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Synthesis and thermal studies on new Co(II), Ni(II), Cu(II) and Cd(II) mixed ligand complexes with 3-benzyl-4-amino-1,2,4-triazole-5-thione Schiff bases and α,α′-bipyridyl

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ABSTRACT

New octahedral mixed ligand complexes of cobalt(II), nickel(II), copper(II) and cadmium(II) have been synthesized with neutral bidentate N, S donor ligands such as 3-benzyl-1H -4-[(2-methoxybenzylidine)amino]-1,2,4-triazole-5-thione(MBT) , 3-benzyl-1H -4-[(4-chlorobenzylidine)amino]-1,2,4-triazole-5 -thione(CBT), 3-benzyl-1H -4-[(4-nitrobenzylidine)amino]-1,2,4-triazole-5-thione(NBT) and α,α′-bipyridyl(bipy) which coordinate to the metal atom through two nitrogen atoms. The synthesized complexes have been characterized by elemental analyses, spectroscopic measurements (IR, UV-Vis.), molar conductance, magnetic measurements and thermal studies. The stoichiometry of these mixed ligand complexes is metal ion: L_1: L_2=1:1:1, 1:2:1 or 1:1:2; L_1=NBT, MBT or CBT and L_2=8-hydroxyquinoline. The thermal decomposition study of the prepared mixed ligand complexes was monitored by TG, DTG and DTA analysis in dynamic nitrogen atmosphere. TG, DTG and DTA studies confirmed the chemical formulations of theses complexes. The kinetic parameters were determined from the thermal decomposition data using the graphical methods of Coats-Redfern and Horwitz-Metzger. Thermodynamic parameters were calculated using standard relations. NBT was found to form the most stable Cu(II) and Ni(II) mixed ligand complexes while MBT forms the most stable Co(II) and Cd(II) mixed ligand complexes.

INTRODUCTION

Since the metal complexes of S,N-heterocycles ligands exhibit enhanced biological activities compared to the uncomplexed ligands[1-3]. This paper reports the formation of new mixed ligand complexes containing S,N-donor ligands. These ligands used are capable of undergoing thione-thiol tautomerism. While the α,α′-bipyridyl (bipy) ligand is a neutral bidentate and can coordinate to the metal atom through two nitrogen atoms. Also the present paper reports the thermal analysis studies of some mixed ligand complexes. The associated thermal decomposition mechanisms are reported.

EXPERIMENTAL

Materials and measurements

All chemicals used in the preparative work were of analytical grade, they include the following: α,α′-bipyridyl (bipy), carbon disulphide, potassium hydroxide, dimethylformamide(DMF), methanol, absolute ethanol, phenylacetic acid, o-methoxybenzaldehyde, p-nitrobenzaldehyde, p-chlorobenzaldehyde, $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $CdCl_2.2.5H_2O$. They were used without further purification.

Synthesis of the trial containing ligands

The triazole containing ligands 3-benzyl-1H -4-[(2-

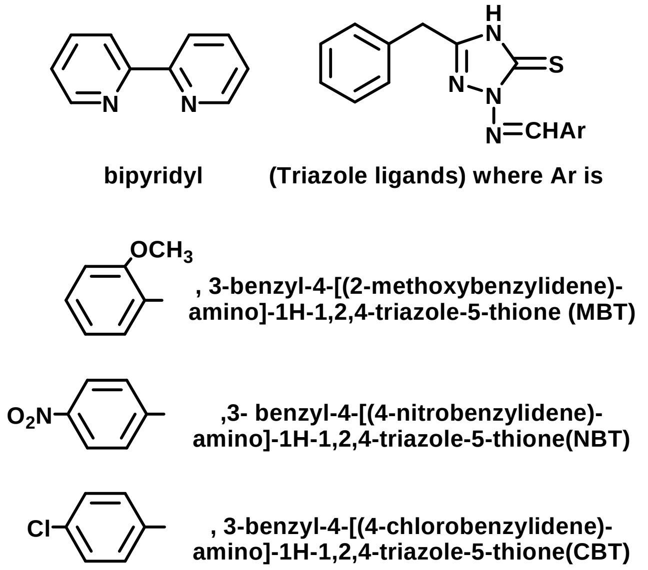


Figure 1 : The structure of different ligands

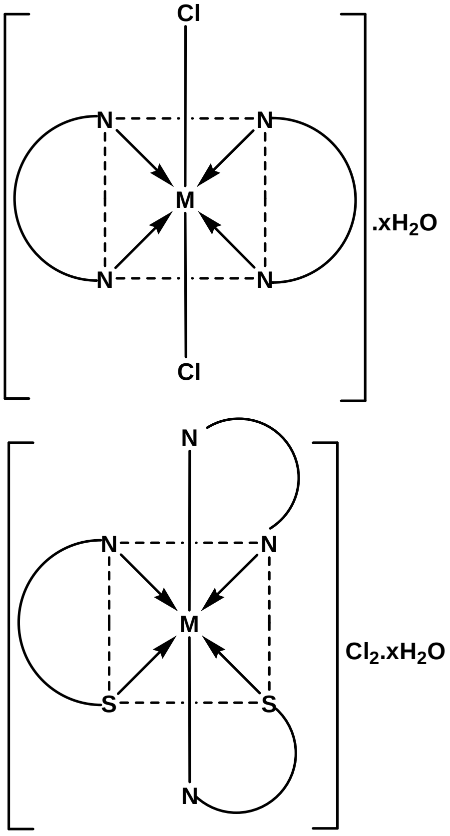
methoxybenzylidine)amino]-1,2,4-triazole-5 -thione (MBT), 3-benzyl-1H -4-[(4-chlorobenzylidine)amino]-1,2,4-triazole-5-thione (CBT) and 3-benzyl-1H -4-[(4-nitrobenzylidine)amino]-1,2,4-triazole-5 -thione (NBT) were synthesized according to literature survey[4-6]. The purity of the ligands was checked by elemental analysis. The structures of the triazole ligands as well as bipyridyl are shown below (Figure 1).

