Design, synthesis and characterization of macrocyclic ligand based transition metal complexes of Mn(II), Fe(II), Co(II), Ni(II)and Cu(II) metal ions

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Abstract

Some new complexes of Mn(II), Fe(II), Co(II), Ni(II)and Cu(II) metal ions were synthesized of macrocyclic ligand derived from 2,6,diacetyl pyridine and 4-Hydrazino-4-oxobutanoic acid(succinic acid hydrazide) and the chelates were characterized by analysis ,magnetic , electronic and infrared spectral studies. The electronic spectra of the metal complexes indicate trigonal bipyramidal geometry of the complexes.

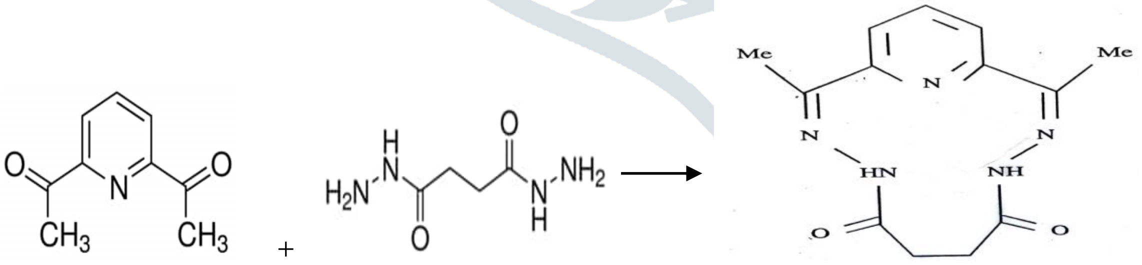
Keywords : Chelates, Geometry, spectra, Trigonal bipyramidal

Preparation of Dihydrazide :

Diethyl succinate was procured from Siscochem laboratories, Bombay. 0.1 mole (16 ml) of diethyl succinate was dissolved in 100 ml of ethanol and 0.2 mole (25ml) of hydrazine hydrate was added. The mixture was refluxed for one hour, concentrated to one third of its volume and cooled. The white crystals of dihydrazide precipitated were filtered ,washed with acetone ,ether and dried. Yield ~ 80%.

Synthesis and Isolation of Chelates:

0.05 mole of diacetylpyridine and 0.10 mole of succinic acid dihydrazide was dissolved in 100 ml of ethanol by refluxing for an hour. Divalent manganese, Iron , cobalt, nickel or copper salt (0.05 mole) dissolved in 100 ml of ethanol was added to each ligand solution separately. 1-2 drops of Glacial acetic acid were added and the solution is refluxed for four to six hours over a water bath. Different coloured solutions were concentrated to half of their volumes and kept in a vaccum dessicator for three days. The coloured crystals separated were filtered off, washed with water and recrystallized with ethanol and dried under vacuo over P_4O_{10} , Yield ~ 50%



2,6 diacetyl pyridine Succinic acid hydrazide Macrocyclic ligand

The nitrato complexes were prepared from metal nitrates. The bromo and thiocyanate salts were prepared by adding slowly potassium bromide and potassium thiocyanate solutions to ethanolic solutions of metal chlorides and stirring for three hours. The potassium chloride was filtered off and the filtrate was used to synthesize bromo and thiocyanate complexes of divalent metal ions.

The complexes are soluble in hot methanol and hot ethanol, but are insoluble in water and their thermal stability varies from 150^{o} to 300^{o}.

Physical Measurements :

(i)Magnetic measurements The magnetic measurements were made using Princeton Allied Research' vibrating sample Magnetometer, Model 155 incorporating digital read out. The electromagnet of the magnetometer was fed from a polytronic constant current regulator, type CP-200. The current was so adjusted as to produce a magnetic field of 5000 gauss. The instrument was calibrated using a standard nickel pellet and cross checked against $HgCo(CNS)_4$.

(ii) Infrared Spectral Measurements

Infrared spectra of the complexes in the conventional region (4000- 250 cm^{-1l}) were recorded on a Beckman IR-12 spectrophotometer in potassium bromide pellets.. Far infrared spectra (650-200 cm-I) were recorded in nujol mull on a Beckman IR-12 spectrophotometer.

