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SYNTHESES AND SPECTRAL PROPERTIES OF IRON(II) COMPLEXES WITH TETRAAZA(12) MACROCYCLIC LIGANDS.

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ABSTRACT

The iron(II) complexes of 1,4,7,10-tetraazacyclododeca-1,3-diene (L^1) and 2,3-dimethyl-1,4,7,10-tetraazacyclododeca-1,3-diene (L^2) have been prepared and studied by means of vibrational and electron spin resonance (esr) spectroscopy. Based on elemental analysis and spectroscopic properties, the structure for the complexes are proposed as follows: square pyramidal for [Fe(L^1-2H) H_2O] and [Fe(L^2-2H) H_2O] and distorted octahedral for [Fe(L^1-H) Py (OAC)].

Key words: Tetraazamacrocycle, Iron(II) complex, Vibrational, esr, spectra.

INTRODUCTION

The chemistry of metal porphyrins and metal corrins having cyclic N_4 donor atoms has been widely investigated up to the present time, because of their biochemical interest (Bowman-James, 1994) The iron-porphyrin complexes have been interesting subject for study (Walker, 1994) but the complexes of synthetic unsaturated N_4-macrocyclic ligands are scanty (Smith,1975). The physicochemical properties of transition metal macrocyclic complexes have been reported (Malik et al, 1983). The coordination nature of macrocyclic ligands depend on the ring size or coordination sites in the ring, the degree of flexibility of the ring and the hard or soft Lewis base behaviour of the donor atoms. (Drew et al, 1983). The M-N bond lengths for which the strain energy is a minimum in the transition metal complexes of 12 to 16 membered tetraaza macrocyclic have been calculated and the values range from 1.83 to 2.38A (Chantson and Hancock 1995). The much effort has been made towards the study of tetraaza(14) annulene macrocyclic ligands containing benzene (Sakata et al, 1985) pyridine (Sakata et al, 1989) and pyrazine (Hashimoto et al, 1988) rings. Further the tetraaza (14) annulene containing nitrile groups, which has no benzene and/or pyridine ring has been employed for preparing transition metal macrocyclic complexes (Sakata and Hashimoto, 1991 and 1992). The interest in the area is so much that several reports dealing with syntheses, reactivities and spectral properties of macrocyclic ligands and their complexes have been published (Kaden, 1992, Saha and Saha,1992, Shourong et al, 1995, Singh and Rana, 1989). From the literature search it appears that the information on tetraaza(12) macrocyclic ligands and their metal complexes are rare (Cummings and Sievers 1970, Rai and Prasad, 1994). The present article describes the syntheses and characterization of iorn(II) complexes containing macrocyclic ligands, which have been prepared by condensation of carbonyl compounds with triethylene tetraamine (trien) in the presence of iorn(II) cation.

MATERIALS AND METHODS

Materials:

Butane-2,3-dione, glyoxal (technical), N,N-dimethyl formamide (AnalaR), iron(II) sulphate heptahydrate (AnalaR), sodium acetate, and triethylene tetramine (technical) were obtained from BDH and used as they were received. All other reagents were supplied by Aldrich Company.

Physical Measurements:

Carbon, hydrogen and nitrogen analyses were carried out at Regional Sophisticated Instrumentation centre, CDRI, Lucknow, India. The IR and ESR spectra were recorded at Regional Sophisticated Instrumentation centre, I.I.T., Mumbai, India. The other physical properties were obtained as reported previously (Akinchan, et al, 1994)

Syntheses of Iron(II) macrocyclic complexes

(a) Synthesis of aqua (1,4,7,10-tetraazacyclododeca 1,3-dienato) Iron(II): [Fe(L^1-2H)H_2O]

A mixture of 10 mmol 1,8-diamino 3,6-

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diaza-octane (triethylene tetramine, trien) and glyoxal (10 mmol) in a blended solvent composed of N,N-dimethyl formamide (15 cm^3) and ethanol (15 cm^3) was refluxed under nitrogen with stirring for one hour. An aqueous solution of sodium acetate (20 mmol) and ethanolic solution ($20cm^3$) of iron(II) sulphate heptahydrate (10 mmol) was added successively to the above solution. The reaction mixture was further refluxed under nitrogen with stirring for four hours. On slow cooling at room temperature dark brown microcrystalline product was isolated by filteration and washed with ethanol and then with diethylether.

M. pt. 145-6°c, Anal: (found; C=39.78, N =28.19, H=6.68; calc for Fe C_8 $N_4H_{16}0$; C= 39.98, N=28.41, H =6.71%) IR/cm^{-1}; v(OH) 3414,v/C =N) 1598, v(C=C) 1418, diimine stretch 1214, rocking (H_20) stretch 858, wagging (H_20) stretch 573, v(Fe-N) 537, v(Fe-0) 451.

