RJC

RASĀYAN *J. Chem.*
Vol. 5 | No.3 | 311-320 | July-September | 2012
ISSN: 0974-1496 | CODEN: RJCABP
http://www.rasayanjournal.com

SYNTHESIS, THERMAL AND SPECTRAL CHARACTERIZATION OF AXIALLY BRIDGED POLYMERIC AND MONOMERIC LEWIS BASE ADDUCTS OF BIS (2-MERCAPTOBENZOTHIAZOLATO) COBALT (II)

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ABSTRACT

Octahedrally coordinated monomeric and axially bridged polymeric compounds from four coordinated cobalt(II) species have been synthesized and characterized by elemental analysis, infra red and electronic spectroscopy, magnetic susceptibility measurements and thermal analysis. The four coordinated system used was tetrahedral bis(2-mercaptobenzothiazolatocobalt(II), $Co(mbt)_2$ and ligands used were bidentate opposite end donors such as 4-aminopyridine, 4,4'-bipyridine and pyrazine. For comparison a monodentate ligand pyridine was also used. The complexes synthesized have the molecular formula $[Co(mbt)_2L_2]$ where L= pyridine and 4-aminopyridine and $[Co(mbt)_2L']n$ where L'= pyrazine and 4,4'-bipyridine. The infra red and thermal studies indicate that 4-aminopyridine is coordinated through its pyridyl nitrogen only, eventhough it is bidentate while others behave as bridging bidentate. These adducts have a trans octahedral structure which is preferable for extended linear framework, eventhough two isomeric forms are possible viz. cis and trans. The variation of magnetic moment on adduct formation was also carried out. The thermal decomposition of $Co(mbt)_2$ is seen taking place in two stages, in nitrogen atmosphere, with CoS, a stable residue. In the case of adducts an additional step was observed due to the loss Lewis bases used. The kinetic and mechanistic parameters were also evaluated from different decomposition stages. In most of the cases it follows Random nucleation, one nucleus on each particle obeying Mampel equation.

Keywords: coordination sphere expansion, 2-mercapto benzothiazole, Lewis base adducts, pyrazine, 4,4' bipyridine, 4-aminopyridine.

INTRODUCTION

A few monomeric and polymeric array systems have been reported by the inorganic chemists, adopting macrocyclic species like pthallocyanines, porphyrins and substituted porphyrins as core ligands, which are MN_4 chromophoric systems with square planar geometry. These types of compounds are belonging to Shiskabob polymers, a special class of coordination polymers containing stacked macrocyclic metal complexes which generates linear chains and have the ability to conduct electricity along the stacking axis through bridging ligands. These types of systems with metal complexes stacked together in wide variety of structural dispositions have been of intense interest to chemists, physicists, material scientists and theoreticians alike. Their concerned efforts backed by the skill of synthetic chemists have yielded multitudes of interesting and novel polymeric materials with extensive applications. Unlike pure organic or pure inorganic polymers the coordination polymers show the properties of both. A variety of such systems could be developed and characterized using various spectroscopic methods [1-7].

From the literature survey it was found that earlier studies focused on the synthesis and characterization of polymeric species from square planar MN_4 systems using macrocyclic ligands and the compounds of simple chelating bidentate ligands were found to be rare. Among those compounds tetrahedral cobalt (II) complexes have been studied to a limited extent and their thermal studies were not discussed in detail [8-13]. So we have been interested in synthesizing the monomeric and axially bridged polymeric complexes of 4-

coordinated tetrahedral cobalt (II) using bidentate bridging ligands coordinating through its end donor nitrogen centers using coordination sphere expansion method. These adducts are highly stable even at high temperature but yielded back the parent complex on heating at a constant rate. So their thermal studies are highly interesting. In the present study attempts are made to synthesize axially linked heteroleptic polymeric and monomeric species of Bis(2-mercaptobenzothiazolato)cobalt(II) using N bases with extensive conjugation in solution as well as in solid-vapour phase.

