Synthesis and characterisation of Lewis-base adducts of Ni(II) and Co(II) complexes of 2-mercaptobenzothiazole

4.1 Introduction

As discussed in Chapter 1 and referred in Chapter 2, 4-coordinated metallomacrocycles show appreciable tendency to coordination sphere expansion with Lewis-base. Their MS_4 analogues, on the other hand, are seen to show relatively much less affinity towards them. This is partly due to the electropositive nature of S (as compared to N) which would try to put more electron density on M on ligation, thereby making the M opt for acquiring higher oxidation state (formal) in MS_4 than it can in MN_4 ligand field. In such cases Lewis-base adduct formation would be the least preferred reaction for MS_4 system as it would burden the M with unwanted electron density. This accounts for the absence of any reasonably well characterisable Lewis-base adducts in literature for MS_4 compounds. In between these two extreme case of MN_4 and MS_4 are species with MN_2S_2 configuration. These are expected to show reasonably good affinity for Lewis-bases and hence bidentate conjugated bases like 4,4'-azopyridine, 4,4'-bipyridine and pyrazine are capable of generating linearly extended polymeric metal complexes with the Lewis-bases acting as bridging ligands.

Mercapto ligands like 2-mercaptobenzothiazole(mbtH), 2-mercapto benzoxazole (mboH) and 2-mercaptobenzimidazole (mbmH) are potential S,N

donor ligands in their anionic form and hence can generate MN_2S_2 chromophore with divalent metal ions like Co(II), Ni(II) and Cu(II). These ligands are very close in their structural features and have only a difference in one of the hetero atoms. The present chapter describes our attempts to generate CoN_2S_2 and NiN_2S_2 chromophores with mbtH and their adducts with various bidentate Lewis-bases.

2-Mercaptobenzothiazole is a potential bidentate ligand with three donor sites. This is known to exist in two tautomeric forms, namely, thione and thiol[1] (**50**).

(thione-form)   (thiol-form)
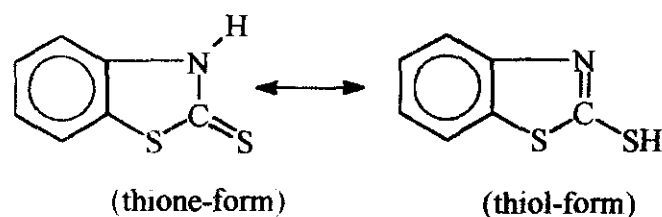
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The bicyclic mbtH has the unique feature of having one N and two S atoms connected to a single carbon in a five membered heterocyclic moiety. This ligand on deprotonation would produce an anionic mbt⁻, which has possibility of attaining aromatic character (6π-electrons) to the five-membered heterocyclic moiety. In such case the ring has to stay planar and the entire anionic molecule including exocyclic S has to be lying in the same plane. This necessitates all the C, N and S including exocyclic S to be sp^2 hybridised. In such a situation the lone pairs of electrons available on the hetero atoms are as shown in Fig 4.1. All these are in sp^2 orbitals which form the potential donor orbitals. The interesting feature of these donor orbitals is that their orientation permits coordination either through the two S atoms (case I) or through N and exocyclic S (case II). The point marked A in Fig.4.1(a) indicates the position of metal ion in the case I and B for case-II in the resulting complexes. It is instructive to note that in case I the mbt gets coordinated to the metal through S and S as in the case of dithiocarbamate species.[2-4]
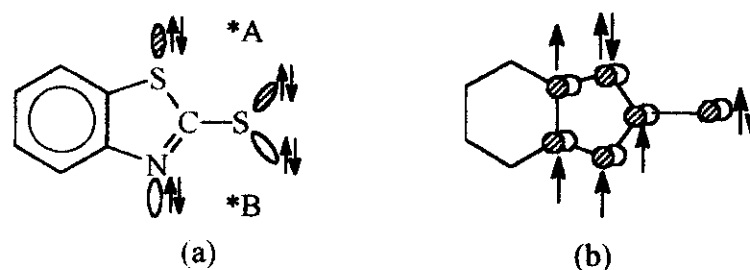
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Fig. 4.1(a) Relative orientation of donor orbitals in mbt⁻ and
(b) the constituent orbitals of the π system and electron count
from them

There are many reports on the interaction of 2-mercaptobenzothiazole with various metal ions. Among these references about bis(2-mercaptobenzothiazolato) nickel(II), -cobalt(II) and -copper(II) were made but with some controversy.[5] Preparation of paramagnetic six-coordinate adducts from diamagnetic four coordinated square planar Ni(II) complexes using monodentate Lewis-bases such as pyridine, picolines,1,10-phenanthroline and 2,2'-bipyridine were also reported.[5] Dipyridine octahedral adduct of Co(mbt)₂ was also reported. In all these cases, it was reported that the coordination of the core ligand (mbt) is through N and S (case II).

In this study attempts are made to generate polymeric complexes of Co(mbt)₂ and Ni(mbt)₂ using N-bases with extensive conjugation and having donor atoms oriented in such a manner that they can link the complex monomer moieties linearly and in polymeric form. The possible π-interactions of these conjugated bases through their end donor groups with the metal d-orbitals along the polymer chain make them very interesting system. The conjugated bidentate N-bases chosen in the present study for axially bridging the M(mbt)₂ to generate polymer like complexes are pyrazine(pyz), 4-aminopyridine(amp), 4,4'-bipyridine(bipy) and 4,4'-azopyridine(azpy). All these have the donor N-atoms positioned at the two ends of the molecules suitable to link M(mbt)₂ moieties to form linearly extended array. We could successfully prepared such polymeric metal complex species except with 4-aminopyridine which gave only monomeric 1:2 adduct. The bidentate ligands chosen are given in Fig. 4.2.
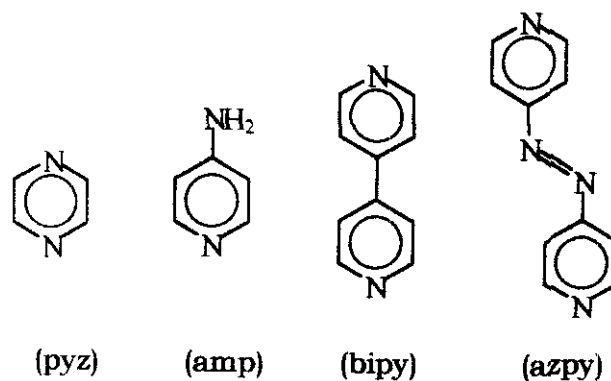
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Fig. 4.2 Lewis-bases used for axial bridging

4.2 Experimental

4.2.1 Reagents used

2-Mercaptobenzothiazole, pyridine, 4-aminopyridine, 4,4'-bipyridine, pyrazine, $NiCl_2.6H_2O$ and $CoCl_2.6H_2O$ used were either BDH, Fluka or Merck samples.