(b) Synthesis of aqua. (2,3-dimethyl-1,4,7,10-tetraazacyclododeca-1,3-dienato) iron(II):

[Fe(L^2-2H)H_2O]

It was prepared exactly as described above by replacing butane-2, 3-dione for glyoxal for the condensation reaction with iron (II) cation.

M. PT. 154-6°C, Anal: (found; C= 44.67, N = 20.84, H= 7.44; calc for $FeC_{10}N_4H_{16}0$; C =44.75, N=20.96, H=7.51%) IR/cm $^{-1}$; v(OH) 3412, v/C=N) 1596, v(C =C) 1418, diimine stretch 1216, rocking (H_20) stretch 828, wagging (H_20) 564, v(Fe-N) 530, v(Fe-0)452.

(c)Synthesis of acetato, pyridine, (1,4,7,10-tetaazacyclododeca-1,3-dienato) iron(II): [Fe(L^1-H)Py(OAC)]:

A mixture of trien (10 mmol) and glyoxal (10 mmol) in a blended solvent composed of N,N-dimethyl formamide (15cm) and ethanol (15cm) was refluxed under nitrogen with stirring for one hour, An aqueous solution of sodium acetate (20 mmol) was added, followed by ethanolic solution (10 mmol) of iron(II) sulphate heptahydrate. The reaction mixture was refluxed under nitrogen with stirring for four hours and to it pyridine (10 mmol) was introduced. The refluxing continued for another one hour. On slow cooling at room temperature the dark brown microcrystalline product was isolated, washed with ethanol and then with diethylether.

M. pt. 160°c(D), Anal: (found; C = 49.56, N = 19.45,H =7.10;calc for $FeC_{15}N_5H_{22}0_2$; C=50.01, N=19.44, H=6.16%) IR/cm^{-1}; v(NH) 3228, v_{as} (COO^-) 1630, v(C=N) 1594, v(C=N) Py 1552, v(C=C) 1422, v_s (COO^-), 1386, diimine strech 1214, v(Py in plane vibration) 612, v(Fe-N) $_{ring}$ 526 v(Py out of plane vibration) 436.

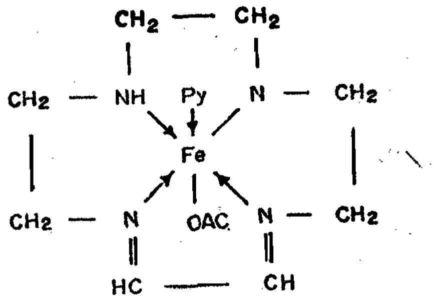


Figure1: Structure [Fe L^1-H) Py(OAC]

RESULTS AND DISCUSSION:

On the basis of analytical data the iron (11) macrocyclic compexes could be formulated as Fe(L^1-2H) H_20, Fe(L^2-2H)H_20 and Fe(L^1-H) Py(CH_3COO). The esr parameters of each iron(II) complexes have been reported in Table 1. The data presented in experimental section will be used to discuss the coordination modes of macrocyclic ligands.

Infrared Spectra of [Fe(L^1-2H)H_2O] and [Fe(L^2-2H)H_2O]:

The following observations are made after examining the ir spectra of iron(II) complexes under inrestigation. The ir spectra of these complexes show bands in the region 1590-1600, and 1410-$1420cm^{-1}$ assignable to V(C=N) and V(C=C) stretehing vibrations respectively (Sakata et al, 1991, 1992). The presence of these bands coupled with absence of any absorption attributable to NH_2 and free; C=O groups provide strong evidence that both terminal NH_2 groups of trien must have condensed with both oxygen atoms of glyoxal or butane-2, 3-dione. Similar observations have been made by Cummings and Sievers (1970), as well as, Rai and Prasad (1994). Although, the iron(II) sulphate was used for the preparation, but the ir spectra of these complexes are unable to show the stretching vibrations due to either ionic or coordinated sulphate anion (Nakamoto, 1978). Furthermore, the ir spectra of these iron(II) complexes exhibit

Table1: Electron spin resonance (esr) spectral parameters for iron(II) tetraaza macrocyclic complexes.