Synthesis Cu(II) mixed ligand complexes

To a solution of copper chloride (1 mmol in 10 mL methanol), a solution of MBT, CBT or NBT ligands (1mmol in 25 mL hot methanol) was added dropwise with constant stirring in one direction. When the precipitate was formed, a solution of α,α'-bipyridyl (2 mmols in 10mL methanol) was added. Refluxing of the resulting solution carried for 8 hours. The product obtained was left overnight, filtered through sintered glass, washed with methanol and dried in vacuum over $CaCl_2$.

Synthesis of Co(II), Ni(II) and Cd(II) mixed ligand complexes

To a solution containing (1 mmol of $CoCl_2.6H_2O$/ $NiCl_2.6H_2O$ or $CdCl_2.2.5H_2O$ and 2 mmols of sodium acetate in 25 mL methanol), a solution of MBT, CBT or NBT ligand (1mmo in 25 mL hot methanol) was added dropwise with constant stirring in one direction. When the precipitate was formed, a solution of α,α'-bipyridyl (2 mmols in 10mL methanol) was added. Refluxing of the resulting solution carried for 8 hours. The mixed ligand complex appears on cooling the solution after 4-6 hours. The product obtained was left overnight, filtered through sintered glass, washed with methanol and dried in vacuum over $CaCl_2$.



M=Cu, Co, Ni, Cd; x=0-2

Figure 2 : Proposed structures of some complexes

Physical measurements

The carbon, hydrogen, nitrogen and sulfur of the solid mixed ligand complexes were determined by Elementar analyzer system Gmbh Vario El. Conductivity measurements for the various complexes were carried out using Jenway 4320 meterlab conductivity meter in DMF solutions at 10^{-3} M concentrations at room temperature. Electronic spectra of the mixed ligand complexes were run on perkin Elmer UV/VIS spectrophotometer Lambda 40 using 1-cm matched silica cells. Magnetic susceptibility measurements were carried out at room temperature using a magnetic susceptibility balance of the type MSB-Auto. Molar susceptibilities were corrected for diamagnetism of the component atoms by the use of Pascal's constants. The calibrant used was $Hg[Co(SCN)_4]$. The infrared spectra of the

TABLE 1 : Analytical and physical data for the mixed ligand complexes

No.	Complex [Empirical formula] (Formula weight)	Color	Analytical Data % Found (Calculated) C	 H	 N	 S	Λ_o ohm^{-1} cm^2 mol^{-1}	μ_{eff} (BM)
1	$[Cu(NBT)_2(bipy)]Cl_2.H_2O$ $CuC_{42}H_{36}N_{12}\ O_5S_2Cl_2$(987.39)	Green	51.40 (51.08)	3.60 (3.67)	17.31 (17.02)	6.23 (6.49)	142.6	-
2	$[Cu(CBT)(bipy)Cl_2].2H_2O$ $CuC_{26}H_{25}N_6O_2SCl_3$(655.48)	Green	47.78 (47.64)	4.12 (3.84)	13.17 (12.82)	5.01 (4.89)	13.3	-
3	$[Cu(MBT)(bipy)Cl_2].2H_2O$ $CuC_{27}H_{28}N_6O_3SCl_2$(651.06)	Green	47.85 (49.80)	4.33 (4.33)	12.99 (12.90)	4.63 (4.92)	7.08	-
4	$[Co(NBT)(bipy)_2]Cl_2.1.5H_2O$ $CoC_{36}H_{32}N9O_{3.5}SCl_2$(808.60)	Green	53.02 (53.47)	3.71 (3.98)	15.47 (15.58)	3.57 (3.96)	139.5	5.41
5	$[Co(CBT)(bipy)Cl_2].H_2O$ $CoC_{26}H_{23}N_6OSCl_3$(632.85)	Green	49.95 (49.34)	3.28 (3.66)	13.58 (13.27)	5.84 (5.06)	16.7	5.18
6	$[Co(MBT)(bipy)Cl_2]$ $CoC_{27}H_{24}N_6OSCl_2$(610.42)	Green	53.81 (53.12)	3.97 (3.96)	13.69 (13.76)	5.99 (5.25)	17.0	5.20
7	$[Ni(NBT)(bipy)Cl_2]$ $NiC_{26}H_{21}N_7O_2SCl_2$(625.15)	Yellow	49.13 (49.95)	3.62 (3.38)	16.14 (15.68)	5.04 (5.12)	31.8	2.86
8	$[Ni(CBT)(bipy)Cl_2].2H_2O$ $NiC_{26}H_{25}N_6O_2SCl_3$(650.63)	Green	47.02 (47.99)	3.23 (3.87)	12.61 (12.91)	4.13 (4.92)	9.63	2.96
9	$[Ni(MBT)(bipy)Cl_2].2H_2O$ $NiC_{27}H_{28}N_6O_3SCl_2$(646.21)	Green	50.32 (50.18)	3.90 (4.36)	13.88 (13.00)	4.79 (4.96)	16.4	3.20
10	$[Cd(NBT)_2(bipy)]Cl_2.H_2O$ $CdC_{42}H_{36}N_{12}O_5S_2Cl_2$(1036.26)	White	49.09 (48.67)	3.19 (3.50)	16.65 (16.21)	6.24 (6.18)	1 67.3	-
11	$[Cd(CBT)(bipy)Cl_2].H_2O$ $CdC_{26}H_{23}N_6OSCl_3$(686.33)	White	45.12 (45.49)	3.65 (3.37)	12.15 (12.24)	4.90 (4.67)	29.6	-
12	$[Cd(MBT)(bipy)Cl_2]$ $CdC_{27}H_{24}N_6OSCl_2$(663.90)	White	49.04 (48.84)	3.56 (3.64)	12.93 (12.65)	5.21 (4.82)	25.0	-

-: diamagnetic

free ligands and the mixed ligand complexes were recorded on a shimadzu 470 infrared spectrophotometer (4000-400 cm^{-1}) using KBr discs. Thermogravimetric studies of these complexes was carried out using a shimadzu DTG-60Hz thermal analyzer, at heating rate 10°C min^{-1} in dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

Elemental analyses and conductivity measurements

The stoichiometry of the mixed ligand complexes together with their molecular formula, molecular weight, colour, effective magnetic moment and molar conductance in dimethylformamide (DMF) solution are decipted in TABLE 1. The results The data clearly indicate that NBT, CBT, MBT and α,α′-bipyridyl ligands act as neutral bidentate ligands.

