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## Synthesis and characterisation of monomeric and polymeric Lewis-base adducts of 2-mercaptobenzoxazolate complexes of Co(II) and Ni(II)

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### 6.1 Introduction

In the preceding chapter while discussing the 4-coordinated Co(II) and Ni(II) complexes of mbtH and their Lewis-base adducts we have demonstrated that the 2-mercaptobenzothiazolato moiety acts as a bidentate ligand resulting in  $MN_2S_2$  chromophore.<sup>(1)</sup> As discussed, the mbtH has three donor centres involving two S atoms and one N atom. The ligation is seen to be occurring via tautomerisation and consequent deprotonation through exocyclic S and cyclic N atoms.<sup>(2)</sup> A very closely related ligand moiety associated with mbtH is 2-mercaptobenzoxazole, mboH. Unlike mbtH which contains one cyclic N, one cyclic S and one exocyclic S, the mboH has one cyclic N, one cyclic O and one exocyclic S atom. So mboH can be considered as the O-analogue of mbtH. It is instructive to note that mboH has three different hetero atoms connected to a  $sp^2$  carbon. Since S and O have comparable ligation characteristics but with varying electronic effects it would be worthwhile to study the Co(II) and Ni(II) complexes of mboH and their Lewis-base adducts and compare their properties with those of the mbt species. The present chapter deals with the preparation, isolation and characterisation of 4-coordinated complexes of Co(II) and Ni(II) with  $mbo^-$  and their various adducts involving different Lewis-bases mentioned in Chapter 4.



## 6.2 Experimental

### 6.2.1 Preparative Details

#### 6.2.2.1 Four-coordinated complexes of 2-mercaptobenzoxazole, mboH

##### a) *Bis(2-mercaptobenzoxazolato)nickel(II), Ni(mbo)<sub>2</sub>*

A solution of NiCl<sub>2</sub>.6H<sub>2</sub>O was prepared by dissolving 1.65g (0.01 mol) in 25 ml of ethanol. This salt solution was added dropwise to a solution of mboH(3.00g, 0.02 mol) in 150 ml of ethanol with continuous stirring. This was followed by the dropwise addition of 5M NH<sub>3</sub> solution when a dark brown solid was obtained. The precipitate was digested on a water bath for 2h and filtered. The dark brown complex was then washed with water, then with ethanol followed by diethyl ether. The complex obtained was dried at 100°C for 3h. Yield was 90%.

##### b) *Bis(2-mercaptobenzoxazolato)cobalt(II), Co(mbo)<sub>2</sub>*

The preparative procedure adopted for this complex was also similar to that employed for Ni(mbo)<sub>2</sub>. The metal salt used was CoCl<sub>2</sub>.6H<sub>2</sub>O(2.38g, 0.01 mol) which was dissolved in ethanol and added dropwise to 3.00g (0.02 ml) of mboH in 100 ml ethanol with stirring. The dark green compound precipitated after the addition of 5M NH<sub>3</sub> in dropwise was washed repeatedly with water, ethyl alcohol and finally with diethyl ether. The compound was dried *in vacuo* at 80°C. Yield was found to be 90%.

#### 6.2.1.2 Lewis-base adducts of M(mbo)<sub>2</sub>

##### a) *Ni(mbo)<sub>2</sub>(pyr)<sub>2</sub>*

A solid-gas phase reaction was adopted for the preparation of the pyridine adduct from Ni(mbo)<sub>2</sub>. About 0.36g (1mmol) of Ni(mbo)<sub>2</sub> was kept in a watch glass in a desiccator which contained about 25 ml of pyridine kept in a petridish at its base. The brown coloured complex was seen to be changing its colour to light green after 12h. The exposure to pyridine atmosphere was



continued to about 48h to complete the conversion. The adduct formed was washed with acetone and with diethyl ether. It was dried *in vacuo*. Yield was 100%.

b)  $M(mbo)_2(pyr)_2$

An alternate method was also used for the preparation of pyridine adducts of  $M(mbo)_2$  in solution phase. A solution of pyridine was prepared in benzene by mixing 1ml of pyridine in 10 ml of benzene. This pyridine solution was added dropwise to a solution of  $Co(mbo)_2$  ( 0.36 g, 1 mmol) prepared from benzene (20 ml). The adduct was separated out when the reaction mixture was heated for about 5min. This was washed with benzene followed by diethyl ether and dried *in vacuo*. Yield noted was 85%.

c)  $M(mbo)_2(amp)_2$

About 0.19 g(0.002 mol) of 4-aminopyridine was dissolved in 10 ml of acetone and this was added dropwise to a solution of  $M(mbo)_2$  prepared by dissolving 0.36 g (0.001 mol) in 25 ml of acetone. Benzene was used as solvent for the preparation of  $[Co(mbo)_2(amp)_2]$ . While on mixing a rose-violet coloured compound was separated out in the case of  $Co(mbo)_2$ , a green coloured compound was formed after heating on a water bath (15 min) for  $Ni(mbo)_2$ . This precipitate was washed with acetone, diethyl ether followed by petroleum ether. These compounds were dried *in vacuo*.

d)  $[Co(mbo)_2(pyraz)]_n$

A solution of pyrazine (0.16 g, 0.002 mol) was prepared in 10 ml of acetone, and was added to a solution of  $Co(mbo)_2$  (0.39 g, 0.001 mol) with constant stirring. The solution mixture was heated for about 15 min on a water bath. The brown coloured complex precipitated was washed with acetone repeatedly followed by diethyl ether and dried *in vacuo*.



e)  $[M(mbo)_2(bipy)]_n$

About 1.0 mmol.(0.156 g) of 4,4'-bipyridine was dissolved in 10 ml of benzene and it was added dropwise to a milli molar solution (0.39 g) of  $M(mbo)_2$ . This solution was heated on a water bath for 15min. The precipitated complex was washed with benzene, acetone then with diethyl ether. The resulting complexes were dried *in vacuo*.

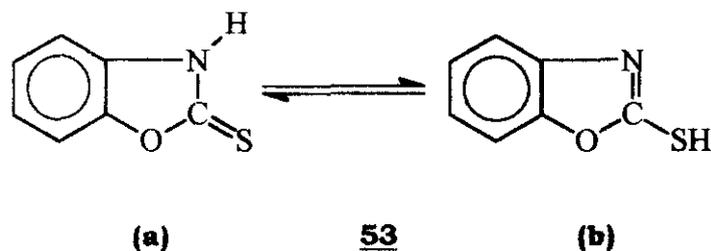
f)  $[M(mbo)_2(azpy)]_n$

The method employed for the preparation of  $[M(mbo)_2(bipy)]_n$  was used for the preparation of these complexes also.

