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# Synthesis, Spectroscopic and Thermal Investigation of New Nickel (II) Amino Acid Complexes

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**ABSTRACT**

The new mixed-ligand Nickel (II) complexes of the type [Ni (AB) $(H_2O)_2$] with bidentate amino acids like proline, glycine, valine have been synthesized and characterized on the basis of elemental analysis, spectroscopic, thermal analysis, magnetic measurements and x-ray diffraction data. The spectral studies suggest octahedral symmetry for these complexes.

**KeywordS:** Mixed ligand complexes, bidentate amino acids, spectral studies and octahedral symmetry.

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## INTRODUCTION

The mixed ligand complexes play an important role in biological process [1-2]. Amino acids containing active –NH2 and –COOH groups are well known for their tendency to form complexes with metals and have great significance in biological and pharmaceutical [3-4] fields and are directly involved in all the metabolic enzymatic activities [5] of living organism.

The stabilities of mixed chelates are of great importance in biological system as many metabolic and toxicological functions are dependent upon this stability. Many attempts have been made to correlate the stability of the metal-lignad complexes with their antimicrobial activity [6-10]. It is well established that ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances [11].

The literature survey reveals that very limited work of ternary complexes of transition metals with drugs and amino acids have been reported in the past[12-16]. During the recent years a systematic study has been done for the synthesis, stability constant and magnetic studies of some mixed ligand complexes of Ni (II) [17-21].

## MATERIALS AND METHOD

During the study analytical A.R. grade chemicals were used. 0.025 Molar aqueous solution of proline, glycine or valine was heated with freshly prepared nickel hydroxide on water both for 2 ½ hr. The solution was filtered when it was hot and filtrate containing ternary complexes was kept on water bath. It was then allowed to cool with ice for better crystallization. Green crystals of Nickel (II) ternary complexes were separated out, then filtered and washed with triply distilled water four times. The crystals were dried in vacuum at 60$^{o}$C.

## RESULTS AND DISCUSSION

The physico-chemical data in Table –1 shows that the complexes correspond to the formula [Ni(AB)($H_2O$)$_2$], where A is proline and B is glycine or valine.

**Table 1: Physico-chemical data of the Complexes.**

| Mole. formula of complexes | Color | Molecular wt. | | Dec. stage | ($T_{max}$) $^{o}$C | % Analysis | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | | H | | N | | O | | M | |
| | | Obs | Cal | | | Obs | Cal | Obs | Cal | Obs | Cal | Obs | Cal | Obs | Cal |
| Ni($C_7H_{12}N_2O_4$) $2H_2O$ | Green | 282.57 | 284.93 | I<br>II<br>III | 164<br>367<br>424 | 30.081 | 29.48 | 4.589 | 4.21 | 7.122 | 9.83 | 39.91 | 40.1 | 19.32 | 20.60 |
| Ni($C_{10}H_{20}N_2O_4$)2H $_2$O | Green | 323.55 | 324.86 | I<br>II<br>III | 155<br>363<br>398 | 30.507 | 36.94 | 6.193 | 5.54 | 7.721 | 8.62 | 30.83 | 34.24 | 18.82 | 18.07 |

The DTA curves show three stage decomposition patterns. The main stage is observed at 424 $^{o}$C and 398 $^{o}$C respectively for [Ni(Pro)(Gly)($H_2O$)$_2$] and [Ni(Pro)(Val)($H_2O$)$_2$] afterwards the

process of oxidation and decomposition take place. The final product is NiO. Water molecules eliminated at around 170°C may be coordinate water [22].

The visible spectrum data is shown in Table –2. Both the Nickel (II) complexes show two well defined bands $\upsilon_2$ and $\upsilon_3$ arising from the spin allowed transitions $^3A_{2g}(F) \rightarrow T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. This indicates that the geometry of Nickel (II) complex is octahedral [23-24]. The ratio of $\upsilon_3 / \upsilon_2$ is practically equal to 1.70 which also supports the octahedral structure [25].

