

SYNTHESIS, CHARACTERIZATION AND PHYSICO-CHEMICAL STUDIES OF SOME MACROCYCLIC COMPLEXES WITH TRANSITION METAL IONS

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The chemistry of the macrocyclic ligands and their complexes are of significant general interest due to the use of such complexes as dyes and pigments, as MRI contrast agents as well as models for many naturally occurring biological systems. Several synthetic methods have recently been developed to prepare porphyrines, an interesting class of tetrapyrroles in which the pyrrolic subunits are held together by aza bridges. Polyether cryptands along with their two-dimensional analogues, the crown ethers, have been synthesized and their metal complexation behaviour have been studied in considerable detail, with applications in catalysis, separations and in chemical sensors being reported. The synthesis of tetrapyrrolic or related complexes in which the formal symmetry of the macrocyclic framework is altered by a peripheral substitution is a topic of growing interest. The interest in the chemistry of these macrocyclic systems still continues unabated.

With a view to improving our knowledge on the macrocyclic chemistry, a series of furan, thiophene or imidazole based porphyrin macrocycles have been synthesized. The series includes (i) tetraphenylfuran/thiophenoporphyrin (TPF/ TPT) (ii) Monopyridyltriphenylfuran/thiophenoporphyrin (MPyF/ MPyT) (iii) *cis*-Dipyridyldiphenylfuran/thiophenoporphyrin (DPyF/DPyT) (iv) *trans*-Dipyridyldiphenylfuran/thiophenoporphyrin (DPyF/ DPyT) (v) Tripyridylmonophenylfuran/thiophenoporphyrin (TrPyF/TrPyT) (vi) Tetrapyrityldiphenylfuran/thiophenoporphyrin (TPyF/TPyT). A series of four isomeric tetraphenylimidazoloporphyrin (TIP1-4) macrocyclic ligands have also been synthesized. A number of their transition metals complexes have been synthesized and characterized.

The synthesis of these O₄ or S₄ macrocyclic ligands involve the attack of respective carbonium ions generated in the reaction from benzaldehyde and pyridinecarboxaldehyde under acidic conditions, on furan or thiophene moiety giving their respective secondary alcohols. Polymerization condensation of these alcohols followed by reduction by 2,3-Dichloro-5,6-dicyanobenzoquinone or *p*-chloranil yield the desired macrocyclic ligands. Tetraphenylimidazoloporphyrin macrocyclic ligands (N₄) have been similarly prepared. The formation of these ligands has been ascertained by absorption spectra. The compositions of these macrocyclic ligands have been established by elemental analysis. The ligands are characterized by infrared, ¹H NMR, UV-Visible and mass spectral data. The observance of IR spectral bands assignable to the bridging methene group and other macrocyclic ring vibrations are consistent with the assigned structures of these ligands and are further indicative of the presence of a

2,5-disubstituted furan, thiophene or imidazole moieties. The ^1H NMR spectral data confer a D_{4h} symmetry for TPT/TPF/TPyT/TPyF ligands as indicated by equivalence of the peripheral phenyl- or pyridyl- substituents and β -protons. On the basis of NMR data a C_{2h} symmetry has been assigned to *trans*-(DPyF/DPyT), while *cis*-(TrPyF/ TrPyT) and (MPyF/ MPyT) are assigned a C_{2v} symmetry. The upfield shifts observed for the peripheral β -protons are suggestive of anti-aromatic character of these ligands. In the case of tetraazaimidazoloporphyrins a higher order symmetry has been assigned instead of the theoretically predicted lower symmetry probably due to the chemical exchange taking place between internal protons. The observed spectral pattern of the UV-Visible spectra are supportive of the $(4n)p$ anti-aromatic character of the O4 and S4 ligands while the N4 ligands possess a $(4n+2)p$ aromatic character.

A number of metal complexes of these ligands have been synthesized. The analytical data indicate that the complexes are formed in a 1:1 (metal: ligand) ratio and are in conformity with their proposed compositions as MLCl_2 ($M = \text{Fe, Co, Ni, Cu or Zn}$; $L =$ furanoporphyrins or thiophenoporphyrins) and ML ($M = \text{Co, Ni or Cu}$; $L =$ tetraphenylimidazoloporphyrins). The complexes have been characterized by infrared and electronic spectra and magnetic susceptibility measurements. The observed negative shift of $50\text{--}10\text{ cm}^{-1}$ in the $\nu(\text{C}=\text{O})$ / $\nu(\text{C}=\text{S})$ or $\nu(\text{C}=\text{N})$ stretching frequency in the IR spectra of the complexes is indicative of coordination of these ligands through oxygen, sulphur or nitrogen atoms, respectively. The complexation is further supported by the appearance of a single absorption band at 627 cm^{-1} due to reduced macrocyclic vibrations and decrease in their intensities. The non-ligand bands in the $520\text{--}400\text{ cm}^{-1}$ region confirms the existence of M-O , M-S or M-N bonds in the complexes. The calculated B values are indicative of moderate degree of covalency in the metal ligand bonds. The order of covalency is: imidazolo > thiopheno > furanoporphyrins for the same metal. On the basis of magnetic moment values and the electronic spectral data an octahedral geometry has been proposed for MLCl_2 complexes ($L =$ furanoporphyrins or thiophenoporphyrins; $M = \text{Fe, Co, Ni, Cu or Zn}$). However, the ML complexes ($M = \text{Co, Ni or Cu}$; $L =$ tetraphenylimidazoloporphyrins) have been assigned a square planar geometry. The ligand field parameters, $10Dq$, B and b have also been evaluated for most of the complexes. A comparison of the $10Dq$ values of these ligands indicate the following order of their field strengths: imidazolo @ thiopheno > furanoporphyrins. The results and conclusions that flow from these experiments add a new perspective to our understanding of this broad and fascinating field of macrocyclic chemistry. However, our present knowledge on the macrocyclic metal chemistry is still rather limited and much further research in this area is needed.