

Spectroscopic Investigation on Some Macrocyclic Complexes of Cu(II), Ni(II) and Co(II)

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Transition metal complexes of Cu(II), Ni(II) and Co(II) with the macrocyclic ligands have been synthesized. These macrocyclic complexes were characterized on the basis of spectroscopic investigation using infrared spectra, electronic spectra and NMR spectra. Additional evidence for the structure of the macrocyclic complexes have been collected from ESR spectra while conclusive evidence has been obtained from X-ray crystallography.

Key Words: Cu(II), Ni(II), Co(II) Complexes, Macrocyclic, NMR, IR, UV.

INTRODUCTION

A variety of complexes of macrocyclic ligands with first row transition metals have been reported. Macrocyclic ligands have ability to stabilize coordination ions in wide range of oxidation states, such as 20- and 22-membered binuclear macrocyclic complexes of Co(II) and Ni(II) with 2,3,6,7,12,13,16,17-octamethyl-1,4,5,8,11,14,15,18-octaazacyclododecane-1,3,5,7,11,13,15,17-octane and 2,3,6,7,13,14,17,18-octamethyl-1,4,5,8,12,15,16,19-octaazacyclodecaaza-1,3,5,7,12,14,16,18-octene have been synthesized¹ by reaction of 2,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione with 1,2-diaminoethane and 1,3-diamino propane in the presence of the respective metal ions.

EXPERIMENTAL

All the metal salts solution were prepared from AR Grade Chemicals. Different macrocyclic ligands have been prepared by methods as reported in the literature¹⁻⁷.

Preparation of complexes from macrocyclic ligands: Both Cu(II) and Ni(II) react directly with the macrocyclic ligands in aqueous methanolic, ethanolic solution to give respective metal complexes⁸.

Cobalt(II) on interaction with the ligand in aqueous solution gives the corresponding cobalt(III) oxygen adducts $LCo^{III} \cdot O-O-Co^{III}L$ called the peroxo complexes. Mixtures of cobalt(II) and macrocyclic ligand solutions on oxygenation (aeration) and subsequent treatment with concentrated HCl gives⁹, the green coloured *trans* dichloro complexes, *trans* $(CoLCl_2)^{2+}$. In the case of *C-rac*-Me₂ cyclam and *C-meso*-Me₂ cyclam, following this route the pink coloured *cis*-dichloro complexes (*cis*-

(CoLCl₂)²⁺, have also been isolated. The *trans*-dichloro complex can also be prepared by reacting the macrocyclic ligand hydrochloride or perchloric acid with this (carbonato) cobalt(II) in methanolic solutions and subsequent treatment with conc. HCl. This route leads only to the *trans*-dichloro species. The *trans*-dichloro complexes are highly stable and undergo axial substitution reaction to give a variety of *cis*- and *trans*-cobalt(III) macrocyclic complexes.

Spectral characteristics: The infrared spectra of the macrocyclic complexes exhibit quite complicated patterns. However, certain important features can be identified which give valuable information about their structures (Table-1). The infrared spectra of the macrocyclic complexes show bands at (3200 cm⁻¹) due to ν(NH)¹⁰ and 1600 cm⁻¹ due to ν(C=N). The frequency of the secondary amine group, (NH), is lowered by hydrogen bonding and raised by increasing the coordination number of the metal to which it is bound. In the case of Co(III), Cu(II)¹² and Ni(II) complexes, the spectra show bands corresponding to the axial ligands in addition to the above bands. The skeletal vibrations of the macrocycles reflect changes in the geometry of macrocycle. Marked changes occur with different ring conformations. The spectra in 1350-750 cm⁻¹ region is used to distinguish the isomeric compounds.

TABLE-1
TYPICAL INFRARED ABSORPTION BANDS FOR
SOME MACROCYCLIC COMPLEXES

Compounds	ν(N-H)	ν(C=N)	Prominent absorption band (cm ⁻¹)	
			C-10	Other ligands bands
L ⁺ 2H ClO ₂	3160	1655	1100,625	-
NiL ⁺ (ClO ₄) ₂	3220	1650	1095,627	-
CuL ⁺ (ClO ₄) ₂	3240	1668	1100,628	-
<i>trans</i> -CoL ⁺ (Cl ₂)(ClO ₄)	3225	1660	110,625	
<i>trans</i> -CoL ⁺ (NO ₂) ₂ (ClO ₄)	3180	1658	1090,624	1400 asy (NO ₂) 3141 sym (NO ₂) 823 (NO ₂)
<i>trans</i> -CoL ⁺ (NH ₃) ₂ (ClO ₄) ₃	3300	1665	1095,626	3140,3000 NH 825
<i>trans</i> -CoL ⁺ (SCN ₂)(SCN)	3160	1660	-	2100 (O N Coord) 2040 (O N ionic) 840 (S-C Coord)
<i>cis</i> -(CoL ⁺ CO ₃)(ClO ₄)·5H ₂ O	3160	Masted	1095,626	1660 CO non bonded 1630 1250 810 (C + CO) 755

Rac- and *meso*[Ni(*trans*[14]diene)]²⁺ and [Ni(*cis*[14]diene)]²⁺ can be easily distinguished on the basis of their IR spectra.

