Chemistry: Bulgarian Journal of Science Education *Volume 24 Number 5, 2015* *Природните науки в образованието*

Experiments
Учебен експеримент в природните науки

SPECTRAL, MAGNETOCHEMICAL AND THERMOGRAVIMETRIC ANALYSIS (TGA) OF TRANSITION METAL COMPLEXES WITH N^O TYPES LIGANDS

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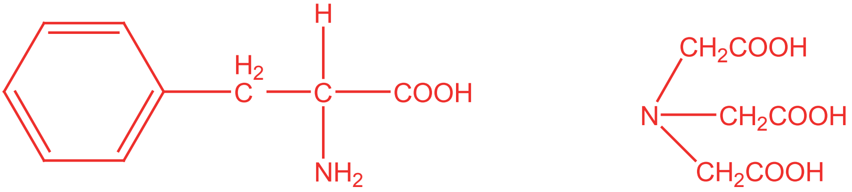
Abstract. Transition metal complexes, $Na_2[M(L_1L_2)].H_2O$, where M = Cu(II), Co(II) and Ni(II) ions ; L_1 and L_2 are the anions of phenylalanine (Phe^-) and nitrilotriacetic acid (NTA^{3-})respectively have been synthesized and characterized by elemental analysis, spectral (IR,UV in solidstate), magnetic susceptibility and thermogravimetric analysis (TGA). All the complexes have been suggested to show six fold octahedral geometry around the metal ion. Phenylalanine and nitrilotriacetic acid demonstrate bidentate and tetradentate behavior respectively, coordinating through their respective nitrogen atom and the oxygen atom (s) of the carboxylate group. Thermal behavior of Ni(II) complex is quite different from those of Cu(II) and Co(II) complexes which show similar type of thermal behavior. Based on their decomposition temperature, the thermal stability of the three complexes can be rated as Cu > Ni > Co.

Keywords: transition metal complexes, octahedral, phenylalanine, nitrilotriacetic acid, thermal analysis

Introduction

Transition metal ions play a vital role in several biological processes in human body (Raja Balan et al., 2013). Divalent metals (Cu, Co and Ni) amino acid complexes have been of importance as model for the metal ligand systems and proved to be useful antibacterial agents against staphylococcus aureus, Escherichia coli, nutritive supplies for human and animals (Fitzsimmons et al., 1985; Martin et al., 1973; Rusu et al., 2009).Such complexes have also been found to act as active catalysts in many environmental and chemical reactions (Iakovidiset al., 1989). Studies on the synthesis, characterization and biological activities of mixed ligand transition metals complexes involving various amino acids including phenylalanine have been carried out by many researchers (Rusu et al., 2009; Sanap & Patil., 2013; Patil et al., 2012; Kabbani et al., 2005; Gupta & Srivastava., 1985; Reddy & Reddy., 2000; 2002; Shivankaret al., 2007; Kumar et al., 2013; 2014). Synthesis, spectral and magneto chemical studies of mixed ligand amino acid chelates of divalent transition metals with nitrilotriacetic acid and glycine, α-alanine, valine, or leucine have also been reported (Saxena& Srivastava., 1990). Studies on the octahedral structure of Cu(II), Co(II), Cd(II) and Zn(II) ternary complexes of nitrilotriacetic acid and alanine or phenylalanine prepared in acidic medium between pH 2.8 and 4.0 have been reported (Khalil et al., 2010).The formation, determination of structure, and the mode of coordination involved in a transition metal complex depend upon many factors such as, metal ions and their oxidation state, reaction medium and the structure of the ligands. Thus the, present paper describes the synthesis, spectral, magnetochemical and thermogravimetric studies of the mixed ligand Cu(II), Co(II) and Ni(II) complexes formed with nitrilotriacetic acid and phenylalanine between pH 4.20 and 8.93.

Structures of phenylalanine and nitrilotriacetic acid ligands are shown below in Fig. 1.