## 6.3 Results and Discussion

### 6.3.1 Four-Coordinated $Co(mbo)_2$ and $Ni(mbo)_2$

Just as mbtH, its O-analogue 2-mercaptobenzoxazole also can be expected to exist in tautomeric forms as shown in **53**.



The thiol form, being acidic, is prone to deprotonation and hence can act as an anionic ligand ( $mbo^-$ ). The overall electronic features and bonding pattern in its complexes can be expected to be somewhat similar to that in  $mbt^-$  species. The donor orbitals on the various hetero atoms and the  $\pi$ -electron system of  $mbo^-$  are depicted in **54**.



**54a** shows its bidentate character either through N and S or through O and S. In either case a neutral bis-chelate is expected to form for both Co(II) and Ni(II). In **54b** the electronic contribution from each of the atoms of the five membered ring to the  $\pi$ -framework is shown which indicates the possibility of attaining aromatic character ( $6\pi$ -electrons) if O and N are  $sp^2$  hybridised. The extended conjugation is expected with the exocyclic S contributing 2 electrons to the  $\pi$ -system in which case the negative charge of  $mbo^-$  can be expected to be highly delocalised within the  $\pi$ -framework.

The analytical data show a strict 1:2 composition for  $Co(mbo)_2$  and  $Ni(mbo)_2$ . (Table 6.1). The  $\nu_{NH}$  and  $\delta_{NH}$  observed at  $3250$  and  $1612\text{cm}^{-1}$  respectively in the IR spectrum of ligand  $mboH$  are seen missing in its Co(II) and Ni(II) complexes. This indicate the deprotonation of the  $mboH$  possibly from its thiol form **53b**.<sup>(3,4)</sup> The strong band observed for  $mboH$  at  $1500\text{ cm}^{-1}$  is essentially  $\nu_{N=C=S}$ . This was found shifted to  $1450\text{ cm}^{-1}$ , and  $1440\text{ cm}^{-1}$  in its  $Co(mbo)_2$  and  $Ni(mbo)_2$ . The combination band ( $\nu_{C=S} + \nu_{CN}$ ) at  $1340\text{ cm}^{-1}$  for  $mboH$  is also seen shifted to lower regions in its complexes ( $1250\text{ cm}^{-1}$  for  $Co(mbo)_2$  and  $1255\text{ cm}^{-1}$  for  $Ni(mbo)_2$ ). Further, the  $672\text{ cm}^{-1}$  peak assignable to  $\nu_{C-S}$  in  $mboH$  is found to be shifted upwards ( $735-740\text{ cm}^{-1}$ ) in  $Co(mbo)_2$  and  $Ni(mbo)_2$ . All these data indicate the coordination of the ligand through N and S in its complexes<sup>(2,5)</sup> (Tables 6.2 and 6.4).

**Table 6.1** Analytical data of the adducts of  $M(\text{mbo})_2$ 

Complex Empirical formula	Formula weight	Elemental content % obsvd. (calcd.)				Colour
		C	H	N	M	
$[\text{Co}(\text{mbo})_2]$ $\text{CoC}_{14}\text{N}_2\text{H}_8\text{O}_2\text{S}_2$	358.93	46.82 (46.80)	2.24 (2.22)	7.82 (7.80)	16.45 (16.41)	Green
$[\text{Co}(\text{mbo})_2(\text{pyr})_2]$ $\text{CoC}_{24}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2$	516.93	55.77 (55.71)	3.40 (3.48)	10.81 (10.83)	11.41 11.39	Brown
$[\text{Co}(\text{mbo})_2(\text{amp})_2]$ $\text{CoC}_{24}\text{H}_{20}\text{N}_6\text{O}_2\text{S}_2$	546.93	52.55 (52.65)	3.70 (3.65)	15.35 (15.35)	10.85 (10.77)	Rose red
$[\text{Co}(\text{mbo})_2(\text{bipy})]_n$ $\text{CoC}_{24}\text{H}_{16}\text{N}_4\text{O}_2\text{S}_2$	514.93	55.93 (55.92)	3.17 (3.10)	10.80 (10.87)	11.45 (11.44)	Brown
$[\text{Co}(\text{mbo})_2(\text{azpy})]_n$ $\text{CoC}_{24}\text{H}_{16}\text{N}_4\text{O}_2\text{S}_2$	542.93	53.07 (53.04)	2.99 (2.94)	10.30 (10.31)	10.80 (10.85)	Brown
$[\text{Co}(\text{mbo})_2(\text{pyz})]_n$ $\text{CoC}_{18}\text{N}_4\text{H}_{12}\text{O}_2\text{S}_2$	438.93	49.20 (49.21)	2.74 (2.73)	12.80 (12.75)	13.49 (13.42)	Dark brown
$[\text{Ni}(\text{mbo})_2]$ $\text{NiC}_{14}\text{H}_8\text{N}_2\text{O}_2\text{S}_2$	358.69	46.71 (46.84)	2.12 (2.23)	7.92 (7.80)	16.47 (16.36)	Dark brown
$[\text{Ni}(\text{mbo})_2(\text{pyr})_2]$ $\text{NiC}_{24}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2$	516.69	55.64 (55.73)	3.52 (3.48)	10.88 (10.84)	11.40 (11.36)	Greenish
$[\text{Ni}(\text{mbo})_2(\text{amp})_2]$ $\text{NiC}_{24}\text{H}_{20}\text{N}_6\text{O}_2\text{S}_2$	546.69	52.70 (52.68)	3.63 (3.65)	15.34 (15.36)	10.80 (10.74)	Greenish yellow
$[\text{Ni}(\text{mbo})_2(\text{bipy})]_n$ $\text{NiC}_{24}\text{H}_{16}\text{N}_4\text{O}_2\text{S}_2$	514.69	55.94 (55.95)	3.21 (3.10)	10.84 (10.88)	11.38 (11.40)	Yellowish green
$[\text{Ni}(\text{mbo})_2(\text{azpy})]_n$ $\text{NiC}_{24}\text{H}_{16}\text{N}_4\text{O}_2\text{S}_2$	542.69	53.00 (53.06)	2.98 (2.94)	15.45 (15.47)	10.78 (10.81)	Pale orange

Magnetic measurement showed the diamagnetic character for  $\text{Ni}(\text{mbo})_2$  indicating its square planar geometry for the complex.<sup>(6)</sup> The  $\text{Co}(\text{mbo})_2$  is found to be paramagnetic and has the room temperature  $\mu_{\text{eff}}$  value of 4.34BM. Cobalt(II) is a  $d^7$  system and has the ability to take either low spin configuration (with one unpaired electron) or high spin state (with three unpaired electrons). In its 4-coordinated form the low spin state should be of square planar geometry and high spin state of tetrahedral configuration. The observed  $\mu_{\text{eff}}$  value of 4.34BM clearly indicates the high spin character of the complex. The high  $\mu_{\text{eff}}$  value shows the orbital contribution to the spin-only value (3.9BM) which is possible in the tetrahedral state of any complex (Table 6.3).