The methods used for the preparation and isolation of these mixed ligand complexes give materials of good purity as supported by their analyses. All the mixed ligand complexes are colured except Cd(II) complexes are white. They are stable in air and nonhygroscopic. The synthesized mixed ligand complexes are sparingly soluble in the common organic solvents but they are completely soluble in DMF or DMSO.

All the mixed ligand complexes except $[Cu(NBT)_2(bipy)]Cl_2.H_2O$ **(1)**, $[Co(NBT)(bipy)_2]Cl_2.1.5H_2O$ **(4)** and $[Cd(NBT)_2(bipy)]Cl_2.H_2O$ **(10)** are expected to be nonelectrolytes[7] since their molar conductance values in dimethylformamid(DMF) solutions cover the range 7.08-29.6 Ohm^{-1} cm^2 mol^{-1} (TABLE 1). While the molar conductance values of dimethylformamide (DMF) solutions of the mixed ligand complexes **(1)**, **(4)**, **(10)** within the range 139.5-167.3 Ohm^{-1}cm^2 mol^{-1} (TABLE 1) indicate that these complexes are 1:2 electrolytes since the resonable range for 1:2 electrolytes is 130 - 170 Ohm^{-1} cm^2 mol^{-1}[7].

UV-Visible spectra and magnetic susceptibility measurements

The electronic spectra of the mixed ligand complexes have been recorded as DMF solutions in the wavelength range 250-1100 nm, The υ_{max} in kK. and ε_{max} in cm^{2}mol^{-1} are depicted in TABLE 2. The cor-

TABLE 2 : Electronic spectral dat (υ_{max} in k.K, ε_{max} in mol^{-1}cm^2) of the synthesized mixed ligand complexes in DMF solutions

No.	Complex	υ(k.K) (ε_{max}cm^{2}mol^{-1})	assignment
1	$[Cu(NBT)_2(bipy)]Cl_2.H_2O$	30.88(44581.07)	Intraligand
		15.18(83.00)	$^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2E_g$
2	$[Cu(CBT)(bipy)Cl_2].2H_2O$	37.15(124651.03)	Intraligand
		29.45(19984.15)	LMCT
		24.16(21299.83)	LMCT
		15.95(46.31)	$^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2E_g$
3	$[Cu(MBT)(bipy)Cl_2].2H_2O$	36.90(43725.16)	Intraligand
		31.71(25413.60)	Intraligand
		15.16(79.46)	$^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2E_g$
4	$[Co(NBT)(bipy)_2]Cl_2.1.5H_2O$	30.08(38945.12)	Intraligand
		17.12(3.65)	$^4T_{1g}(F)\rightarrow{}^4A_{2g}(\upsilon_2)$ $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\upsilon_3)$
5	$[Co(CBT)(bipy)Cl_2].H_2O$	36.73(34819.25)	Intraligand
		17.16(14.15)	$^4T_{1g}(F)\rightarrow{}^4A_{2g}(\upsilon_2)$ $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\upsilon_3)$
6	$[Co(MBT)(bipy)Cl_2]$	30.76(88456.17)	Intraligand
		17.45(3.49)	$^4T_{1g}(F)\rightarrow{}^4A_{2g}(\upsilon_2)$ $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\upsilon_3)$
7	$[Ni(NBT)(bipy)Cl_2]$	36.89(13465.82)	Intraligand
		31.54(8456.71)	Intraligand
			$^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$
8	$[Ni(CBT)(bipy)Cl_2].2H_2O$	36.27(21785.46)	Intraligand
		15.71(9.61)	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$
9	$[Ni(MBT)(bipy)Cl_2].2H_2O$	37.03(16743.52)	Intraligand
		30.58(10753.20)	Intraligand
		15.49(9.81)	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$
10	$[Cd(NBT)_2(bipy)]Cl_2.H_2O$	36.64(91977.06)	Intraligand
		26.15(15379.57)	LMCT
11	$[Cd(CBT)(bipy)Cl_2].H_2O$	30.06(45297.65)	Intraligand
		32.19(10573.45)	Intraligand
12	$[Cd(MBT)(bipy)Cl_2]$	36.72(36717.64)	Intraligand
		35.22(30524.30)	Intraligand
		30.81(16982.52)	Intraligand

rected magnetic moment (μ_{eff}) in Bohr magneton units of the mixed ligand complexes are given in TABLE 1.

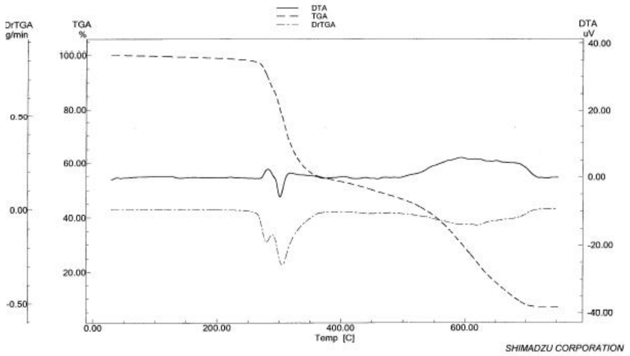


Figure 3 : TG-DTG curves of complex (1)

Three sets of bands could be recognized in the electronic spectra of the obtained mixed ligand complexes. The first with υ_{max} in the range 30.06-37.15 kK., could be attributed to intraligand charge transfer transitions[8]. The second set of includes bands having υ_{max} in the range 24.16 - 29.45 kK. These bands are assigned as LMCT transitions[8].

The third set of bands of Cu(II) mixed ligand complexes have υ_{max} in the range 15.16-15.95 kK. and is assigned for all the three transitions $^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2A_{1g}$ and $^2B_{1g}\rightarrow{}^2E_g$ which are usually found for tetragonal distorted octahedral Cu(II) complexes[9].

The d-d transition bands observed for Co(II) mixed ligand complexes are found to have υ_{max} in the range 17.12-17.45 kK. could be attributed to $^4T_{1g}(F)\rightarrow{}^4A_{2g}(\upsilon_2)$ and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\upsilon_3)$transitions, suggesting distorted octahedral environment around Co(II) ions[9,12].