(a) L-phenylalanine

(b) Nitrilotriacetic acid

Fig. 1. Structure of the ligands

Experimental

The two ligands, L-phenylalanine (Aldrich) and nitrilotriacetic acid (Fluka) and the metal salts, $CuCl_2.2H_2O$ (BDH), $CoCl_2$ (Rochelle chemicals) and $NiCl_2$ (Rochelle chemicals) were used as purchased without any further purification. Ligands were dissolved in one equivalent of sodium hydroxide (UNIAR)and metal ions solution were prepared in one equivalent of hydrochloric acid (Rochelle chemicals). IR spectra of ligands and synthesized metal complexes were recorded on a Perkin – Elmer FT-IR 2000 spectrophotometer in 4000 – 400 cm^{-1} range using KBr disc. Vario El C H N O/S elemental analyzer was used for the elemental analysis (C H N) of the complexes and magnetic susceptibility measurements were carried out on Johnson Matthey Alfa product magnetic susceptibility balance (University of Botswana). Electronic spectra of the complexes in solid state were recorded in the range 200-1300 nm (UV-NIR) on a

Perkin-Elmer UV/Vis/NIR spectrometer Lambda 750 and thermogravimetric analysis (TGA) was carried out on Mettler Toledo TGA/SDTA 851 instrument between 20° C and 1000°C temperature at a heating rate of 10° C /minute under the nitrogen atmosphere (Indian Institute of Sciences, Bangalore, India).

Synthesis of complexes

Equimolar (0.1M) solutions of ligands were mixed with metal ion (0.1M) solution separately in 1:1:1 molar ratio and the pH of the mixture solution was adjusted to an appropriate value between 4.20 and 8.93 to synthesize Cu(II), Co(II) and Ni(II) complexes.

Copper(II) complex

After mixing the above solutions, the pH of the resulting mixture solution was adjusted to ~ 4.20 by adding sodium hydroxide solution. The color of the solution remained blue throughout the experiment. The dark blue solution was then concentrated on a steam bath to reduce the volume of the solution between 25-30 ml and allowed to crystallize overnight. Blue crystalline product was then filtered and washed first with 50% alcohol-water mixture followed by acetone and dried in a vacuum desiccator.

Cobalt(II) complex

After mixing the solutions of both ligands and $CoCl_2$ solution, the pH of the resulting mixture solution was adjusted to ~ 8.93 by the addition of sodium hydroxide. The pink solution was then concentrated on a steam bath to reduce the volume between 20-25 ml and allowed to crystallize for about 24 hours. The pink powder product was then filtered and washed first with 50% alcohol-water mixture followed by acetone and dried in a vacuum desiccator.

Nickel(II) complex

The pH of the mixed solution of both ligands and $NiCl_2$ was adjusted to ~ 6.93 by adding sodium hydroxide. Bright blue solution was then concentrated on a steam bath and the volume of the solution was reduced between 25-30 ml and allowed to crystallize for about 24 hours. Light green powder product was then filtered and washed first with 50% alcohol – water mixture followed by acetone and dried in a vacuum desiccator.

Results and discussion

Elemental analysis

Elemental analysis (C H N) analytical data Calcd (found)for the suggested formula, $Na_2[M\{C_6H_5CH_2CH(NH_2)COO)\}\{N(CH_2COO)_3\}]H_2O$, [M=Cu(II), Co(II), Ni(II)], of the metal complexes and their respective color are given in Table 1.

Table 1. Elemental analysis and magnetic measurements data for the metal complexes

Complex	Color	Calcd(found)%			Magnetic measurements				
		C	H	N	Temp (K)	χ_g x 10^6 cgs	χ_M x 10^6 cgs	χ_M' x 10^6 cgs	μ_{eff} BM
$Na_2[Cu(Phe)(NTA)].H_2O$ $Na_2[Cu(C_{15}H_{18}N_2O_9]$	Blue	37.54 (37.55)	3.79 (3.49)	5.83 (5.56)	302	2.357	1131.19	1252.15	1.73
$Na_2[Co(Phe)(NTA)].H_2O$ $Na_2[Co(C_{15}H_{18}N_2O_9]$	Pink	37.91 (38.42)	3.82 (3 43)	5.89 (5.90)	301	18.63	8858.18	8979.14	4.65
$Na_2[Ni(Phe)(NTA)].H_2O$ $Na_2[Ni(C_{15}H_{18}N_2O_9)]$	Light green	37.92 (37.80)	3.83 (4.21)	5.89 (5.69)	297	1012.77	4811.37	4932.33	3.42

Note: Phe and NTA represent anions of phenylalanine and nitrilotriacetic acid respectively.