The electronic spectrum of  $\text{Ni}(\text{mbo})_2$  (Fig. 6.4) showed a weak absorption at  $21970 \text{ cm}^{-1}$  with no other low energy peak. This is very characteristic of



square planar Ni(II) species in which case the above transition could be assigned to  ${}^1B_{1g} \rightarrow {}^1A_{1g}$ . The  $\text{Co(mbo)}_2$  gave an absorption peak in the region 15000-17000  $\text{cm}^{-1}$  with fine structure which is typical of tetrahedral Co(II) complexes<sup>(7,8)</sup> (Fig. 6.1). The peak could be assigned to  ${}^4A_2 \rightarrow {}^4T_1(P)$ . The lower energy transition expected for Co(II) species in tetrahedral geometry could not be measured, being outside the limit of the instrument used. All the foregoing data indicated the strict four-coordinated character of both the complexes, with  $\text{Ni(mbo)}_2$  taking square planar geometry and  $\text{Co(mbo)}_2$  assuming tetrahedral configuration (Table 6.5).

### 6.3.2 Lewis-base Adducts of $\text{Co(mbo)}_2$

The bidentate Lewis-bases chosen are amp, pyz, bipy and azpy which have the donor N atoms disposed at the two ends of the molecule and have the extensive conjugation. The various adducts separated are  $[\text{Co(mbo)}_2(\text{amp})_2]_n$ ,  $[\text{Co(mbo)}_2(\text{pyz})]_n$ ,  $[\text{Co(mbo)}_2(\text{bipy})]_n$  and  $[\text{Co(mbo)}_2(\text{azpy})]_n$ . As a reference molecule the pyridine adduct  $[\text{Co(mbo)}_2(\text{pyr})_2]$  was also prepared. The analytical data shown (Table 6.1) confirm the 1:1 (complex : Lewis-base) composition for pyz, bipy and azpy complexes, and 1:2 ( $\text{Co(mbo)}_2$  : Lewis-base) for amp and pyr complexes. It is interesting to note the thermal reversibility of pyr, bipy and pyz complexes which show simple Lewis-base loss in the temperature range 95-135°C leaving back the parent  $\text{Co(mbo)}_2$ .

#### 6.3.2.1 Infra-red spectra

As compared to the IR spectrum of  $\text{Co(mbo)}_2$ , its Lewis-base adducts of pyz, amp, bipy, azpy and pyr gave several additional and modified peaks. The additional peaks in all the cases correspond to the Lewis-base moiety present in the complex. The absorption at 1440, 1480, 1580 and 1595  $\text{cm}^{-1}$  observed for pyridine molecule are known to have their origin to  $\text{C}=\text{C}$  and  $\text{C}=\text{N}$  ring stretching skeletal vibrations.<sup>(9)</sup> These bands are reported to be characteristic of any pyridine bearing molecule or its derivatives. Only very slight variation in position is known to be observed among them. In addition to this the peaks at 604  $\text{cm}^{-1}$  (in-plane ring deformation) and 405  $\text{cm}^{-1}$  (out of plane ring deformation) are typical of pyridine moiety.<sup>(3)</sup> In  $\text{Co(mbo)}_2(\text{pyr})_2$  the three skeletal stretching bands are found to occur at 1460, 1570 and 1600  $\text{cm}^{-1}$



and the in-plane ring deformation at  $690\text{ cm}^{-1}$ , and the out-of-plane ring deformation at  $425\text{ cm}^{-1}$ . These shifts observed for these bands in the complex indicate the coordination of pyridine moiety to the metal through its N.

4-Aminopyridine is a bidentate species with no possibility of chelation but with the potential ability to coordinate to metal through ring N and also through exocyclic-NH<sub>2</sub> group. If such a bidentate character is manifested, a linearly linked polymeric array system would be resulted for Co(mbo)<sub>2</sub> with amp. The IR spectrum of Co(mbo)<sub>2</sub> (amp)<sub>2</sub> gave all peaks characteristic of amp in addition to Co(mbo)<sub>2</sub>. Our observation that the Co(mbo)<sub>2</sub> form only 1:2 (complex:amp) complexes rather than 1:1 species indicates that only one of the N atoms of amp is involved in the coordination. The -NH<sub>2</sub> vibrations of free amp molecule are seen to occur at  $3300$  and  $3200\text{ cm}^{-1}$  which could be assigned to  $\nu_{\text{NH}}(\text{sym})$  and  $\nu_{\text{NH}}(\text{asym})$  vibrations respectively.<sup>(3)</sup> The bending  $\delta_{\text{NH}}$  mode is seen as a weak band at  $1640\text{ cm}^{-1}$  in the spectra. The characteristic pyridine vibrations for the molecule appear at  $1470$ ,  $1500$ ,  $1520$  and  $1590\text{ cm}^{-1}$  (C=C and C=N ring stretching skeletal bands) and at  $610\text{ cm}^{-1}$  and  $405\text{ cm}^{-1}$  (in-plane and out of plane ring deformations). In Co(mbo)<sub>2</sub>(amp)<sub>2</sub> all the bands corresponding to -NH<sub>2</sub> group are seen almost unaltered ( $3305$  and  $3200\text{ cm}^{-1}$ ), as compared to free amp. This clearly indicates the non-coordination of amino group of the Lewis-base. However the characteristic peaks corresponding to pyridyl function of amp are found to be perceptibly shifted (ring stretching skeletal bands to  $1460$ ,  $1510$ ,  $1555$ , and  $1610\text{ cm}^{-1}$  respectively). Further, both the in-plane and out-of plane ring deformations of pyridine moiety are found shifted upwards to  $640$  and  $420\text{ cm}^{-1}$  respectively. These observations indicate the coordination of amp through its pyridyl N in the complex. The non-participation of -NH<sub>2</sub> group in coordination could be attributed to the involvement of the -NH<sub>2</sub> group in  $\pi$ -conjugation with the aromatic pyridyl moiety. These are discussed in detail in Chapter 4.