EXPERIMENTAL

2-mercaptobenzothiazole, pyridine, 4-aminopyridine, 4,4'-bipyridine, pyrazine, benzene, diethyl ether, $CoCl_2.6H_2O$, $Co(NO_3)_2.6H_2O$ were either BDH or Merck analaR samples. The metal content in all the compounds were estimated by complexometric titration using murexide indicator. The C, H and N analyses were carried out using Heracus CHNO rapid analyzer. The infra red spectra were recorded in the range 400-4000cm^{-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 magnetic susceptibilities were measured on a Sartorious semimicro Gouy balance. The fields were calculated using a standard calibrant $Hg[Co(SCN)_4]$. The thermal analyses were carried out using either Seiko Thermal analyzer or Delta Series TGA7 Thermal analyzer in an atmosphere of dry nitrogen with a heating rate of 10^0K/min. The thermal decomposition features of all the complexes developed were studied and the thermodynamic and kinetic parameters calculated using a computer programme.

Synthesis of coordinatively unsaturated four cordinated Bis(2-mercapto benzothiazolato)cobalt(II), $Co(mbt)_2$ (1)

A solution of $CoCl_2.6H_2O$ (2.38g, 0.01 mol) in 25 mL ethyl alcohol was added to a solution of mbtH (3.34g, 0.02 mol) in 100ml ethanol while stirring. Then the addition of 5M ammonia (or very dilute NaOH) solution precipitated the green coloured complex. It was digested on a water bath for 1h and then filtered, washed with water, ethyl alcohol followed by diethyl ether. It was then dried at 100^0C for 3h.Yield 90%. The preparation of the complex was also carried out using $Co(NO_3)_2.6H_2O$ to check the authenticity of a literature product with different composition [11-12].

Synthesis of monomeric Lewis base adducts

(a) Pyridine adduct – $[Co(mbt)_2(pyr)_2]$(2)

About 2mmol of pyridine in benzene was added dropwise to a solution of $Co(mbt)_2$, (approx. 0.39g, 1mmol) in benzene. This mixture was refluxed for about 15min.on a water bath. The precipitated brown coloured complex was filtered washed with diethyl ether and dried in vacuo. But we are also reporting a different solid-vapour phase reaction was used for its preparation. About 0.39g (1mmol) of $Co(mbt)_2$ was kept in a petridish in an air tight vessel. Then about 25ml of pyridine was also kept in a beaker in the same vessel. The vapourised pyridine was seen reacting with the solid complex resulted into a green complex after 24h. The unreacted pyridine was removed by keeping it at about 50^0C for 30min. Then it was washed with acetone and diethyl ether. The compound was then dried *in vacuo* and its yield was found to be 99.9%.

(b) 4-aminopyridine adduct – $[Co(mbt)_2(amp)_2]$(3)

A solution of 4-aminopyridine was prepared by dissolving 0.19g (2mmol) in 10 ml of acetone. This solution was added drop wise to a solution of $Co(mbt)_2$ (0.39g, 1mmol) in 10 ml of benzene. The reaction mixture was gently heated for about 15 min and then cooled. The precipitated compound was separated by filtration and then washed with acetone followed by ether. Yield 98%.

Synthesis of polymeric Lewis-Base adducts

(a)Pyrazine adduct, $[Co(mbt)_2(pyz)]n$ (4)

A solution of pyrazine prepared by dissolving 0.12 g (1.5 mmol) in benzene was added to a solution of $Co(mbt)_2$ (0.39g, 1mmol) in 10ml of benzene. The mixture was gently heated in a water bath for 30 min. The brown coloured compound formed was repeatedly washed with benzene, acetone followed by diethyl ether. Yield 90%.

(b) 4,4'-bipyridine adduct,$[Co(mbt)_2(bipy)]n$ (5)

About 0.16g (1mmol) of 4,4'-bipyridine dissolved in10 ml of acetone was added to a solution of 1 mmol of $Co(mbt)_2$. On slow cooling a brown coloured compound was precipitated. The compound is purified by washing with acetone followed by ether. Yield 95%.

RESULTS AND DISCUSSION

2-mercaptobenzothiazole (mbtH) is a potential bidentate ligand with three donor sites exist in two tautomeric forms thiol and thione. The thiol form has an ability to deprotonate and hence to generate the anionic mbt-, a bidentate ligand with N and S donors. It will interact with metal (II) ions generates four coordinated square planar or tetrahedral systems. In this present study the interaction of Co(II) with mbtH was studied and the analytical data showed that the complex is $Co(mbt)_2$ without the involvement of any other anion in them. Some of the literature reports, however have indicated that the cobalt complex formed has a composition Co(mbt)X, but we could not separate any such species [9]. We have verified by taking various Co (II) salts, that whatever may be the anions from the salt the cobalt (II) complex formed has the same composition $Co(mbt)_2$.