Infrared studies

In an earlier report (Khalil et al., 2010),the presence of bands in 1738-1728cm^{-1} range in the IR spectra of ternary Co(II), Ni(II) and Cu(II) complexes was attributed to the presence of uncoordinated free carboxylic acid group of nitrilotriacetic acid and hence it has been shown to act as a tridentate ligand in the octahedral complexes coordinating through the oxygen of two carboxylic acid groups and the nitrogen atom. Phenylalanine has been suggested to act as a monodentate ligand.

In the present IR studies, nitrilotriacetic acid shows characteristic ν(OH) absorption band for COOH group at ~1712 cm^{-1} which vanishes in case of metal complexes. Instead, $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ absorption bands are observed between 1614-1582 cm^{-1} and 1400-1383 cm^{-1} range respectively(Saxena & Srivastava., 1990; Tomita &Uneo., 1963). The absence of bands in 1738-1728 cm^{-1} range in the IR spectra of the metal complexes does not show the possibility of the presence of any uncoordinated carboxylic acid group of the nitrilotriacetic acid. In nitrilotriacetic acid, ν(CN) band is observed at 1331 cm^{-1} which lowers in case of metal complexes. Hence, nitrilotriacetic acid coordinates through the nitrogen and oxygen atom of the carboxylate groups with the metal ions. In the free phenylalanine, the asymmetric (N-H) and symmetric(N-H) bands observed at ~ 3040 cm-^{1}and ~ 2963 cm^{-1} respectively are shifted to higher frequencies in the metal complexes indicates that the nitrogen of the amino group coordinates with the metal ions (Shivankar et al., 2007). The IR spectrumof phenylalanine also shows ν_{as}(COO$^-$) and ν_s (COO$^-$) bands at 1556 cm^{-1} and 1408 cm^{-1} respectively. In metal complexes, the shifting of ν_{as}(COO$^-$) band to the higher frequency range (1614-1582) cm^{-1}and ν_s (COO$^-$) band to the lower frequency range (1400-1383) cm^{-1} suggest the coordination of the carboxylic group via oxygen atom. In addition, metal complexes also show characteristic ν (OH) frequency around ~3300 cm^{-1}in the region 3400-3200 cm^{-1} attributed to the lattice water molecule and a strong band in the region 1614-1550 cm^{-1} is also the indicative of the presence of water molecule (Shivankar et al., 2007; Bellamy, 1975; Nakamoto, 1970). The difference in the COO$^-$ frequencies for the complexes are greater than the difference in the corresponding frequencies in phenylalanine suggesting monodentate behavior of its carboxylic acid group(Devereux et al., 1998; Mitie et al., 2009; Danyi et al., 2006). Thus it can be inferred that the coordination in metal complexes takes place through the oxygen atom of the carboxylic acid group and the nitrogen of the amino group, suggesting a bidentate behavior for the phenylalanine. However, tentative assignment of the main IR bands for the ligands and metal complexes are given in Table 2.

Table 2. Main IR frequencies (cm^{-1}) of ligands and their metal complexes

Compound	**ν(OH)**	**ν_{as} (N-H)**	**ν_{as} (N-H)**	**ν_{as} COO$^-$**	**ν_s COO$^-$**	**ν CO COOH**	**ν HOH**	**ν_s (CH)**	**ν_s (CN)**
Phenylalanine	-	3040	2963	1556	1408	-	-	-	-
Nitrilotriacetic acid	-	-	-	-	-	1712	-	3040 2992	1331
$Na_2[Cu(Phe)(NTA)].H_2O$ $Na_2[Cu(C_{15}H_{18}N_2O_9]$	3247	3173	3032	1614	1383	-	1614	2962	1322
$Na_2[Co(Phe)(NTA)].H_2O$ $Na_2[Co(C_{15}H_{18}N_2O_9]$	3358	3172	2967	1579	1396	-	1578	2967	1323
$Na_2[Ni(Phe)(NTA)].H_2O$ $Na_2[Ni(C_{15}H_{18}N_2O_9)]$	3354	3291	3022	1582	1400	-	1582	2942	1322

Note: Phe and NTA represent anions of phenylalanine and nitrilotriacetic acid respectively.