The IR spectrum of [Co(mbo)<sub>2</sub>(bipy)]<sub>n</sub> offers some interesting features as observed in the case of its Co(mbt)<sub>2</sub> analogue. The additional peaks found in the adducts as compared to the parent complex are indicative of the presence of bipyridine in the complex. Just as in the case of [Co(mbt)<sub>2</sub>(bipy)]<sub>n</sub> several diagnostic peaks could be used for inferring the mode of coordination and the overall disposition of the bipy moiety in the molecule.



As mentioned in Chapter 4, if bipy is to act as a monodentate ligand (forming 1:2 adduct with  $\text{Co(mbo)}_2$ ) the appearance of six bands at 800, 1070, 1215, 1402, 1483 and 1589  $\text{cm}^{-1}$  is anticipated.<sup>(10)</sup> In its 1:1 adducts wherein it acts as a bridging bidentate ligand three of these absorptions at 1215, 1402 and 1589  $\text{cm}^{-1}$  are expected to be absent. The 1215  $\text{cm}^{-1}$  peak is essentially due to in-plane C-H bending and 1589  $\text{cm}^{-1}$  due to ring vibration of pyridyl moiety. In the IR spectrum of the  $[\text{Co(mbo)}_2(\text{bipy})]_n$  disappearance of these peaks is seen. The bands at 800, 1080 and 1480  $\text{cm}^{-1}$  however are present in the complex, with almost no intensity loss. These data strongly indicate the bridging character of the bipy moiety with both its pyridyl Ns involved in bonding with the Co atom at its two ends. This necessitates strict 1:1 composition and overall polymeric character to the adduct. Careful analysis of the IR spectrum of the complex showed that the characteristic peak of bipy at 1215  $\text{cm}^{-1}$  which is an in-plane vibration is not altogether absent in the complex but is seen as a very weak band. As mentioned, this is diagnostic of the relative dispositions of the pyridyl moieties in bipy which indicates that the two rings are not coplanar but remain tilted. This is discussed in Chapter 4 in detail.

The 4,4'-azopyridine ligand has four possible sites of coordination, namely the two pyridyl nitrogens and the two azo nitrogens. The former are much more accessible for coordination due to steric reason, and for the binuclear complex reported by Lawray<sup>(11)</sup> et al the two pentammine ruthenium groups are assumed to be fixed through its pyridyl nitrogen. The appearance of new absorption bands at 1420, 1460, 1560 and 1590  $\text{cm}^{-1}$  in the IR spectrum of  $[\text{Co(mbo)}_2(\text{azpy})]_n$ , assignable to C=C and C=N ring stretching skeletal vibrations of pyridine moiety, and new IR bands at 680  $\text{cm}^{-1}$  and 420  $\text{cm}^{-1}$  (in plane and out of plane ring deformations of pyridyl moiety) indicate the coordination of pyridine moiety to the metal ion through its pyridyl N.

As discussed in Chapter 4 there was some slight mismatch in composition of the adduct of  $\text{Co(mbt)}_2$  with pyrazine from the theoretically expected value of 1:1 stoichiometry. In contrast the overall yield and the chemical composition of  $[\text{Co(mbo)}_2(\text{pyz})]_n$  are seen to be more accurate than that of  $[\text{Co(mbt)}_2(\text{pyz})]_n$ . No peaks in the range 950-1000, 1230 and 1600  $\text{cm}^{-1}$  are observed for the present complex which clearly indicate the high local symmetry of the



pyrazine moiety in the adduct.<sup>(12)</sup> This strongly indicates the absence of any monodentate pyrazine fragment in the system. So the overall structure of the adduct could be considered as linearly linked (through pyrazine) polymeric system with a very long chain length. The important IR stretching frequencies and their assignments are given in Table 6.2.

**Table 6.2** IR spectral data of Co(mbo)<sub>2</sub> and its Lewis-base adducts(cm<sup>-1</sup>)

Compound	ν <sub>C-C</sub> + CN	ν <sub>C=N</sub> s	ν <sub>C-S</sub>	*C=C and C=N	**Ring deformation		ν <sub>NH2</sub>	δ <sub>NH</sub>
					Out of Plane	In plane		
mboH	1340	1500	672	-	-	-	3250	1612
[Co(mbo) <sub>2</sub> ]	1250	1450	740	-	-	-	-	-
[Co(mbo) <sub>2</sub> (pyr) <sub>2</sub> ]	1250	1440	735	1460, 1570, 1600	425	690	-	-
[Co(mbo) <sub>2</sub> (amp) <sub>2</sub> ]	1250	1460	735	1460, 1510, 1555, 1610	420	640	3200 3300	1630
[Co(mbo) <sub>2</sub> (bipy)] <sub>n</sub>	1242	1410	735	1420, 1460, 1525, 1600	425	670	-	-
[Co(mbo) <sub>2</sub> (azpy)] <sub>n</sub>	1250	1410	735	1420, 1460, 1560, 1590	420	680	-	-
[Co(mbo) <sub>2</sub> (pyz)] <sub>n</sub>	1250	1410	740	-	-	-	-	-