The d-d transition bands observed for Ni(II) mixed ligand complexes are found to have υ_{max} in the range 15.49-16.41 kK. could be attributed to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ transitions, suggesting octahedral geometry[9].

All the mixed ligand Cd(II) complexes are diamagnetic as expected for d^{10} electronic configuration. On the basis of elemental analyses, infrared spectra, molar conductance values and thermal analyses, octahedral geometry is proposed for all the mixed ligand complexes.

All the Cu(II) mixed ligand complexes **(1-3)** display a diamagnetic nature (TABLE 1) which is attributed either to their polymeric nature or super exchange interaction[10] in the complex molecules and/or high polarizability[11] of the ligands which supplies more electron density to copper ion and consequently the ions interact more strongly. The room temperature magnetic moment values of the Co(II) mixed ligand complexes are within the range 5.18-5.41 B.M. expected for octahedral Co(II) complexes[9,13], The lower magnetic moment values (5.18, 5.20 B.M.) of these complexes may be attributed to the presence of low symmetry component in the ligand field as well as the covalent nature of the metal ligand bonds[14]. The room temperature magnetic moment values of Ni(II) mixed ligand complexes are 2.86, 2.96 and 3.20 B.M., respectively suggesting octahedral geometry[13,15].

IR Spectra

The assignment of the IR bands of all the mixed ligand complexes will be shown in TABLE 3. The free triazole ligands (NBT, CBT and MBT) show four bands at 1588-1540, 1282-1340, 1008-1040 and 780-814 cm^{-1} which are assignable to thioamide I, II, III and IV vibrations, respectively. In the mixed ligand complexes, these bands shift to higher frequency suggesting the coordination of the sulfur atom to the metal ions[16].

Coordination via the sulfur atom shifts the thioamide III band to lower wavenumbers and reduces its intensity. All the triazole ligands and the mixed ligand complexes show a band at within the range 3102-3030 cm^{-1} attributed to ν(NH) vibration, indicating that the free ligands and the mixed ligand complexes are in the thione form. The strongest bands observed in the range 1619-1625 cm^{-1} in the IR spectra of NBT, CBT and MBT ligands can be assigned to ν(C=N) vibrations of the azomethine group. This band in the synthesized mixed ligand complexes shifted to lower frequency indicating the coordination of the azomethine nitrogen to the metal ions. The bands observed in the region 480-520 cm^{-1} may be assigned to υ(M-N) vibration[17].

The IR spectrum of the free bipy ligand exhibit a series of significant IR absorption bands appearing in the vibrational regions 3041, 1576, 1552 and 753 cm^{-1}, these bands are apparently the characteristic absorptions of the free bipy ligand[18,19], these bands suffer a negative shift to a lower wavenumber on complexation. This shift has been attributed to the coordination of the bipy ligand to form the mixed ligand complexes.

The IR spectra of the mixed ligand complexes containing hydration and/or coordination water molecules display a broad band within the range 3340-3489 cm^{-1} due to ν(OH) vibrational modes of the water molecules[20] and this was confirmed by the results of thermal analysis. Figure 2 show the proposed structure for some synthesized complexes.

Thermal decomposition studies

The measured curves obtained during TGA scanning were analysed to give the percentage mass loss as a function of temperature .The different kinetic parameters were computed from thermal decomposition data using Coats-Redfern. And Horwitz-Metger methods[21,22]. Thermodynamic parameters: entropy ($\Delta S^{\#}$), enthalpy ($\Delta H^{\#}$) and free energy ($\Delta G^{\#}$) of activation were calculated(TABLE 4) using standard relations[23].

Thermal analysis of $[Cu(NBT)_2(bipy)]Cl_2.H_2O$

The TGA of the octahedral complex $[Cu(NBT)_2(bipy)]Cl_2.H_2O$ gave three steps (Figure 3). The first step (T=30.52-206.34°C, $E^{\#}$=141.28KJ/mol) is assignable to removal of one water molecule (calcd.=1.824 %; found=1.784 %). Step two (T =207.55 - 382.05°C, $E^{\#}$=298.88 KJ/mol) is assignable to removal of NBT molecule and two chlorine atoms and two oxygen atoms (calcd.= 44.791 %; found=43.997 %). The third step (T=383.26-725.53°C, $E^{\#}$=198.91 KJ/mol) is assignable to removal of bipy molecule and $C_{16}H_{13}N_5S$ moiety (calcd.=46.974 %; found =46.885 %). The residual product is assignable to be Cu (calcd.=6.435 %; found =7.334 %).

Thermal analysis of $[Cu(CBT)(bipy)Cl_2].2H_2O$

The TGA of the octahdral complex $[Cu(CBT)(bipy)Cl_2].2H_2O$ gave three steps. The first step (T =24.59 - 201.21°C, $E^{\#}$=121.66 KJ/mol) is assignable to removal of two water molecules (calcd.=5.496 %; found=5.858 %). Step two (T =202.43-359.15°C, $E^{\#}$=254.64 KJ/mol) is assignable to removal of C_5H_4N and C_7H_5NCl moieties and two chlorine atoms (calcd.= 43.870 %; found=43.622 %). The third step (T = 360.37-751.77°C, $E^{\#}$=307.23 KJ/mol) is assignable to removal of C_5H_4N and CHN_3 moieties (calcd.=20.309%; found =20.208%) giving $CuS+C_8H_7$ as residual products (calcd.=30.321%; found=30.290%).