A comparison of the spectra of *cis*(CoL(aa)ⁿ⁺ (where aa = CO₃²⁻ or acac⁻¹) with that of *trans*-(CoL Cl₂)⁺¹ reflects the difference between the folded geometry of the microcycle in the former and the planar geometry of the latter. Bands observed in

the chlorocomplex are either not observed in the holded complex or are shifted in their position. Further the $\nu(\text{NH})$ band generally appears as a doublet in the $\text{cis}(\text{CuLX}_2)^{\text{n+}}$ complexes.

Electronic spectra: The electronic spectra of the macrocyclic complexes (Table-2) have been assigned on the basis of molecular orbital diagrams and the ligand field parameters evaluated in a number of cases. The appearance of characteristics bands in the spectra of these complexes is taken as an indication of the geometry associated with these complexes. The Cu(II) complexes show colours varying from red to blue, depending on the strength of macrocyclic ligand field. The four coordinate square planar, Cu(II) complexes show a single $d-d$ band¹¹ in the visible region between 19300 and 16000 cm^{-1} . This broad band is due to an overlap of the ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transition¹².

TABLE-2
TYPICAL ELECTRONIC SPECTRAL BANDS FOR
SOME MACROCYCLIC COMPLEXES

Complex	λ_{max} (cm^{-1})	$\text{M}^{-1} \text{cm}^{-1}$
$(\text{CuL}^1)(\text{ClO}_4)_2$	19,685	(92)
$(\text{CuL}^2)(\text{ClO}_4)_2$	19,900	(100)
$(\text{NiL}^1)(\text{ClO}_4)_2$	21,413	(64)
$(\text{NiL}^2)(\text{ClO}_4)_2$	21,600	(116)
$\text{trans}-(\text{CoL}^1\text{Cl}_2)(\text{Cl}_2\text{H}_2\text{O})$	16,026	(33)
$\text{trans}-(\text{CoL}^1(\text{NO}_2)_2)(\text{ClO}_4)$	22,624	(185)
$\text{cis}-(\text{CoL}^3(\text{glycine}))(\text{ClO}_4)_2$	20,405	(89)
$\text{cis}-\text{CoL}^4(\text{acac})(\text{ClO}_4)_2$	20,080	(162)
$\text{cis}-\text{CoL}^5\text{Cl}_2(\text{ClO}_4)$	18,726	(77)
$\text{cis}-\text{CoL}^5\text{CO}_3(\text{ClO}_4)$	15,873	(34)
$\text{cis}-\text{CoL}^5\text{CO}_3(\text{ClO}_4)$	19,048	(215)
$\text{trans}-\text{CoL}^5\text{ClNO}_2(\text{ClO}_4)$	19,685	(71)

${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$
 where: $\text{L}^1 = \text{Me}_2$ 14 ane; $\text{L}^2 = \text{Cyclam}$; $\text{L}^3 = \text{Me}_2$ 14 diene; $\text{L}^4 = \text{Me}_4$ 14 diene;
 $\text{L}^5 = \text{C-rac Me}_2$ 14 ane

The ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transitions is equal to the difference in the energies of d_{xy} and $d_{x^2-y^2}$ orbitals, *i.e.* equal to the inplane 10 Dq or $10 \text{ Dq } xy$ ¹³. This is close to the other two transition and hence appears merged with them. The maximum of this band approximately gives the values of $10 \text{ Dq } xy$. The square planar Ni(II) complexes also show a characteristics transition around 22,500 cm^{-1} corresponding to ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ transition. A number of Ni(II) complexes show a broad band in this region with a low extinction coefficient, the value of which increases with an increase in temperature or an increase in the ionic strength. This behaviour is due to an equilibrium (octahedral planar) existing in these complexes. The broad band is due to a combination of ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ of octahedral Ni(II) and ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{1g}$ of square planar Ni(II). The thermodynamic parameters and the percentage octahedral, % planar species at a

particular temperature can be evaluated by studying the spectral changes at different temperatures.

The octahedral Ni(II)¹⁴ complexes exhibit bands at 28000 cm⁻¹ (³A_{2g}→³T_{1g}(P), 19000 cm⁻¹ ³A_{2g}→³T_{1g}(F) and 1300 cm⁻¹ (³A_{2g}→³T_{2g}. In case of complexes with a symmetry lower than octahedral the ³A_{2g}→³T_{2g} band shows splitting.

