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Synthesis and Characterisation of Chiral Cobalt Complexes

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ABSTRACT   *The reactions of Cobalt(II) sulphateheptahydrate with two different ligands such as sodium salt of p-methylisonitrosoacetophenone (MINAP) and various chiral amino acids (aa) formed a series of Ternary Chiral Mixed Ligand (CML) Co(II) metal complexes with general molecular formula [Co(MINAP)(aa).2H2O]. All the complexes have been characterised on the basis of elemental analysis, molar conductance, magnetic susceptibility, specific optical rotation, electronic absorption, infrared spectral and thermal studies. On the basis of results the bonding and structure of the complexes discussed in details.*

KEYWORDS : Cobalt, Chiral Amino acid, Ternary Chiral Mixed Ligand Complexes

INTRODUCTION
In recent years, the coordination complexes having two different ligands have importance from various chemical and biological point of view. Mixed ligand complexes of transition metals are commonly found in biological processes[1,2]. Schiff bases and their metal complexes have importance as biochemical[3], analytical[4], industrial[5] and antimicrobial[6] agents. Amino acids are well known chelating agents and play an important role in biological processes[7]. The amino acid compounds are biologically active having metabolic enzymatic activities[8] creating considerable interest in their metal complexes[9]. Ternary complexes containing an amino acid as a secondary ligand are potential models for enzyme metal ion substrate complexes[10]. The use of chiral additives in kinetic optical resolution of metal complexes is well known[11]. Light catalysed inversion[12] and diastereoisomeric equilibration[13] in chiral metal complexes have been studied extensively.

In continuation to our studies on chiral complexes the present paper reports the synthesis and characterisation of chiral mixed ligand Co(II) complexes of sodium salt of p-methylisonitrosoacetophenone as primary ligand and various chiral amino acids as secondary ligands.

EXPERIMENTAL
Materials and Methods
All the chemicals having Analytical Grade purity were used as received without further purification.The sodium salt of p-methylisonitrosoacetophenone which is a primary ligand in this study was prepared[14] by using the reported method. The various chiral amino acids which had a role of secondary ligand in this study were purchased from THOMAS BAKER.The solvents were distilled and purified according to standard procedures[15] before their use.

The Specific Optical Rotation (SOR) values $[\alpha]_D$ of all the Cobalt complexes in 0.01% DMF solution at 25°C were measured by using Jasco P-2000 Polarimeter. The FTIR spectra of all the ligands and their metal complexes in KBr were recorded on a Perkin-Elmer Precisely Spectrum 100 FT-IR Spectrometer between 4000-400 cm⁻¹region.

Synthesis of Ternary Chiral Mixed Ligand Co (II) complexes:
The mixture of an aqueous solutions (1 mmol) of Co(II) sulphateheptahydrate and sodium salt of p-methylisonitrosoacetophenone was stirred and kept in a boiling water bath for 30 minutes. An aqueous solution of the sodium salt of chiral amino acid (1 mmol) was added to this mixture. The final mixture (1:1:1 molar proportion) was heated for three hours in a hot water bath. Finally the solid complexes obtained by filteration, 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.

Co(II) + Na-MINAP + Na-aa → (-)[Co(MINAP)(aa)] + 2Na⁺
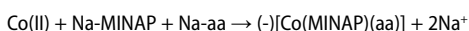
Where Na-MINAP is sodium salt of p-methylisonitrosoacetophenone and Na-aa is sodium salt of L-amino acid.

RESULTS AND DISCUSSION
Characterisation of metal complexes
All the complexes are brown 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 [Co(MINAP)(aa)·2H₂O]. The SOR $[\alpha]_D$ values at 25°C in 0.01% DMF solution were found to be negative and lie between -13.1° to -90.1° for all the complexes (Table-1) which supports to the chiral nature of complexes. The molar conductance values are very low indicating non-electrolytic nature of the complexes.

The complexes were prepared only in aqueous medium without use of any toxic or hazardous solvents. This process is non-polluting and eco-friendly which supports Green Chemistry approach.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.