The absorption at 3050cm^{-1} which is assigned to ν_{NH} is seen absent in the $Co(mbt)_2$. This indicates the deprotonation of mbtH. The thioamide band ($\nu_{N=C=S}$) is known to occur at 1480 cm^{-1} as a strong band in the free ligand was found shifted to 1440 cm^{-1}. The $\nu_{(C=S)}$at 667 cm^{-1} in the ligand was also shifted to 700 cm^{-1}. These shifts in the IR spectra of the complex indicate chelation is through N and exocyclic S of the mbt moiety in agreement with earlier reports [12].

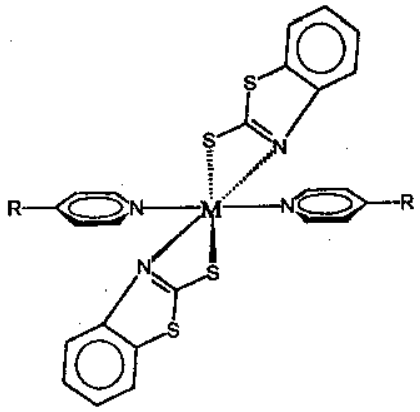
The electronic spectrum of this compound shows a broad absorption consisting of three close lying peaks at 16450, 15150 and 14325 cm^{-1}. This is very typical of tetrahedral Co(II) species due to $^4A_2 \rightarrow {}^4T_1(P)$ transition [14]. The effective magnetic moment of this compound was found to be 4.40 BM which is also typical of tetrahedral Co(II) species. The elemental analysis data, infra red and electronic spectral data of parent compound and all the adducts were presented in tables 1,2,3 respectively

Elemental Analysis

From the analytical data (Table.1) it could be suggested that the adducts have the following composition $[Co(mbt)_2L]n$, where L= pyrazine and 4,4'-bipyridine and $[Co(mbt)_2L^*_2]$ where L* = pyridine and 4-aminopyridine.

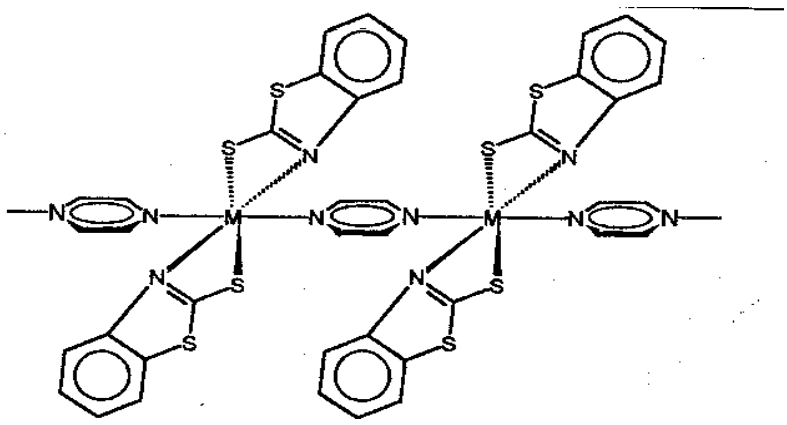
Infrared Spectra

The IR spectra of adducts showed the presence of characteristic peaks of the Lewis bases in them (Table.2). The peaks due to mbt- moiety were also present but with some shift in their position. The $\nu_{(N=C=S)}$ band observed at 1440 cm^{-1} in $Co(mbt)_2$ was seen in the range 1405-1430 cm^{-1} in the adducts. The $\nu_{(C=S)}$ band observed at 700 cm^{-1} was also found lowered to 680-692 cm^{-1} in adducts [15]. These lowering can be attributed to the following reason. Since Lewis bases are very good electron donors, they increase the electron density on the metal ion through coordination. So back donation from metal to mercaptobenzothiazole moiety is possible and which would strengthen M-C bond but weakens C-S bond. The C=C and C=N ring stretching skeletal bands in pyridine were observed in the range 1430-1600 cm^{-1} (4 peaks at 1440,1480,1580 and 1595 cm^{-1}). These bands were seen present in the IR spectra of all adducts except those of pyrazine. The in-plane and out of plane ring deformation at 604 and 405 cm^{-1} respectively of pyridine moiety were seen shifted in the range 635-680 cm^{-1} and 420-425 cm^{-1} support the coordination of pyridyl nitrogen to the metal upon adduct formation [15].