(iii) Electronic Spectral Studies

The electronic spectra of the complexes at room temperature were recorded in nujol mull or dimethyl formamide on Carl Zeiss Specord UV-vis spectrophotometer .

(iv) Chemical Analyses and Estimation Of Metal Contents

The analyses of C. H and N were carried out by Micromalytical techniques. Halides were determined by Volhard's method.

The metal content in all the complexes were estimated as follows :

A known quantity of the complex was heated with a very small amount of concentrated sulphuric acid and then repeatedly with nitric acid until all the organic matter was decomposed. The residue was dissolved in doubly distilled water and made upto known volume from which the metals were estimated by standard methods . Mostly 0.1M EDTA was added to determine the metal contents volumetrically using Erichrome Black T, Sulphosalicylic acid r murexide as indicators.

Result and Discussion :

The analytical data shows that the chelates have the molecular formulae as **$[M(C_{13}H_{15}N_5O_2)X_2]$** where M =Mn(II), Fe (II) ,Co (II) , Ni (II) and Cu (II); and X = Cl, Br, NO_3 and NCS

The tests for anions are given only after decomposition of complexes, showing their presence inside the coordination sphere. The conductance measurements show them to be non electrolytes.

Table :1 Analytical data of Manganese ,Iron ,Cobalt ,Nickel and Copper Complexes

		Found % Calculated %					
Complex	**Colour**	**C**	**H**	**N**	**M**	**X**	**Mol wt**
$[Mn(C_{13}H_{15}N_5O_2)Cl_2]$	Brown	39.19(39.20)	3.76(3.80)	17.58 (17.52)	13.81(13.78)	17.58(17.52)	398
$[Mn(C_{13}H_{15}N_5O_2)Br_2]$	Light Brown	32.32--	3.01--	14.05 (14.00)	11.04 (11.00)	34.91(34.20)	498
$[Mn(C_{13}H_{15}N_5O_2)(NO_3)_2]$	Dark Brown	34.51---	3.31 ---	21.68(21.50)	12.16(12.20)	----	452
$[Mn(C_{13}H_{15}N_5O_2)(NCS)_2]$	Brown	40.54 --	3.37 --	22.07 (22.00)	12.39 (12.40)	-----	444
$[Fe(C_{13}H_{15}N_5O_2)Cl_2]$	Orange red	39.10(38.92)	3.76(3.58)	17.54 (17.60)	14.01(14.00)	17.54 (17.60)	398.9
$[Fe(C_{13}H_{15}N_5O_2)Br_2]$	Brown	31.26--	3.00---	14.03 (14.00)	11.28(11.20)	34.07(34.00)	498.9
$[Fe(C_{13}H_{15}N_5O_2)(NO_3)_2]$	Brown	34.44--	3.31---	21.63 (21.50)	12.34(12.40)	---	452.9
$[Fe(C_{13}H_{15}N_5O_2)(NCS)_2]$	Brown red	40.45--	3.37---	22.02 (22.00)	12.56(12.42)	---	444.9
$[Co(C_{13}H_{15}N_5O_2)Cl_2]$	Reddish	38.8(38.6)	3.37(3.75)	17.41 (17.50)	14.06(14.5)	17.41(17.38)	402