Iron(11) Complexes	Matrix	Temp	g_{iso}	Peak to peak width gauss) G
Fe(L^2-2H) H_20	Solid	RT	2.015	980
Fe(L^1-2H) H_20	Solid	RT	2.018	850
Fe(L^1-H)Py(OAC)	Solid	RT	2.021	620

RT =Room Temperature

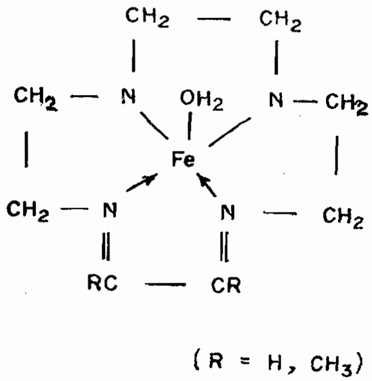
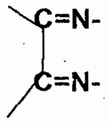


Figure2: Structures [Fe L^1-2H)H_20]and [Fe L^2-2H)H_20]

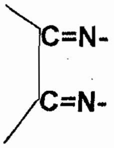
an absorption band in the region of 1200-1220cm^{-1} characteristic of the α-diimine moiety



of the tetraaza macrocyclic complexes. This ir spectral band has been observed in the spectra of several tetraaza macrocyclic complexes regardless of the nature of the metal ions (Rai and Prasad,1994). Thermogravimetric studies show that the H_2O molecule is not lost until 170^oC is reached, suggesting that it is coordinated H_2O, rather than hydrate, H_2O (Akinchan et al, 1994). The bands in the region of 3410-3415, 825-860, 560-575 and 450-455cm^{-1} are assignable to V(OH), rocking (H_2O), wagging (H_2O) and V(Fe-O) respectively (Nakamoto, 1978 and Akinchan et al, 1994) Further the coordination mode of tetraazan(12) macrocycles are confirmed by the presence of V(Fe-N) in the region of 530-540cm^{-1}

Infrared Spectrum of [Fe(L^1-H)Py(OAC):

The ir spectrum of this complex shows strong bands at 1594 and 1422 cm-1 attributable to V(C=N) and V(C=C) indicating the skeletal stretehing vibrations of macrocycles (Sakata et al, 1991, 1992). The absorption bands due to NH_2 and >C=O groups are absent from the spectrum of this complex, suggesting condinsation of both carbonyl oxygen atoms of glyoxal with both terminal NH_2 groups of trien (Rai and Prasad, 1994). Further, the stretching vibration due to α- diimine moiety



has been located at 1214cm-1 (Rai and Prasad, 1994). The observation of ir bands at 1630 and 1386cm^{-1} assignable to Va(COO-) and Vs(COO-) respectively suggest the presence of monodentate acetate in the iron(II) complex. (Nakamoto, 1978). The presence of pyridine is supported by locating V(C=N), Py(inplane vibration), Py(out of plane vibration) at 1552, 612 and 436 cm^{-1} respectively (Nakamoto, 1978). The coordination mode of tetraaza macrocycles is further supported by the observation of V(Fe-N) ring at 526cm^{-1}. Due to either possible overlaping of ligand bands or weak nature of the metal-ligand vibrations, it has not been possible to assign V(Fe-N) Py and VFe-O) acctate in the spectrum of the iron(II) complex. The low value of conductance data indicate non-electrolytic nature of this complex (Geary, 1971).

Electron spin resonance (esr) spectra of iron(II) complexes:

The esr spectra of the iron(II) tetraaza (12) macrocycles have been recorded for polycrystalline samples at room and liquid nitrogen temperatures. The esr spectra taken at liquid nitrogen temperature is unable to provide any useful information. The results obtained at room temperature are presented in Table 1. A polycrystalline sample gives one broad isotropic signal (g_{iso}) centred around 2.015-2.021 with peak to peak width higher than 600 Gauss. The appearance of broad isotropic esr signal for all the iron(II) macrocyclic complexes suggest strong interaction between iron(II) centres. The addition of pyridine in the coordination sphere must have weakened the in plane bonding (higher g_{iso},2.021) and lessen the iron-iron interaction (smaller peak to peak width, 620G). The results presented suggest octahedral structure for the [Fe(L^1-H) Py(OAC)] and square pyramidal for [Fe(L^1-2H)H_2O] and [Fe(L^2-2H)$H_2$0].

CONCLUSIONS

The reactions described demonstrate the templating effect of iron(II) cation to form tetraaza(12) macrocyclic iron(II) complex. The tetraaza(12) macrocycles (Figure 2) are able to encircle iron(II) cation forming four chelate rings and coordination takes place through four cyclic nitrogen atoms. Considered collectively, the results presented here and elsewhere (Rai and Prasad, 1994, Cummings and Sievers, 1970, Sakata et al, 1991, 1992) indicate that the stability of a particular macrocycle or macrocyclic metal ion complex depends on several factors. Here, a major controlling factor appears to be the attainment by the iron(II) cation of the best possible coordination geometry. Based on analysis, physical properties and spectral data discussed earlier, the octahedral (Figure 1) for [Fe(L^1-H) Py(OAC] and square pyramidal structures (Figure,2) for [Fe(L^1-2H)H_2O] and [Fe(L^2-2H)H_2O] are suggested.

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