4.2.2 Preparative Details

a) Preparation of 4,4'-azopyridine

4,4'-azopyridine was prepared by oxidative coupling of 4-aminopyridine with hypochlorite with some modification of reported procedure[6-7] (for detail, refer Chapter 3, section 3.2.1).

b) Bis(2-mercaptobenzothiazolato)nickel(II),[Ni(mbt)₂]

A slightly modified method of a reported procedure[5,8], was employed for the preparation of Ni(mbt)₂. A solution of $NiCl_2.6H_2O$ (1.65 g, 0.01 mol) in ethyl alcohol (25 ml) was added dropwise to a solution of mbtH (3.34 g, 0.02 mol) in ethanol (100 ml) while stirring. The dropwise addition of 5M ammonia solution yielded a brown coloured solid. The precipitate was digested on a water bath for 1h after which it was filtered. The brown complex was washed with water and

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then with ethanol followed by diethyl ether. The Ni(mbt)$_2$ obtained was dried at 100°C for 3h. (yield 90%).

c) Bis(2-mercaptobenzothiazolato)cobalt(II), [Co(mbt)$_2$]

The preparative procedure adopted for the complex was almost similar to that employed for Ni(mbt)$_2$. The metal salt employed was Co(NO$_3$)$_2$.6H$_2$O with metal to ligand ratio of 1:2. The unreacted metal salt and the ligand were removed by repeated washing with water and cold ethanol. The preparation of the complex was also carried out using CoCl$_2$.6H$_2$O to check the authenticity of a literature[8] product with a different composition. Both the methods yielded same green coloured complex disproving the earlier report. The product obtained was dried at 100°C for 3h.(yield 90%).

d) Dipyridinebis(2-mercaptobenzothiazolato)nickel(II) and -cobalt(II), [M(mbt)$_2$(pyr)$_2$]
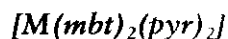
A solution method for the preparation of these compounds was already reported. About 2 mmol of pyridine in benzene was added dropwise to a solution of M(mbt)$_2$, (approx. 0.39 g, 1 mmol) in benzene. This mixture was refluxed for about 15 min on a water bath. The precipitated green complex (in the case of Ni(mbt)$_2$) and brown complex(in the case of Co(mbt)$_2$) was filtered and washed with diethyl ether repeatedly and dried in vacuo.

A different solid state reaction was also adopted for the preparation of these compounds. About 0.39 g (1 mmol) of M(mbt)$_2$ was kept in a petridish in an air-tight vessel. Then about 25 ml of pyridine was also kept in beaker in the same vessel. The vapourised pyridine was seen reacting with the solid complex and a green coloured adduct was formed after 24h in the case of Ni(mbt)$_2$. But a brown coloured compound was obtained when Co(mbt)$_2$ reacted with pyridine. The unreacted pyridine was removed by keeping it at about 50°C for 30 min. Then it was washed with acetone and diethyl ether. The compound was then dried in vacuo.

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e) **M(mbt)$_2$(amp)$_2$**

A solution of 4-aminopyridine was prepared by dissolving 0.19 g (2 mmol) of 4-aminopyridine in 10 ml of acetone. This solution was added dropwise to a solution of M(mbt)$_2$ (about 0.39 g, 1 mmol) in 10 ml of benzene. This reaction mixture was gently heated for about 15 minutes and then cooled. (Heating is not necessary in the case of Co(mbt)$_2$). The precipitated compounds were separated out by filtration which was washed with acetone followed by diethyl ether. The complex was finally dried *in vacuo.*

f) **[M(mbt)$_2$(pyz)]$_n$**

A solution of pyrazine prepared by dissolving 0.12 g (1.5 mmol) in benzene was added to a solution of M(mbt)$_2$ (0.39 g, 1 mmol) in 10 ml of benzene. This mixture was gently heated for 30 min. An yellow coloured compound separated out in the case of Ni(mbt)$_2$ and brown in the case Co(mbt)$_2$. The precipitated compounds were repeatedly washed with benzene, acetone followed by diethyl ether, which was then dried *in vacuo.*

g) **[M(mbt)$_2$(bipy)]$_n$**

About 0.16 g (1 mmol) of 4,4'-bipyridine was dissolved in 10 ml of benzene and this solution was added to a solution of M(mbt)$_2$ (1 mmol) in benzene. On cooling, a green coloured compound was precipitated when Ni(mbt)$_2$ reacted with this solution, but in the case of Co(mbt)$_2$ acetone was used as solvent and the adduct obtained was brown in colour. The separated compounds were washed with benzene followed by the diethyl ether. The compounds were dried *in vacuo*

h) **[Ni(mbt)$_2$(azpy)]$_n$**

The method adopted for the preparation of this compound was almost similar to that one employed in the case of 4,4'-bipyridine. The solvent used was benzene and the colour of the complex was orange brown.

4.2.3 Analytical Methods

All the complexes were analysed for the metal content by the complexometric titration method. Murexide indicator was used for the estimation of nickel but xylenol orange for cobalt[9]. The infra-red spectra of the complexes and their adducts were recorded in the range 400-4000 cm^{-1} on a Shimadzu IR 470 spectrophotometer. Electronic spectra were recorded in the solid state using Nujol mull paste employing a Shimadzu UV 160A spectrophotometer in the range 200-1100nm. The C, H and N analyses were carried out using Heracus CHNO rapid analyser. The magnetic susceptibilities were measured on a Sartorious semimicro Gouy balance. The fields were calculated using a standard calibrant $Hg[Co(SCN)_4]$.

4.3 Results and Discussion

4.3.1 Four-coordinated $Co(mbt)_2$ and $(Ni(mbt)_2$

As mentioned in the introductory section 4.1, the ligand mbtH is capable of existing in thiol-thione tautomeric forms. The thiol form indicates its acidic character and the ability to deprotonate to generate the anionic mbt^- species. As evident from preparative details both Co(II) and Ni(II) complexes of the ligand are generated in basic medium. Hence both the metal complexes can be expected to be formed from the anionic ligand. The analytical data clearly showed that both the Co(II) and Ni(II) complexes have the composition $M(mbt)_2$ (Table 4.1.) without the involvement of any other anion in them. Some of the literature reports, however, have indicated that the cobalt (II) complex formed has a composition $Co(mbt)X$.[8,10] But we could not separate such species, eventhough we followed the same preparative procedure. We have verified, by taking various Co(II) salts, that whatever may be the anions from the salt the Co(II) complex generated is always the same with $Co(mbt)_2$ composition. Some controversial reports about Cu(II) complexes also are seen in literature about which a brief mention is made in Chapter 9 of the present work.

