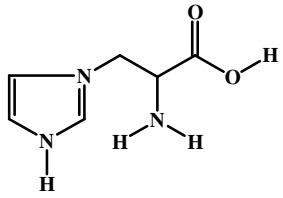

Fig. 1. Structure of histidine (α-amino, imidazolepropanoic acid)

molecule is to determine the chemical basis (binding, reactions, structural effects) for the biological roles and physiological effects of metal ions. Proteins and peptides that are rich in cysteine (Cys) or histidine (His) amino acids are potential ligands for metal ions[5]. A number of proteins involved in metal transport contain amino acid sequences that are rich in histidines. Since histidine is an excellent ligand for Cu(II), Ni(II) and other metal ions, it helps to quantify the metal-binding stoichiometry and affinity of histidine-rich sequences to understand metal ion selectivity by these proteins. One example is the unique peptide sequence, -PHGHGHGHGP- (P = proline, H = histidine, G = glycine), found in an intracellular loop of IRT1, a transmembrane Fe-transporting protein identified in *Arabidopsis thaliana*. Another example is Hpn, a unique small protein from *Helicobacter pylori* that has 28 histidines among its 60 residues and may play a role in Ni metabolism in this microorganism[6]. Study of the coordination chemistry of so-called zinc fingers that bind Zn(II) with four cysteines and histidines is a part of program, toxic metal

interactions with cellular proteins. The goals here are to quantify the binding of As, Ni, Cr and other toxic metals to certain target proteins (transcription factors, enzymes, DNA repair proteins), characterize metal-induced changes in the structure and function of the protein and determine the products of metal-protein reactions, which may be as molecular "biomarkers" of toxic metal exposure[5].

EXPERIMENTAL

All the chemicals used were of analytical grade, the reactions were carried out in three conical flasks of equal size. The α-amino, imidazolepropanoic acid (0.388 g; 0.1 mol) dissolved in sodium carbonate (0.262 g; 0.1 mol) in water (25 mL) in each of the three conical flasks. In the first flask added ferric chloride (0.675 g; 0.1 mol) in water (25 mL), in the second flask added nickel chloride (0.592 g; 0.1 mol) in water (25 mL) and in the third flask added chromium nitrate (1.00 g; 0.1 mol) in water (25 mL) slowly but with constant stirring (pH; 8). The red precipitates of complex(A) *i.e.*, Fe + histidine, light green precipitates of complex (B) *i.e.*, Ni + histidine and greish blue precipitates of complex (C) *i.e.*, Cr + histidine thus obtained were filtered off, washed several times with hot water and finally with alcohol. The products was dried in air and kept under vacuum for 48 h to get red product (0.255 g; 23.9 %) (decomposition point = 215 ºC) the complex (A), the light green product (0.23 g; 23.3 %) (decomposition point = 223 ºC) the complex (B) and greish blue product (0.260 g; 18.73 %) (decomposition point = 251 ºC), the complex (C) (Table-1).

TABLE-1
DECOMPOSITION POINTS AND YIELD OF THE COMPLEXES

No.	Complex	Reaction product	Decomposition points (ºC)	Yield (%)
1	A	Iron + histidine	215	23.90
2	B	Nickel + histidine	223	23.30
3	C	Chromium + histidine	251	18.73

Characterization of complexes: Thermal analysis (TGA) was measured by the Shimadzu (TGA-40) thermal analyzer at Pakistan Council of Scientific and Industrial Research (PCSIR) Laboratory Complexes, Lahore Pakistan. Ultravoilet-visible spectra were measured by Hitachi UV-vis U-2800 spectrometer, fourier transform infrared spectra were measured by MIDAC, M-2000 series spectrophotometer and the atomic absorption spectra were recorded on Zeemans Z-5000 series Polarized Atomic Absorption Spectrometer at Central Laboratory of Lahore College for Women University, Lahore Pakistan and the antimicrobial activity of the complexes was checked by "Antimicrobial Diffusion Technique" at the Institute of Microbiology; University of The Punjab, Lahore Pakistan.

RESULTS AND DISCUSSION

All the complexes are insoluble in common organic solvents and do not possess sharp melting points but decompose on heating above 210 ºC (Table-1).

The thermogravimetric (TG) data of complexes is depicted in (Figs. 2-4, Table-2). It is clear that complex(A) loses excess water endothermically up to about 97 ºC, complex (B) upto 129 ºC and complex (C) at 99.30 ºC. During this process of desorption the weight loss of 30.1 g (12.26 %) of complex