Magnetic measurements and electronic spectra

Copper(II) complex

The observed magnetic moment for the copper(II) complex is 1.73 B.M which is well in the expected range (1.70 – 2.20 BM) for the presence of one unpaired electron corresponds to the spin free octahedral geometry for the complex (Figgis & Lewis, 1960).Copper(II) with d^9 configuration shows main absorption band for the d-d transition at 657 nm (15 220 cm^{-1}) which can safely be assigned to ^2E_g $^2T_{2g}$ transition and a charge transfer band is observed at 265 nm (37 735 cm^{-1}) (Lever, 1984). The electronic spectra of copper(II) complex is shown in Fig. 2.

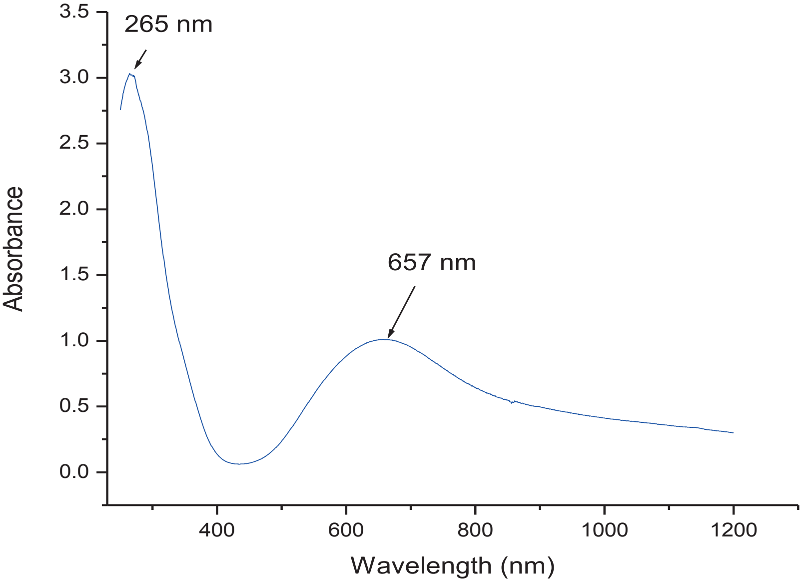


Fig. 2. Electronic spectrum of copper(II) complex

Cobalt(II) complex

The observed magnetic moment, 4.65 BM for cobalt(II) complex suggests a six fold octahedral structure (Figgis& Lewis., 1960; Cotton et al., 1999).This value is higher than the required value for a free spin d^7state corresponding to three unpaired electrons. Co(II) ion with d^7 configuration with an octahedral geometry should show three absorption bands corresponding to three spin allowed transitions in its electronic spectrum; (ν_1) $^4T_{1g}(F)$ $^4T_{2g}(F)$ observable near infer red region; (ν_2)$^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ and (ν_3) $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$. Since, ν_2 transition involves a two electron process and should be weaker by ~ 10^{-2} than the other transitions (Cotton et al., 1999), hence its position may however be ambiguous and is rather difficult to locate with certainty (Lever, 1984; Cotton et al., 1999). Sometimes it appears as a shoulder on either side of the main absorption band (ν_3 transition) and in some cases it may be unobservable. Besides, the spectra should also show charge transfer bands. In the present cobalt (II) complex, the main absorption band (ν_3) is observed at 509 nm (19 646 cm^{-1}) which can safely be assigned to $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition. The band observed at 1188 nm (8418cm^{-1}) in the NIR can be attributed to (ν_1),$^4T_{1g}$ (F) $\longrightarrow$ $^4T_{2g}$(F) transition. The charge transfer band is observed at 261nm (38 314 cm^{-1}). The electronic spectra of cobalt (II) complex is shown in Fig. 3.