A look at the donor orbital components of the mbt$^-$ species indicates two possibilities of ligating modes as mentioned in Fig. 4.1a. The nature of IR spectra of the complexes gives us enough proof about the mode of bonding (Table 4.2). The absorption at 3050cm^{-1} which is assigned to ν_{NH} is seen absent in both Co(II) and Ni(II) complexes. This indicates the deprotonation of the mbtH. The thioamide band (ν_{NCS}) is known to occur at 1480 cm^{-1} as a strong band in the free ligand. This was found shifted to 1400 cm^{-1} when coordinated to Ni(II) in Ni(mbt)$_2$ and to 1440 cm^{-1} when ligated to Co(II) in Co(mbt)$_2$. The $\nu_{(C=S)}$ at 667 cm^{-1} in the free ligand was seen shifted to 700 cm^{-1} in both Co(mbt)$_2$ and in Ni(mbt)$_2$. These shifts in the IR spectra of complexes indicate chelation through N and exocyclic S of the mbt moiety in agreement with earlier reports. Hence both Co(II) and Ni(II) complexes can be considered to have MN$_2$S$_2$ chromophore. The planar structure and the aromatic nature of the mbt$^-$ moiety in its complexes is evident from the discussion made in section 4.1 it can also be expected the ligand moiety would be conjugatively interacting with the metal in both its complexes.

The electronic spectra of Co(mbt)$_2$ give a broad absorption consisting of three close lying peaks at 16450, 15150 and 14325 cm^{-1} (Fig.4.6). This is very characteristic of tetrahedral Co(II) species. This transition is essentially due to $^4A_2 \rightarrow {}^4T_1(P)$.[11,12] Ni(mbt)$_2$ in benzene solution gave three peaks at 25975, 22220 and 16000 cm^{-1}. These are typical of square planar Ni(II). While 25975 peak could be assigned to the CT transition the peaks at 22220 and 16000 cm^{-1} could be attributed to $^1B_{1g} \rightarrow {}^1A_{1g}$.[13] The magnetic susceptibility measurements showed that the Co(mbt)$_2$ is paramagnetic while Ni(mbt)$_2$ is diamagnetic. The μ_{eff} value of Co(mbt)$_2$ was evaluated to be 4.40 BM which is typical of tetrahedral Co(II) species.

4.3.2 Lewis-Base Adducts of M(mbt)$_2$

The polymeric adduct formation was carried out in hot or cold conditions. It was interesting to see that some of the adducts could be prepared by solid-gas state reaction. Attempts were also made to prepare M(mbt)$_2$ adducts with Lewis-bases in 1:2 composition. Analytical data (Table 4.1) could confirm the composition of the adducts. While bipy and pyz yielded 1:1

adducts with both $Co(mbt)_2$ and $Ni(mbt)_2$, amp and pyr always yielded 1:2 adducts with the parent complex. While we could successfully prepare a 4,4'-azopyridine adduct of $Ni(mbt)_2$ with 1:1 composition $Co(mbt)_2$ failed to yield an adduct with a definite stoichiometry. The reaction between the complex and the ligands used for adduct formation may be shown by the following scheme.

$$[M(mbt)_2] + 2L' \rightarrow [M(mbt)_2L'_2]$$

$$n[M(mbt)_2] + nL'' \rightarrow [M(mbt)_2L'']_n$$
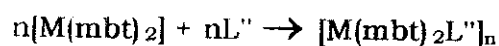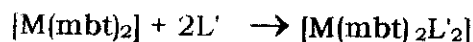
where $\quad$ M $=$ Co(II), Ni(II)

$\qquad$ L' $=$ pyr, amp

$\qquad$ L'' $=$ pyz, bipy, azpy.

Table 4.1 Elemental analytical data

Sl. No.	Complex Emperical formula	Formula weight	Elemental content (%) Obsvd. (calcd)				Colour
			C	H	N	M	
1	$[Ni(mbt)_2]$ $NiC_{14}H_8N_2S_4$	391.24	42.85 (43.00)	2.02 (2.05)	7.25 (7.20)	15.15 (15.00)	Brown
2	$[Ni(mbt)_2(pyr)_2]$ $NiC_{24}H_{18}N_4S_4$	549.17	52.20 (52.00)	3.20 (3.20)	10.15 (10.20)	10.80 (10.72)	Green
3	$[Ni(mbt)_2(amp)_2]$ $NiC_{24}H_{20}N_6S_4$	579.24	49.70 (49.72)	3.45 (3.50)	14.45 (14.40)	10.10 (10.13)	Green
4	$[Ni(mbt)_2(pyz)]_n$ $NiC_{18}H_{12}N_4S_4$	471.24	45.82 (45.83)	2.55 (2.54)	11.90 (11.88)	12.44 (12.45)	Greenish yellow
5	$[Ni(mbt)_2(bipy)]_n$ $NiC_{24}H_{16}N_4S_4$	547.17	52.61 (52.63)	2.90 (2.94)	10.30 (10.23)	10.78 (10.72)	Green
6	$[Ni(mbt)_2(azpy)]_n$ $NiC_{24}H_{16}N_6S_4$	577.24	49.82 (49.89)	2.71 (2.79)	14.60 (14.55)	10.15 (10.16)	Orange
7	$[Co(mbt)_2]$ $CoC_{14}H_8N_2S_4$	391.48	42.90 (42.91)	2.02 (2.05)	7.12 (7.15)	15.02 (15.05)	Green
8	$[Co(mbt)_2(pyr)_2]$ $CoC_{24}H_{18}N_4S_4$	549.41	52.40 (52.42)	3.31 (3.30)	10.21 (10.20)	10.78 (10.80)	Brown
9	$[Co(mbt)_2(amp)_2]$ $CoC_{24}H_{20}N_6S_4$	579.48	49.69 (49.70)	3.47 (3.48)	14.50 (14.49)	10.16 (10.17)	Brown
10	$[Co(mbt)_2(pyz)]_n$ $CoC_{18}H_{12}N_4S_4$	471.48	45.79 (45.81)	2.56 (2.54)	11.86 (11.87)	12.47 (12.49)	Brown
11	$[Co(mbt)_2(bipy)]_n$ $CoC_{24}H_{16}N_4S_4$	547.41	52.60 (52.61)	2.94 (2.95)	10.24 (10.23)	10.79 (10.80)	Brown

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4.3.2.1 Infra red spectra

The IR spectra of all the adducts of $M(mbt)_2$ showed the presence of characteristic peaks of the Lewis-bases in them. The peaks due to mbt moiety were also present but with some shift in their position. The $v_{(N=C=S)}$ band occurring at 1400 cm^{-1} in $Ni(mbt)_2$ was found shifted to 1370-1385 cm^{-1} in its Ni(II) adducts. The same band observed at 1440 cm^{-1} in $Co(mbt)_2$ was seen in the range 1405-1430 cm^{-1} in the adducts with Lewis-bases. The $v_{(C=S)}$ band observed at 700 cm^{-1} for $M(mbt)_2$ was found lowered to 680-692 cm^{-1} in all the $M(mbt)_2$ adducts. This lowering can be attributed to the following reasons. Since Lewis-bases are very good electron donors, they increase electron density on the metal ion through coordination. So back donation from metal to mercaptobenzothiazole moiety is possible in the adduct. This would strengthen M-C bond but weaken C-S bond and as a result $v_{(C=S)}$ gets lowered. The important stretching frequencies of $M(mbt)_2$ and their adducts are given in Table 4.2.