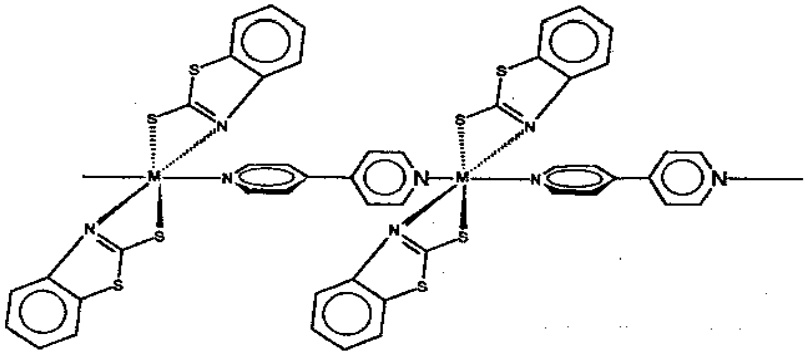


(a)

Fig.-1(a): The proposed structure of Lewis base adducts of Co $(mbt)_2$ (where M=Co)
$[Co(mbt)_2(pyr)_2]$ if R= H, and $[Co(mbt)_2(amp)_2]$ if R = NH_2



(a)



(b)

Fig.-1b: The proposed structure of polymeric Lewis base adducts of Co $(mbt)_2$ with varying metal to metal distance (where M=Co, in the figure)
(a) $[Co(mbt)_2(pyz)]n$, and (b) $[Co(mbt)_2(bipy)]n$.

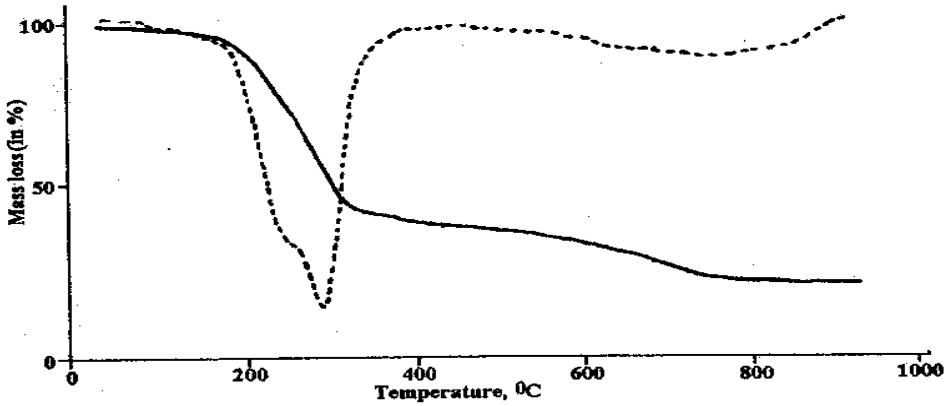


Fig.-2: TG/DTG curve of $Co(mbt)_2$ in nitrogen atmosphere.

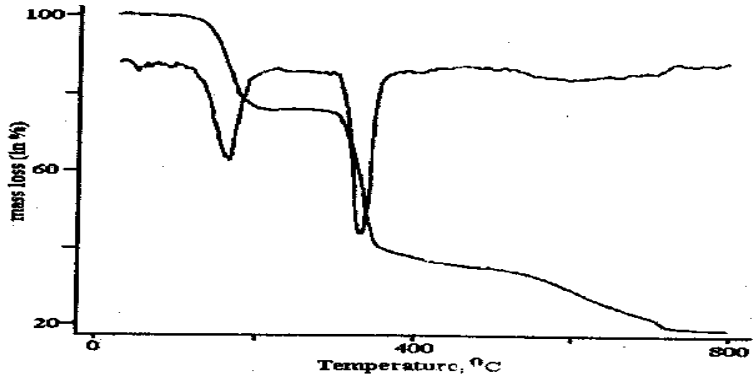


Fig.-3: TG/DTG curve of $[Co(mbt)_2(pyr)_2]$ in nitrogen atmosphere.

