



Synthetic and Structural Studies on Chiral Nickel Complexes

KEYWORDS

Nickel, Chiral Amino acid, Ternary Chiral Mixed Ligand Complexes.

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ABSTRACT Ternary Chiral Mixed Ligand (CML) Ni(II) metal complexes of general molecular formula $[\text{Ni}(\text{MINAP})(\text{aa})\cdot 2\text{H}_2\text{O}]$; where, MINAP is sodium salt of *p*-methylisonitrosoacetophenone and aa is a chiral amino acid have prepared. The complexes have characterised by several physico-chemical techniques like molar conductance, specific optical rotation, magnetic susceptibility, electronic absorption, infrared spectral and TG-DTA analysis. On the basis of results the bonding and structure of the complexes discussed in details.

INTRODUCTION

In recent years, the study of mixed ligand transition metal complexes have attracted the interest of most of the chemists because of their applications in various fields. It is well known that mixed ligand complexes are biologically active against pathogenic microorganisms¹⁻⁵. Ternary complexes containing an amino acid as a secondary ligand are potential models for enzyme metal ion substrate complexes⁶. Chiral metal complexes are known to be used as catalysts in asymmetric synthesis^{7,8}, asymmetric epoxidations or Sharpless epoxidations⁹ and resolution of racemic compounds¹⁰. Some of the ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances¹¹. The binary and ternary transition metal complexes have shown biological activity^{12,13}. The mixed ligand complexes are suitable for mimicking the role of metal ions, detoxification mechanism and drug designing. In continuation to our studies on chiral complexes the present paper reports the synthesis and characterisation of chiral mixed ligand Ni(II) complexes of sodium salt of *p*-methylisonitrosoacetophenone as primary ligand and various chiral amino acids as secondary ligands.

EXPERIMENTAL

Materials and Methods

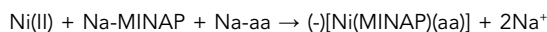
The Analytical Grade chemicals were used. The primary ligand sodium salt of *p*-methylisonitrosoacetophenone was prepared¹⁴ by using the reported method. The secondary ligands were various chiral amino acids such as L-alanine, L-valine, L-leucine, L-methionine and L-phenylalanine obtained from THOMAS BAKER. The solvents were distilled and purified according to standard procedures¹⁵ before their use.

The 10^{-3} M solution in DMF of each of the complexes were prepared to measure molar conductance using CM-180 Elico digital conductivitymeter with a dip-type conductivity cell fitted with a platinum electrode (cell constant = 1.0 cm^{-1}). The magnetic susceptibilities at room temperature were measured using Gouy's method and diamagnetic corrections for the ligand components applied using Pascal's constants¹⁶ to calculate effective magnetic moments. The Jasco P-2000 Polarimeter instrument was used to measure Specific Optical Rotation (SOR) values, $[\alpha]_D$ of all the Nickel complexes in 0.01% DMF solution at 25°C. The UV and Visible spectra of all the complexes were recorded in DMF on a Shimadzu UV-160A spectrophotometer. A Perkin-Elmer Precisely Spectrum 100 FT-IR Spectrometer was used to record FTIR spectra of all the ligands and their metal complexes in KBr between $4000\text{-}400 \text{ cm}^{-1}$ region. The

Rigaku Thermo Plus-8120 TG-DTA instrument was used for TG-DTA analysis of all the Nickel complexes.

Synthesis of Ternary Chiral Mixed Ligand Ni (II) complexes:

The complexes were prepared using an aqueous solutions (1 mmol) of Ni(II) sulphate heptahydrate and sodium salt of *p*-methylisonitrosoacetophenone. The mixture was stirred and kept in a boiling water bath for 30 minutes and added an aqueous solution of the sodium salt of chiral amino acid (1 mmol). The final mixture (1:1:1 molar proportion) was heated for three hours in a hot water bath and the solid complexes were obtained by filtration, washed first with ice-cold water and then with 1:1 ethanol:water. The complexes were dried under vacuum. The synthesis of present complexes may be represented by the following equation.