Thermal analysis of $[Cu(MBT)(bipy)Cl_2].2H_2O$

The TGA of the octahedral complex

TABLE 3 : Relevant IR Spectral data for the mixed ligand complexes

Compound	υ(O-H) (H_2O)	Thioamide Bands				bipy characterstic bands			
		I δ(C-H)+ δ(N-H)	II υ(C=S)+ υ(C-N)+ δ(C-H)	III υ(C-N)+ υ(C-S)	IV υ(C=S)				
$[Cu(NBT)_2(bipy)]Cl_2.H_2O$	3420	1590	1310	1025	830	2950	1495	1460	670
$[Cu(CBT)(bipy)Cl_2].2H_2O$	3420	1590	1305	1030	800	2970	1480	1460	680
$[Cu(MBT)(bipy)Cl_2].2H_2O$	3450	1590	1350	1030	810	2950	1480	1460	620
$[Co(NBT)(bipy)_2]Cl_2.1.5H_2O$	3400	1580	1290	1030	820	2950	1490	1465	665
$[Co(CBT)(bipy)Cl_2].H_2O$	3350	1595	1320	1030	810	2945	1480	1460	680
$[Co(MBT)(bipy)Cl_2]$	-	1595	1360	1020	870	2950	1490	1430	620
$[Ni(NBT)(bipy)Cl_2]$	-	1590	1290	1030	820	2950	1490	1460	660
$[Ni(CBT)(bipy)Cl_2].2H_2O$	3050	1590	1340	1030	820	2950	1495	1460	660
$[Ni(MBT)(bipy)Cl_2].2H_2O$	3400	1590	1320	1040	810	2990	1480	1440	710
$[Cd(NBT)_2(bipy)]Cl_2.H_2O$	3350	1590	1280	1015	840	2960	1490	1460	720
$[Cd(CBT)(bipy)Cl_2].H_2O$	3400	1590	1290	1040	840	2950	1490	1450	710
$[Cd(MBT)(bipy)Cl_2]$	-	1610	1310	1050	820	2950	1480	1440	720

$[Cu(MBT)(bipy)Cl_2].2H_2O$ gave three steps. The first step (T =23.87 - 160.79°C, $E^{\#}$=35.70 KJ/mol) is assignable to removal of two water molecules (calcd.=5.534 %; found=6.170 %). Step two (T =161.60 - 407.00°C, $E^{\#}$=39.58 KJ/mol) is assignable to removal of two chlorine atoms and CH_3 moiety and bipy molecule (calcd.=37.187 %; found =37.002 %). The third step (T = 408.22 – 751.53°C, $E^{\#}$=149.24 KJ/mol) is assignable to removal of $C_8H_6N_4O$ moiety (calcd.= 26.749 %; found=26.223%). The residual products are assignable to be CuS + C_8H_7 (calcd.=30.527 %; found=30.605 %).

Thermal analysis of $[Co(NBT)(bipy)_2]Cl_2.1.5H_2O$

The TGA of the octahedral complex $[Co(NBT)(bipy)_2]Cl_2.1.5H_2O$ gave three steps. The first step (T =26.58 - 187.33°C, $E^{\#}$=50.93 KJ/mol) is assignable to removal of one and half water molecules (calcd.=3.341 %; found=3.547 %). Step two (T =187.33 - 330.72°C, $E^{\#}$=28.95 KJ/mol) is assignable to removal of bipy molecule and chlorine atom (calcd.=23.699 %; found=23.561 %). The third step (T=332.74-431.30°C, $E^{\#}$=161.81 KJ/mol) is assignable to removal of bipy molecule and $C_7H_5N_3O_2$ moiety and chlorine atom (calcd.=43.837 %; found =43.619 %). The residual products are assignable to be CoS + C_2HN_2 + C_5H_4N (calcd.=29.083 %; found=29.273 %).

Thermal analysis of $[Co(CBT)(bipy)Cl_2].H_2O$

The TGA of the octahedral complex $[Co(CBT)(bipy)Cl_2].H_2O$ gave three steps. The first step (T =38.13-188.73°C, $E^{\#}$=84.21 KJ/mol) is assignable to removal of one water molecule (calcd.=2.846 %; found=3.312 %). Step two (T =190.72-461.64°C, $E^{\#}$=95.90 KJ/mol) is assignable to removal of two chlorine atoms and C_6H_4Cl (calcd.=28.829 %; found =28.884 %). The third step (T = 462.43-751.67°C, $E^{\#}$=112.68 KJ/mol) is assignable to removal of C_7H_7 moiety (calcd.= 14.399 %; found=14.575 %) giving CoS + $C_3H_2N_4$ + bipy as residual products (calcd.=53.923 %; found=53.229 %).

Thermal analysis of $[Co(MBT)(bipy)Cl_2]$

The TGA of the octahedral complex $[Co(MBT)(bipy)Cl_2]$ gave two steps. The first step (T =28.49-381.63°C, $E^{\#}$=294.62 KJ/mol) is assignable to removal of C_7H_7O moiety, chlorine atom and bipy molecule (calcd.=48.944 %; found=48.968 %). The second step (T=383.65-751.71°C, $E^{\#}$=82.55 KJ/mol) is assignable to removal of chlorine atom and $C_{10}H_9N_4$ moiety (calcd.= 36.147 %; found=36.382%). The residual product is CoS (calcd.=14.907 %; found=14.650 %).

Thermal analysis of $[Ni(NBT)(bipy)Cl_2]$

The TGA of the octahedral complex

TABLE 4 : Kinetic and thermodynamic parameters for the thermal decomposition of the synthesized mixed ligand complexes