\*C=C and C=N ring stretching of pyridine ring

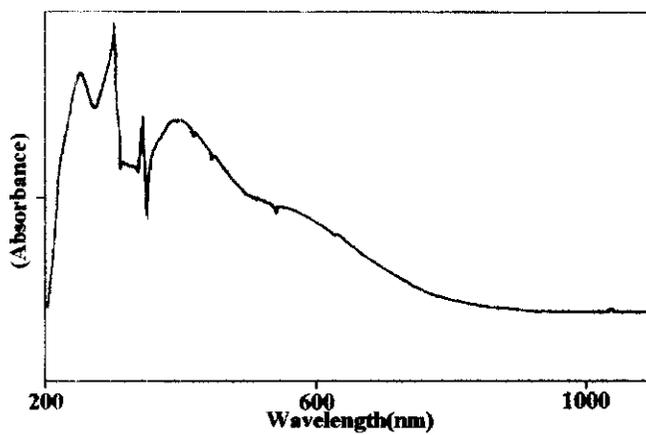
\*\* Ring deformation of pyridine

### 6.3.2.2 Electronic spectra and magnetic properties

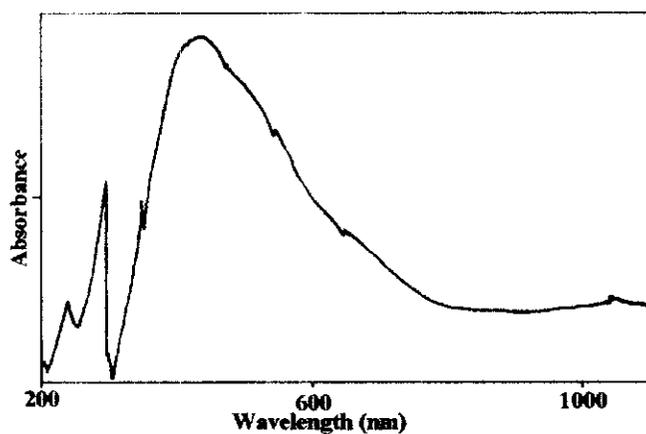
Just as in the case of mbt analogue the tetrahedral Co(mbo)<sub>2</sub> also shows significant change in its electronic spectra on adduct formation (Fig.6.1-6.3). The characteristic fine features in the bands of Co(mbo)<sub>2</sub> are seen disappearing in the adducts. The new absorptions found for the adducts are in the range 17700-18400 and 15450-15850 cm<sup>-1</sup>. These bands are typical of octahedral high spin Co(II) complexes. The transitions corresponding to these peaks could be assigned to <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P)(17700-18400 cm<sup>-1</sup>) and <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>1</sub>



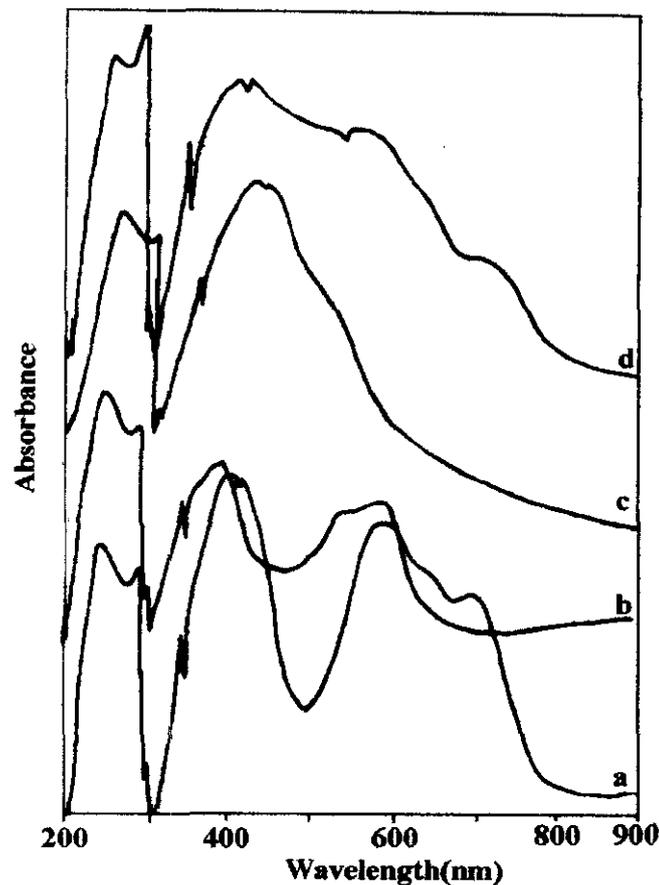
(15450-15850  $\text{cm}^{-1}$ ).<sup>6)</sup> The electronic spectrum of  $\text{Co}(\text{mbo})_2$  and its adducts are given in Fig. 6.1, 6.2 and 6.3.



**Fig. 6.1** Electronic spectrum of  $\text{Co}(\text{mbo})_2(\text{pyr})_2$



**Fig. 6.2** Electronic spectrum of  $[\text{Co}(\text{mbo})_2(\text{bipy})]_n$



**Fig. 6.3** Electronic spectra of  $\text{Co(mbo)}_2$  and its Lewis-base adducts

- |  |   |
|--|---|
| (a) $\text{Co(mbo)}_2$ ,                 | (b) $\text{Co(mbo)}_2(\text{amp})_2$ ,  |
| (c) $[\text{Co(mbo)}_2(\text{pyz})]_n$ , | (d) $[\text{Co(mbo)}_2(\text{azpy})]_n$ |

The room temperature magnetic susceptibility measurements were carried out and  $\mu_{\text{eff}}$  values evaluated for all the adducts. The magnetic moment values for the complexes are found to be in the range 4.62-4.73BM.<sup>(13,14)</sup> No definite trend in  $\mu_{\text{eff}}$  values could be seen for the complexes. These high values however indicate high spin octahedral structure for the complexes. The electronic transitions, their assignments and magnetic moment values of  $\text{Co(mbo)}_2$  and their adducts are given in Table 6.3. The high spin rather than low spin state for all these Lewis-base adducts indicate the weak ligation property of the Lewis-bases with the parent  $\text{Co(mbo)}_2$ . The overall structure for all the complexes (adducts) could therefore expected to be distorted octahedral.

**Table 6.3** Electronic spectral and magnetic moment data of Co(mbo)<sub>2</sub> and its adducts

Compound	$\nu$ (cm <sup>-1</sup> )	Assignments	Magnetic moment (BM)	Geometry*
[Co(mbo) <sub>2</sub> ]	16891 15527 14347	<sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>1</sub> (P)	4.34	T <sub>d</sub>
[Co(mbo) <sub>2</sub> (pyr) <sub>2</sub> ]	17700 15827	<sup>4</sup> Tig(F) → <sup>4</sup> Tig(P) <sup>4</sup> Tig → <sup>4</sup> T <sub>1</sub>	4.73	O <sub>h</sub> or dist. O <sub>h</sub>
[Co(mbo) <sub>2</sub> (amp) <sub>2</sub> ]	18350 15625	<sup>4</sup> Tig(F) → <sup>4</sup> Tig(P) <sup>4</sup> Tig → <sup>4</sup> T <sub>1</sub>	4.62	"
[Co(mbo) <sub>2</sub> (bipy)] <sub>n</sub>	18490 15480	<sup>4</sup> Tig(F) → <sup>4</sup> Tig(P) <sup>4</sup> Tig → <sup>4</sup> T <sub>1</sub>	4.69	"
[Co(mbo) <sub>2</sub> (azpy)] <sub>n</sub>	18020 15820	<sup>4</sup> Tig(F) → <sup>4</sup> Tig(P) <sup>4</sup> Tig → <sup>4</sup> T <sub>1</sub>	4.65	"
[Co(mbo) <sub>2</sub> (pyz)] <sub>n</sub>	18382 16640	<sup>4</sup> Tig(F) → <sup>4</sup> Tig(P) <sup>4</sup> Tig → <sup>4</sup> T <sub>1</sub>	4.67	"