Where Na-MINAP is sodium salt of *p*-methylisonitrosoacetophenone and Na-aa is sodium salt of L-amino acid

RESULTS AND DISCUSSION

Characterisation of metal complexes

All the complexes are light green solids, insoluble in water and shows varying solubility in common organic solvents. The complexes are non-hygroscopic and thermally stable indicating a strong metal-ligand bond. The elemental analysis data Table-1 of the metal complexes are consistent with their general formulation as mixed ligand complexes $[\text{Ni}(\text{MINAP})(\text{aa})\cdot 2\text{H}_2\text{O}]$. The values observed for molar conductance of all the complexes fall between 0.005 to 0.011 mhos. $\text{cm}^2\text{mol}^{-1}$ in 10^{-3} M DMF solution (Table-1) indicate the complexes are non-electrolytic in nature¹⁷. The SOR $[\alpha]_D$ values at 25°C in 0.01% DMF solution were found to be negative and lie between -32.2° to -90.6° for all the complexes (Table-1) which supports to the chiral nature of complexes.

All the complexes were prepared only in aqueous medium by solvent free approach which is non-polluting green approach and does not employ any toxic materials. Therefore, the complexes are obtained by a green chemistry synthetic route without use of any toxic solvent. Thus, apart from being a new simple route for synthesizing Chiral Mixed Ligand metal complexes, the present method could be a new technique for optical resolution of amino acids. The possibility of application of this system for resolution of other racemic compounds can be employed.

Table 1: Analytical data of the metal complexes prepared from chiral amino acids

Complex ^a	Empirical Formula (Formula wt.)	Yield %	Color	Decomposition Temperature (°C)	%Elemental analysis Found(Calculated)					μ_{eff} (B.M.)	$[\alpha]_{\text{D}}$
					Ni	C	N	H	S		
[Ni(MINAP)(Ala)·2H ₂ O]	C ₁₂ H ₁₈ NiN ₂ O ₆ (344.97)	75	Light Green	252	17.02 (17.01)	41.77 (41.78)	8.11 (8.12)	5.27 (5.26)	-	2.72	-32.2
[Ni(MINAP)(Val)·2H ₂ O]	C ₁₄ H ₂₂ NiN ₂ O ₆ (373.03)	76	Light Green	258	15.72 (15.73)	45.07 (45.08)	7.52 (7.51)	5.95 (5.94)	-	2.94	-37.8
[Ni(MINAP)(Leu)·2H ₂ O]	C ₁₅ H ₂₄ NiN ₂ O ₆ (387.05)	74	Light Green	246	15.18 (15.16)	46.54 (46.55)	7.22 (7.24)	6.26 (6.25)	-	2.87	-90.6
[Ni(MINAP)(Met)·2H ₂ O]	C ₁₄ H ₂₂ NiN ₂ O ₆ S (405.09)	77	Light Green	272	14.50 (14.49)	41.49 (41.51)	6.89 (6.91)	5.49 (5.47)	7.93 (7.92)	3.02	-14.0
[Ni(MINAP)(Phe)·2H ₂ O]	C ₁₈ H ₂₂ NiN ₂ O ₆ (421.07)	81	Light Green	241	13.95 (13.94)	51.32 (51.34)	6.67 (6.65)	5.26 (5.27)	-	3.04	-71.6

Where ^a : MINAP represents the desalted primary ligand p-methylisnitrosoacetophenone, whereas Ala, Val, Leu, Met and Phe represent deprotonated chiral secondary ligands alanine, valine, leucine, methionine and phenylalanine respectively.

