Vol.2, No.8, 817-827 (2010)
http://dx.doi.org/10.4236/ns.2010.28103

Natural Science

Synthesis and thermal studies of mixed ligand complexes of Cu(II), Co(II), Ni(II) and Cd(II) with mercaptotriazoles and dehydroacetic acid

Dina M. Fouad*, Ahmed Bayoumi, Mohamed A. El-Gahami, Said A. Ibrahim, Abbas M. Hammam

Chemistry department, Faculty of Science, Assiut University, Assiut, Egypt; *Corresponding Author: dinafouad93@hotmail.com

Received 15 January 2010; revised 25 February 2010; accepted 2 March 2010.

ABSTRACT

A series of new mixed ligand complexes of cobalt(II), nickel(II), copper(II) and cadmium(II) have been synthesized with 3-benzyl-1H-4-[(2-methoxybenzylidine) amino]-1, 2, 4-triazole-5-thione (MBT), 3-bezyl-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 dehydroacetic acid sodium salt (Nadha). The mixed ligand complexes have been characterized by elemental analysis, spectroscopic spectral measurements (IR, UV-Vis.), molar conductance, magnetic measurements and thermal studies. The stoichiometry of these complexes is M:L_1:L_2 = 1:1:1, 1:2:1 or 1:1:2 where L_1 = NBT, CBT and MBT and L_2 = Nadha. Tetrahedral structure was proposed for all Cd(II) mixed ligand complexes while the square planar geometry was proposed for Cu(II) mixed ligand complex with NBT. Octahedral structure was proposed for Ni(II), Co(II) mixed ligand complexes and Cu(II) mixed ligand complexes with CBT and MBT ligands. The thermal decomposition study of the prepared 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 the thermal decomposition data using the graphical methods of Coats-Redfern and Horwitz-Metzger. Thermodynamic parameters were calculated using standard relations.

Keywords: Mix Ligand Complexes; Mercaptotriazoles; Dehydroacetic Acid

1. INTRODUCTION

3-acetyl-6-methyl-2H-pyran-2, 4(3H)-dione, a commercially available compound usually obtained through the auto condensation of ethyl acetoacetate [1], it has been shown to posses modest antifungal properties [2]. The importance of similar pyrones as potential fungicides is reinforced by the existence of several natural fungicides possessing structures analogous to 5, 6-dihydro dehydroacetic acid, like alternaric acid, the podoblastins and lachnelluloic acid [3-5], studies have shown that such compounds and their complexes have very interesting biological properties[6-13]. Like dehydroacetic acid, mercaptotriazoles and their complexes have been shown to posses enhanced biological activities [14-27]. The work of the present paper is devoted to the synthesis and characterization of some new mixed ligand complexes containing mercaptotriazoles and dehydroacetic acid. The mercaptotriazole ligands containing the thioamide groups which are capable of undergoing thione-thiol (HN – C = S←→ N = C – SH) tautomerism and can coordinate to the metal atom through both nitrogen and sulphur atoms. While the sodium salt of dehydroacetic acid behaves as a monobasic bidentate ligand through two oxygen atoms. Hence the present paper reports the thermal analysis studies of some mixed ligand complexes. The associated thermal decomposition mechanisms are reported.

2. EXPERIMENTAL

2.1. Materials and Measurements

All chemicals used in the preparative work were of analytical grade, they include the following: dehydroacetic acid sodium salt (Nadha), carbon disulphide, potassium hydroxide, absolute ethanol, methanol, Dimethylformamide (DMF), phenylacetic acid, o-methoxy benzaldehyde, p-nitrobenzaldehyde, p-chlorobenzaldehyde, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CdCl_2 \cdot 2.5H_2O$. They were used without further purification.

Copyright © 2010 SciRes.

2.2. Synthesis of the Mercaptotriazole Ligands

The ligands 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) and 3-benzyl-1H-4-[(4-nitrobenzylidine)amino]-1, 2, 4-triazole-5-thione (NBT) were synthesized according to literature survey [28-30]. The purity of the ligands was checked by elemental analysis (**Table 1**). The structures of ligands are shown in **Figure 1**.