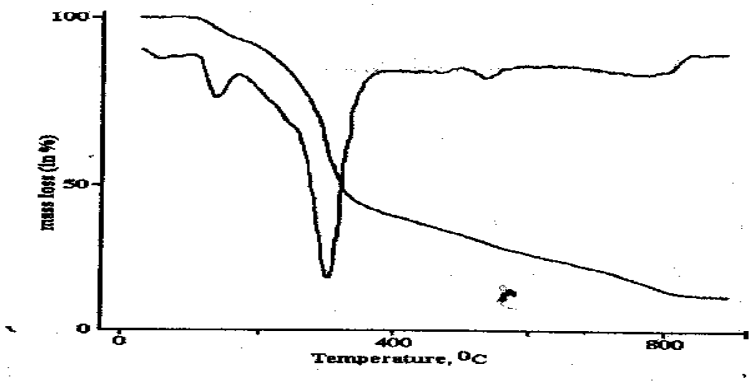


Fig.-4: TG/DTG curve of $[Co(mbt)_2(amp)_2]$ in nitrogen atmosphere.

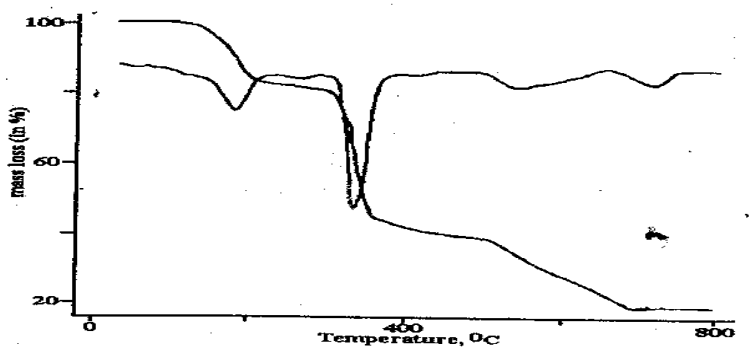


Fig.-5: TG/DTG curve of [Co(mbt)$_2$(pyz)]n in nitrogen atmosphere.

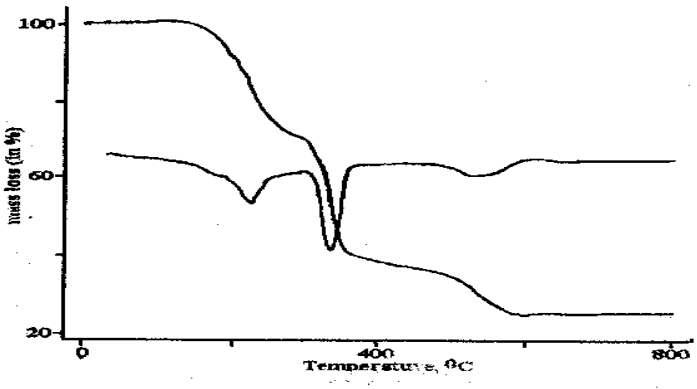


Fig.-6: TG/DTG curve of [Co(mbt)$_2$(bipy)]n in nitrogen atmosphere.

Primary amines show two absorptions in the range 3400-3500 cm^{-1} assignable to asymmetric and symmetric N-H stretching modes. The ν(N-H) bending mode of primary amine is usually observed in the range 1650-1580 cm^{-1}. These bands were observed at 3480, 3390, 3400 and 1620 cm^{-1} respectively in 4-aminopyridine adduct. But as compared to free 4-aminopyridine these bands remain almost unaltered indicate the non coordination of NH_2 group to the metal [16]. In the IR spectrum of [Co(mbt)$_2$(pyz)]n there is a negligible absorption occurring at 1590 cm^{-1} but with no peaks at 950-1000 cm^{-1} and 1230 cm^{-1}. These data strongly indicate the polymeric nature of the pyrazine adduct [17,18].

The monomeric derivatives of 4,4'-bipyridine give rise to bands at 800,1070,1215,1402,1483 and 1589 cm^{-1} . The predominant spectral difference observed for monomeric compounds containing unidentate terminal and bidentate bridging ligand is the disappearance of absorptions at about 1215, 1402 and 1589 cm^{-1}. The IR spectrum of [Co(mbt)$_2$(bipy)]n shows the presence of new bands at 800,1080,1480 cm^{-1} indicating that 4,4'-bipyridine is coordinated to Co(mbt)$_2$ through both its pyridyl moieties resulting in a polymeric compound. The appearance of a very weak band at 1215 cm^{-1}, strong band at 1405 cm^{-1} and an another weak band at1600 cm^{-1} also supports its polymeric nature. The centre of symmetry of 4, 4'-bipyridine vanishes when pyridyl planes are tilted or when it was acts as monodentate making the 1215 cm^{-1} band IR active. The appearance of a weak band at 1215 cm^{-1} indicates that the pyridyl groups are not in the same plane but tilted in the complex [19].