Infrared Spectra

The FTIR spectra of the metal complexes were recorded in KBr over the range 4000-400 cm⁻¹. The structurally important vibrational bands have been assigned on the basis of the reported assignments of infrared spectral bands of several carbonyl oxime, amino acids and their metal complexes¹⁸⁻²⁰

A broad band observed in the range between 3600-3300 cm⁻¹ due to asymmetric (asym) and symmetric (sym) O-H stretching modes are indicative of the presence of lattice water²¹. The ν_{asym} (N-H) and ν_{sym} (N-H) vibrations observed between 3037-3027 cm⁻¹ and 2981-2944 cm⁻¹, respectively, in the free amino acids are shifted to higher wave number i.e. in the range 3351-3263 cm⁻¹ and 3087-2953 cm⁻¹ respectively, in the spectra of the complexes, suggesting coordination of the amino group through nitrogen with the metal ion. The ν_{sym} (C-N) stretching frequency observed in the region 978-913 cm⁻¹ in the spectra of free amino acids is found to be shifted to lower wave number i.e. 958-818 cm⁻¹ in the spectra of the complexes, confirming coordination through the amino group of the amino acids.

The ν_{asym} (COO) band of the free amino acids observed in the range 1596-1563 cm⁻¹ is shifted to higher wave number, i.e. in the range 1652-1594 cm⁻¹ and the ν_{sym} (COO) mode observed between 1425-1407 cm⁻¹ in the spectra of free amino acids is found to be shifted to lower wave number i.e. 1404-1351 cm⁻¹, in the spectra of the CML complexes indicating the coordination of the carboxylic acid group via oxygen with the metal ion. Nakamoto, Morimoto and Martell showed that for a given ligand, the difference ($\nu_{\text{asym}} - \nu_{\text{sym}}$) would increase as the M-O bond becomes more covalent, since the carboxylate stretching becomes correspondingly more asymmetrical²². In the present investigation, this difference being in the range 243-248 cm⁻¹ indicates that the Ni-O bond have covalent character²³.

An important feature of the infrared spectra of the pre-

sent complexes is the absence of the band due to O-H stretching vibrations of the -COOH group of amino acid. This observation leads to the conclusion that the complex formation takes places by deprotonation of the carboxylic group of amino acid moiety. The C=N stretching frequency observed at 1543 cm⁻¹ in the spectrum of Na-MINAP is found to be shifted to the range 1539-1461 cm⁻¹ in the spectra of the complexes, indicating bonding through the nitrogen donor atom of the oxime group. This conclusion is further supported by the observation that a new band attributed to $\nu(\text{N} \rightarrow \text{O})$ is observed in the range 1274-1172 cm⁻¹ in the spectra of the complexes.

The C=O stretching frequency observed at 1603 cm⁻¹ in the spectrum of Na-MINAP is found to be shifted to the range 1608-1549 cm⁻¹ in the spectra of the complexes, indicating coordination through the oxygen donor atom of the oxime group. This is confirmed by the appearance of some new bands of weak intensity observed in the regions around 698-613 cm⁻¹ and 475-433 cm⁻¹ may be ascribed to the Ni-O and Ni-N vibrations, respectively²³. It may be noted that these vibrational bands are absent in the infrared spectra of Na-MINAP as well as the amino acids. Some of the important IR bands and their assignments are shown in Table-2 and the FTIR spectra of representative complex [Ni(MINAP)(Val)·2H₂O] is shown in Figure-1.

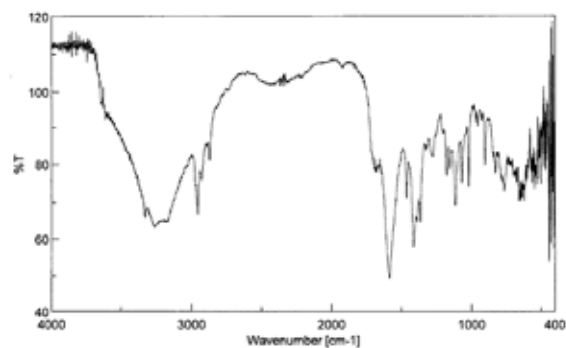


Fig. 1: FTIR Spectrum of [Ni(MINAP)(Val)·2H₂O]