Magnetic Susceptibility Measurements
TheGouy's method was used to measure magnetic susceptibility of all the Cobalt complexes at room temperature using the complexHg[Co(SCN)₄] as calibrant. The diamagnetic corrections were applied for the ligand components using Pascal's constants[16] and the effective magnetic moments were calculated. The μ_{eff} values for the Co(II) complexes are in the range 4.93-5.35 B.M., which are well within the range expected for octahedral Co(II) complexes[17].

Electronic Spectra
The10⁻⁴M solution of each of the complexes in DMF were used to record the electronic spectra in the ultraviolet region. Four bandswere observed in the ultraviolet region. The first two bands may be assigned to the π→π* transitions of the aromatic chromophore. The third band can be attributed to the n→π* transitions.Fourth band may be due to the ligand to metal charge transfer (LMCT) transitions. The visible and near-infrared region electronic absorption spectra of the Co(II) complexes in DMF solution shows two transition bands which may be attributed to d-d transitions.

Thermal Measurements
TheTG and DTA studies of the complexes were recorded in nitrogen atmosphere on Rigaku Thermo Plus-8120 TG-DTA instrumentby increasing the temperature from room temperature upto 900°C at the heating rate of 10°C/min. The thermograms of all the complexes consists of three steps. In the first step the two water molecules gets lost from complex at above 100°C temperature indicating the complexes

are thermally stable upto 100℃. The DTA curve of complex also displays an endothermic peak at about this region. The second and third steps can be due to simultaneous loss of ligands from dehydrated complex.

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)					μeff (B.M.)	[α]$_D$ (Degrees)
					Co	C	N	H	S		
[Co(MINAP)(Ala)·2H$_2$O]	C$_{12}$H$_{18}$CoN$_2$O$_6$ (345.21)	72	Brown	251	17.03 (17.07)	41.79 (41.75)	8.10 (8.11)	5.26 (5.25)	-	5.21	-23,2
[Co(MINAP)(Val)·2H$_2$O]	C$_{14}$H$_{22}$CoN$_2$O$_6$ (373.27)	72	Brown	255	15.81 (15.79)	45.02 (45.05)	7.52 (7.50)	5.93 (5.94)	-	5.02	-13.1
[Co(MINAP)(Leu)·2H$_2$O]	C$_{15}$H$_{24}$CoN$_2$O$_6$ (387.29)	74	Brown	248	15.23 (15.22)	46.50 (46.52)	7.20 (7.23)	6.29 (6,25)	-	5.35	-27.4
[Co(MINAP)(Met)·2H$_2$O]	C$_{14}$H$_{22}$CoN$_2$O$_6$S (405.33)	77	Brown	267	14.52 (14.54)	41.50 (41.49)	6.92 (6.91)	5.45 (5.47)	7.92 (7.91)	4.93	-90.1
[Co(MINAP)(Phe)·2H$_2$O]	C$_{18}$H$_{22}$CoN$_2$O$_6$ (421.31)	80	Brown	244	13.96 (13.99)	51.33 (51.31)	6.63 (6.65)	5.28 (5.27)	-	5.18	-41.2

Where [a] : MINAP represents the desalted primary ligand p-methylisonitrosoacetophenone, 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 complexes[18-20]

A broad band observed in the range 3632-3603 cm^{-1} due to asymmetric (asym) and symmetric (sym) O-H stretching modes are indicative of the presence of lattice water[21]. The v_{asym}(N-H) and v_{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 3571-3360 cm^{-1} and 3035-3028 cm^{-1} respectively, in the spectra of the complexes, suggesting coordination of the amino group through nitrogen with the metal ion. The v_{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. 851-810 cm^{-1} in the spectra of the complexes, confirming coordination through the amino group of the amino acids.

The v_{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 1652-1633 cm^{-1} and the v_{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. 1406-1384 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 (v_{asym}- v_{sym}) would increase as the M-O bond becomes more covalent, since the carboxylate stretching becomes correspondingly more asymmetrical[22]. In the present investigation, this difference being in the range 285-246 cm^{-1}

indicates that the Co-O bond have covalent character[23].