UV-Visible Electronic Spectra and Magnetic Susceptibility measurements

While the tetrahedral Co(mbt)$_2$ has a broad envelop consisting of three peaks in the range 14000-16500 cm^{-1}, its adducts have three sets of bands around 9000,15000 and 19000 cm^{-1}(Table.3). The absorption maxima appearing around 15000 cm^{-1} was due to $^4T_{1g} \rightarrow {}^4A_{2g}$ and the higher energy band appearing around 19000 cm^{-1} was $^4T_{1g} \rightarrow {}^4T_{1g\ (P)}$ [20]. These are typical of octahedral Co(II) complexes. As compared

to the parent tetrahedral $Co(mbt)_2$ (μ=4.4 BM) these adducts are seen to have higher μ(eff) values 4.6-4.7 BM which is also typical for octahedral Co (II) species [21,22]. Since the number of unpaired electrons in both the parent $Co(mbt)_2$ and its adducts are same (three) the difference in their magnetic moments could be attributed to varying extend of spin-orbit coupling in them. From all these experimental evidences it was concluded that $[Co(mbt)_2]$ has to undergo a structural transformation from tetrahedral to square planar geometry somewhere in the reaction pathway. And it is also obvious that in all the adducts the trans structure is the preferable one because cis structure would cause severe steric problem.
From the elemental analysis, infra red and electronic spectra and magnetic susceptibility measurements the Lewis base adducts could have the following tentative structures (Fig.-1.)

Table-1: Physical properties and elemental analysis data

S.No.	Complex Formula Empirical Formula	Weight/ Geometry	Elemental Analysis Observed (Calculated) C H N M				color
1	$[Co(mbt)_2]$ $CoC_{14}H_8N_2S_4$	391.48 Tetrahedral	42.90 (42.91)	2.02 (2.05)	7.12 (7.15)	15.02 (15.05)	Green
2	$[Co(mbt)_2(pyr)_2]$ $CoC_{24}H_{18}N_4S_4$	549.41 Octahedral	52.40 (52.42)	3.31 (3.30)	10.21 (10.2)	10.78 (10.8)	Brown
3	$[Co(mbt)_2(amp)_2]$ $CoC_{24}H_{20}N_6S_4$	579.48 Octahedral	49.69 (49.7)	3.47 (3.48)	14.50 (14.49)	10.16 (10.17)	Brown
4	$[Co(mbt)_2(pyz)]n$ $CoC_{18}H_{12}N_4S_4$	471.48 Octahedral	45.79 (45.81)	2.56 (2.54)	11.86 (11.87)	12.47 (12.49)	Brown
5	$[Co(mbt)_2(bipy)]n$ $CoC_{24}H_{16}N_4S_4$	547.41 Octahedral	52.60 (52.61)	2.94 (2.95)	10.24 (10.23)	10.79 (10.80)	Brown

Table-2: Infra red spectral data of Lewis base adducts (in cm^{-1})

Compound	$\nu_{C=N=S}$	$\nu_{C=S}$	$\nu_{C=C+C=N}$	$\nu_{C=N}$	ν_{NH2}	ν_{NH} bending	ring deformation out of plane	ring deformation in plane
$[Co(mbt)_2]$	1440	700	-	-	-	-	-	-
$[Co(mbt)_2(pyr)_2]$	1430	690 1450	1595 1550	-	-	-	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

Thermal Analysis

The thermogram of $Co(mbt)_2$ in nitrogen atmosphere is given in Fig.2 shows a two stage thermal decomposition . The initial mass loss of about 54% was starting at 192^0C and ending at 392^0C. The second stage of decomposition was initiating immediately at 395^0C and progressing till 900^0C with a mass loss of 23%. A stable baseline after the second stage indicates the completion of the reaction with a residual percentage of 23%. The first mass loss corresponds to the decomposition of mbt- moieties from the complex yielding its thiocyanate $Co(SCN)_2$. The observed weight loss is in close agreement with the calculated value of 55.32%. The second stage is due to the decomposition of the thiocyanate intermediate to CoS [23]. The percentage of residue observed (23%) is in good agreement with the calculated value

(23.23%). The mass loss, peak temperature, probable reactions and the residue obtained after the decomposition were presented in Table-4.