Table 2: Some important infrared spectral bands (cm⁻¹) of CML Ni(II) complexes

Complex	v(O-H) (H ₂ O)	v(N-H) (asym.) (aa)	v(N-H) (sym.) (aa)	v(COO-) (asym.) (aa)	v(COO-) (sym.) (aa)	v(C-N) (sym.) (aa)	(C=O) (MINAP)	v(C=N) (MINAP)	v(N→O) (MINAP)	v(M-O)	v(M-N)
[Ni(MINAP)(Ala)·2H ₂ O]	3585w	3344w	2958w	1608s	1375m	818s	1608s	1461m	1274s	638 ^a w 618 ^b w	473 ^a w 435 ^b w
[Ni(MINAP)(Val)·2H ₂ O]	3329w	3263w	2956w	1652s	1365w	904s	1585s	1539m	1204s	651 ^a w 628 ^b w	475 ^a w 436 ^b w
[Ni(MINAP)(Leu)·2H ₂ O]	3357w	3298w	2953w	1634s	1351w	834s	1559m	1508w	1172s	698 ^a w 613 ^b w	461 ^a w 437 ^b w
[Ni(MINAP)(Met)·2H ₂ O]	3578w	3351W	3067w	1594s	1386w	958s	1549s	1510m	1274s	687 ^a w 640 ^b w	473 ^a w 444 ^b w
[Ni(MINAP)(Phe)·2H ₂ O]	3356w	3301w	3087w	1636s	1404s	909s	1558m	1498m	1207m	696 ^a w 640 ^b w	468 ^a w 433 ^b w

Magnetic Susceptibility Measurements

The magnetic susceptibility measured for all the Nickel complexes at room temperature by the Gouy's method using [Ni(en)₃]SO₄ as a calibrant. The effective magnetic moments were calculated after applying diamagnetic corrections for the ligand components using Pascal's constants¹⁶. The μ_{eff} values for the Ni(II) complexes are in the range 4.89-5.29 B.M., which are well within the range expected for octahedral Ni(II) complexes²⁴. The magnetic moments of the compounds investigated are in agreement with the findings of electronic absorption spectra.

Electronic Spectra

The electronic spectra in the ultraviolet region of the metal complexes in DMF solution (10⁻⁴M) was recorded. The bands observed in the range 40,816-48,077 cm⁻¹ are assigned to the π→π* transitions of the aromatic chromophore. In addition, the band observed in the range 39,526-40,984 cm⁻¹ can be attributed to the n→π* transitions. The bands in the range 38,760-39,526 cm⁻¹ can be assigned to the ligand to metal charge transfer (LMCT) transitions.

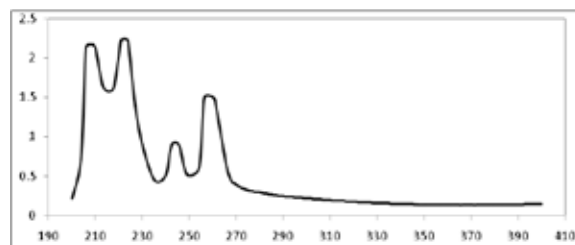
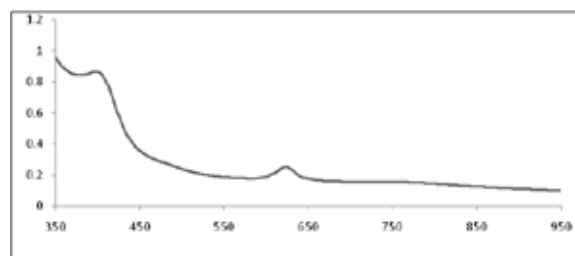
The electronic absorption spectra in the visible and near-infrared region of the Ni(II) complexes in DMF solution shows two transition bands. The bands around 25,126 and 15,106 cm⁻¹, are attributed to d-d transitions (Table-3). The ultraviolet and visible spectrum of the representative complex [Ni(MINAP)(Leu)·2H₂O] are shown in Figure-2 and Figure-3 respectively.