\* T<sub>d</sub> = tetrahedral. O<sub>h</sub> = octahedral and Dist.O<sub>h</sub> = Distorted octahedral

### 6.3.3 Lewis-base Adducts of Ni(mbo)<sub>2</sub>

The set of Lewis-bases chosen for the adduct formation with Ni(mbo)<sub>2</sub> were same as those used for Co(mbo)<sub>2</sub> and the mbo complexes. All the four bidentate Lewis-bases and pyridine were tried but those complexes which could be isolated are [Ni(mbo)<sub>2</sub>(pyr)<sub>2</sub>], [Ni(mbo)<sub>2</sub>(amp)<sub>2</sub>], [Ni(mbo)<sub>2</sub>(bipy)]<sub>n</sub> and [Ni(mbo)<sub>2</sub>(azpy)]<sub>n</sub>. In our hands pyrazine failed to form adduct with the Ni(mbo)<sub>2</sub>, even though preparations were tried by various techniques. All the complexes were chemically analysed which showed 1:2 adduct formation for Ni(mbo)<sub>2</sub>(pyr)<sub>2</sub> and Ni(mbo)<sub>2</sub>(amp)<sub>2</sub>. The bipy and azpy yielded only 1:1 adduct with polymeric nature, the overall composition being [Ni(mbo)<sub>2</sub>(bipy)]<sub>n</sub> and [Ni(mbo)<sub>2</sub>(azpy)]<sub>n</sub>.

#### 6.3.3.1 Infra-red spectra

As discussed in the case of Co(mbo)<sub>2</sub> and its Lewis-base adducts, the Ni(mbo)<sub>2</sub> and its Lewis-base adducts also show their characteristic peaks in their infra-red spectra (Table 6.4). The main difference between the parent Ni(mbo)<sub>2</sub> and its adducts is the appearance of several additional and



modified peaks in the latter. These additional bands have been verified and found to be due to the Lewis-base moiety. The appearance of new absorptions at 1460, 1480 and 1595  $\text{cm}^{-1}$ <sup>(9)</sup> in the IR spectrum of  $\text{Ni(mbo)}_2(\text{pyr})_2$  (assignable to C=C and C=N ring stretching skeletal vibrations) and new IR bands at 690 and 435  $\text{cm}^{-1}$  (in-plane and out-of-plane deformations respectively) indicate the coordination of pyridine moiety to the metal ion through its N atom in the adduct.<sup>(3)</sup>

The IR spectrum of  $[\text{Ni(mbo)}_2(\text{amp})_2]$  gave all characteristic peaks of 4-aminopyridine in addition to those observed for the parent compound,  $[\text{Ni(mbo)}_2]$ . The formation of 1:2 complex rather than 1:1 and almost unaltered symmetric  $\nu_{\text{NH}}$ (3300  $\text{cm}^{-1}$ ) asymmetric  $\nu_{\text{NH}}$ (3200  $\text{cm}^{-1}$ ), stretching vibrations and bending  $\delta_{\text{NH}}$  mode (1630  $\text{cm}^{-1}$ ) clearly indicate the non-coordination of amino group of Lewis-base (amp) on adduct formation. However the appearance and perceptible change in the characteristic peaks of pyridyl group in the range 1430-1600  $\text{cm}^{-1}$  (1460, 1515, 1560 and 1600  $\text{cm}^{-1}$ ) and upward shift of in-plane (690  $\text{cm}^{-1}$ ) and out-of-plane (470  $\text{cm}^{-1}$ ) ring deformation of pyridine moiety from 604 and 405  $\text{cm}^{-1}$  respectively indicate the coordination of amp through its pyridyl nitrogen.

The infra red spectrum of the bipyridyl adduct of  $\text{Ni(mbo)}_2$ ,  $[\text{Ni(mbo)}_2(\text{bipy})]_n$ , is exactly similar to that of its  $\text{Co(mbo)}_2$  analogue. As discussed earlier, the absence of peaks at 1402 and 1589  $\text{cm}^{-1}$  and appearance of three new peaks at 805, 1080 and 1480  $\text{cm}^{-1}$  in the IR spectrum of this Lewis-base adduct in addition to that of pyridyl moiety strongly indicate the bridging character of bipy with both its pyridyl Ns.<sup>(10)</sup> Consequently the resulting complex can be considered as a linearly linked polymeric array system. We could observe the appearance of a very weak band at 1210  $\text{cm}^{-1}$  which could be assigned to the in-plane vibration of bipyridyl moiety. This indicates that the two pyridyl fragments of the bipy molecule are not in the same plane but slightly distorted.

The IR spectra of  $[\text{Ni(mbo)}_2(\text{azpy})]_n$  has been found to be quite similar to that of the  $[\text{Co(mbo)}_2(\text{azpy})]_n$ . All the peaks characteristic of azpy like C=C and C=N ring stretching vibration (1460, 1500, 1560 and 1600  $\text{cm}^{-1}$ ), out of plane ring deformation (at 470  $\text{cm}^{-1}$ ) and in-plane ring deformation (at 680  $\text{cm}^{-1}$ ) could



be observed in the IR spectrum. All these values are as appeared in the  $[\text{Co}(\text{mbo})_2(\text{azpy})]_n$  with only slight variation. The overall composition and nature of the IR spectra indicate the coordination of azpy through its pyridyl Ns.