2.3. Synthesis Cu(II) Mixed Ligand Complexes

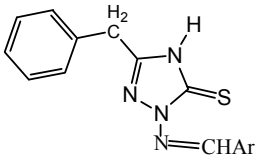
To a solution of copper chloride 1 mmol in 10 mL methanol, a solution of the (MBT, CBT or NBT) ligands (1 mmol in 25 mL hot methanol was added dropwise with constant stirring in one direction. When the precipitate was formed, 2 mmols in 10mL methanol of (Nadha) ligand was added. Refluxing of the resulting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

2.4. Synthesis of Co(II), Ni(II) and Cd(II) Mixed Ligand Complexes

To 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 (1 mmol in 25 mL hot methanol) was added dropwise with constant stirring in one direction. When the precipitate was formed, 2 mmols: 0.3802 grams in 10mL methanol of Nadha 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 anhydrous $CaCl_2$.

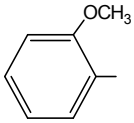
Table 1. The Analytical data for the mercaptotriazole ligands.

Free ligand (Empirical formula) Formula weight	Analytical Data % Found (Calculated)			
	C	H	N	S
MBT ($C_{17}H_{16}N_4OS$) M.Wt.= 324.401	63.09 (62.94)	5.11 (4.97)	17.47 (17.27)	9.71 (9.88)
NBT ($C_{16}H_{13}N_5O_2S$) M.Wt.= 339.379	56.55 (56.62)	3.282 (3.86)	19.82 (20.63)	9.39 (9.44)
CBT ($C_{16}H_{13}N_4SCl$) M.Wt.= 328.820	58.79 (58.44)	4.10 (3.98)	17.04 (17.03)	9.64 (9.75)

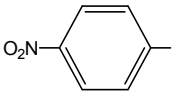


triazole ligands

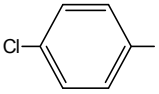
where Ar is:



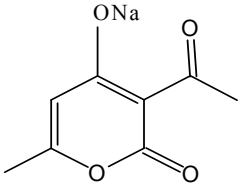
, 3-benzyl-4-[(2-methoxybenzylidene)amino]-1H-1,2,4-triazole-5-thione (MBT)



,3- benzyl-4-[(4-nitrobenzylidene)amino]-1H-1,2,4-triazole-5-thione(NBT)



, 3-benzyl-4-[(4-chlorobenzylidene)amino]-1H-1,2,4-triazole-5-thione(CBT)



Dehydroacetic acid(Sodium salt)

Figure 1. structures for the ligands.

Copyright © 2010 SciRes.

2.5. Physical Measurements

The carbon, hydrogen, nitrogen and sulfur of the solid 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 solid 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 free ligands and the metal complexes were recorded on a shimadzu 470 infrared spectrophotometer (4000-400 cm^{-1}) using KBr discs. Thermogravimetric studies of the various complexes was carried out using a shimadzu DTG-60Hz thermal analyzer, at heating rate $10^{o}C\ min^{-1}$ in dynamic nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1. Elemental Analyses and Conductivity Measurements

The analytical data of the metal complexes are given in **Table 2**. The data reveal the formation of complexes having 1:1:1, 1:1:2 or 1:2:1 (metal ion: mercaptotriazole ligand: Nadha) ratio with Co(II), Ni(II), Cu(II) and Cd(II). The methods used for the preparation and isolation of the mixed ligand complexes give materials of good purity as supported by their analyses. All the mixed ligand complexes are colored except Cd(II) complexes are white. They are stable in air and nonhygroscopic. The synthesized complexes are sparingly soluble in the common organic solvents but they are completely soluble in DMF or DMSO.

The molar conductance values for complexes (2, 4-9) recorded as DMF solutions are within the range 8.14-30.9 $Ohm^{-1}cm^{2}mol^{-1}$ (**Table 2**) which indicates the nonelectrolyte nature of these complexes. While the mixed ligand complexes (1, 3, 10-12) show molar conductance values within the range 71.0-84.9 Ohm^{-1} $cm^{2}mol^{-1}$ indicating that these complexes are 1:1 electrolytes [31].

3.2. UV-Visible Spectra and Magnetic Susceptibility Measurements

The electronic spectra of the Cu(II), Ni(II),Co(II) and Cd(II) 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 3**. The corrected magnetic moment (μ_{eff}) in Bohr magneton units of the mixed ligand complexes are given in **Table 2**.

