INTERNATIONAL JOURNAL OF RESEARCH IN PHARMACY AND CHEMISTRY

Available online at www.ijrpc.com

Research Article

SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC OF SOME TRANSITION METAL COMPLEXES WITH2-(6-METHOXYNAPHTHALEN-2-YL) PROPANOIC ACID

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ABSTRACT

Metal complexes of naproxen (Nap) have been synthesized and characterized by vibrational and electronic data,[1]HNMR, molar conductance measurement and the magnetic susceptibility. Cr (III), Fe (III) have (3:1) and Co (II), Hg (II) have (2:1) (ligand: metal) mole ratio and the carboxylate group of Nap acts as bidentate ligand. The suggested formula $[ML_3]$ where M= Cr (III), Fe (III) and $[ML_2]$ where M= Co (II), Hg (II). Conductivity measurement in DMF solvent showed that the complexes were non-electrolytic. From the result data monomer structure for all complexes were proposed, octahedral geometry for Cr (III), Fe (III) complexes and tetrahedral geometry for Co (II), Hg (II) were suggested.

Keywords: Naproxen, complexes of 2-(6-methoxynaphthalen-2-yl) propanoic acid

INTRODUCTION

Naproxen, 2-(6-methoxynaphthalen-2-yl) propanoic acid, is a member of the aryl acetic acid group of non-steroidal anti-inflammatory drugs (NSAIDs), that has been used as over the counter analgesic ,anti-inflammatory and antipyretic agent for decades[1]).Rare earth(III) complexes of Naproxen(HNap) have been synthesized and characterized. The elemental analyses reveal the presence of 1:3 (metal:ligand) stoichiometry and the IR spectra suggest the carboxylate group of HNap functions, as a bridging ligand to coordinate to RE(III) ions. The electronic spectra recorded in solid exhibit only slight shifts in visible regions, on which β, δ and $b^{\frac{1}{2}}$of covalent parameters have been calculated[2]. Naproxen is a poorly soluble anti-inflammatorydrug, the solubility of which canbe enhanced by complexation withbeta-cyclodextrin. Besides that, the inclusioncomplex reduces the incidence of gastrointestinal side effects of the drug. Complexes prepared using supercritical fluid technology showed similar properties to those of freeze-drying andspray-drying complexes as proved by DSC, FT-IRandUV[3].Copper(II) complexes with the non-steroidal anti-inflammatory drugs (NSAIDs) naproxen and diclofenac have been synthesized and characterized in the presence of nitrogen donor heterocyclic ligands (2,2'-bipyridine, 1,10-phenanthroline or pyridine) and biological properties of thecomplexes been also evaluated[4].The use of naproxen sodium–chitosan complexes (NSC) in retarding the drug release was explored and the effects of drying methods [SD and tray drying (TD)] used in preparing NSC on particle size, surface morphology, density, flow properties and compactability were evaluated[5].Industrial applications rely on the microencapsulation of solids and liquids by polymer coating and entrapment into polymer matrices, naproxen was successfully encapsulated in the enteric microparticales by the quasi-emusion solvent diffusion method[6].The present work investigates the synthesis and properties of Cr (III), Fe (III), Co (II) ,Hg (II) and characterize

their geometrical structures by using different physical techniques.

INSTRUMENTION

Melting points were recorded using Gallenkamp M.F.B. 600.01F of melting point apparatus. Infrared spectra were recorded using FTIR 8300 Shimadzu as KBr disk in the range (4000 - 600) cm^{-} .UV-Visible spectra were measured using Shimadzu UV-Vis 160A Ultra-violet spectrophotometer at room temperature using silica cells of 1.0 cmlength.^{1}H nuclear resonance analysis spectra wererecorded on a jeol 400 MHz spectrometer using DMSOas solvent and tetramethylsilane (TMS) as internal standard.Conductivity measurements of 0.001M ethanol solution of the complexes were measured at 25˚C by BC3020 Professional Benchtop conductivity meter Trans instruments.Magnetic susceptibility for the prepared complexes were obtained at room temperature using magnetic susceptibility balance JohnsonMattey catalytic system division

MATERIAL AND METHODS

Synthesis of potassium salt of naproxen (Nap)

Naproxen was dissolved with an equimolaramount of KOH solution in ethanol (10ml) and refluxed for 3 hours to give yellow precipitate which formed was isolated by filteration and recrystallized from ethanol.

Synthesis of naproxen complexes

Addition of ethanol solution of the[$CrCl_3.6H_2O$, $FeCl_3$., $CoCl_2.6H_2O$, $HgCl_2$] to an ethanol solution of potassium salt of naproxen was the starting point. The ratio (ligand: metal) of trivalent and divalent ions used were (3:1) and (2:1), respectively .After the reaction mixture has been refluxed for 2 hours, colored precipitateformed at room temperature. The solid complexes were isolated by filtration, washed with ethanol and finally driedin a desiccator over molecular sieves under vacuum.

RESULTS AND DISCUSSION

^{1}H NMR spectrum

^{1}H-NMR spectrum of the ligand (Nap), showed the following characteristics chemical shifts (DMSO as solvent),Table1: the doublet signal at δ (1.54) ppm is suggested to be of the proton of (C-CH_3), a signal at δ (3.72) ppm. is suggestedto be of the protons of (O-CH_3), The protons of (CH) occurs as atripletaround at δ (3.79) ppm. The multipletsignals at δ (7.02-7.84) ppm. is suggestedto be of protons of benzene ring. All these protons shiftsare up-field in the complexes[7].This is due to the lesser electron-withdrawing capacity of metal ions in the complexes relative to that of the carboxy proton in the ligand.