The C=C and C=N ring stretching skeletal bands in pyridine were observed in the range of 1430-1600 cm^{-1} (4 peaks at 1440,1480, 1580 and 1595 cm^{-1})[14]. These bands were seen present in the IR spectra of all the adducts except those of pyrazine.

Upon complex formation, the characteristic in-plane ring deformation at 604 cm^{-1} and out of plane ring deformation at 405 cm^{-1} of free pyridine moiety were seen shifted to higher frequencies. The bands observed in the range 635-680 cm^{-1} in the adducts could be assigned to in-plane ring deformation of coordinated pyridine moiety. The bands appear in the range 420-425 cm^{-1} were assigned to the out of plane ring deformation of pyridine upon coordination. These data support the coordination of pyridyl nitrogen to the metal upon adduct formation.

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Table 4.2 IR spectral data of M(mbt)$_2$ and its Lewis-base adducts(cm^{-1})

Compound	ν_{N-C-S}	ν_{C-S}	^{a}C=C + C=N	$^b\nu_{CN}$	$^c\nu_{NH_2}$	NH bending	^{d} Ring deformation	
							Out of plane	In plane
MbtH	1480	667	-	-	-	1590	-	-
[Ni(mbt)$_2$]	1400	700	-	-	-	-	-	-
[Ni(mbt)$_2$(pyr)$_2$]	1380	692	1590, 1480, 1445	-	-	-	425	635
[Ni(mbt)$_2$(amp)$_2$]	1385	685	1560, 1505, 1450	1340	3480, 3390	1622	422	670
[Ni(mbt)$_2$(pyz)]$_n$	1382	685	-	-	-	-	-	-
[Ni(mbt)$_2$(bipy)]$_n$	1380	685	1560, 1530, 1450	-	-	-	420	685
[Ni(mbt)$_2$(azpy)]$_n$	1370	682	1580, 1560, 1448	-	-	-	420	680
Co(mbt)$_2$	1440	700	-	-	-	-	-	-
[Co(mbt)$_2$(pyr)$_2$]	1430	690	1595, 1550, 1450	-	-	-	420	690
[Co(mbt)$_2$(amp)$_2$]	1380	680	1550, 1510, 1450	1350	3480, 3400	1620	430	680
[Co(mbt)$_2$(pyz)]$_n$	1380	687	-	-	-	-	-	-
[Co(mbt)$_2$(bipy)]$_n$	1405	680	1560, 1525, 1480	-	-	-	430	680

^{a} C=C and C=N ring stretching in pyridine
^{b} uncoordinated ν_{CN} in aromatic primary amine
^{c} ν_{NH_2} of aromatic primary amine
^{d} ring deformation of pyridine moiety

Primary amines show two absorption in the range 3400-3500cm^{-1} assignable to asymmetric and symmetric N-H stretching modes.[15] $\nu_{(NH)}$ bending mode of primary amine is usually observed in the range 1650-1580 cm^{-1}.[16,17] These bands were observed at 3480, 3390, 3400 ($\nu_{(NH)}$) and 1620 cm^{-1} (δ_{NH}) respectively in [M(mbt)$_2$ (amp)$_2$]. But as compared to free 4-aminopyridine these bands remain almost unaltered. This strongly indicates the non-coordination of NH$_2$ group[18,19] to the metal in its adducts. *The unavailability of amino*

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nitrogen can be attributed to the resonance stabilisation of 4-aminopyridine and its planar structure, as illustrated in Fig. 4.3.
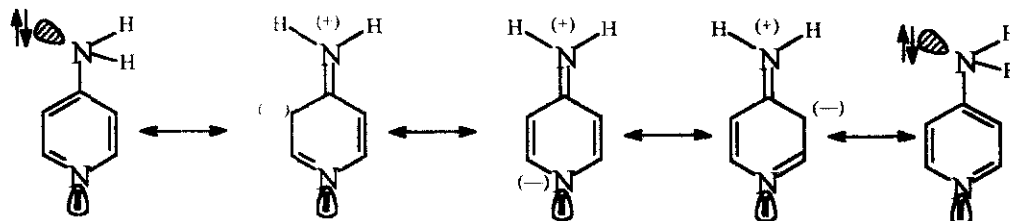

Fig.4.3. Resonance structures of 4-aminopyridine

The NH_2 group present in amp is electron releasing so that lone pairs of amino nitrogen gets delocalised to the pyridyl nitrogen. In addition to this the NH_2 group tends to remain in the molecular plane and p-orbitals which contain the lone pair of electrons tries to lie perpendicular to the plane of the molecule. These situations make the lone pair of NH_2 group not available for coordination.

Lever et al[20-23] reported that the complexes in which pyrazine is bonded to metal only through one of its nitrogen atoms show a band in the region 950-1000 cm⁻¹. But this band is generally seen absent in pyrazine bridged polymers of long chain and is appearing as a weak band in oligomeric species. Hanack[24] et al prepared and characterised a large number of monomeric and polymeric species in porphyrins and phthalocyanines with pyrazine. According to them pyrazine has a characteristic centrosymmetric ring stretch at about 1600 cm⁻¹, $v_{(pyz)}$, which is both IR and Raman allowed for unidentate pyrazine complexes. But it is only Raman allowed (not IR active) for bidentate polymeric compounds and for the free pyrazine. Therefore it is possible to classify pyrazine complexes based on the stretching absorption at 1600 cm⁻¹. It is also reported that the bands present in pyrazine at 1230 and 695 cm⁻¹ also vanish on polymerisation. Hanack[24] reported a negligible absorption at 1582 cm⁻¹ in the IR spectrum of polymeric [PcFe(pyz)]ₙ but a strong intense peak in monomeric [PcFe(pyz)₂]. In the IR spectrum of the M(mbt)₂(pyz) is a negligible absorption occurring at 1590 cm⁻¹ but with no

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peaks at 950-1000 cm^{-1} and 1230 cm^{-1}. These data strongly indicate the polymeric nature of the pyrazine adducts of M(mbt)$_2$.