Table 2. Analytical and physical data for the 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)(dha)]Cl $CuC_{24}H_{20}N_5O_6SCl$(605.51)	Red	47.59 (47.60)	3.10 (3.32)	11.92 (11.56)	4.43 (5.29)	79.83	-
2	[Cu(CBT)(dha)Cl(H_2O)] $CuC_{24}H_{22}N_4O_5SCl_2$(612.97)	Green	47.45 (47.02)	4.02 (3.61)	9.43 (9.14)	5.81 (5.23)	16.47	-
3	[Cu(MBT)$_2$(dha)]Cl.H_2O $CuC_{42}H_{41}N_8O_7S_2Cl$(932.95)	Green	54.85 (54.07)	3.58 (4.42)	11.43 (12.01)	6.38 (6.87)	71.0	-
4	[Co(NBT)(dha)$_2$].H_2O $CoC_{32}H_{29}N_5O_{11}S$(750.59)	Green	51.08 (51.20)	3.92 (3.89)	9.20 (9.33)	4.18 (4.27)	24.2	5.12
5	[Co(CBT)(dha)Cl(H_2O)].H_2O $CoC_{24}H_{24}N_4O_6SCl_2$(626.37)	Grey	46.56 (46.01)	3.72 (3.86)	9.12 (8.94)	5.38 (5.11)	30.9	4.86
6	[Co(MBT)(dha)Cl(H_2O)] $CoC_{25}H_{25}N_4O_6SCl$(603.94)	Grey	49.63 (49.71)	4.60 (4.17)	9.16 (9.27)	5.49 (5.30)	8.14	4.55
7	[Ni(NBT)(dha)$_2$].2H_2O $NiC_{32}H_{31}N_5O_{12}S$(768.37)	Green	49.96 (50.02)	3.90 (4.06)	8.96 (9.11)	4.09 (4.17)	22.6	3.16
8	[Ni(CBT)(dha)Cl(H_2O)].H_2O $NiC_{24}H_{24}N_4O_6SCl_2$(626.13)	Green	46.21 (46.03)	4.24 (3.86)	8.19 (8.94)	5.34 (5.12)	14.3	2.98
9	[Ni(MBT)(dha)Cl(H_2O)] $NiC_{25}H_{25}N_4O_6SCl$(603.70)	Green	49.25 (49.73)	4.02 (4.17)	8.83 (9.28)	5.26 (5.31)	17.2	3.05
10	[Cd(NBT)(dha)]Cl.H_2O $CdC_{24}H_{22}N_5O_7SCl$(672.39)	White	42.70 (42.87)	3.10 (3.29)	9.65 (10.41)	4.84 (4.76)	71.8	-
11	[Cd(CBT)(dha)]Cl.H_2O $CdC_{24}H_{22}N_4O_5SCl_2$(661.83)	White	43.88 (43.55)	3.23 (3.35)	12.72 (8.46)	4.66 (4.84)	84.9	-
12	[Cd(MBT)(dha)]Cl $CdC_{25}H_{23}N_4O_5SCl$(639.40)	White	47.35 (46.96)	3.67 (3.62)	8.93 (8.76)	4.93 (5.01)	75.2	-

-: diamagnetic

Copyright © 2010 SciRes.

Table 3. Electronic spectral data of the synthesized mixed ligand complexes.