$[Co(C_{13}H_{15}N_5O_2)Br_2]$	Brownish yellow	31.08--	2.98---	33.86(34.00)	11.75(11.72)	33.86(33.82)	502
$[Co(C_{13}H_{15}N_5O_2)(NO_3)_2]$	Brown	34.21--	3.28---	21.49(21.50)	12.93(12.82)	----------	456
$[Co(C_{13}H_{15}N_5O_2)(NCS)_2]$	Red brown	41.47(41.50)	3.45(3.50)	22.58(22.60)	13.59(13.53)	-------------	434
$[Ni(C_{13}H_{15}N_5O_2)Cl_2]$	Dark green	38.32(38.80)	3.73(3.72)	17.42(17.50)	14.63(14.65)	17.42(17.40)	401.8
$[Ni(C_{13}H_{15}N_5O_2)Br_2]$	Green	31.08--	2.98---	13.94(13.92)	11.71(11.70)	33.87(33.90)	501.8
$[Ni(C_{13}H_{15}N_5O_2)(NO_3)_2]$	Dark Green	39.71----	3.81---	24.94(24.98)	14.94(14.96)	---------	392.8
$[Ni(C_{13}H_{15}N_5O_2)(NCS)_2]$	Dark Green	40.19--	3.34---	21.88(21.80)	13.13(13.20)	-----------	447.8
$[Cu(C_{13}H_{15}N_5O_2)Cl_2]$	Dark brown	38.37(38.50)	3.68(3.62)	17.20(17.25)	15.62(15.60)	17.22(17.25)	406.5
$[Cu(C_{13}H_{15}N_5O_2)Br_2]$	Brown	30.79--	2.95---	13.82(13.80)	12.53(12.60)	33.56(33.60)	506.5
$[Cu(C_{13}H_{15}N_5O_2)(NO_3)_2]$	dark Brown	33.87--	3.25---	21.28(21.30)	13.78(13.80)	---------	460.5
$[Cu(C_{13}H_{15}N_5O_2)(NCS)_2]$	Brown	39.77--	3.31---	21.65(21.70)	14.03(14.00)	---------	452.5

Infrared spectra : A free amide group may coordinate through its oxygen or nitrogen. Changes in the IR spectra of these chelates indicate that due to the absence of vibrations of free carbonyl and hydrazinic groups -NH_2 groups of dihydrazide have condensed with -C=O group of diacetyl pyridine. This is also clear that in these chelates nitrogen of amide moieties and pyridine nitrogen take part in coordination.

Pyridine ring Vibrations

The four v (C=C) and v (C=N) skeletal frequencies are found in the regions: 1590-1610 cm^{-I} (band I), 1560-1580 cm-I (band II), 1430- 1490 cm^{-1} (band III), and 1430-1440 cm^{-1} (band IV). In the spectra of the ligands these bands are found 1580 ,1500, 1505 and 1440 cm-I, respectively. On coordination with bivalent metal ions, a general shift of 2-4 cm^{-I} has been observed almost in every band. But the band 1580 cm^{-1} shows an upward shift (10-15 cm^{-1}). The increase in the frequency of vibrations is associated with C=C or C=N stretching (originating from the pyridine ring) vibration is indicative of coordination of the pyridine nitrogen to the metal atom. The magnitude of shift though small, is meaningful.

The ring breathing mode or vibration near 990 cm^{-I} is a reliable guide to coordination or the pyridine residue. Generally, on coordination of the pyridine nitrogen, this band increases in energy above 1000 cm^{-I}. In the spectra of the complexes, this band disappears and new bands appears at ~ 1014-1020 cm^{-I}. This small shift in the ring breathing mode suggests the coordination of pyridine nitrogen to the metal atoms.

Two strong bands are observed in the spectra of pyridine based ligands at ~ 795 cm^{-I} and 730 cm^{-I} are assignable to v (C- H) and θ (C-C) respectively .The band at ~ 730 cm^{-I} split into two components lying between 720 and 755 cm^{-I} Which indicates pyridine to metal coordination These ligands exhibited two bands ~ 810 cm^{-I} and ~ 730 cm^{-I} assignable to v (C-H) and θ (C-H) vibrations, respectively. The band assigned to θ (C-C) disappears and two bands appear ~ 720 and 800 cm^{-I}, respectively, indicating the pyridine-nitrogen coordination.

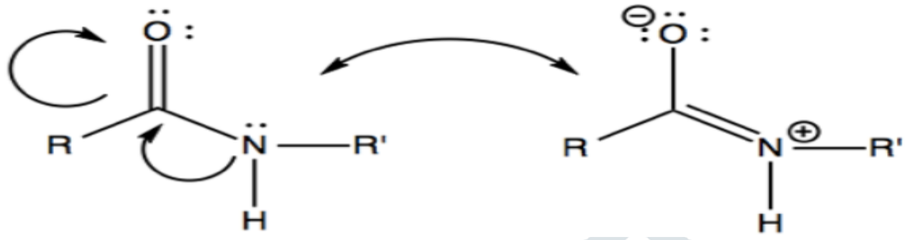
Pyridine and substituted pyridines generally exhibit one band near 400 cm^{-I} assignable to C-C deformation mode. which increases in frequency on coordination. The frequency increase depends upon the metal. In general, the more strongly bound the metal ion is, the greater increase in the frequency . In the spectra of complexes, these bands have been located around 415-432 and 430-434 cm^{-I}, respectively; this indicating the pyridine-metal coordination.