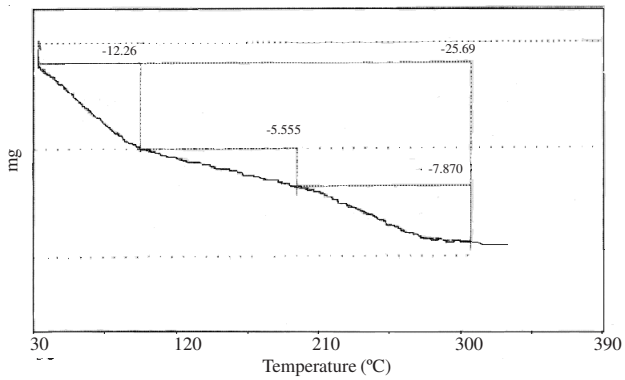

Fig. 2. Thermogravimetric analysis of iron of histidine complex

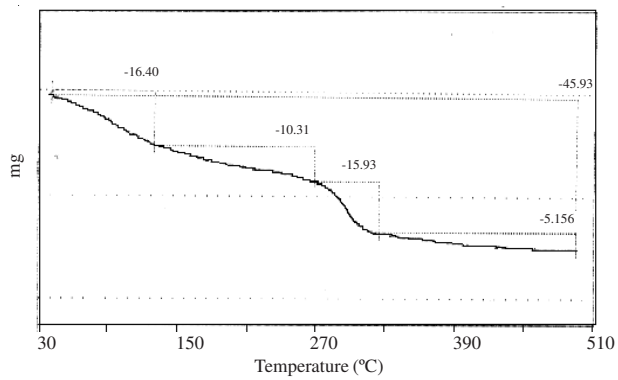

Fig. 3. Thermogravimetric analysis nickel complex of histidine

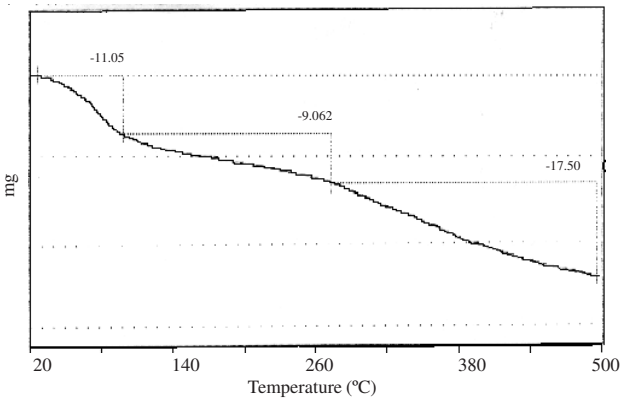

Fig. 4. Thermogravimetric analysis of chromium complex of histidine

TABLE-2
THERMOGRAVIMETRIC DATA OF THE METAL COMPLEXES

No.	Chelate	Temperature (ºC)	Weight loss (%)	Weight loss (g)
A	Fe^{3+}	97.0	12.26	30.10
		196.0	5.55	13.60
		306.0	7.870	19.35
B	Ni^{2+}	129.0	16.40	40.80
		268.0	10.31	25.67
		325.0	15.93	39.60
		495.0	5.15	12.82
C	Cr^{3+}	99.30	11.25	27.21
		273.2	9.062	21.90
		496.4	17.52	42.33

(A), 40.8 g (16.40 %) of complex (B) and 27.21 g (11.25 %) of complex (C) corresponds to the loss of two water molecules. Further on, no weight loss takes place but it is considered to undergo fusion decomposition during this temperature change. Later on, the oxidative degradation starts and complex (A) loses weight of 13.6 g (5.55 %) up to 196 ºC, complex (B) loses weight of 25.67 g (10.31 %) at 268 °C and complex (C) 0f 21.90 g (9.062 %) up to 273 ºC due to the evolution of CO_2. Thereafter the remnant loses weight 19.35 g (7.87 %) at 306 ºC of complex (A), 39.60 g (15.93 %) up to 325 ºC of complex (B) and 42.33 g (17.52 %) of complex (C) is recorded at 496.4 ºC, due to the evolution of the nitrogen molecules of the complexes. The oxides are formed at about these temperatures. By the results obtained from the data, it is concluded that complex (A) is thermally stable complex (B) showed intermediate stability while complex (C) is least stable.

The atomic absorption spectra showed that the metal concentration in complex (A) is 1.26 ppm, in complex (B) it is 1.32 ppm and in complex (C) metal concentration is 1.16 ppm. Calculation of the metal amount showed that the ligand to metal ratio is 1:1 in all of the three complexes (Figs. 5-7, Table-3).