**Table 2: Electronic Spectral Data of the Complexes**

| Complexes | $\upsilon_1$ $cm^{-1}$ cal. | $\upsilon_2$ $cm^{-1}$ obs. | $\upsilon_3$ $cm^{-1}$ obs. | $\beta cm^{-1}$ | Dq/B | $\upsilon_3 / \upsilon_2$ |
|---|---|---|---|---|---|---|
| $Ni(C_7H_{12}N_2O_4)\ 2H_2O$ | 8960 | 16129 | 27027 | 2279 | 0.39 | 1.68 |
| $Ni(C_{10}H_{20}N_2O_4)2H_2O$ | 8546 | 15384 | 27548 | 2292 | 0.37 | 1.79 |

The IR spectrum of the complexes shows strong absorption maxima at around 540 $cm^{-1}$ confirming the presence of Ni-O bond [26-27]. Ni-N bonding is manifested by the appearance of bands at 412-420 $cm^{-1}$. Also the spectrum exhibits a strong broad band at 1610 – 1630 $cm^{-1}$ indicative of (COO) as stretching mode, while a peak corresponding to $(COO)_s$ vibration appeared at 1450 -1500 $cm^{-1}$ . The position of these bands in the spectrum of the metal-complex allows the assignment of the coordination mode for the amino acids ligand in the complex. The complexes further display a band in the range 3250-3280 $cm^{-1}$ attributed to ($\upsilon NH_2$), typical of coordination amino groups[28]. Ni-N bonding is manifested by the appearance of bands at 412-420 $cm^{-1}$. The OH stretching vibrations of coordinated water are located in the range 3200-3500 $cm^{-1}$. No free carboxylic (COOH) groups could be detected from the IR spectral data indicating coordination of both of the studied metal ions to the carboxylate anions, from the foregoing band positions of $\upsilon$ ($NH_2$), $\upsilon$ ($COO^-$), $\upsilon$ (M-O) and $\upsilon$ (M-N) and comparison with similar compound [28], it may be concluded that the involved amino acids in the complexes are bidentate coordinating through the $–NH_2$ and $COO^-$ groups.

The magnetic moments of the Ni (II) ternary complexes are 3.09-3.14 B.M. These values are in the range reported for octahedral Ni (II) complexes [23], having two unpaired electrons.

**Table 3: IR Spectral data and Magnetic measurement of the complexes (cm-1).**

| S.N. | Complexes | $\upsilon_s(COO^-)$ | $\upsilon_{as}(COO^-)$ | $\upsilon(NH_2)$ | $\upsilon$(OH) | $\upsilon$(M-O) | $\upsilon$(M-N) | $\mu$ eff (BM) |
|---|---|---|---|---|---|---|---|---|
| 1 | $Ni(C_7H_{12}N_2O_4)\ 2H_2O$ | 1450 | 1610 | 3250 | 3500 | 540 | 412 | 3.09 |
| 2 | $Ni(C_{10}H_{20}N_2O_4)2H_2O$ | 1500 | 1630 | 3280 | 3200 | 535 | 420 | 3.14 |

The XRD data of [Ni (Pro) (Val) $(H_2O)_2$] is shown in **Table-4**. The XRD study of this complex shows that the complex is crystalline in nature. The diffractogram shows 14 reflections for 2θ value ranging from 10° to 73° with 2 θ maxima at 16.8161 which corresponds to *d* value of 5.26801 Å. λ value for this peak is 1.4487Å. The unit cell parameters are calculated by indexed data. It is also clear from the data that Nickel (II) complex has tetragonal symmetry.

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**Table 4: Crystal parameter.**

| Complex | Lattice const. | Atomic radius | Λ | Crystal system | Rel. ref. |
|---|---|---|---|---|---|
| $Ni(C_7H_{12}N_2O_4)$ $2H_2O$ | 8.9131 | 3.1508 | 1.4487 Å | Tetragonal | 16 |

## CONCLUSION

The results of thermal analysis show stability of Nickel (II) amino acid complexes. The complexes were thermal stable up to about 350°C. Most thermally stable complex is [Ni (Pro) (Gly) $(H_2O)_2$]. Electronic and IR spectral studies suggest that both the Nickel (II) complexes have octahedral geometry. From the XRD studies this may confirm the formation of the mixed ligand complexes and indicates the presence of a mixture of two binary complexes.

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