No.	Complex	υ(k.K) (ε_{max}cm^{2}mol^{-1})	assignment
1	[Cu(NBT)(dha)]Cl	33.17(35140.84) 25.80(5948.31) 12.40(29.60)	Intraligand LMCT $^2B_{1g}\rightarrow{}^2A_{1g}$
2	[Cu(CBT)(dha)Cl(H_2O)]	36.27(23049.82) 34.29(21219.11) 15.44(26.69)	Intraligand Intraligand $^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2E_g$
3	[Cu(MBT)$_2$(dha)]Cl.H_2O	36.93(53248.13) 30.79(25121.52) 13.33(48.33)	Intraligand Intraligand $^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2E_g$
4	[Co(NBT)(dha)$_2$].H_2O	34.85(84126.39) 26.91(20410.62) 17.24(143.6)	Intraligand LMCT $^4T_{1g}(F)\rightarrow{}^4A_{2g}(\upsilon_2)$, $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\upsilon_3)$
5	[Co(CBT)(dha)Cl(H_2O)].H_2O	37.09(57420.32) 15.62(131.05)	Intraligand $^4T_{1g}(F)\rightarrow{}^4A_{2g}(\upsilon_2)$, $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\upsilon_3)$
6	[Co(MBT)(dha)Cl(H_2O)]	36.76(38944.24) 31.21(55761.13) 15.71(131.62)	Intraligand Intraligand $^4T_{1g}(F)\rightarrow{}^4A_{2g}(\upsilon_2)$, $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\upsilon_3)$
7	[Ni(NBT)(dha)$_2$].2H_2O	32.30(45142.33) 22.42(56013.97) 15.89(118.74)	Intraligand LMCT $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$
8	[Ni(CBT)(dha)Cl(H_2O)].H_2O	34.39(12535.04) 15.64(26.70)	Intraligand $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$
9	[Ni(MBT)(dha)Cl(H_2O)]	35.66(12174.10) 31.42(14453.81) 15.02(12.30)	Intraligand Intraligand $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$
10	[Cd(NBT)(dha)]Cl.H_2O	37.12(16417.18) 33.46(8509.42) 29.47(5046.47)	Intraligand Intraligand LMCT
11	[Cd(CBT)(dha)]Cl.H_2O	36.92(46607.37) 32.11(12100.81) 29.54(6728.32)	Intraligand Intraligand LMCT
12	[Cd(MBT)(dha)]Cl	37.10(115683.04) 30.96(78832.13)	Intraligand Intraligand

Three sets of bands could be recognized in the electronic spectra of the obtained mixed ligand complexes as listed in **Table 3**. The first set with υ_{max} in the range 30.79-37.12 kK., could be attributed to intraligand charge transfer transitions [32]. The second set of includes bands having υ_{max} in the range 22.42-29.54 kK. These bands are assigned as LMCT transitions [32].

The third set of bands of Cu(II) complexes 2 and 3 have υ_{max} at 15.44, 13.33 kK. and is assigned for a d-d transition which is typical for distorted octahderal Cu(II) complexes [33]. These bands are assigned to all the three transitions $^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2A_{1g}$ and $^2B_{1g}\rightarrow{}^2E_g$ [33]. While complex (1) shows an absorption d-d band at 12.40 kK. which has been attributed to $^2B_{1g}\rightarrow{}^2A_{1g}$ transition suggesting square planar geometry [33,34].

The d-d transition bands observed for Co(II) mixed ligand complexes(4-6) are found to have υ_{max} in the range 15.62-17.24 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 [33,34].

The d-d transition bands observed for Ni(II) mixed ligand complexes (7-9) are found to have υ_{max} in the range 15.02-15.89 kK. could be attributed to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ transitions, suggesting octahedral geometry for the Ni(II) complexes [33].

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, tetrahedral geometry is proposed for all the complexes.

The corrected magnetic moment values for Cu(II), Co(II) and Ni(II) mixed ligand complexes are reported in **Table 2**. All the Cu(II) mixed ligand complexes (1-3) display a dimagnetic nature which is attributed either to their polymeric nature or super exchange interaction [35]

Copyright © 2010 SciRes.

in the complex molecules and/or high polarizability [36] 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 (4-6) are within the range 4.55-5.12 B.M. expected for octahedral Co(II) complexes [35,37]. These lower magnetic moment values of the 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 [38]. The room temperature magnetic moment values of Ni(II) mixed ligand complexes (7-9) are 3.16, 2.98 and 3.05 B.M., respectively suggesting octahedral geometry [37,39].

3.3. IR Spectra

Relevant IR bands that provide considerable structural evidence for the formation of mixed ligand complexes are reported in **Table 4**.

The IR spectrum of the free (Nadha) ligand exhibit a series of significant IR absorption bands appearing in the vibrational regions at 1713, 1642 and 1252 cm^{-1} have been ascribed to the stretching vibrations of υ(C=O) lactone, υ(C=O)carbonyl and υ(C–O) phenolic, respectively [40,41]. In all the complexes υ(C=O) lactone remains unaltered while the other two peaks shift to lower frequency. This shift has been attributed to the coordination of the ligand to form the mixed ligand complexes.