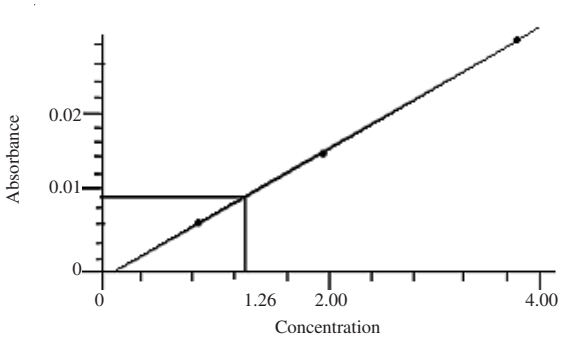

Fig. 5. Atomic absorption spectra of iron complex of histidine

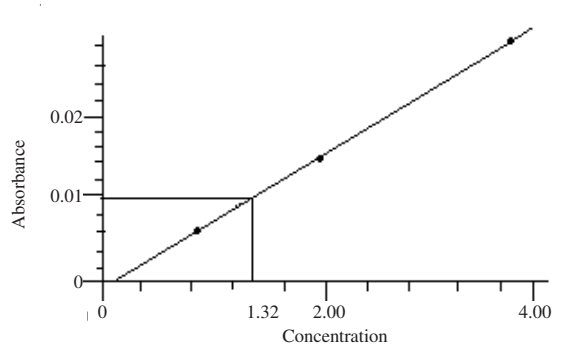

Fig. 6. Atomic absorption spectra of nickel complex of histidine

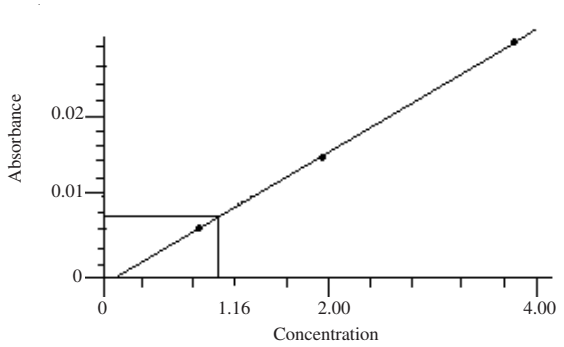

Fig. 7. Atomic absorption spectra of chromium complex of histidine

TABLE-3
ATOMIC ABSORPTION SPECTRA OF COMPLEXES

No. of obs.	Complexes	Theoretical yield (%)	Practical yield (%)	Ligand-metal ratio
1	(A)	26.49	25.20	1:1
2	(B)	27.59	26.40	1:1
3	(C)	24.91	23.20	1:1

The FTIR spectrum of ligand was studied and compared to those of its complexes, the important band frequencies are listed in Table-4. The IR spectrum of histidine molecule shows broad and intense one at 1720 and 1418 cm^{-1} due to the stretching and bending frequencies of the C=O and C-H group, respectively. The stretching vibrational band of NH group appears at 2850 cm^{-1} while that of ν(C=N) appears at 1650 cm^{-1}. The stretching vibrational frequency of the C=C appears at 1606 cm^{-1}. On the other hand, the IR spectra of the complexe (B), show the absence of the stretching vibrational band of the C=N group, so it seems that coordination process precludes. This is taken as an evidence for the contribution of this nitrogen atom to complex formation, which is supported by the shift of the band due to the N-H group to lower frequency. On the other hand, the frequencies of C-H, O-H, C-O and C=O have altered in metal complexes. A further support for the contribution of the N-H groups of histidine ligand to complex formation is the appearance of only one new band at 425-407 cm^{-1} due to (M-N) stretching.

TABLE-4
FTIR SPECTRA OF COMPLEXES

No. of obs.	Complex	IR (cm^{-1})	Assignments
1	α-Amino, imidazolepropanoic acid	2850	N-H stretching
		1720	C=O carbonyl
		1650	C=N stretching
		1606	C=C stretching (aromatic)
		1418, 1409	C-H bending (aromatic)
		1339	C-H bending (-CH_2-)
		1170	C-O bending (acid)
		979	O-H bending
		822	C=C bending
2	(A)	1912	C=O stretching
		1771	C=O carbonyl
		1636	C=N stretching
		1381	C-H bending (-CH_2-)
		1226	C-O stretching
		1188	C-O bending (acid)
		930	O-H bending
		407	ν(M-N)
3	(B)	1330	C-H bending (-CH_2-)
		1180	C-O bending (acid)
		691	C-H bending
		422	ν(M-N)
4	(C)	1625	C=N stretching
		1467	C-H Bending (aromatic)
		1086	O-H bending
		519	C-H bending
		425	ν(M-N)

Hence the salt solutions were coloured *i.e.* iron (reddish-orange), copper (blue), nickel (green) and chromium (bluish-green). The UV-visible wavelength range of coloured solutions is given in (Table-5)[7].

TABLE-5
COLOURS OF VISIBLE RADIATIONS

No.	Approximate wavelength range (nm)	Colour
1	465-482	Blue
2	498-530	Green
3	597-617	Reddish-orange

Also the wavelength range of α-amino, imidazole-propanoic acid is given as (200-350 nm). The wavelength range of the chelates formed is (180-300 nm), as shown in Table-6.

TABLE-6
MAXIMUM WAVELENGTH (λ_{max}) OF METAL COMPLEXES

No.	Complexes	λ_{max}
1	A	215
2	B	208
3	C	225

Measurements of "zones of inhibition" of the compounds were noted, results showed that compounds posses antimicrobial activity against three strains; *Escherichia coli*, *S. aureus* and *Pseudomonas*. Among the four complexes, complex(A) showed strong antimicrobial activity against all the three strains especially *E. coli*,that is a gram-ve bacteria, it causes intestinal disease complex (B) and complex (C) do not showed any activity against *Pseudomonas* and some activity against *S. aureus* that causes skin acceny (Table-7).

TABLE-7
ANTIMICROBIAL ACTIVITY DATA OF METAL COMPLEXES

Compound	Zone of inhibition (mm)		
	Escherichia coli (gram –ve)	*S. aureus* (gram +ve)	*Pseudomonas*
Complex (A)	21	14	17
Complex (B)	16	12	–
Complex (C)	13	10	–

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