**Table 6.4** Infra red spectral data of  $\text{Ni}(\text{mbo})_2$  and its adducts ( $\text{cm}^{-1}$ )

Compound	$\nu_{\text{C}=\text{N}}$	$\nu_{\text{C}-\text{N}-\text{S}}$	$\nu_{\text{C}-\text{S}}$	*C=C and C=N	**Ring deformation		$\nu_{\text{NH}_2}$	$\delta_{\text{NH}}$
					Out of plane	In plane		
$[\text{Ni}(\text{mbo})_2]$	1255	1440	740	-	-	-	-	-
$[\text{Ni}(\text{mbo})_2(\text{pyr})_2]$	1250	1420	690	1460, 1480, 1600	435	690	-	-
$[\text{Ni}(\text{mbo})_2(\text{amp})_2]$	1250	1430	720	1460, 1515, 1560	470	690	3200 3300	1630
$[\text{Ni}(\text{mbo})_2(\text{bipy})]_n$	1250	1430	690	1465, 1480, 1505, 1600	470	680	-	-
$[\text{Ni}(\text{mbo})_2(\text{azpy})]_n$	1245	1430	700	1460, 1500, 1560, 1600	470	680	-	-

\*C=C and C=N ring stretching of pyridine ring

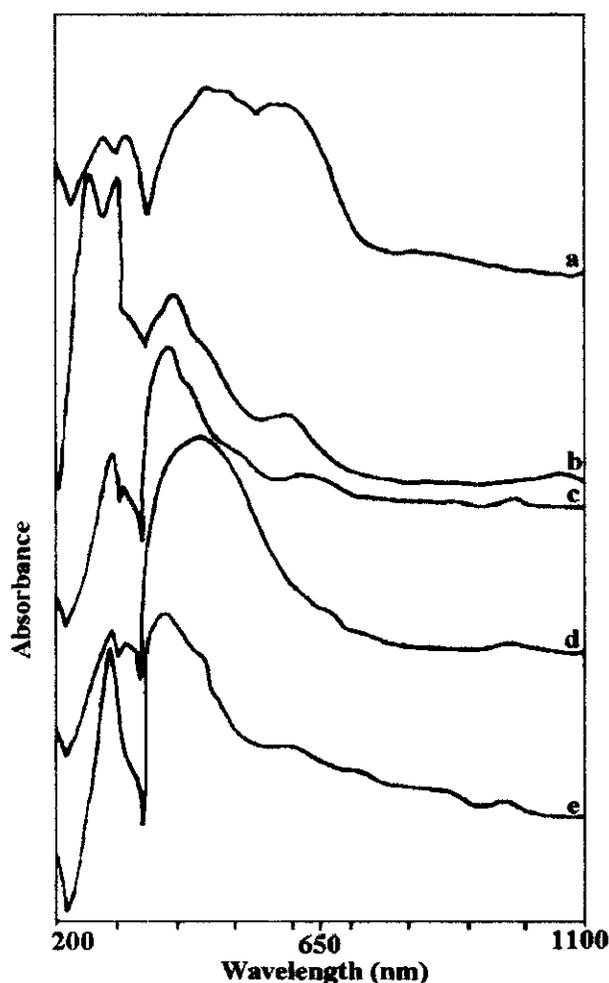
\*\* Ring deformation of pyridine

### 6.3.3.2 Electronic spectra and magnetic properties

The electronic spectra of various adducts of  $\text{Ni}(\text{mbo})_2$  as shown in Fig. 6.4. The significant change that is observed when  $\text{Ni}(\text{mbo})_2$  undergoes adduct formation is the disappearance of broad band at  $21970 \text{ cm}^{-1}$  and the appearance of three new bands in the range  $22320\text{-}23640 \text{ cm}^{-1}$ ,  $16310\text{-}18590 \text{ cm}^{-1}$  and  $9570\text{-}10470 \text{ cm}^{-1}$ , (Fig. 6.4) while the  $\text{Ni}(\text{mbo})_2$  peak at  $21970 \text{ cm}^{-1}$  is due to  ${}^1\text{B}_{1g} \rightarrow {}^1\text{A}_{1g}$  transition in a square planar geometry, the three bands mentioned above for the adducts are characteristic of octahedral Ni(II) species. The bands could be assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ , ( $\nu_3$ ),  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ , ( $\nu_2$ ), and



${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ , ( $\nu_1$ ) respectively<sup>(7)</sup> in agreement with typical Ni(II) octahedral complexes. We have evaluated the ligand-field parameters  $Dq$ , for all the adducts employing the methods as discussed earlier (Chapter 4). These show interesting trend. The  $Dq$  order for various adducts is seen to be as  $[Ni(mbo)_2(pyr)_2] < [Ni(mbo)_2(amp)_2] < [Ni(mbo)_2(azpy)]_n < [Ni(mbo)_2(bipy)]_n$ . The trend appears to be depended on the  $pK_a$  value of the Lewis-bases. The  $pK_a$  order is  $5.17 < 9.11$ .<sup>(15)</sup> The Racah parameter ( $B$ ) and Nephelauxetic parameter ( $\beta$ ) evaluated are also given in the Table 6.5. Significant changes are seen in these values for the various adducts.



**Fig. 6.4** Electronic spectra of  $Ni(mbo)_2$  and its Lewis-base adducts

(a)  $Ni(mbo)_2$ , (b)  $Ni(mbo)_2(pyr)_2$ , (c)  $Ni(mbo)_2(amp)_2$ ,  
 (d)  $[Ni(mbo)_2(azpy)]_n$ , (e)  $[Ni(mbo)_2(bipy)]_n$

While the parent Ni(mbo)<sub>2</sub> is diamagnetic all its adducts were seen to be paramagnetic to the extent of 2 electrons. The  $\mu_{\text{eff}}$  values evaluated are seen to be in the range 3.08-3.14BM for the adducts.<sup>(16)</sup> The electronic transitions, their assignments, Dq,  $\beta$ , B and magnetic moment  $\mu_{\text{eff}}$  data are given in Table 6.5.

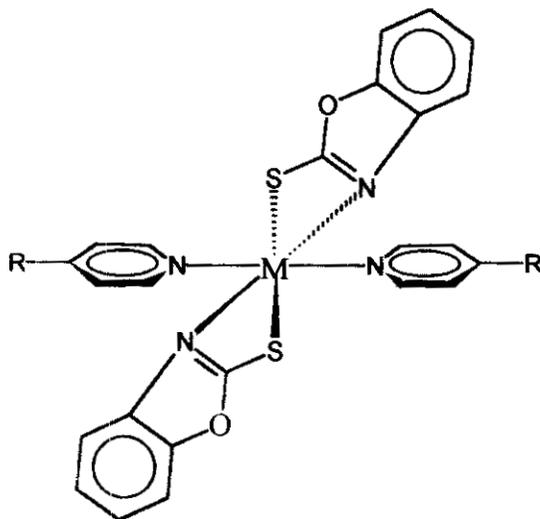
**Table 6.5** Electronic spectral data and ligand field parameters of the Ni(mbo)<sub>2</sub> adducts