The various changes Observed in the spectra of complexes indicate the metal pyridine-nitrogen coordination. However, the shifts observed in the vibrations associated with v (C=C) or v (C=N), v ~(1580 cm") and C-C out-of-plane deformation (~400 and 415 cm^{-I}) are comparatively small . These small shifts may be interpreted in terms of weak interactions between metal and pyridine nitrogen. This fact is also supported by the appearance of weak to very weak v (M-N) (py) vibrations in the far infrared region. It, therefore, appears that pyridine nitrogen is feebly coordinated to the metals studied in present case.

Amide Group Vibrations

An amide group has two donor atoms, nitrogen and oxygen, and it depends upon the experimental conditions as to which one of them coordinates to the metal ion. The vibrations of interest are: amide I band [consists mainly of v (C=0) around 1680 cm-I, amide ll , amide Ill bands (arise from CN as well as from N-H) near 1520 and , 1240 cm^{-I} respectively, amide IV near 660 cm^{-I}, and amide VI around 480 cm^{-1} (arise through C=0 out-of-plane and C-O in-plane deformations modes), respectively.

The amide group generally exhibit characteristic bands ~ 1650, 1550 and ~ 1260 cm-I. These vibrations may be assigned to amide I, Il and amide Ill bands, respectively. In the spectra of all the complexes studied, amide I band shifts to higher frequencies (1670-1680 cm^{-I}), while amide Il band decreases in frequency (1535-1540 cm^{-1}) and amide Ill band appearing in regions ~ 1280 cm^{-1} showing an increase in frequency. These changes in the amide group bands indicate, the coordination of amide nitrogen to the metal atoms ,which may be explained by considering the structure of an amide group.
In a free acid amide out of these two resonance structures, structure Il predominates. On coordination through its oxygen atom, the contribution of structure Il increases. If coordination occurs through the nitrogen atom, its hybridisation would be sp^3 and the bond will become a complete double bond with the loss of the resonance energy.



Structure I **Structure II**

For an amide group coordinated through the oxygen atom, the amide I band will shift to a lower frequency and amide Il and Ill bands go to higher frequencies. On the other hand. if the amide-nitrogen atom coordinates, the amide I, Il and Ill bands would shift to the opposite directions. In other words, these changes may be explained by assuming the decrease of the double bond character of C=O group and the subsequent increase of the C-N double bond character.

The nitrogen coordination of amide group may further be confirmed by following the pattern of changes in amide IV and VI bands. In the spectra of the complexes. these two bands appeared ~630-640 cm^{-1} and 495-505 crn^{-1}, respectively. The shift in the frequency of the latter bond, thus indicates coordination through amide nitrogen. Finally. the coordination of nitrogen of amide group to the metal atoms is confirmed by the appearance of v(M-N) in the far infrared region or the spectra.

Strong absorption ~1580-1640 cm^{-I} are usually associated with phenyl ring vibrations. but the (C=N) group could also be responsible for it, as conjugated systems containing C=C and C=N both linkages often exhibit one or more strong bands between 1700 and 1500 cm^{-I}. It is usually not possible to identify such bands with particularly (C=C) or (C=N) linkage. On comparing the spectra of hydrazides and hydrazones a band ~1630 cm^{-I} with a shoulder ~1610 cm^{-I} may be assigned to symmetric and antisymmetric stretching vibrations of this group. These vibrations indicate that azomethine group is not taking part in these metal chelates.

Thus, the changes in the infrared spectra of these chelates it is apparent : due to the absence of the vibrations of free carbonyl and hydrazinic groups that -NH2 groups of dihydrazide have condensed with -C=O group of 2,6-diacetyl pyridine. This is also clear that in these chelates nitrogen of amide moieties and pyridine nitrogen take part in coordination.