Complex No.	Step	N	Coats-Redfern equation (Kinetic Pararmeters) (Thermodynamic parameters)						Horwitz-Metzger equation (Kinetic Pararmeters) (Thermodynamic parameters)					
			r	E	Z	ΔS	ΔH	ΔG	r	E	Z	ΔS	ΔH	ΔG
1	1	2.0	1.0000	141.28	2212.54	-183.52	144.69	219.96	1.0000	148.27	1.29×10^{17}	80.02	151.66	118.84
	2	2.0	0.9928	298.88	4799.04	-179.93	303.68	407.63	0.9921	308.30	6.09×10^{25}	243.20	313.08	172.57
	3	2.0	0.9795	198.91	3204.78	-186.61	206.07	366.71	0.9813	213.25	2.28×10^{10}	-55.42	220.37	268.08
2	1	1.0	0.9996	121.66	1921.04	-185.03	125.20	204.15	0.9992	128.85	6.49×10^{13}	16.52	132.38	125.33
	2	1.0	0.9996	254.74	4092.02	-180.48	259.11	354.06	0.9993	263.87	1.21×10^{24}	211.42	268.22	157.00
	3	2.0	1.0000	307.23	4942.22	-182.97	314.35	471.16	0.9999	321.90	2.29×10^{17}	78.65	328.99	261.58
3	1	0.0	0.9994	35.70	576.80	-194.28	38.94	114.70	0.9953	43.50	1462.27	-186.55	46.73	119.47
	2	0.0	0.9999	39.58	640.82	-195.64	43.82	143.64	1.0000	48.00	143.53	-208.08	52.22	158.39
	3	2.0	0.9950	149.24	2370.31	-186.6	154.53	273.17	0.9946	159.79	1.21×10^{11}	-39.03	165.05	189.87
4	1	0.0	0.9364	50.93	819.21	-191.32	54.15	128.39	0.9887	13.23	0.07	-268.12	16.36	117.71
	2	0.33	1.0000	28.95	470.01	-199.00	33.61	145.13	1.0000	38.43	7.20	-233.73	43.07	174.05
	3	0.0	1.0000	161.81	2577.59	-186.94	167.80	302.45	1.0000	174.20	6.32×10^{9}	-64.61	180.16	226.71
5	1	1.0	0.9999	84.21	1344.06	-188.11	87.80	169.13	1.0000	91.36	9.44×10^{8}	-76.18	94.94	127.88
	2	1.0	0.9895	95.90	1534.34	-188.65	100.28	199.66	0.9897	104.63	1.02×10^{8}	-96.29	108.99	159.72
	3	0.0	0.9995	112.68	1814.09	-191.16	119.69	280.81	0.9998	126.89	1.16×10^{5}	-156.57	133.86	265.82
6	1	2.0	0.9786	294.62	4728.44	-179.73	299.24	399.07	0.9896	322.53	1.84×10^{29}	310.16	327.12	154.84
	2	2.0	0.9416	82.52	1332.07	-192.39	88.49	226.57	0.9975	188.28	9.74×10^{10}	-41.85	194.21	224.25
7	1	2.0	0.9930	186.19	2913.87	-183.29	190.55	286.76	0.9923	194.81	3.62×10^{17}	86.53	199.15	153.73
	2	0.66	1.0000	14.85	7463968	-119.70	20.18	96.95	1.0000	25.16	0.09	-271.21	30.47	204.40
8	1	0.33	0.9995	34.62	559.51	-194.95	38.03	117.93	0.9998	41.39	812.93	-191.84	44.78	123.41
	2	1.0	1.0000	61.40	990.18	-192.16	65.71	165.41	0.9999	70.11	22877.04	-166.06	74.40	160.55
	3	2.0	0.9999	262.88	4227.67	-182.59	268.70	396.55	1.0000	274.89	9.82×10^{18}	111.57	280.68	202.56

[Ni(NBT)(bipy) Cl_2] gave two steps. The first step (T =31.75-524.63°C, $E^{\#}$=186.19 KJ/mol) is assignable to removal of one bipy molecule and $C_7H_5NO_2$ moiety (calcd.=46.956 %; found=46.462 %). The second step (T=526.64-749.76C, $E^{\#}$=14.85 KJ/mol) is assignable to removal of two chlorine atom and CHN_3 moiety (calcd.=20.146 %; found =20.325 %) giving NiS + C_8H_7N as residual products (calcd.=33.256 %; found =33.213 %).

Thermal analysis of [Ni(CBT)(bipy)Cl_2].$2H_2O$

The TGA of the octahedral complex [Ni(CBT)(bipy)Cl_2].$2H_2O$ gave three steps. The first step (T =28.15-189.96 oC, $E^{\#}$=34.62 KJ/mol) is assignable to removal of two water molecules (calcd.=5.537 %; found=5.062 %). Step two (T =190.77-450.84°C, $E^{\#}$=61.40 KJ/mol) is assignable to removal of teo chlorine atoms and $C_{16}H_{13}N_4Cl$ moiety (calcd.=56.507 %; found =56.512 %). The third step (T = 452.06-751.77°C, $E^{\#}$=262.88 KJ/mol) is assignable to removal of bipy molecule (calcd.= 24.004 %; found=24.468 %) giving NiS as a residue (calcd.=13.949 %; found =13.958 %).

Thermal analysis of [Ni(MBT)(bipy)Cl_2].$2H_2O$

The TGA of the octahedral complex [Ni(MBT)(bipy)Cl_2].$2H_2O$ gave four steps. The first step (T =25.30 - 202.65°C, $E^{\#}$=22.42 KJ/mol) is assignable to removal of two water molecules (calcd.=5.575 %; found=5.419 %). Step two (T =203.86-289.70°C, $E^{\#}$=150.99 KJ/mol) is assignable to removal of bipy molecule (calcd.=24.169 %; found=23.884 %). The third step (T=290.92-356.11°C, $E^{\#}$=276.17 KJ/mol) is assignable to removal of two chlorine atoms and CH_3 moiety (calcd.=13.298 %; found =13.392 %). The fourth step (T = 358.13-750.48°C, $E^{\#}$=213.31 KJ/mol) is assignable to removal of $C_8H_6N_3O$ moiety (calcd.=24.783 %; found=23.884

$$[Cu(NBT)_2(bipy)]Cl_2.H_2O \xrightarrow[-H_2O]{} [Cu(NBT)_2(bipy)]Cl_2 \xrightarrow[-NBT,\ -2Cl,\ -O_2]{} [Cu(C_{16}H_{13}N_5S)(bipy)] \xrightarrow[\substack{-C_{16}H_{13}N_5S,\\ -bipy}]{} Cu$$

$$[Cu(CBT)(bipy)Cl_2].2H_2O \xrightarrow[-2H_2O]{} [Cu(CBT)(bipy)Cl_2] \xrightarrow[\substack{-2Cl,\\ -C_7H_5NCl,\\ -C_5H_4N}]{} [Cu(C_9H_8N_3S)(C_5H_4N)] \xrightarrow[\substack{-C_5H_4N\\ -CHN_3}]{} CuS + C_8H_7$$

$$[Cu(MBT)(bipy)Cl_2].2H_2O \xrightarrow[-2H_2O]{} [Cu(MBT)(bipy)Cl_2] \xrightarrow[\substack{-CH_3\\ -2Cl\\ -bipy}]{} [Cu(C_{16}H_{13}N_4SO)] \xrightarrow[-C_8H_6N_4O]{} CuS + C_8H_7$$