Table 3: Absorption spectral data for the CML Ni(II) complexes

Complex	Electronic spectral data in DMF		Proposed Assignments
	Peak Position v(cm ⁻¹) {ε M ⁻¹ cm ⁻¹ }		
[Ni(MINAP)(Ala)·2H ₂ O]	46948(1.9×10 ⁴)	-	Intra-ligand
	434782.5(10 ⁴)	-	Intra-ligand
	40000(1.0×10 ⁴)	-	Intra-ligand
	38911(1.2×10 ⁴)	-	Charge transfer
	-	24938(3.5×10 ³)	d-d transition
	-	15873(1.2×10 ³)	d-d transition
[Ni(MINAP)(Val)·2H ₂ O]	46296(2.2×10 ⁴)	-	Intra-ligand
	41494(2.6×10 ⁴)	-	Intra-ligand
	40486(1.2×10 ⁴)	-	Intra-ligand
	38910(1.5×10 ³)	-	Charge transfer
	-	24876(1.4×10 ³)	d-d transition
	-	16639(5.0×10 ²)	d-d transition
[Ni(MINAP)(Leu)·2H ₂ O]	48077(2.2×10 ⁴)	-	Intra-ligand
	45045(2.3×10 ⁴)	-	Intra-ligand
	40984(9×10 ³)	-	Intra-ligand
	38760(1.5×10 ⁴)	-	Charge transfer
	-	25063(8.7×10 ²)	d-d transition
	-	16026(2.5×10 ²)	d-d transition

[Ni(MINAP)(Met)·2H ₂ O]	46729(2.0×10 ⁴)	-	Intra-ligand
	41841(2.2×10 ⁴)	-	Intra-ligand
	40650(1.0×10 ⁴)	-	Intra-ligand
	39526(1.2×10 ⁴)	-	Charge transfer
	-	24876(4.0×10 ²)	d-d transition
	-	15106(1.7×10 ²)	d-d transition
[Ni(MINAP)(Phe)·2H ₂ O]	44053(2.1×10 ⁴)	-	Intra-ligand
	40816(2.5×10 ⁴)	-	Intra-ligand
	39526(9×10 ³)	-	Intra-ligand
	38911(1.6×10 ⁴)	-	Charge transfer
	-	25126(9.1×10 ²)	d-d transition
	-	15848(4.0×10 ²)	d-d transition

Where ^a : at 10⁻⁴M concentration; ^b : at 10⁻³M concentration.

Fig. 2: Ultraviolet Spectrum of [Ni(MINAP)(Leu)·2H₂O]Fig. 3: Visible Spectrum of [Ni(MINAP)(Leu)·2H₂O]

Thermal Measurements

The simultaneous TG-DTA studies of the complexes was recorded in nitrogen atmosphere by increasing the temperature from room temperature upto 900°C at the heating rate of 10°C/min. All the complexes investigated shows similar behaviour in their thermograms. The thermogram of the representative complex [Ni(MINAP)(Val)·2H₂O], is shown in Figure-4 exhibit three steps. In the first step the complex losses two water molecule in the temperature range between 100°C to 260°C indicates that the complex is thermally stable up to nearly 100°C above which it loses the water molecule. The DTA curve of complex displays an endothermic peak at 100°C, which is attributed to the loss of two water molecules.

The dehydrated product is stable up to 260°C above that temperature the second step starts. The complex loses some moiety in the temperature range between 260°C to 375°C which could be attributed due to loss of the amino acid ligand. The third step involving the loss of MINAP ligand in the temperature range between 375°C to 540°C Table-4. In thermogram the sudden decrease in the slope suggests a simultaneous loss of ligands from the complex which is also reflected by the strong endothermic peak by the DTA curve. There can also be significant contribution to this effect from the spontaneous oxidation of the final metal powder formed in the decomposition process into NiO which is confirmed by X-ray analysis ²⁵.