The bridging ability of 4,4'-bipyridine to generate polymeric metal complexes have been demonstrated with several metallomacrocycles. The synthesis of polymers with bidentate equitorial (basal) ligands like, dimethyl glyoxime and diphenyl glyoxime, with Fe(II) and Co(II) as the central metal ion and 4,4'-bipyridine as the bridging ligand have been reported. Single crystal X-ray measurements were been made on bis(dimethylglyoximato) 4,4'-bipyridine cobalt(II)[25] and it was found that the Co(II) ion and the midpoint of the 4,4'-bond of bipyridine ligand occupy centres of symmetry and the two pyridyl units of the bipyridine lie in the same plane. In the case of bipyridyl compounds, IR spectroscopy is seen to be a useful tool to distinguish monomeric from polymeric and dimeric compounds.[26] The monomeric derivatives [PcM(bipy)$_2$], (M=Fe, Ru, Co) give rise to bands at 800, 1070, 1215, 1402, 1483, and 1589 cm^{-1}. These absorptions are caused by the ligand and agree with the bands exhibited by free bipyridine. The predominant spectral difference observed for monomeric compounds containing unidentate terminal 4,4'-bipyridine, compared with those containing bidentate bridging ligand is the disappearance of absorptions at about 1215,1402 and 1589 cm^{-1}. The bands around 1215 and 1585 cm^{-1} are also present in the pyridine derivatives [PcCo(pyr)$_2$],[PcCo(pyr)] and (PcFe(pyr)$_2$], which are assigned to be the in-plane C-H bending vibration and the ring vibration respectively.[27] Considering non-bridging 4,4'-bipyridine as a coordinating pyridine derivative suggests a similar assignment for the monomeric 4,4'-bipyridine complexes.[28]
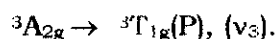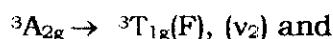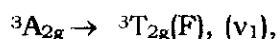
The IR spectrum of [Ni(mbt)$_2$(bipy)]$_n$ shows the presence of new bands at 800,1080,1480 cm^{-1} indicating that 4,4'-bipyridine is coordinated to Ni(mbt)$_2$ through both its pyridyl moieties resulting in a polymeric compound. The appearance of a very weak absorption peak at 1215 cm^{-1}, strong absorption at 1405 cm^{-1} and a very weak band at 1600 cm^{-1} also supports the polymeric nature for the adduct. The appearance of new bands at 810,1075,1480 cm^{-1} and weak absorptions at 1210,1405 and 1600 cm^{-1} in the IR spectrum of [Co(mbt)$_2$(bipy)]$_n$ also suggest a similar polymeric structure for the compound.

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If both pyridyl units are arranged in same plane, bidentate 4,4'-bipyridine is centrosymmetric to its 4,4'-bond centre. Consequently the above assigned in-plane vibration at 1215 cm^{-1} of the monomeric complexes loses its IR activity in dimeric and polymeric compounds, if one assumes a coplanar arrangement of the pyridyl groups. The centre of symmetry vanishes when pyridyl planes are tilted or when 4,4'-bipyridine acts as a monodentate ligand, making the 1215 cm^{-1} band IR active. Since the analytical data and thermal analyses (discussed in Chapter **5**) of [M(mbt)$_2$(bipy)]$_n$, [M=Ni(II), Co(II)], indicate 1:1 stoichiometry for the adducts. The appearance of IR band at 1215 cm^{-1} in these complexes indicates that pyridyl groups are not in the same plane but tilted.

4.3.2.2 Electronic spectra of Lewis-base adducts of Ni(mbt)$_2$

The electronic spectra of all the adducts of Ni(mbt)$_2$ are recorded in solid state by the method already suggested. The authenticity of all the peaks was confirmed by recording the spectra by repeated sample preparation. Some of the spectra are reproduced in Fig. 4.4. Octahedral complexes of nickel (II) differ from the square planar ones in their absorption characteristics below 10000 cm^{-1}, which is not seen in square planar complexes because of their very high crystal field strength. Orgel diagram suggests that six-coordinate octahedral Ni(II) complexes can have generally three bands in the electronic spectrum. They originate from the following transitions[11]

$$^3A_{2g} \rightarrow {}^3T_{2g}(F), \ (\nu_1),$$

$$^3A_{2g} \rightarrow {}^3T_{1g}(F), \ (\nu_2) \text{ and}$$

$$^3A_{2g} \rightarrow {}^3T_{1g}(P), \ (\nu_3).$$

On examining the electronic spectra of all the Ni(mbt)$_2$ adducts it can be seen that all of them have three absorptions maxima in the ranges 7000-13000 cm^{-1}, 11000-20000 cm^{-1} and 19000-27000 cm^{-1} (Table 4.3). These are very characteristic of octahedral Ni(II) complexes and can be assigned to $A_{2g} \rightarrow {}^3T_{2g}(F)$, ($\nu_1$), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, ($\nu_2$) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, ($\nu_3$) transitions respectively.
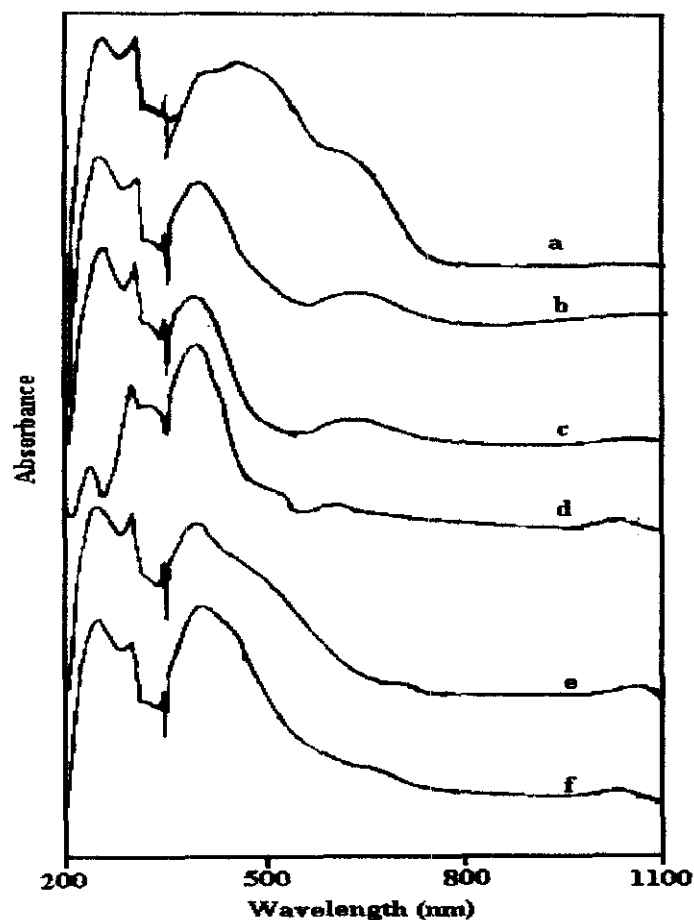
Fig.4.4 Electronic spectra of Lewis-base adducts of Ni(mbt)$_2$
(a) Ni(mbt)$_2$,   (b) Ni(mbt)$_2$(pyr)$_2$,
(c) Ni(mbt)$_2$(amp)$_2$,   (d) [Ni(mbt)$_2$(bipy)]$_n$,
(e) [Ni(mbt)$_2$(azpy)]$_n$,   (f) [Ni(mbt)$_2$(pyz)]$_n$

From Orgel diagram of octahedral Ni(II) ion and electronic transitions observed by the complexes it is possible to calculate Dq (CFSE), Racah's parameter B, and the Nephelauxetic parameter (β) for all the octahedral Ni(II) complexes. From Orgel diagram and Tanabe and Sugano diagrams, it was seen that the energies of both $^3T_{2g}$ and $^3A_{2g}$ are linearly varying with Dq. For any ligand that produces a spin-free octahedral nickel complex the difference in energy between the $^3T_{2g}$ state and the $^3A_{2g}$ state in the complex is 10 Dq.