An important feature of the infrared spectra of the present 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 1514-1498 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 v(N→O) is observed in the range 1274-1223 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 1562-1546 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 700-618 cm^{-1} and 480-431 cm^{-1} may be ascribed to the Co-O and Co-N vibrations, respectively[21]. 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 [Co(MINAP)(Leu)·2H$_2$O] is shown in Figure-1.
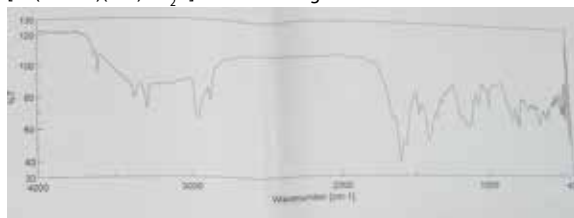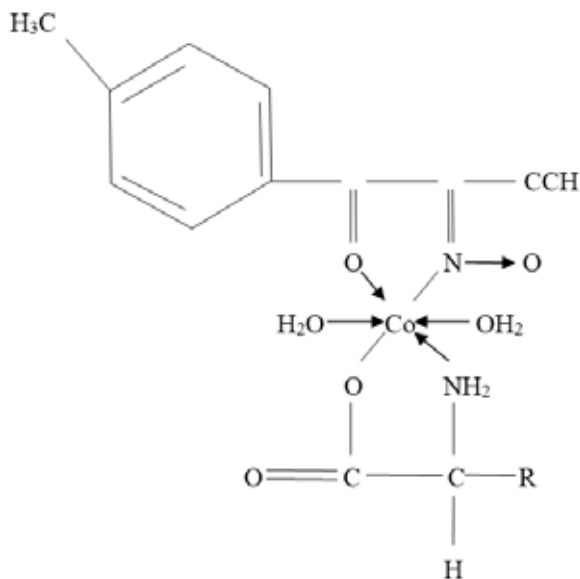

Fig. 1: FTIR Spectrum of [Co(MINAP)(Leu)·2H$_2$O]

Table 2: Some important infrared spectral bands (cm^{-1}) of CML Co(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)	v(C=O) (MINAP)	v(C=N) (MINAP)	v(N→O) (MINAP)	v(M-O)	v(M-N)
[Co(MINAP)(Ala)·2H$_2$O]	3631 W	3571 w	3035 w	1643 s	1384 s	817 S	1548 s	1514 m	1274 s	647[a] w 618[b] w	480[a] w 434[b] w
[Co(MINAP)(Val)·2H$_2$O]	3632 W	3568 w	3034 w	1640 s	1385 s	815 S	1546 s	1511 m	1269 s	676[a] w 635[b]w	469[a] w 454[b] w
[Co(MINAP)(Leu)·2H$_2$O]	3629 W	3549 w	3032 w	1652 s	1404 m	851 M	1562 m	1502 w	1271 s	678[a] w 619[b] w	467[a] w 442[b] w
[Co(MINAP)(Met)·2H$_2$O]	3603 W	3460 w	3033 w	1652 w	1406 w	810 S	1561 s	1507 m	1223 s	700[a] w 622[b] w	459[a] w 442[b] w
[Co(MINAP)(Phe)·2H$_2$O]	3603 W	3360 w	3028 w	1633 s	1401 s	813 M	1560 m	1498 w	1272 m	697[a] w 654[b] w	452[a] w 431[b] w

Fig. 2: Proposed structure of the complexes

Where, R= (CH$_3$) for Alanine

R=CH(CH$_3$)$_2$ for Valine

R=CH$_2$CH(CH$_3$)$_2$ for Leucine

R=(CH$_2$)$_2$SCH$_3$ for Methionine

R=CH$_2$C$_6$H$_5$ for Phenylalanine

CONCLUSIONS
Based on the above results the following conclusion may be drawn. The higher decomposition temperature shows the presence of strong metal-ligand bonding in the complexes. Specific rotation measurement studies are indicative of the chirality of the complexes.The IR spectra show bonding of the metal through N- and O- donor atoms of the two ligands. The magnetic, electronic and thermal studies supports the octahedral geometry of the complexes.

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