

Chapter 2

Scope and objectives

The bridged macrocyclic systems (Shiskabob) mentioned in previous chapter (Section 1.1.2.9), show conductivity in one dimension and the conduction pathway has been described as originating from π - π overlap of stacked metallomacrocycles which are separated by small distances (O^2 , S^2 , F^2 , $C\equiv C^2$ etc). The generation of a conduction pathway by π - π overlap of the stacked macrocycles, is not the only possibility allowing charge migration in bridged metal complexes.

Another pathway can be brought about by bridging groups which allow electron migration from one metal atom to the other. For this purpose organic bridging ligands, containing conjugated π -electrons allowing delocalisation along the chain are necessary. To obtain a stacked one-dimensional arrangement of a bridged polymer, the bridging ligand L, axial to the metal M, must be linear or at least have a sufficiently small M-L-M angle. Additionally the central atom must be a transition metal with a preferred octahedral coordination. The π -electron containing bridging group L may be cyanide or a polyatomic organic molecule, such as pyrazine, or 4,4'-bipyridine. In this case the interplanar distances of the metallomacrocycles are comparatively large and thereby excluding a conduction pathway by π - π overlap.

The combination of transition metal macrocycles with linear bridging ligands containing delocalisable π -electrons, can lead to a conduction pathway along



the central axis of this new type of polymer. The structural flexibility of such bridged macrocyclic transition metal complexes provides a unique possibility to study systematically the physical properties of such compounds and to develop new conducting materials.

The Shiskabob approach yields a class of coordination polymers of stacked macrocyclic metal complexes which are linked together by axial coordination of bridging ligands. Until recently, 'Shiskabob' polymers with bridging ligands larger than a single atom were rather rare. An interesting development is reporting of a class of compounds wherein coordinatively unsaturated metal complexes (4-coordinated species) are linked through bidentate ligands with ligation centres disposed in such a way that they are capable of coordinating to two different metal atoms, instead of one, through opposite end-donor centres. Of particular interest in this context are ligand systems with extensively conjugated π -framework so that by making use of appropriate d-orbitals and π/π^* orbitals of the spacer system electronic communications can be made possible between metal centres along the link axis. In the late 1970's Hanack et al⁽¹⁾ developed a large family of such polymers employing phthalocyanines of the type $[M(Pc)(L-L)]_{\infty}$.⁽²⁻¹²⁾

4- Coordinated MN_2S_2 chromophores are of special interest, especially because of their enzyme model capacity and also because of their special tunable electronic properties. As the earlier studies have focussed exclusively on MN_4 chromophores,⁽²⁻¹²⁾ it is pertinent to investigate on hetero-dentate chromophore systems of MN_2S_2 essentially because the presence of S around M can impart novel electronic properties. The present study is aimed at developing some of these chromophoric systems and linearly linking them through bidentate Lewis-bases with extended conjugation so that molecular systems with polymeric array could be formed. These are expected to have novel electronic, magnetic and related material properties.

The present study is aimed at investigating following aspects.

1. Developing simple coordinatively unsaturated metal complexes, especially of Co(II) and Ni(II) with ligands with potential N and S donor ability. The



ligand chosen are 2-mercaptobenzothiazole (mbtH), 2-mercaptobenzoxazole (mboH) and 2-mercaptobenzimidazole (mbmH) which have three donor centres and have similar structures except the presence of a hetero group which is different in each of the ligands.

2. The detailed characterisation of the resulting 4-coordinate complexes using analytical, spectroscopic and magnetic measurements and thermal analysis is also intended. The complexes formed are seen to prefer always 1:2 composition and have structure and electronic properties expected of typical 4-coordinated Co(II) and Ni(II) complexes.
3. Since some of the literature reports are seen to present conflicting reports,^(13,14) it is intended to checkup the authenticity of some of the parent compounds.
4. Selection and synthesis of various conjugated bidentate ligand systems capable of acting as bridging ligand and by suitable synthetic strategy to develop extensively bridged metal complexes. The bidentate ligands employed are N-containing Lewis-bases like 4-aminopyridine (amp), pyrazine (pyz), 4,4'-bipyridine (bipy), and 4,4'-azopyridine (azpy). For comparison monomeric 1:2 adducts of monodentate pyridine (pyr) are also synthesized.
5. Preparation and characterisation of various adducts of the above mentioned Lewis-bases of the parent Co(II) and Ni(II) complexes of mbtH developed using analytical, spectroscopic, and magnetic measurements.
6. Preparation and characterisation of all possible polymeric and monomeric Lewis-base adducts of 2-mercaptobenzoxazolate complexes of Ni(II) and Co(II) using relevant techniques.
7. To establish the structural and bonding features of monomeric and polymeric Lewis-base adducts of $M(\text{mbm})_2$, and compare them with those of $M(\text{mbt})_2$ and $M(\text{mbo})_2$.
8. To evaluate various spectroscopic parameters like Dq, Nephelauxetic parameter (β) and Racah parameter (B) of all the octahedral Ni(II) adducts developed.⁽¹⁵⁾



9. Compare the ligating features of the basal ligands mbt, mbm and mbo for each set of Lewis-base adducts and account for the possible molecular effects.
10. Evaluate and gradate the various Lewis-bases in terms of their ligating ability based on spectroscopic parameter separately for adducts of Ni(mbt)₂, Ni(mbo)₂ and Ni(mbm)₂. It is also intended to look at the possible molecular effects on these properties.
11. The structural features of mbtH, mboH and mbmH offer some interesting thermal decomposition features. So it is intended to look in detail phenomenological, kinetic, and thermodynamic aspects of their decompositions based on their thermograms employing nine-mechanism based equations proposed by Satava.⁽¹⁶⁾
12. Some of the adducts formed are expected to be reversible in nature and yield back the parent complex on slow heating at low temperature. The phenomenological, kinetic and thermodynamic parameters associated with these are expected to be interesting. Hence a detailed investigation on their thermal features is intended for all the adducts of Ni(mbt)₂, Ni(mbm)₂, Ni(mbo)₂, Co(mbt)₂ and Co(mbo)₂.
13. Since pentacoordinated vanadyl complexes have one vacant coordination site, it is possible to develop dimeric Lewis-base adducts. These are expected to be very interesting model systems. By employing the bidentate Lewis-bases mentioned above, it is also intended to develop all possible adducts of VO(acac)₂, (acac = acetylacetonate), which is a MO₅ chromophore. Detailed spectral characterisation is intended using electronic and ESR studies.
14. The thermal decomposition of the adducts of VO(acac)₂ is expected to be interesting. It is also planned to investigate their decomposition characteristics (phenomenological, kinetic and thermodynamic) and discuss some of their salient features.



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