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Table 4.3 Electronic spectral data and magnetic moments of Ni(mbt)$_2$ and their Lewis-base adducts

Compound	Abs Max cm^{-1}	*Tendative Assignments	B cm^{-1}	Dq cm^{-1}	β	$\frac{\nu_2}{\nu_1}$	μ_{eff} (BM)
[Ni(mbt)$_2$]	25975 22220 16000	Charge transfer $^1B_{1g}{\rightarrow}^1A_{1g}$	-	-	-	-	Dia
[Ni(mbt)$_2$(pyr)$_2$]	25445 15850 9300	ν_3* ν_2* ν_1*	8924	930	0.957	1.7	3.15
[Ni(mbt)$_2$(amp)$_2$]	25905 16180 9520	ν_3 ν_2 ν_1	901.0	952	0.866	1.69	3.14
[Ni(mbt)$_2$(pyz)]$_n$	25250 16390	ν_3 ν_2	-	-	-	-	3.10
[Ni(mbt)$_2$(bipy)]$_n$	25575 16390 10520	ν_3 ν_2 ν_1	692.7	1052	0.665	1.56	3.01
[Ni(mbt)$_2$(azpy)]$_n$	24630 16130 10320	ν_3 ν_2 ν_1	653.7	1032	0.628	1.56	3.02

* $^3A_{2g}{\rightarrow}^3T_{1g}(P) = \nu_3$, $^3A_{2g}{\rightarrow}^3T_{1g}(F) = \nu_2$, $^3A_{2g}{\rightarrow}^3T_{2g}(F) = \nu_1$

It is also possible to calculate the value of β from the electronic transitions.[11] The Nephelauxetic parameter (β) is a measure of covalent character and it can evaluated using the equation.

$$\beta = \left(\frac{B - B'}{B} \right) \times 100 \qquad\qquad \text{------------(4.1)}$$

where B is the Racah parameter for the free gaseous ion and B' is the same for the complex.

A simple method was also reported by some authors[29] for the calculation of the Racah parameters (B)[30] which can be given by

$$B = \left(\frac{v_2 + v_3 - 3v_1}{15} \right) \qquad \text{------------(4.2)}$$

In the case of octahedral Ni(II), the value of v_1 directly can be taken as 10Dq.

$$v_1 = 10Dq \qquad \text{----------(4.3)}$$

It is possible to evaluate 10Dq from v_2, v_3 and B as

$$10Dq = \left(\frac{v_2 + v_3 - 5B}{3} \right) \qquad \text{----------(4.4)}$$

The Nephelauxetic parameter(β) could be obtained by using the relation

$$\beta = \frac{B(complex)}{B(free\ ion)} \qquad \text{------------(4.5)}$$

where the value of B for free ion is about 1041 cm^{-1}

It is generally seen that the ratio v_2/v_1 in octahedral Ni(II) complexes lies in the range of 1.5-1.7. Table 4.3 gives the calculated Dq values for the various Ni(mbt)$_2$ adducts prepared in the present study along with their B and β. The energy ratio v_2/v_1 evaluated for the complexes are also given in the table. The values clearly indicate that all the adducts have octahedral geometry.

It is instructive to note that the Dq and β of Ni(II) adducts increase in the order [Ni(mbt)$_2$(pyr)$_2$]=[Ni(mbt)$_2$(amp)$_2$]<<[Ni(mbt)$_2$(azpy)]$_n$=[Ni(mbt)$_2$ (bipy)]$_n$. Among these the Dq and β values of polymeric adducts (involving azpy and bipy) are seen to have higher than that of monomeric species. This could be attributed to the extended π conjugation of the orbitals of the bidentate ligand and the metal ion in one dimension in the polymeric products. Because of this π-bonding ability, the M-N bond can acquire some amount of π-character or double bond character which would increase their relative stability. When a metal complex combines with N-base the electron density on the metal ion would increase since N-bases are good σ-donors. This would consequently

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increase the back bonding tendency of the metal in order to decrease the electron density on the metal ion. Due to this back bonding, the covalent character (β) of the metal and coordinating atom is expected to be higher.

The structural features of both monomeric and polymeric adducts are given in Fig. 4.5(a) and the orbital interaction in them in Fig. 4.5(b). Both σ- and π- bonding features are also presented in Fig. 4.5(b).

The Dq value of [Ni(mbt)$_2$(pyr)$_2$] is seen to be slightly smaller than that of [Ni(mbt)$_2$(amp)$_2$]. This could be attributed to strong ligating capacity (coordination ability) of 4-aminopyridine as compared to pyridine which is evident from the pKa values. The pKa value of pyridine is (5.17) while that of 4- amino pyridine is 9.11[31] which implies that the 4-aminopyridine is more basic than pyridine. Consequently amp is a better ligand than pyridine which is manifested in the difference in their Dq values.
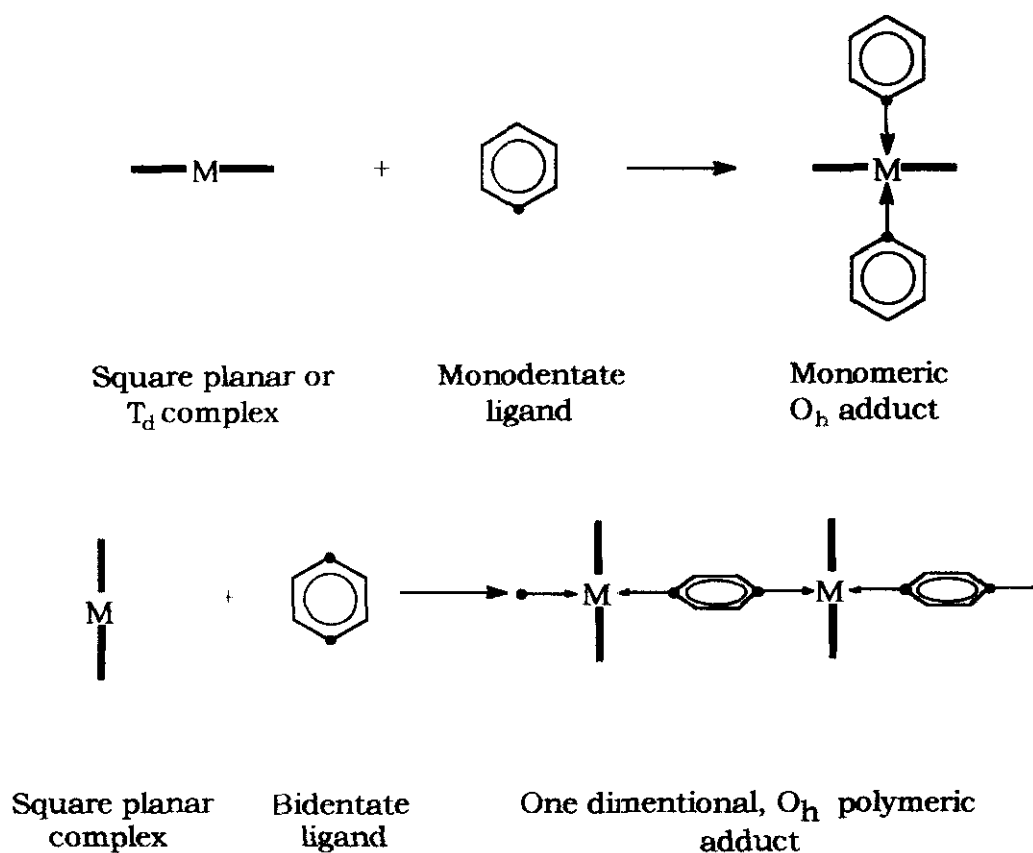