Magnetic and electronic spectral studies :

The magnetic moments of Manganese II , Iron II , Cobalt II ,Nickel II and Copper II complexes (5.80-5.88 , 5.20-5.30, 4.20-4.50 ,2.42-2.65 and 1.65- 1.73 B.M. respectively) are well within the range reported for five coordinate geometry of the complexes.

The diffuse reflectance spectra of Manganese II complexes show bands at ~ 16500-17000 , 19200-20000 and 21500-22000 cm^{-1} which confirms the trigonal bipyramidal geometry with ligand molecules occupying a trigonal plane and anions are present on axial positions .Thus assuming D_{3h} symmetry for manganese ion , a d^5 system .The five d orbitals split into three orbital singlets and a doublet as $b_1(d_{x2-y2})$, $a_1 (d_{z}^{2})$,e (d_{xy} , d_{yz}) and $b_2(d_{xy})$.

The electronic spectra of iron II complexes show mainly one band in visible region ~ 12000 cm^{-1} and another one in near infrared region ~ 4000 cm^{-1}. The band in the region 12000 cm^{-1} indicate the five coordinate geometry of these complexes. The band at 12000 cm^{-1} can be assigned to $5_A \rightarrow 5_{E1}$ and possible band at ~ 4000 cm^{-1} may be $5_A \rightarrow 5_{E2}$ in trigonal bipyramidal field .

The electronic spectra of the Cobalt II complexes exhibit bands in the region ~ 6230-6350 ,13150-13250, 19750-19850 and 28400-28600 cm^{-1} which are comparable to high spin five coordinate geometry. Thus assuming the effective geometry to be D_{3h} for these complexes the spectral bands can be assigned to ~ 6300 , 4_{A4} -$4'_{E'}$, ~ 13200 , $4_{A'2}$- $4''_{E}$ and 19850 cm^{-1} $4_{A'2}$ -$4''_{E}$ (P) respectively which is well consistent with high spin five coordinate geometry.

The electronic spectra of the Nickel II complexes exhibit bands in the region ~ 7300-7500 ,10850-10950 ,15450-15550 ,23550-23650 and 27750-27850 cm^{-1} which exhibit five coordinate geometry around metal ion. Bands observed in the spectra may be assigned to 7500,$3_{E'1}$-$3_{E''}$,10900, $3_{E'1}$-$3_{A''2,}$ 15500 $3_{E'1}$-$3_{A\,2}$,23600 $3_{E'1}$-$3_{E'}$ (P) +$3_{A'\,2}$ (P) and 27800 cm^{-1} may be a charge transfer band. Therefore these complexes have a trigonal bipyramidal geometry.

Electronic spectra of copper complexes exhibit various bands in the region ~10300-10420, ~13650-13750 and 27000-27250 cm^{-1} consistent with five coordinate geometry. Thus assuming the effective geometry to be D_{3h} the spectral bands can be assigned to ~ 10350 ,$2_{A'1}$ -$2_{E'1}$ and 13700 cm^{-1} $2_{A'1}$ -$2_{E'1}$ respectively.

Far Infrared spectral studies

Some Of the important bands appear in the far infrared spectra of chelates at around 620, 550, 430 and 280 cm^{-1} and these may be assigned to in-plane ring deformation, NH

rocking, C-C out-of-plane deformation and C-C torsional modes, respectively. The bands appearing around 610 and 410 cm^{-1} are designated as 6a and 16b according to a terminology suggested by Eline and Turkevich some unassigned bands occur around 494, 360 , 235 ,226 and 204 cm^{-I}.

Out of the various pyridine ring vibrations the two appearing around 400 cm^{-1} (vibration16 b , of b_2 symmetry in the point group C_{2v} Of the molecule, an out-of-plane deformation) and at 610 cm^{-1}(vibration 6a, of symmetry a_1 , an in-plane ring deformation) suffer significant shifts towards higher frequencies on coordination of pyridine to metal .

Metal-pyridine Stretching Vibrations

The (M-N) stretching vibrations of pyridine complexes with divalent metals of first

transition series have been found to occur in the range 250- 280 cm-I Deviations from this range have also been observed. Only one band is shown between 235 and 334 i.e., at 280 which may be assigned to (C-C) torsional mode.