Compound	$\nu$ (cm <sup>-1</sup> )	*Assignments	B (cm <sup>-1</sup> ) $\frac{\nu_2 + \nu_3 - 3\nu_1}{15}$	Dq (cm <sup>-1</sup> )	$\beta$	$\mu_{\text{eff}}$ (BM)
[Ni(mbo) <sub>2</sub> ]	30865 21980 17095	Charge transfer <sup>1</sup> B <sub>1g</sub> → <sup>1</sup> A <sub>1g</sub>	-	-	-	Dia
[Ni(mbo) <sub>2</sub> (pyr) <sub>2</sub> ]	22320 17450 9570	$\nu_3$ $\nu_2$ $\nu_1$	737	957.0	0.708	3.14
[Ni(mbo) <sub>2</sub> (amp) <sub>2</sub> ]	23640 16315 10280	$\nu_3$ $\nu_2$ $\nu_1$	608	1028.0	0.584	3.14
Ni(mbo) <sub>2</sub> (azpy) <sub>2</sub>	22370 18590 10340	$\nu_3$ $\nu_2$ $\nu_1$	651	1039.5	0.625	3.08
[Ni(mbo) <sub>2</sub> (bipy) <sub>2</sub> ]	22470 17636 10470	$\nu_3$ $\nu_2$ $\nu_1$	579.6	1047.0	0.556	3.06

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

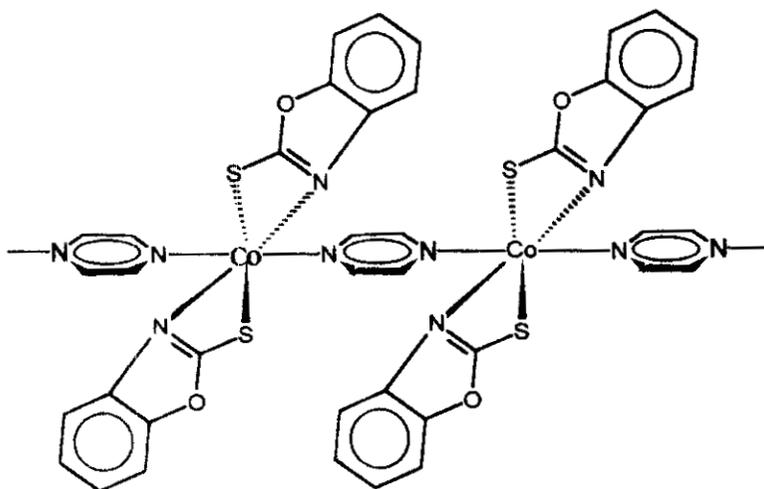
The data presented above indicate that the various Lewis-base adducts of M(mbo)<sub>2</sub> have an over all structure in Fig.6.5-6.8.



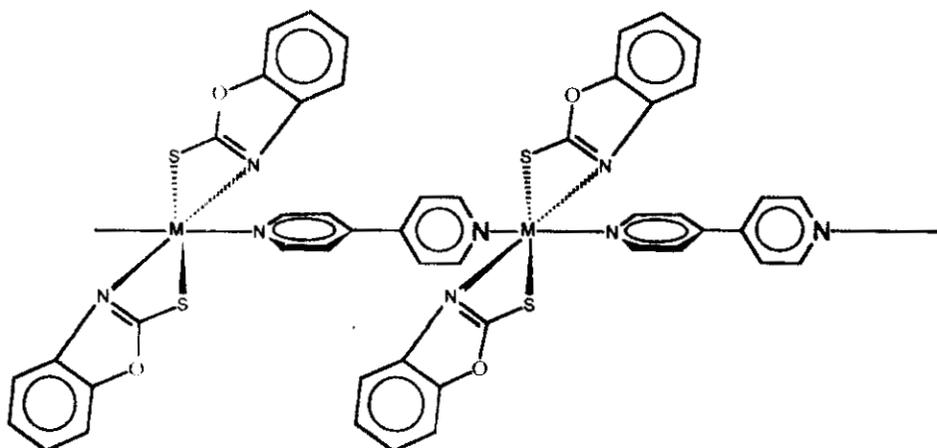


**Fig.6.5** The proposed structure of monomeric Lewis-base adducts of  $M(mbo)_2(LB)_2$

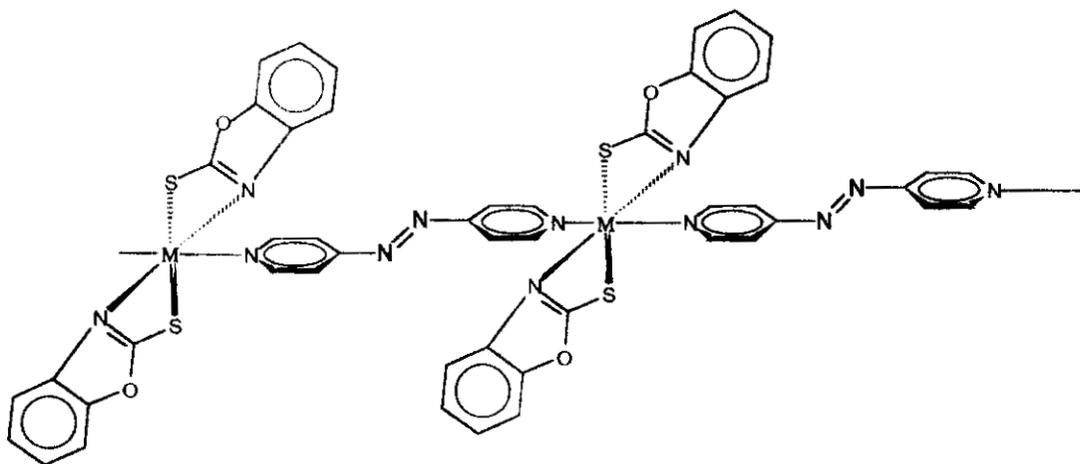
$M=Co(II)$  or  $Ni(II)$ ,  $(LB) = pyr$  ( $R = H$ ),  $amp$  ( $R=NH_2$ )



**Fig.6.6** The proposed structure of polymeric Lewis-base adducts of  $[Co(mbo)_2(Pyz)]_n$



**Fig.6.7** The proposed structure of polymeric Lewis-base adducts of  $[M(mbo)_2(bipy)]_n$ ,  $M=Co(II)$  or  $Ni(II)$ .



**Fig.6.8** The proposed structure of polymeric Lewis-base adducts of  $[M(mbo)_2(azpy)]_n$ ,  $M=Co(II)$  or  $Ni(II)$ .

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