Square planar or   Monodentate   Monomeric
T_d complex   ligand O_h adduct

Square planar   Bidentate   One dimentional, O_h polymeric
complex   ligand   adduct

Fig.4.5a Structural disposition of monomeric and polymeric Lewis-base adducts of M(mbt)$_2$
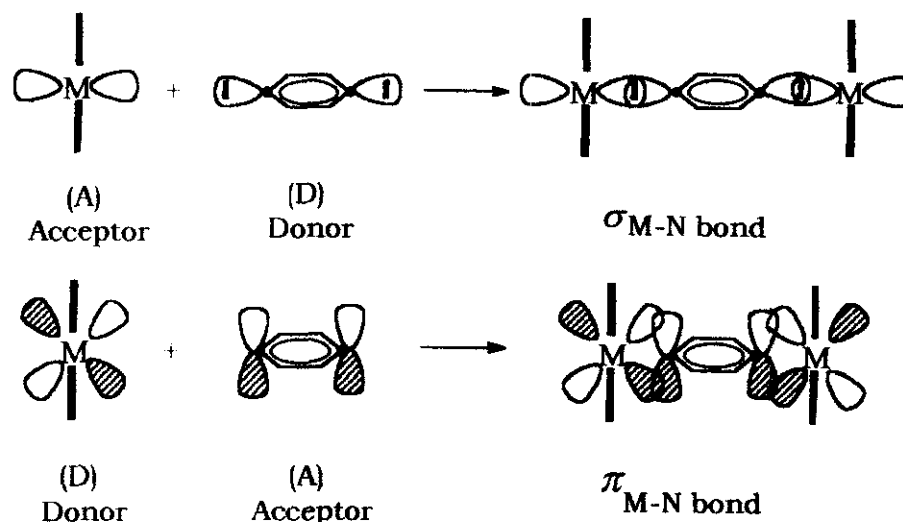
69

Fig.4.5b Possible σ- and π- back bonding in linearly linked Lewis-base adducts of M(mbt)$_2$

4.3.2.3 Electronic spectra of Lewis-base adducts of Co(mbt)$_2$

Like in the Ni(II) systems, the electronic spectra of the Lewis-base adducts of Co(mbt)$_2$ are seen to be distinctly different from the 4-coordinated parent complex. While the tetrahedral Co(mbt)$_2$ has a broad envelop consisting of three peaks in the range 14000-16500 cm^{-1}, its adducts showed three sets of bands around 9000 cm^{-1}, 15000 cm^{-1} and 19000 cm^{-1}. unfortunately the instrument at our disposal could not measure the peak around 9000 cm^{-1}. However the other two peaks could be clearly measured for all the Co(mbt)$_2$ adducts. The data are presented in Table 4.4.

Table 4.4 Electronic spectral data and magnetic moments of Co(mbt)$_2$ and its Lewis-base adducts

Compound	Abs. Max (cm^{-1})	Tentative Assignments	μ_{eff} (BM)
[Co(mbt)$_2$]	16450, 15150, 14325	$^4A_2 \rightarrow {}^4T_1(P)$	4.40
[Co(mbt)$_2$(pyr)]$_2$	15500 18900	$^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^4T_{1g}(P)$	4.70
[Co(mbt)$_2$(amp)]$_2$	15750 18860	$^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^4T_{1g}(P)$	4.60
[Co(mbt)$_2$(pyz)]$_n$	15130 18110	$^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^4T_{1g}(P)$	4.70
[Co(mbt)$_2$(bipy)]$_n$	14925 19120	$^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^4T_{1g}(P)$	4.62

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Some of the characteristic spectra of the adducts are reproduced in Fig.4.6. The absorption maxima appearing around 15000cm^{-1} are assigned to $^4T_{1g} \rightarrow {}^4A_{2g}$. The higher energy band appearing around 19000 cm^{-1} in all the adducts is typical of octahedral Co(II) complexes. Eventhough there is difference in the peak maxima in these adducts, no attempt was made to determine the relative ligand field strengths and other spectroscopic parameters for the adducts. The structural and bonding features in these adducts could be expected to be similar to Ni(mbt)$_2$ adducts, discussed above.
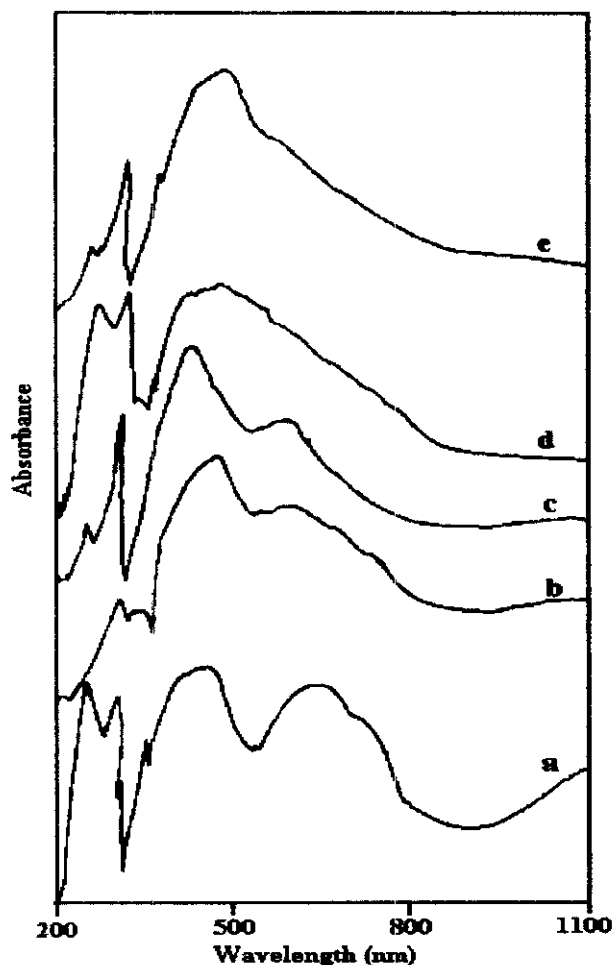