Some new bands are found in the region 250-285 cm-l in the spectra or divalent metal complexes. The exact ranges are: manganese (250-253cm^{-1}). iron (265 cm^{-1}), cobalt (260-270 cm^{-1}) ,nickel(260-274 cm^{-1}l) and copper (275-285 cm^{-1}) and these bands may be assigned to (Mn-py), (Fe-py), (Co-py). (Ni-py) and (Cu-py) stretching vibrations, respectively. These bands are well within the range reported for the respective metals. The weak intensity of metal-pyridine stretching vibrations is probably due to weak coordination of pyridine-nitrogen to the metal ions.

Metal-nitrogen Stretching Vibrations

Metal-nitrogen Stretching vibrations may be assigned by comparing spectra of similar type of complexes, and in turn with those of metal hydrazinic and related ligands. A number of new bands appear in the region 382-418 cm^{-I} for divalent metal complexes. These bands have originated from metal-nitrogen stretching modes.
For various metals the observed ranges are: manganese (382- 387 cm^{-I}), iron (385 cm^{-I}), cobalt (398-410 cm^{-I}). nickel (405-412 cm^{-I}), and copper (408-418 cm^{-I}) and these vibrations may be assigned to v(Mn-N), v(Fe-N). v(Co-N), v(Ni-N) and v(Cu-N) vibrations modes, respectively. In general, these bands are sharp and well defined, indicating the substantial interaction between divalent metal atoms and hydrazinic group.
Comparing the metal-nitrogen stretching frequencies, it becomes evident that increase of vibration modes with decreasing ionic radii and effective metal charge is more pronounced in the case of metal-oxygen stretching bands than metal-nitrogen bands. This is probably due to the greater contribution of the chelate-ring Vibrations which occur in the same range as v(M-N).
Thus, on the basis of infrared (both conventional and far infrared), it has been established that the succinic acid dihydrazide reacts with 2, 6-diacetyl pyridine to form a macrocycle, tridentate in nature, and the coordination takes place through the pyridine nitrogen and amide nitrogen of the macrocycle.

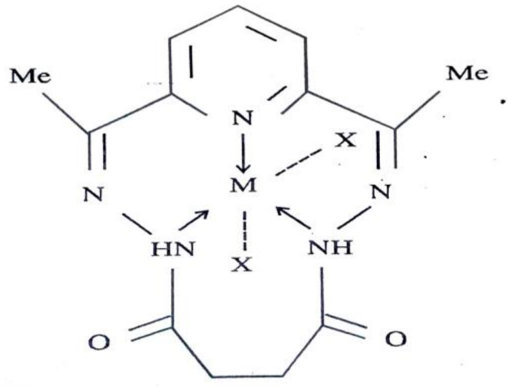
Assignment of Stereochemistry on the basis of 16b and 6a Vibrations of Pyridine Ring

The range of for various metal ions are manganese (410-412 cm^{-1}) iron (415 cm^{-1}), Cobalt (415-420 cm^{-1}) nickel (422-428 cm^{-1}) and Copper (435-436 cm^{-1}I) for 16b vibration; and Mn(620-630 cm^{-1}), Cobalt (335 cm^{-1}), Ni(635-645 cm^{-1}) and Cu(642-650 cm^{-1}), for 6a vibrations, respectively.

The magnitude of the ‘shifts' compared to four and six Coordination molecule is small. Both bands shift (50-80 cm^{-1}) and are weaker in transition metal complexes of the second and third transition metals than they are for those of the first transition series. However, ‘shifts' observed for the present complexes are in the range observed for the weakly-coordinated- pyridine-nitrogen in five coordinate complexes.

Both 16b and 6a bands seem to be the functions either directly of the metallic radii .In fact. as. the size of ionic radii decreases, the magnitude of ‘shifts' increase. The same pattern has been observed for the present complexes, i.e., the order of ‘shifts' in Mn < Fe < Co < Ni < Cu, which is in the decreasing order of ionic radii.

Based on the analysis, conductance', magnetic, electronic and infrared studies the following structure may be proposed for the metal chelates.



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