$$[Co(NBT)(bipy)_2]Cl_2.1.5H_2O \xrightarrow[-1.5H_2O]{} [Co(NBT)(bipy)_2]Cl_2 \xrightarrow[\substack{-Cl\\ -bipy}]{} [Co(NBT)(bipy)]Cl \xrightarrow[\substack{-C_7H_5N_3O_2\\ -bipy\\ -Cl}]{} CoS + C_9H_8N_2$$

$$[Co(CBT)(bipy)Cl_2].H_2O \xrightarrow[-H_2O]{} [Co(CBT)(bipy)Cl_2] \xrightarrow[\substack{-C_6H_4Cl\\ -2Cl}]{} [Co(C_{10}H_9N_4S)(bipy)] \xrightarrow[-C_7H_7]{} CoS + C_3H_2N_4 + bipy$$

$$[Co(MBT)(bipy)Cl_2] \xrightarrow[\substack{-C_7H_7O\\ -bipy\\ -Cl}]{} [Co(C_{10}H_9N_4S)Cl] \xrightarrow[\substack{-Cl\\ -C_{10}H_9N_4}]{} CoS$$

$$[Ni(NBT)(bipy)Cl_2] \xrightarrow[\substack{-bipy\\ -C_7H_5NO_2}]{} [Ni(C_9H_8N_4S)Cl_2] \xrightarrow[\substack{-CHN_3\\ -2Cl}]{} NiS + C_8H_7N$$

$$[Ni(CBT)(bipy)_2Cl_2].2H_2O \xrightarrow[-2H_2O]{} [Ni(CBT)(bipy)Cl_2] \xrightarrow[\substack{-2Cl\\ -C_{16}H_{13}N_4Cl}]{} [Ni(S)(bipy)] \xrightarrow[-bipy]{} NiS$$

$$[Ni(MBT)(bipy)Cl_2].2H_2O \xrightarrow[-2H_2O]{} [Ni(MBT)(bipy)Cl_2] \xrightarrow[-bipy]{} [Ni(MBT)Cl_2] \xrightarrow[\substack{-CH_3\\ -2Cl}]{} [Ni(C_{16}H_{13}N_4S)] \xrightarrow[-C_8H_6N_3O]{} NiS + C_8H_7N$$

$$[Cd(NBT)_2(bipy)]Cl_2.H_2O \xrightarrow[-H_2O]{} [Cd(NBT)_2(bipy)]Cl_2 \xrightarrow[\substack{-NBT\\ -Cl}]{} [Cd(NBT)(bipy)]Cl \xrightarrow[-bipy]{} [Cd(NBT)]Cl \xrightarrow[\substack{-C_{16}H_{13}N_5O_2\\ -Cl}]{} CdS$$

$$[Cd(CBT)(bipy)Cl_2].H_2O \xrightarrow[-H_2O]{} [Cd(CBT)(bipy)Cl_2] \xrightarrow[\substack{-2Cl\\ -C_7H_5Cl}]{} [Cd(C_9H_8N_4S)(bipy)] \xrightarrow[\substack{-bipy\\ -C_3H_3N_4}]{} CdS + C_6H_5$$

$$[Cd(MBT)(bipy)Cl_2] \xrightarrow[\substack{C_8H_8O\\ -C_7H_7}]{} [Cd(C_2HN_4S)(bipy)Cl_2] \xrightarrow[\substack{-Cl\\ -C_5H_4N}]{} [Cd(C_2HN_4S)(C_5H_4N)Cl] \xrightarrow[\substack{-Cl\\ -C_5H_4N\\ -C_2HN_4}]{} CdS$$

Thermal analysis of complexes

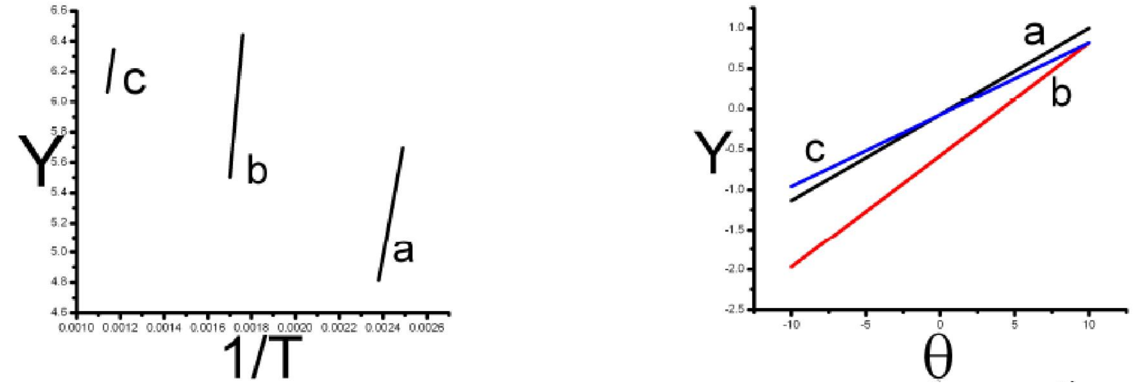


Figure 4 : Coats-Redfern and Horwitz-Metzger plots of complex 1(a: 1st step, b: 2nd step, c: 3rd step)

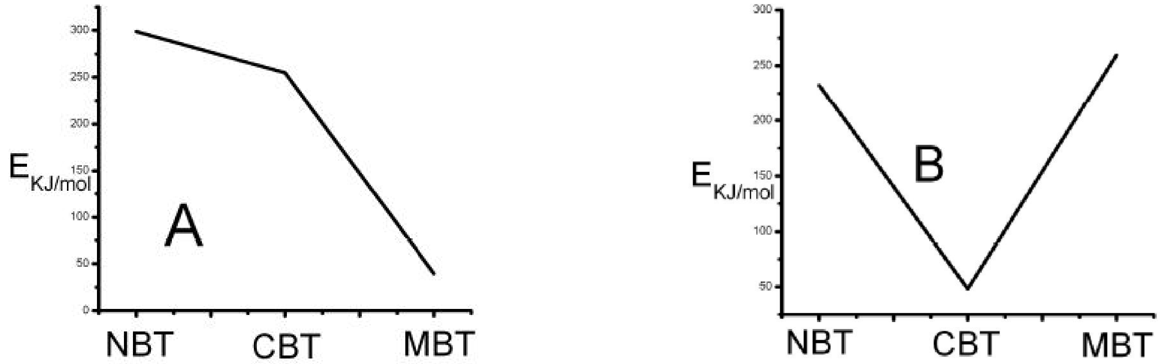


Figure 5 : Relationships between the activation energy and triazole ligand type of Cu(II)(A) and Cd(II)(B) mixed ligand complexes

%). The residual products are NiS + C_8H_7N (calcd.=32.329 %; found=32.845 %).