NBT, CBT and MBT ligands show four bands at 1565-1588, 1275-1340, 1008-1040 and 780-815 cm^{-1} which are assignable to thioamide I, II, III, IV vibrations, respectively [42]. Theses bands have contributions from δ(C-H) + δ(N-H), υ(C=S) + υ(C-N) + δ(C-H), υ(C-N) + υ(C-S) and υ(C=S) modes of vibrations, respectively. These bands are expected to be affected differently by the modes of coordination to the metal ions. In the complexes, these bands shift to lower frequency suggesting the coordination of the sulfur atom to the metal ions [43].

All the ligands and their complexes show a band within the range 3102-3030 cm^{-1} which is attributed to υ(NH) vibration, indicating that the mercaptotriazole ligands and the 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 υ(C=N) vibrations of the azomethine group. This band in the complexes shifts 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 [44].

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 υ(OH) vibrational modes of the water molecules [45] and this was confirmed by the results of thermal analysis. **Figure 2** shows the Proposed structure for some mixed ligand complexes.

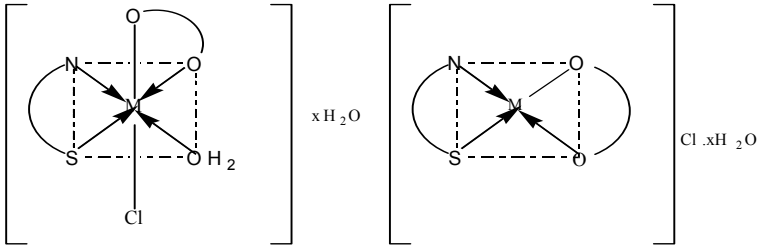
3.4. Thermal Decomposition Studies

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 [46,47]. Thermodynamic parameters: entropy ($\Delta S^{\#}$), enthalpy ($\Delta H^{\#}$) and free energy ($\Delta G^{\#}$) of activation were calculated as shown in **Table 5** using the following standard relations [48].

Table 4. Relevant IR Spectral data for the complexes.

Compound	υ(O-H) (H_2O)	Thioamide Bands				dha 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)	υ(C=O) carbonyl	υ(C–O)
[Cu(NBT)(dha)]Cl	-	1550	1240	1000	790	1630	1240
[Cu(CBT)(dha)Cl(H_2O)]	-	1550	1240	1000	790	1630	1240
[Cu(MBT)$_2$(dha)]Cl.H_2O	3350	1550	1260	1000	780	1630	1230
[Co(NBT)(dha)$_2$].H_2O	3300	1550	1270	1000	790	1640	1220
[Co(CBT)(dha)Cl(H_2O)].H_2O	3350	1540	1260	1010	800	1640	1240
[Co(MBT)(dha)Cl(H_2O)]	3350	1560	1250	1020	770	1620	1240
[Ni(NBT)(dha)$_2$].2H_2O	3400	1560	1270	1000	810	1630	1240
[Ni(CBT)(dha)Cl(H_2O)].H_2O	3350	1560	1270	1010	780	1600	1200
[Ni(MBT)(dha)Cl(H_2O)]	3350	1550	1180	1000	770	1620	1250
[Cd(NBT)(dha)]Cl.H_2O	3400	1540	1250	990	810	1630	1190
[Cd(CBT)(dha)]Cl.H_2O	3440	1560	1260	1010	760	1620	1220
[Cd(MBT)(dha)]Cl	-	1570	1250	1010	750	1620	1230

Copyright © 2010 SciRes.



M = Cu(II), Co(II), Ni(II) or Cd(II); x = 0 or 1

Figure 2. The Proposed structure for some mixed ligand complexes.