The perusal of thermograms shows the presence of water molecule in the complexes which further corroborates the observation made on the basis of infrared spectral studies and is in good agreement with the elemental analysis presented in Table-1. On the basis of physico-chemical studies, the proposed bonding and structure in the metal complexes can be represented as shown in Figure-5.

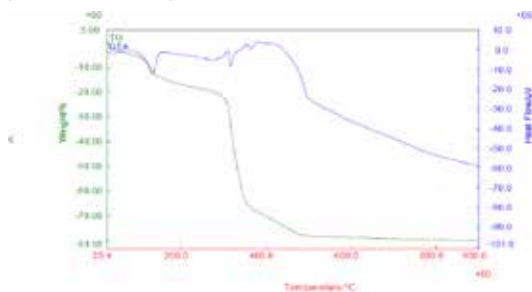


Fig. 4: TG/DTA Thermogram of [Ni(MINAP)(Val)-2H₂O]

Table 4: Thermal data for CML Ni(II) complexes

Complex	Temperature Range (°C)	% Weight loss		Decomposition product
		Found	Calculated	
[Ni(MINAP)(Ala)-2H ₂ O]	100-260	10.34	10.44	[Ni(MINAP)(Ala)]
	260-375	25.43	25.83	[Ni(MINAP)]
	375-540	46.56	46.72	[NiO]
[Ni(MINAP)(Val)-2H ₂ O]	120-260	9.42	9.66	[Ni(MINAP)(Val)]
	260-375	31.22	31.40	[Ni(MINAP)]
	375-540	42.76	43.20	[NiO]
[Ni(MINAP)(Leu)-2H ₂ O]	110-260	9.14	9.31	[Ni(MINAP)(Leu)]
	260-375	33.37	33.89	[Ni(MINAP)]
	375-540	41.42	41.64	[NiO]

[Ni(MINAP)(Met)-2H ₂ O]	100-260	8.64	8.89	[Ni(MINAP)(Met)]
	260-375	36.37	36.83	[Ni(MINAP)]
	375-540	39.42	39.78	[NiS]
[Ni(MINAP)(Phe)-2H ₂ O]	100-260	8.24	8.18	[Ni(MINAP)(Phe)]
	260-375	39.16	39.23	[Ni(MINAP)]
	375-540	38.12	38.27	[NiO]

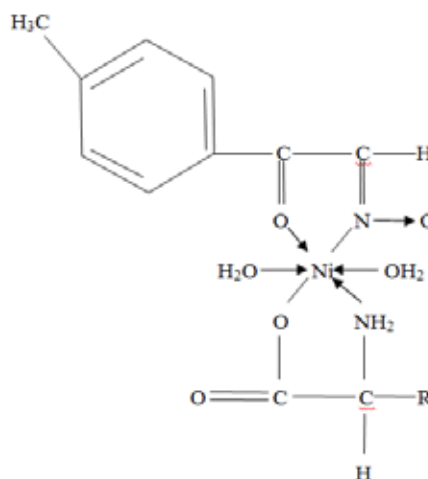


Fig. 5: Proposed structure of the complexes

Where, R = (CH₃) for Alanine

R = CH(CH₃)₂ for Valine

R = CH₂CH(CH₃)₂ for Leucine

R = (CH₂)₂SCH₃ for Methionine

R = CH₂C₆H₅ for Phenylalanine

CONCLUSIONS

Based on the above results the following conclusion may be drawn. The higher decomposition temperature and electrical conductance studies show the presence of strong metal-ligand bonding and non-electrolytic nature of the complexes, respectively. Specific rotation measurement studies are indicative of the chirality of the complexes. Room temperature magnetic studies are indicative of paramagnetic nature and an octahedral geometry of the Ni(II) complexes which is supported by the electronic spectra. The IR spectra show bonding of the metal through N- and O- donor atoms of the two ligands. Thermal analysis confirms the presence of coordinated water molecules.

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