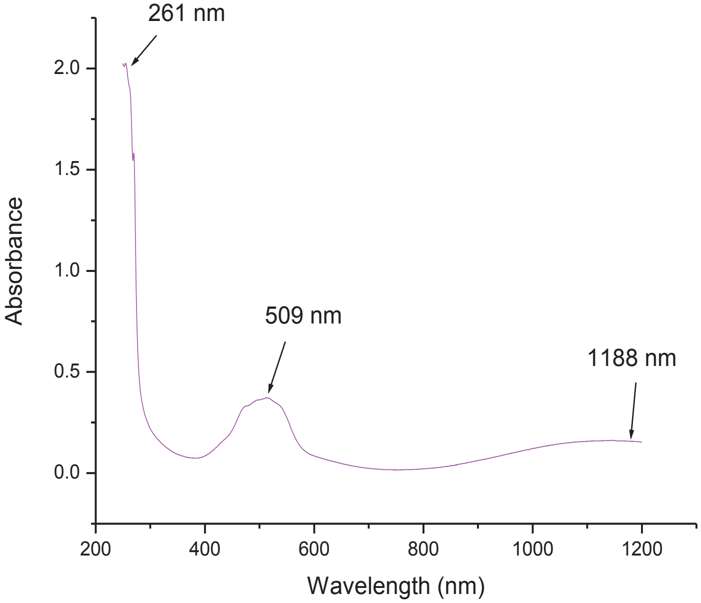


Fig. 3. Electronic spectrum of cobalt(II) complex

Nickel(II) complex

The observed magnetic moment of 3.42 BM indicates an octahedral structure (d^8 configuration) for the nickel(II) complex (Figgis & Lewis., 1960; Cotton et al., 1999),which is supported by its electronic spectrum. Ni(II) has a d^8 electronic configuration and therefore three d-d electronic transitions are expected to occur in addition to charge transfer bands: $^3A_{2g} \rightarrow {}^3T_{1g}(P)$; $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_2 \rightarrow {}^3T_{2g}(F)$. The spectrum for Ni(II) complex is presented in Fig. 4. The maximum at 627 nm (15 948 cm^{-1}) is assigned to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition and the one at 388 nm (25 773 cm^{-1}) corresponds to $^3A_{2g} \rightarrow {}^3T_{2g}(P)$ transition. $^3A_{2g} \rightarrow {}^3T_{2g}$ transition is observed at 1070 nm (9345 cm^{-1}). Charge transfer bands are seen at 258 nm (38 759 cm^{-1}) (Cotton et al., 1999).

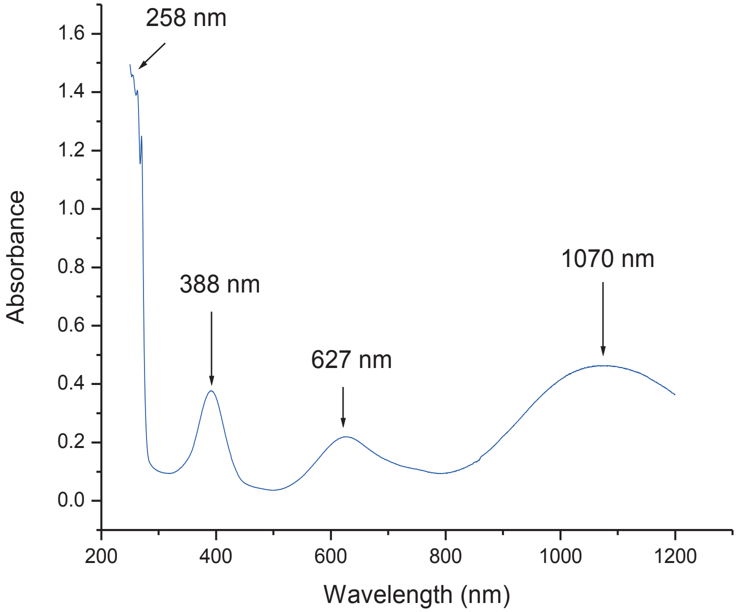


Fig.4. Electronic spectrum of nickel(II) complex

Magnetic susceptibility measurements together with elemental analysis (C,H,N) of the metal complexes are given in Table1.