3.4.1. Thermal Analysis of [Cu(NBT)(dha)]Cl

The TGA of the square planar complex [Cu(NBT)-(dha)]Cl gave three steps (**Figure 3, 4**). The first step (T = 26.04-291.4°C, $E^{\#}$ = 98.78 KJ/mol) is assignable to removal of $C_{15}H_{13}N_5O_2S$ moiety (calcd. = 54.063%; found = 53.829%). Step two (T = 291.61-392.12°C, $E^{\#}$ = 211.85 KJ/mol) is assignable to removal of chlorine atom and $COCH_3$ moiety (calcd. = 12.986%; found = 12.666%). The third step (T = 394.14-751.73°C, $E^{\#}$ = 160.68 KJ/mol) is assignable to removal of carbon atom and $C_6H_4O_3$ moiety (calcd. = 22.477%; found = 23.102%). The residual product is assignable to be Cu (calcd. = 10.494%; found = 10.403%).

$$[Cu(NBT)(dha)]Cl \xrightarrow{I,\ -C_{15}H_{13}N_5O_2S} [Cu(C)(dha)]Cl \xrightarrow{II,-Cl,\ -COCH_3}$$

$$[Cu(C)(C_6H_4O_3)] \xrightarrow{III,\ -C,\ -C_6H_4O_3} Cu$$

3.4.2. Thermal Analysis of Some Complexes

The TGA of the complexes 1, 2, 3, 4, 5, 6, 7, 10 gave three steps. The first step (T = 29.69-208.26°C, $E^{\#}$ = 17-178.34 KJ/mol) is assignable to removal of one water molecule. Step two (T = 169.55-388.84°C, $E^{\#}$ = 35.48-430 KJ/mol) is assignable to removal of $C_{15}H_{13}N_4Cl$ moiety. The third step (T = 321.16-751.62°C, $E^{\#}$ = 93-261 KJ/mol) is assignable to removal of $C_8H_7O_3$ moiety and chlorine atom giving CuO + CS as residual products:

$$[Cu(CBT)(dha)Cl(H_2O)] \xrightarrow{I,\ -H_2O} [Cu(CBT)(dha)Cl] \xrightarrow{II,\ -C_{15}H_{13}N_4Cl}$$

$$[Cu(CS)(dha)Cl] \xrightarrow{III,\ -Cl,\ -C_8H_7O_3} CuO + CS$$

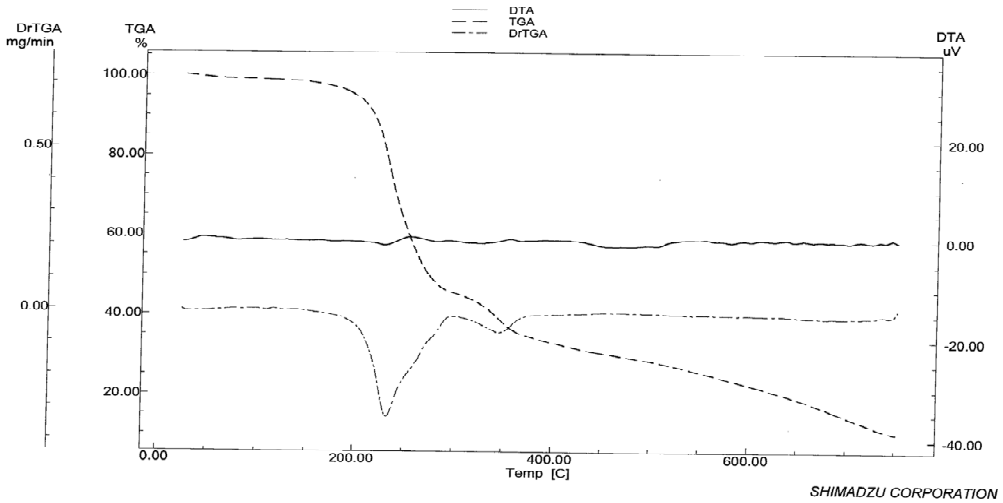


Figure 3. TG-DTG curves of complex 1.

Copyright © 2010 SciRes.