Fig.4.6 Electronic spectra of Lewis-base adducts of Co(mbt)$_2$
(a) Co(mbt)$_2$, (b) Co(mbt)$_2$(pyr)$_2$,
(c) Co(mbt)$_2$(amp)$_2$, (d) [Co(mbt)$_2$(pyz)]$_n$,
(e) [Co(mbt)$_2$(bipy)]$_n$

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4.3.2.4 Magnetic susceptibility measurements

Magnetic susceptibility measurements of all the adducts of $Ni(mbt)_2$ were carried out to determine the spin-state of the complexes. The μ_{eff} values evaluated for the adducts were seen to be in the range 3.0-3.2 BM (Table 4.3). The values are typical of octahedral Ni(II) complexes with some contribution from spin-orbit coupling. It is interesting to note that among the various adducts azpy and bipy derivatives have a slightly lower value for the μ_{eff} (3.01 BM) as compared to the pyr and amp adducts. As discussed earlier the former ones have an extended polymeric structure while the latter ones exist in monomeric form. We expect that the extended system would have lesser orbital contribution to the magnetic moment than the simple monomeric ones and hence the slight change in the μ_{eff} values.

In the case of $Co(mbt)_2$ adducts the μ_{eff} values are seen to be in the range 4.6-4.7 BM.[32] As compared to the parent tetrahedral $Co(mbt)_2$, which has got a μ_{eff} value of 4.4 BM, these adducts are seen to have higher μ_{eff} values. Since the number of unpaired electrons in both the parent $Co(mbt)_2$ and its adducts is same (three unpaired electrons) the difference in μ_{eff} values in these two systems could be attributed to varying extent of spin-orbital coupling in them. The μ_{eff} values in the range 4.6-4.7 BM found in the adducts is typical of octahedral Co(II) species. It is evident that there is the possibility of greater contribution of orbital component to the spin component in octahedral field than in tetrahedral field in a d^7 system. The higher μ_{eff} value observed for the adducts is essentially due to this.

From the detailed study of elemental analysis, infra-red and electronic spectral data and magnetic susceptibility measurements the Lewis-base adducts of $M(mbt)_2$ could be assigned the following tentative structures (Fig.4.7 - 4.10).

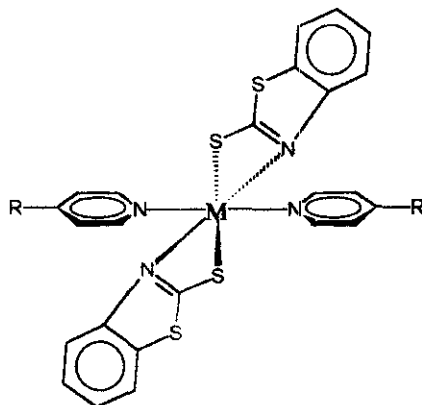**Fig.4.7** The tentative structure of M(mbt)₂ (LB)₂
M = Co(II) or Ni(II), (LB) = pyr, (R = H), amp, (R= NH₂)
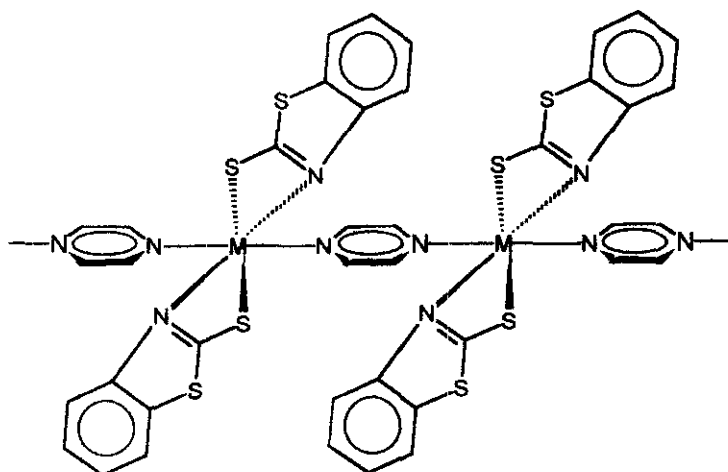
Fig.4.8 The proposed structure of [M(mbt)₂(pyz)]ₙ, M=Co(II), Ni(II).
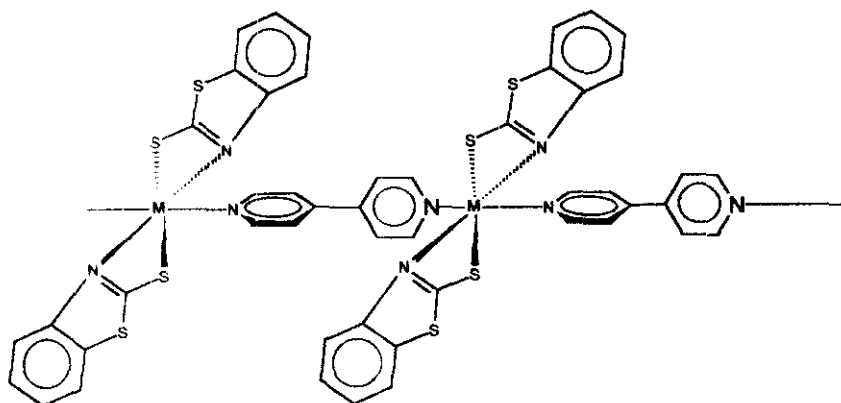
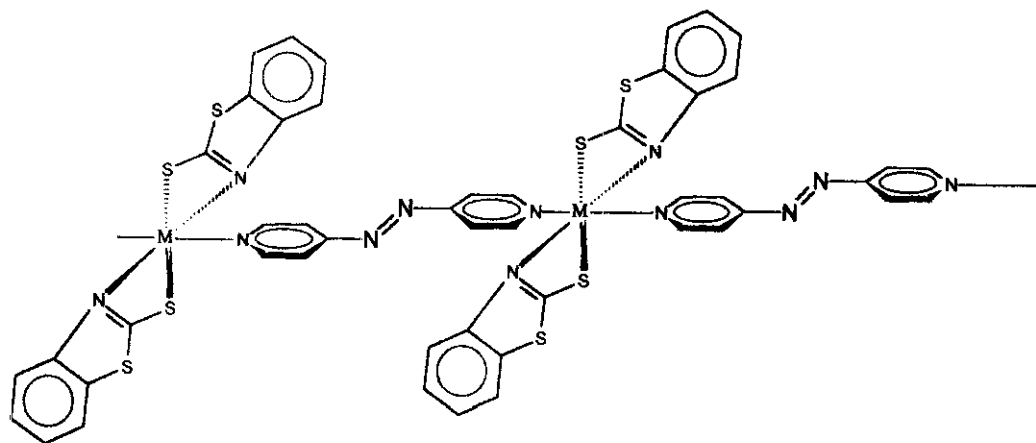**Fig.4.9** The proposed structure of [M(mbt)₂(bipy)]ₙ, M=Co(II), Ni(II).

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Fig.4.10 The proposed structure of [Ni(mbt)$_2$(azpy)]$_n$.

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