Based on the IR results as well as on the magnetic measurements, elemental analysis and electronic spectra, we suggest the general structure of the synthesized complexes as shown in Fig. 5.

Thermogravimetric analysis (TGA) study

Thermogravimetric analysis is used to determine the thermal stability and the fragmentation patterns of materials (Vega-Lizama et al., 2015; Hu et al., 2015). The thermal behavior of copper, cobalt and nickel complexes with phenylalanine and nitrilotriacetic acid was studied in the temperature range 20-1000°C.As a general observation, the fragmentation for all the complexes starts with the loss of lattice water molecule and ends with the metal carbonate residue, MCO_3 (M = Cu, Co, Ni) (Figs. 6-8). The copper complex showed a better thermal stability than the other two complexes (~105°C) while cobalt complex was the least stable (~80°C). The nickel complex was stable up to 95°C. Table 3shows detailed fragmentation patterns for the three complexes.

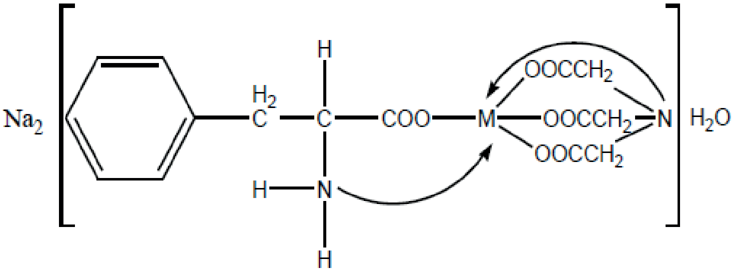


Fig. 5. Structure of complexes; where M=Co(II), Ni(II), Cu(II) ions

The fragmentation pathways as shown by TGA study confirm the structure of the complexes as suggested in Fig. 5.