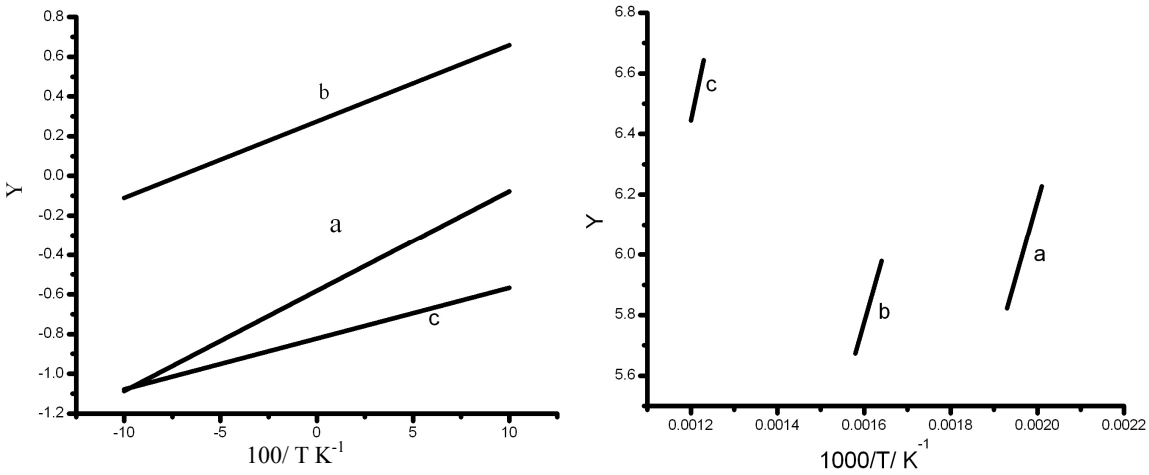


Figure 4. Coats-Redfern and Horwitz-Metzger plots of complex 1(a: 1st step, b: 2nd step, c: 3rd step).

The TGA of the complexes 8, 9, 12 gave four steps. The first step (T = 27.51-316°C, $E^{\#}$ = 42.69-58 KJ/mol) is assignable to removal of two water molecules. Step two (T = 191.98-339.03°C, $E^{\#}$ = 53.18-205.84 KJ/mol) is assignable to removal of $C_8H_7O_3$ moiety and chlorine atom. The third step (T = 318-529.38.57°C, $E^{\#}$ = 136-205.91 KJ/mol) is assignable to removal of C_6H_4Cl moiety. The fourth step (T = 444.59-751.64°C, $E^{\#}$ = 62.35-196.92 KJ/mol) is assignable to removal of $C_{10}H_9N_4$ moiety giving NiO + S as residual products.

$$[Ni(CBT)(dha)Cl(H_2O)].H_2O \xrightarrow{I,\ -2H_2O} [Ni(CBT)(dha)Cl] \xrightarrow{II,\ -C_8H_7O_3,\ -Cl}$$

$$[Ni(CBT)(O)] \xrightarrow{III,\ -C_6H_4Cl} [Ni(C_{10}H_9N_4S)(O)] \xrightarrow{IV,\ -C_{10}H_9N_4} NiO + S$$

3.4.3. Thermal Analysis of [Cd(CBT)(dha)]Cl.H_2O

The TGA of the tetrahedral complex [Cd(CBT)(dha)]Cl.H_2O gave five steps. The first step (T = 37.43-173.98°C, $E^{\#}$ = 94.16 KJ/mol) is assignable to removal of one water molecule (calcd. = 2.722%; found = 2.322%). Step two (T = 175.18-218.69°C, $E^{\#}$ = 67.71 KJ/mol) is assignable to removal of chlorine atom (calcd. = 5.356%; found = 5.289%). The third step (T = 219.89-284.97°C, $E^{\#}$ = 194.96 KJ/mol) is assignable to removal of $C_7H_5N_2Cl$ moiety (calcd. = 23.054%; found = 23.186%). The fourth step (T = 286.97-475.42°C, $E^{\#}$ = 78.45 KJ/mol) is assignable to removal of $C_6H_7O_2$ and CHN_2 moieties (calcd. = 22.988%; found = 22.154%). Step five (T = 477.41-751.71°C, $E^{\#}$ = 193.02 KJ/mol) is assignable to removal of sulphur atom and CO and C_8H_7 moieties (calcd. = 24.661%; found = 23.154%) giving CdO + C as residual products (calcd. = 21.216%; found = 20.804%).

$$[Cd(CBT)(dha)]Cl.H_2O \xrightarrow{I,\ -H_2O} [Cd(CBT)(dha)]Cl \xrightarrow{II,\ -Cl} [Cd(CBT)(dha)]$$

$$\xrightarrow{III,\ -C_7H_5N_2Cl} [Cd(C_9H_8N_2S)(dha)] \xrightarrow{IV,\ -CHN_2\ -C_6H_7O_2} [Cd(C_8H_7S)(C_2O_2)]$$

$$\xrightarrow{V,\ -CO,\ -S,\ -C_8H_7} CdO + C$$

3.5. Thermal Stability

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

MBT rather than CBT and NBT forms the most stable complexes with Cu(II), Co(II) and Cd(II) while the most stable Ni(II) complex in presence of CBT as a S, N donor ligand (**Figure 5**).