Thermal analysis of $[Cd(NBT)_2(bipy)]Cl_2.H_2O$

The TGA of the octahedral complex $[Cd(NBT)_2(bipy)]Cl_2.H_2O$ gave four steps. The first step (T =26.52-198.72°C, $E^{\#}$=202.45 KJ/mol) is assignable to removal of one water molecule (calcd.=1.738 %; found=1.185 %). Step two (T =199.53-290.88°C, $E^{\#}$=232.50 KJ/mol) is assignable to removal of chlorine atom and NBT molecule (calcd.=36.170 %; found=35.636 %). The third step (T=292.09-374.65°C, $E^{\#}$=172.21 KJ/mol) is assignable to removal of bipy molecule (calcd.=15.071 %; found =15.788 %). The fourth step (T = 375.89-751.58°C, $E^{\#}$=64.73 KJ/mol) is assignable to removal of chlorine atom and $C_{16}H_{13}N_5O_2$ moiety (calcd.=33.075%; found=33.245 %). giving CdS as a residue (calcd.=13.942%; found =14.146 %).

Thermal analysis of $[Cd(CBT)(bipy)Cl_2].H_2O$

The TGA of the octahedral complex $[Cd(CBT)(bipy)Cl_2].H_2O$ gave three steps. The first step (T =27.53-155.38°C, $E^{\#}$=37.33 KJ/mol) is assignable to removal of one water molecule (calcd.=2.624 %; found=2.453 %). Step two (T =156.59-314.34°C, $E^{\#}$=48.24 KJ/mol) is assignable to removal of two chlorine atoms and C_7H_5Cl moiety (calcd.=28.480 %; found=28.477 %). The third step (T=314.34-751.69°C, $E^{\#}$=50.02 KJ/mol) is assignable to removal of $C_3H_3N_4$ moiety and bipy molecule (calcd.= 36.609 %; found=36.731 %) giving CdS + C_6H_5 as residual products (calcd.=32.284 %; found =32.339 %).

Thermal analysis of $[Cd(MBT)(bipy)Cl_2]$

The TGA of the octahedral complex $[Cd(MBT)(bipy)Cl_2]$ gave three steps. The first step (T =31.17-313.04°C, $E^{\#}$=242.54 KJ/mol) is assignable to removal of C_8H_8O and C_7H_7 moieties (calcd.=31.823 %; found=32.023 %). Step two (T =315.05-392.37°C, $E^{\#}$=259.64 KJ/mol) is assignable to removal of chlorine atom and C_5H_4N moiety (calcd.=17.102 %; found=17.081 %). The third step

(T=394.38-749.54°C, $E^{\#}$=95.81 KJ/mol) is assignable to removal of chlorine atom and C_5H_4N and C_2HN_4 moieties (calcd.=29.311 %; found =28.892 %). The residual product is CdS (calcd.=21.761 %; found=22.004 %).

Thermal stability

Comparing the values of the initial decomposition temperatures (T_{idec}) of the organic part or the activation energy data for the prepared mixed ligand complexes the following data is obtained:

NBT rather than MBT and CBT forms the most stable mixed ligand complexes with Cu(II) and Ni(II) while MBT forms the most stable complexes with Co(II) and Cd(II) (Figure 5).

For complexes of the same triazole containing ligand; Cu(II) have been found to form the most stable mixed ligand complexes in presence of NBT or CBT while in presence of MBT, Co(II) forms the most stable mixed ligand complex.

CONCLUSION

The presence of more than one exothermic peak in the DTA curves of all the complexes reveals that the pyrolysis occurs in several steps[24].

The difference in the shape of the DTA curves of the complexes containing the same metal ion with respect to each other may be attributed to the structural features of the ligand or the strength of the chelation between the metal ion and the ligand, this also led to the variety in the thermal behaviour of the complexes[25].

On heating the complexes containing water molecules from room temperature, the loss in the weight indicated by the TGA curves is accompanied in some cases by endothermic peaks in the DTA curves. This weight loss may correspond to the evolution of water molecules[25].

Most complexes having DTA curves characterized by the presence of main sharp and strong exothermic peaks in their ends. These peaks are associated with a weight loss on the TGA curves corresponding to the decomposition of one stable intermediate compounds into the corresponding final residue[25].

The relatively low values of values of $\Delta H^{\#}$ for the prepared complexes confirm the M-S or M-N bond rupture[26,27].

The high values of the free energy of activation ($\Delta G^{\#}$) for most of the steps in the decomposition reactions of the complexes mean that the decomposition reactions are slower than that of the normal ones[23].

In general there are no obvious trends in the values of $\Delta H^{\#}$ and $\Delta S^{\#}$ for the studied complexes. This may be attributed to the fact that the thermal decomposition of the complexes is controlled not only by the structure of the ligands but also by the configuration of the coordination sphere[28,29].

The values of the free energy of activation ($\Delta G^{\#}$) of a given complex, generally increase significantly for the subsequent decomposition stages. This is due to the increase $T\Delta S^{\#}$ values significantly from one step to another which overrides the values of $\Delta H^{\#}$[23].

Increasing the $\Delta G^{\#}$ values for the subsequent of a given complex reflects that the rate of removal of a given species will be lower than that of the precedent one[23]. This may attributed be to the structure rigidity of the remaining complex.

There is much closeness in the enthalpy ($\Delta H^{\#}$) values obtained by Coats-Redfern equation and Horwitz-Metzger equation, indicating that the thermal degradation of these complexes follow the standard methods.

In most cases the values of the activation energy for the second stage of decomposition were found to be higher than that of the first stage, which indicates that the decomposition rate of the second stage is lower than the first. This may be attributed to the structural rigidity of the remaining complex[31,32].

The order n of the decomposition reactions does not provide any meaningful information about the decomposition mechanisms of the complex[33].

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