The TG/DTG curve of $[Co(mbt)_2(pyr)_2]$ (Fig.-3) shows an initial decomposition in the range 105^0C to 210^0C with a weight loss of 28.0%. The second stage of decomposition is seen initiating at 305^0C and ending at 450^0C with a mass loss of 39.23%. The third stage is seen starting immediately after the second and progressing till 720^0C with a peak temperature of 617.45^0C. The decrease in mass in this stage is 15.82% with the mass of the residue being 16.95%. On heating the breakage of two bonds at the pyridyl nitrogen and the cobalt (II) ion would make the two pyridine moieties escape from the complex yielding $Co(mbt)_2$ intact. The weight loss corresponding to this decomposition is in close agreement with the calculated value of 28.75%. During the second stage the breaking of two bonds of the five membered heterocycle at N and C takes place yielding an intermediate $Co(SCN)_2$. The mass of the residue after the first two decomposition stages 32.77% is in agreement with the theoretical value of 31.86%. In the third stage the weight loss could be attributed to the decomposition of $Co(SCN)_2$ to CoS, a stable residue. The residual mass 16.95% observed was agrees well with the theoretical value of 16.55%. The mass loss, peak temperature, temperature range, probable reactions etc are tabulated in Table-4.

The thermal decomposition of $[Co(mbt)_2(amp)_2]$ (fig.4) is seen taking place in three different stages. The first stage was in the range 115-160^0C with a mass loss of 9.03%. The mass losses during the second and third stages were found to be 52.52 and 22.02%. It was found that during the first stage of decomposition the observed value of 9.03% was less than that expected (32.44% for the loss of two molecules of 4-aminopyridine). But the total mass loss during the two stages was 61.55% with a residual mass of 38.45%. The calculated value for the two stages, loss of both 4-aminopyridine molecules and mbt moieties leading to the formation of $Co(SCN)_2$ was 69.92%. From these values it was concluded that before the complete decomposition of the first stage the second stage is seen starting and the third stage was also getting initiated before the completion of the second stage. The residual percentage (16.43) was in close agreement with the theoretical value of 15.69%.

The thermal decomposition of polymeric adduct $[Co(mbt)_2(pyz)]n$ (Fig.-5) shows an initial weight loss of 16.98% is seen starting at 105^0C and ending at 200^0C. The second and third stages were in the range 215^0C to 380^0C and 380 to 700^0C respectively. The mass losses were 40.4 and 23.06% respectively with a residual mass of 19.56%. During the first stage the pyrazine molecule escapes leaving back the parent compound. The calculated value of 16.97% is in well agreement with this which corresponds to the loss of only one molecule. The second and third stages are similar to the other adducts.

The thermal decomposition of polymeric adduct $[Co(mbt)_2(bipy)]n$ (Fig.-6) shows an initial decomposition starting at 120^0C and progressing till 270^0C with a peak temperature of 220.62^0C,The weight loss corresponding to this decomposition was 29%. The second stage is seen initiating only at 280^0C and ending at 375^0C with a mass loss of 35.89%. The third stage is starting immediately after the second in the range 380-585^0C. The mass loss observed was 12.7% with the mass of the residue being 22.42%. During heating the breaking of metal-pyridyl nitrogen bond resulted into the loss of one molecule of 4,4'-bipyridine moiety from the adduct giving back the parent compound. The calculated value of 28.51% is in good agreement with this. The second and third stages were similar to that of pyridine adduct but with a different residue of CoS_2. The residual mass observed is in good agreement with theoretical value of 22.46%.

Kinetic and Mechanistic aspects

The kinetic parameters of the thermal decomposition stages of Lewis base adducts are presented in Table.5. The activation energies of first stage decomposition was found to be low in the range 58-126 kJ/mol while second and third stages are in between 118-282 kJ/mol and 32-360 kJ/mol respectively. The corresponding entropy of activation falls in the range -172 to -242kJ/mol (stage 1) -93to-204 kJ/mol (stage 2) and -150 to-290J/mol (stage 3). The negative values of ΔS indicate that the activated complexes have more ordered structure than the reactants and the reactions are slower than the normal [24,25]. In almost all the cases they are obeying Random nucleation, one nucleus on each particle, obeying Mampel equation [26].