Infrared spectra

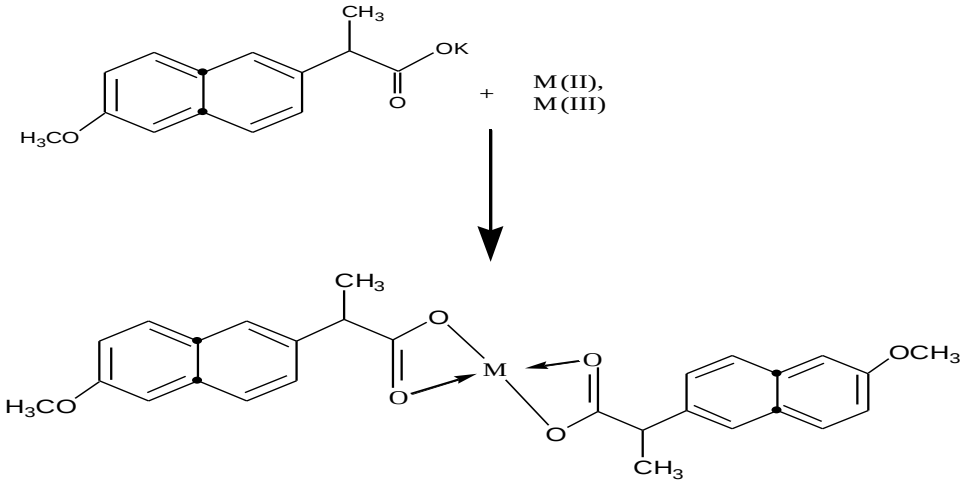
IR spectrum of Nap ligand:The carboxylate ion coordinates to metal ion in one of the three main ways:If the values of $\Delta\upsilon$ COO [$\Delta\upsilon = \upsilon_{asym.}(COO)-\upsilon_{sym.}(COO)$]< 200 cm^{-} ; carboxylate group of these compounds can be considered to be bidentate.If the value of $\Delta\upsilon$ >350cm^{-} ,thenthe carboxylate group binds in a monodentatebehavior. In compounds where $\Delta\upsilon$ >200 cm^{-} and < 350 cm^{-} an intermediate state between monodentatae and bidentateoccurs[8]. The IR data ofNap and its complexes are shown in Table (2). The υ(C=O) stretching mode of the carboxylic acid group is observed at 1729 cm^{-} . This band disappears on deprotonation and in the Nap salt there are two new bands appear at υ_{as}(COO)1600 cm^{-} and(COO)υ_{s}1452 cm^{-} [9].The values of $\Delta\upsilon$ for all complexes appeared in the region 150 - 187 cm^{-} which is less than 200cm^{-} indicating the carboxylate group as bidenate ligand.Stretching vibration bands of metal-oxygen complexes appeared in the region (478-420)cm^{-}.

Ultraviolet-visible spectroscopyand magnetic moment

The ultraviolet visible spectrum of Nap in DMF solvent showed bands at (253 and 310 nm)these transitions attributed to$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions[10-11].Cr (d^3)has three bands at 698,574 and 333nm.Co(d^7) has bandat579 nm. Fe(d^5) and Hg(d^{10})have spin-forbidden d-d bands.These bands are shown in Table (3).The magnetic moment for CrNap andFeNapcomplexesare approximately 3.2 and 5.1 B.M., respectively for octahedral geometry. $\mu_{eff.}$CoNap complex is 4.2 B.M. refer to tetrahedral geometry.HgNapcomplex is diamagnetic[12-13]. Molar conductivity measurement in DMF solvent at 25 ˚C showed that all the prepared complexes have non-electrolytic behavior.

CONCLUSION

Complexes of Nap were synthesized and characterized. The molar conductivity in DMF solvent showed that the complexes were non-electrolytic. The Nap acts as bidentateligand through the carboxylate group. Monomer structure for all complexes was proposed, octahedral geometry for Cr (III), Fe (III) complexes and tetrahedral geometry forCo (II), Hg (II) were suggested.



M(III)=Cr(III),Fe(III)
M(II)=Co(II),Hg(II)

Table 1:[1]HNMR spectral data(δ,ppm) of the ligand and its complexes

Compound	C-CH_3	O-CH_3	CH	CH aromatic ring
Nap	d(1.54)	s(3.72)	t(3.79)	m(7.02-7.84)
Complex	d(1.56)	s(3.70)	t(3.80)	m(7.16-7.86)

Table 2: IR data of Nap with complexes

Compound	$\upsilon_{asym.}$ (COO)	$\upsilon_{sym.}$ (COO)	$\Delta\upsilon$
Nap	1610	1452	148
CrNap	1604	1417	187
FeNap	1600	1423	177
CoNap	1602	1425	177
HgNap	1600	1450	150

Table 3: Electronic spectra, molar conductivity and magnetic moment for ligand and its complexes

Compound	Color	Band, nm	Assignment	Molar Conductivity µs	Magnetic Moment B.M.	Suggested Structure
Nap	Yellow	253 310	π →π* n→π*	-	-	-
CrNap	Light green	574 333 319 274	^4A_2g (F)→ ^4T_2g (F) ^4A_2g (F)→ ^4T_1g (F) n →π* π→π*	17	3.2	Octahedral
FeNap	Dark yellow	332 319 275	Charge transfer n →π* π→π*	19	5.1	Octahedral
CoNap	Blue	579 309 239	^4A_2g (F)→ ^4T_1g (P) n →π* π→π*	12	4.5	Tetrahedral
HgNap	White	333 271	n →π* π→π*	16	0.0	Tetrahedral

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