The *trans*¹⁵(CoN₄X₂)ⁿ⁺ complexes have a basic D_{4h} symmetry with (¹A_{2g}→¹T_{1g} (Oh) splitting into two components, (¹A_{1g}→¹E_{1g} (D_{4h}) and (¹A_{1g}→¹A_{2g} (D_{4h}). When the tetragonal splitting is not very large (where x and n do not differ greatly in the spectrochemical series) only a single absorption band is observed under the ¹A_{1g}→¹T_{1g} (Oh) envelope. The appearance of these bands in a particular region indicates the geometry of these complexes. The CoN₆, CoN₅O or *cis*-CoN₄O₂ chromophores exhibit two bands associated with ¹A_{1g}→¹T_{2g} (Oh) and ¹A_{1g}→¹T_{2g} (Oh) transition¹⁶.

NMR spectra: The ¹H NMR spectra of the macrocyclic complexes helps to identify the macrocyclic structure. ¹H NMR spectra of [Ni(Me₄[14]diene)]²⁺ show resonance corresponding to -CH₂ groups, amine dimethylene, imine dimethylene and methylene protons. The most prominent feature of the spectra is the appearance of three equally strong methyl resonance in the high field position of the spectra, due to the 6 methyl groups on the macrocycle which are pair-wise equivalent. The location of geminal carbon atom produces an axial and equatorial difference between the two geminal methyl groups. The three types of methyl groups associated¹⁷. With the complexes are: (i) CH₃-I, the imine methyl group is oriented in an equatorial manner and is essentially in the NiN₄ plane (ii) CH₃-II, the axial methyl groups of geminal pair lying over the NiN₄ plane and (iii) CH₃-III, the equatorial geminal methyl groups lying out away from the metal in centre with their bond axis roughly parallel to the NiN₄ plane. In the case of an analogous dieno complex, [Ni[14]dieneN₄]⁺, the methyl resonance shows a downfield shift since the methyl groups are now adjacent to localized amine bonds and therefore deshielded to a greater extent. The imine methylene resonance also spreads down field due to the deshielding effect and this downfield shift obscures the NH resonance¹⁸. The ¹H NMR spectra of complexes containing macrocycles with aromatic ring shows additional resonance due to the phenyl ring between 6.7 and 7.6 ppm.

In the case of [CoMe₄[14]diene)]²⁺ the single methyl occurs as a doublet at 1.46 ppm due to coupling with the single proton on C-7 and C-14. The imine methyl occurs further downfield as a singlet at 2.51 ppm.

In the case of Ni(II) complex of this macrocyclic, the axial methyl occurs as a doublet at 1.2-1.3 ppm. There is evidence that the order of assignment of the methyl resonance in cobalt(III) relative to nickel(II) complexes is reversed with the axial substituent at higher field. Therefore for *N-rac*[N₂[Me₆[14]diene)]²⁺, the equatorial methyl occurs at 1.35 ppm and axial methyl at 2.16 ppm. For *trans-N-meso*[Co[Me₆[14]diene)Cl₂]⁺ and the corresponding *N-rac*-isomer, the equatorial methyl occurs at 1.68 ppm and the axial methyl appears at 1.37 ppm.

The NMR spectra can also be used to monitor the course of a reaction to form a macrocyclic complex. The NMR spectra is scanned at regular intervals till no further changes are observed. The structure of some macrocyclic complexes has been established on the basis of ^{13}C NMR spectra also (Table-3).

TABLE-3
 ^1H NMR RESONANCES OF SOME MACROCYCLIC COMPLEXES

Complex	Solvent	CH_3 groups			Resonance amine dimethylene
		III	II	I	
<i>meso</i> -[Ni(Me ₆ [14]diene)](SCN) ₂	D ₂ O	1.76	2.21	2.69	3.11
<i>meso</i> -[Ni(Me ₆ [14]diene)](SCN) ₂	H ₂ O	1.72	2.18	2.67	3.14
[Ni[14]dienoN ₄]PF ₄	CD ₃ COCD ₃	1.93	–	–	–
[Ni[14]dienoN ₄]NO ₃	CDCl ₃	1.90	–	–	–
[Co(PhTIM)Br ₂]Br	CF ₃ COOH	–	–	–	–
[Co(MePhTIM)Br ₂]PF ₆	CD ₃ -O ₂	2.47	–	–	–

Additional evidence for the structure of a macrocyclic complex has been collected from ESR spectra while conclusive evidence has been obtained from X-ray crystallography.

RESULTS AND DISCUSSION

The compounds were found insoluble in common organic solvents and soluble in dimethyl formamide, dimethyl sulfoxide, dichloromethane and nitromethane.

In the case of macrocyclic ligands, configurational isomers are possible, both due to chiral carbon and chiral nitrogen centres. Me₂[14]ane can exist in two, isomeric forms, 'tet a' or *meso* and 'tet b' or *rac*-conformations. Each of these two isomers is capable of forming a blue and red copper(II) complex. The blue and red isomers differ in the relative configurations of two hydrogen on the chiral nitrogen's in the ring. This has been proved by X-ray structures determination. The blue complex is formed in neutral or slightly acidic solutions and is readily converted into thermodynamically more stable red isomer at higher pH^{1,2}.

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