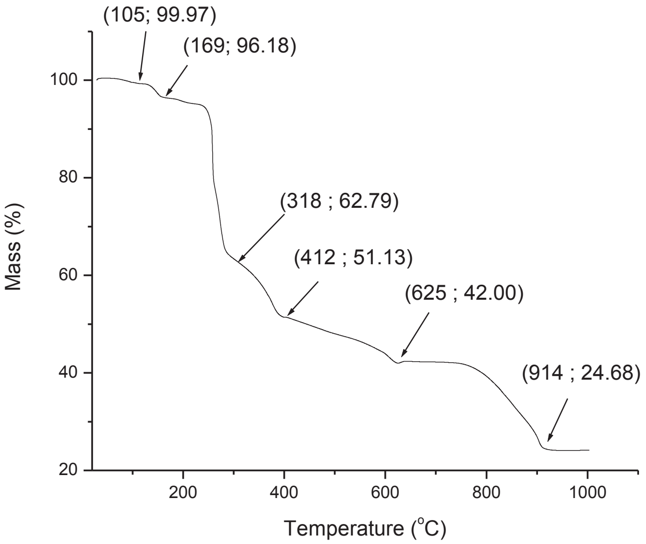


Fig. 6.TGA plot for Cu – Phe - NTA complex

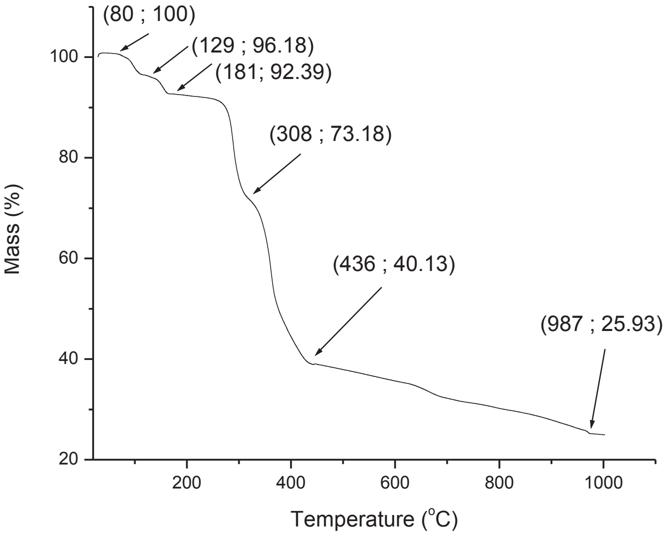


Fig. 7. TGA plot for Co - Phe - NTA complex

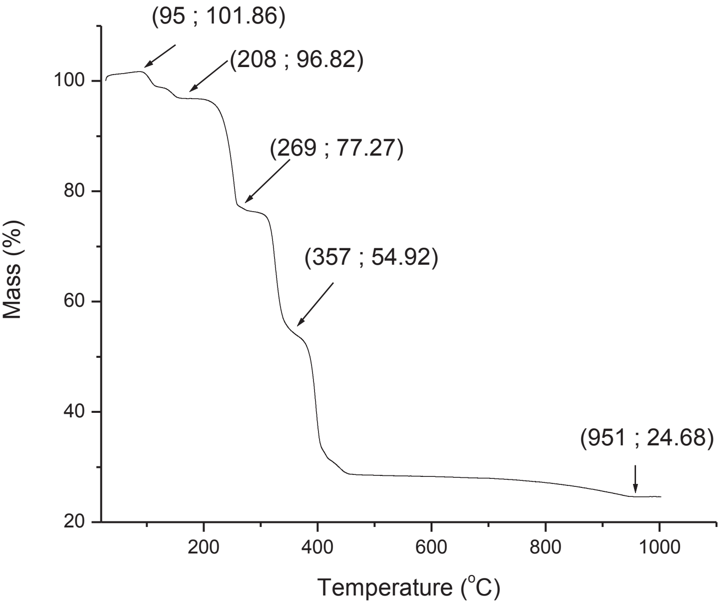


Fig. 8. TGA plot for Ni – Phe - NTA complex

Table 3. Thermogravimetric analysis results for M – Phe - NTA

Complex	**Stability (°C)**	**Temp. range (°C)**	**Removed group(s)***	**Mass loss (%)**	
				Found	Calculated
Cu-Ph-NTA	105	105-169	H_2O	3.82	3.75
		169-318	Na_2, $Ph\text{-}CH_2\text{-}CHNH_2$	37.21	38.34
		318-412	$OOCHCH_2$	48.87	50.42
		412-625	COO	58.00	59.59
		914-	Remaining residue, $CuCO_3$	24.68	25.62
Co-Ph-NTA	80	80-129	H_2O	3.82	3.79
		129-181	Na	7.61	8.63
		181-308	Na, $OOCHCH_2$	26.82	25.68
		308-436	$Ph\text{-}CH_2\text{-}CHNH_2$, COO	59.87	60.21
		987-	Remaining residue, $CoCO_3$	25.93	25.04
Ni-Ph-NTA	95	95-208	H_2O	3.18	3.79
		208-269	$Ph\text{-}CH_2$	22.73	22.96
		269-357	Na_2, $OOCCH_2$	45.08	44.87
		951-	Remaining residue, $NiCO_3$	24.68	24.85

*The groups removed from the second step onwards include the groups removed in the preceding steps.

Conclusion

In view of the evidences obtained above from the IR, electronic spectra, magnetic susceptibility measurements and thermogravimetric analysis, a sixfold octahedral structure has been suggested for all the complexes in which nitrilotriacetic acid and phenylalanine act as a tetradentate and bidentate ligands respectively. Both the ligands coordinate with their respective nitrogen atom and the oxygen atom(s) of the carboxylic acid groups. Based on the temperature decomposition, the thermal stability of the complexes is suggested as Cu > Ni> Co. The suggested structure for the complexes is shown in Fig. 5.

Acknowledgements: Authors gratefully acknowledge the assistance provided by the University of Botswana, the Third World Academy of Science (TWAS) and the India Institute of Sciences, India.

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