Asian Journal of Chemistry Vol. 6, No. 3 (1994), 706–708

NOTES

Synthesis and Characterization of Some Ni(II) Mixed Ligand Complexes with Amino Acids.

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Some Ni(II) complexes of the type [Ni (AB) $(H_2O)_2$] with bidentate amino acids like serin, threonine, α-amino butyric acid have been synthesised and characterized by elemental analysis, electronic, infrared spectra, magnetic moments. Differential thermal analysis data show that these complexes are thermally stable upto ~ 350°C and they decomposed to yield pure NiO at 700°C. The value of magnetic moment shows that the complexes are paramagnetic with two unpaired electrons. The spectral studies suggest octahedral symmetry for these complexes.

Amino acids containing an active NH_2 and COOH group are well known for their tendency to form complexes with metals and have great significance in biological[1,2] pharmaceutical fields and are directly involved in all the metabolic enzymatic activities[3] of every living being. This communication reports the synthesis, composition and structure of Ni(II) complexes with serine (Ser) as primary ligand and threonine (Threo) and α-amino butyric acid (α-Aba) as secondary ligand.

Preparation of the complexes

Freshly precipitated nickel hydroxide was mixed with equimolar solutions of primary ligand *viz* serine and secondary ligand namely α-amino butyric acid or threonine, on waterbath for 3 h. The pH of the solution was kept 7.0 as at this pH ternary complexes are formed easily. The filterate was concentrated on water bath at 90–100°C. The solution was filtered while hot. On cooling blue crystals of nickel-ternary complexes separated out. These were recrystallised with double distilled water. The crystals were dried in vacuum at 50°C.

TABLE-1
ANALYTICAL, MAGNETIC MOMENT AND D.T.A DATA OF THE Ni COMPLEXES.

Complex	Dec. Temp	% Analysis, Found (calc.)			μ_{eff} (B.M.)
		C	H	N	
[Ni(Ser)(Thre)$(H_2O)_2$]	360°C	26.50 (26.58)	5.71 (5.69)	8.90 (8.86)	3.07
[Ni(Ser)(α-Aba)$(H_2O)_2$]	345°C	29.94 (28.00)	6.07 (6.00)	9.29 (9.33)	3.16

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The analytical data Table-1 shows that the complexes correspond to the formula [Ni (AB)$(H_2O)_2$] *i.e.*, [Ni(Ser)(Thre)$(H_2O)_2$] and [Ni (Ser)(α-Aba)$(H_2O)_2$].

The electronic spectra of all the complexes exhibit two well resolved bands ν_2 and ν_{3-1} in the range (14925 and 25974) 14925–19050 and 21050–26670 cm^{-1} which may be assigned to ν_2 and ν_3 bands arising from the transitions $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(p)$ respectively in octahedral geometry. However, it has not possible to assign[4] the ν_1 band appearing at 13600–13770 cm^{-1} arising from the transition $^3A_{2g} \rightarrow {}^3T_{2g}$. ε Values 6–11 show that all the complexes have octahedral structure in the present case. The ratio of ν_3/ν_2 is practically equal to 1.70. It also support the octahedral structure[5].

In the IR spectrum of amino acids there appear five absorption bands. The absorption band at 2580 and 2100 cm^{-1} may be assigned to NH_3^+, the absorption at near about 1630–1640 cm^{-1} may be due to the NH_3^+ deformation and bending. The absorption band near 1110 cm^{-1} show NH_3^+ rocking. The absorption band at 1590 and 1420 cm^{-1} due to COO^- asymmetric and symmetric stretching frequencies respectively. The absorption at 890–900 cm^{-1} is due to the C–N symmetric stretching frequencies.

The absorption band corresponding to NH_3^+ stretching frequencies disappeared on complexation indicating that NH_3^+ group is involved in the complex formation.

The carbonyl asymmetric stretching frequency shifted to lower 20–30 cm^{-1} while symmetric stretching frequency shifted to higher 30–50 cm^{-1} (Table–3). This observation indicate that the carbonyl oxygen is coordinated to metal ion in the complexes.

There is appearance of asymmetric stretching frequencies of NH_2 group in the region 3200–3500 cm^{-1}. Thus it is a decisive proof that complexation take place through amino group[6] and also give clue that Ni–N bond is covalent in nature[7].

TABLE 2
VISIBLE SPECTRAL DATA FOR MIXED LIGAND COMPLEXES OF Ni(II) WITH AMINO ACIDS.

Assignments	Complex	
	[Ni (Ser)(Thre)$(H_2O)_2$]	[Ni (Ser)(α-Aba)$(H_2O)_2$]
ν_1 cm^{-1}	13650	13650
ν_2 cm^{-1}	15698 (6.7)	15625 (6.6)
ν_3 cm^{-1}	26731 (11.1)	26666 (10.8)
B cm^{-1}	729.0	719.4
Dq/B	1.46	1.44
ν_3/ν_2	1.70	1.70

(ε Values given in parentheses)

In all the complexes a band is observed at *ca* 500 cm^{-1}, which may be assigned to Ni–N bond stretching.

It is observed that there is a band around 410 cm^{-1} which may be assigned as Ni–O bond stretching.

TABLE-3
IR SPECTRAL BANDS ASSIGNMENTS FOR AMINO ACIDS AND Ni(II) COMPLEXES.

Compound	νNH_3^+	$\delta(NH_3+)$	$\nu(NH_2)$	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	ν(Ni–O)	ν(Ni–N)
Serine	2564, 2033	1635	—	1600	1410	—	—
Threonine	2520, 2040	1625	—	1595	1418	—	—
α-Aba	2560, 2085	1625	—	1580	1415	—	—
[Ni (Ser)(Thre)$(H_2O)_2$]	— —	—	3500–3200	1575	1430	410	495
[Ni (Ser)(α-Aba)$(H_2O)_2$]	— —	—	3500–3200	1570	1440	415	500

The appearance of a band at 1680 cm^{-1} in the spectra of Ni(II) complexes indicates the presence of coordinated water. The absorption is due to bending modes of H_2O.

The mangnetic moments of the Ni(II) ternary complexes are 3.07 to 3.28 B.M.; these values are in the range reported for octahedral nickel(II) complexes[8] having two unpaired electrons. The magnetic moment values for Ni complexes are stains 58.8705×10^{-6} and 60.35525×10^{-6} values also support paramagnetic nature of the complexes.

The DTA curve show a two stage decomposition pattern. The main decomposition stage is observed at 320–360°C. If we assume that the other decomposition products have completely volatilized off, water eliminated above 150°C can be considered as coordinated water[9]. The final stage is NiO after decomposition in all cases.

ACKNOWLEDGEMENT

Thanks are due to the Principal, Govt. Digvijay College, Rajnandgaon for providing laboratory facilities for the research work.

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(*Received*: 12 August 1993; *Accepted*: 14 October 1993) AJC-725.