Table-3:Electronic absorption spectral data and magnetic susceptibility measurements

Compound	Absorption max.	Assignments	μ(BM)
$[Co(mbt)_2]$	16450,15150,14325	$^4A_2 \rightarrow {}^4T_{1(P)}$	4.40
$[Co(mbt)_2(pyr)_2]$	15500	$^4T_{1g} \rightarrow {}^4A_{2g}$	4.70
	18900	$^4T_{1g} \rightarrow {}^4T_{1g\ (P)}$	
$[Co(mbt)_2(amp)_2]$	15750	$^4T_{1g} \rightarrow {}^4A_{2g}$	4.60
	18860	$^4T_{1g} \rightarrow {}^4T_{1g\ (P)}$	
$[Co(mbt)_2(pyz)]n$	15130	$^4T_{1g} \rightarrow {}^4A_{2g}$	4.70
	18110	$^4T_{1g} \rightarrow {}^4T_{1g\ (P)}$	
$[Co(mbt)_2(bipy)]n$	14925	$^4T_{1g} \rightarrow {}^4A_{2g}$	4.62
	19120	$^4T_{1g} \rightarrow {}^4T_{1g\ (P)}$	

Table.4:Thermal analysis data

Compound	temp.range (^{0}C)	peak temp (^{0}C)	stage	mass % found(calcd)	probable reactions
$[Co(mbt)_2]$	192-392		1	54.0 (55.32)	1→ $Co(SCN)_2$
1	395-900	-	2	23.0(21.46)	$Co(SCN)_2 \rightarrow CoS$
above 900	-	-		23.0(23.23)	CoS (residue)
$[Co(mbt)_2(pyr)_2]$	105-210	168.26	1	28.0(28.75)	2→$[Co(mbt)_2]$+2pyr
2	305-450	332.67	2	39.23(39.4)	$[Co(mbt)_2] \rightarrow Co(SCN)_2$
450-720	617.45		3	15.82(15.29)	$Co(SCN)_2 \rightarrow CoS$
above 720	-	-		16.95(16.55)	CoS (residue)
$[Co(mbt)_2(amp)_2]$	115-160	136.40	1	9.03(32.44)	----------
3	180-335	301.9	2	52.52(37.48)	3→ $Co(SCN)_2$
335-810	543.41		3	22.02(14.40)	$Co(SCN)_2 \rightarrow CoS$
above 810	-	-		16.43(15.69)	CoS (residue)
$[Co(mbt)_2(pyz)]n$	105-200	174.56	1	16.98 (16.97)	4→$[Co(mbt)_2]$ + pyz
4	215-380	333.06	2	40.4(45.94)	$[Co(mbt)_2] \rightarrow Co(SCN)_2$
380-700	535.52		3	23.06(17.80)	$Co(SCN)_2 \rightarrow CoS$
above 700	-	-		19.56(19.29)	CoS (residue)
$[Co(mbt)_2(bipy)]n$	120-270	220.62	1	29.00(28.51)	5→$[Co(mbt)_2]$ + bipy
5	280-375	333.94	2	35.89(39.54)	$[Co(mbt)_2] \rightarrow Co(SCN)_2$
380-585	538.84		3	12.7(9.49)	$Co(SCN)_2 \rightarrow CoS_2$
above 585	-	-		22.42(22.46)	CoS_2 (residue)

Table -5: Kinetic parameters of Lewis Base adducts of $Co(mbt)_2$.

Stage	Parameters	Adducts of $Co(mbt)_2$			
		(pyr)	(amp)	(pyz)	(bipy)
1	Ea (kJ/mol)	84.76	73.81	73.83	58.32
	A (s^{-1})	192.53	84.79	39.32	2.30
	ΔS (J/mol)	-204.43	-210.62	-217.75	-242.14
2	Ea (kJ/mol)	246.54	118.29	220.93	282.24
	A (s^{-1})	2.13×10^7	245.72	231655	1.72×10^8
	ΔS (J/mol)	-110.47	-204.6	-128.95	-93.11
3	Ea (kJ/mol)	98.82	32.13	69.48	260.63
	A (s^{-1})	1.57	1.17×10^{-2}	0.23	220959.2
	ΔS (J/mol)	-250.24	-290.22	-265.21	-150.92

CONCLUSION

The available experimental data suggest that synthesized Co(II) Lewis base adducts from tetrahedral bis(2-mercaptobenzothiazolatocobalt(II) have a trans-octahedral structure. The pyrazine and 4,4'-bipyridine compounds are linearly linked polymeric species similar to Shiskabob polymers but 4-aminopyridine is behaving as monodentate ligand eventhough it contains two donor sites and hence producing only monomeric species. On heating the coordinatively unsaturated system was regenerated in most of the cases and hence this reaction is reversible.

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[RJC-947/2012]