For complexes containing the same mercaptotriazole ligand; Cd(II) have been found to form the most stable complexes in presence of NBT or MBT ligands. While in case of presence of CBT ligand, Cu(II) forms the most stable complex.

Copyright © 2010 SciRes.

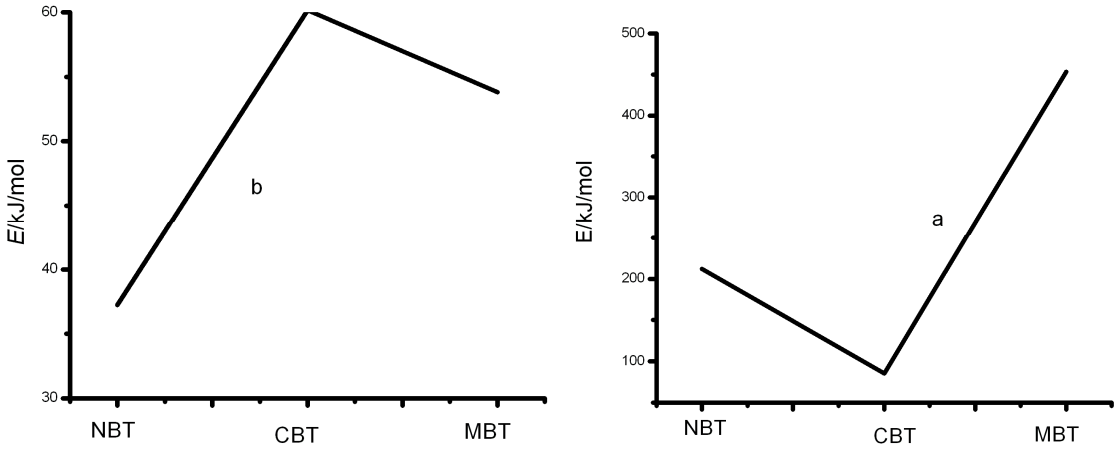


Figure 5. Relationships between the activation energy for the first decomposition step for the mixed ligand complexes and the S, N donor ligand: Cu(II)(A) and Ni(II)(B) complexes.

Table 5. Kinetic and thermodynamic parameters for the thermal decomposition of the synthesized 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	1.0	1.0000	98.78	1578.17	–188.10	103.00	198.39	0.999	107.20	4.75×10^{8}	–83.20	111.39	153.59
	2	2.0	0.9991	211.85	3407.68	–183.36	217.00	330.53	0.9988	222.27	1.97×10^{17}	80.12	227.39	177.77
	3	2.0	0.9997	160.68	2566.76	–188.02	167.48	321.12	0.9997	174.50	3.85×10^{8}	–88.92	181.25	253.92
2	1	0.0	0.9998	58.56	937.11	–188.98	61.35	124.63	1.0000	64.25	2.69×10^{7}	–103.6	67.02	101.72
	2	0.0	1.0000	85.48	1369.69	–189.47	89.79	188.10	1.0000	94.41	8.91×10^{6}	–116.4	98.70	159.13
	3	2.0	1.0000	257.51	4138.54	–181.58	262.56	372.78	0.9999	267.55	3.06×10^{21}	160.51	272.5	175.14
3	1	1.0	0.9995	76.98	1232.71	–189.14	80.71	165.59	0.9992	84.60	3.81×10^{7}	–103.1	88.32	134.61
	2	2.0	0.9988	453.67	7256.60	–176.09	458.25	555.15	0.9602	336.07	7.15×10^{29}	321.52	340.62	163.69
	3	0.5	1.0000	57.76	935.37	–195.66	63.97	210.04	1.0000	70.52	158.19	–210.44	76.69	233.80
4	1	0.5	1.0000	58.72	941.80	–190.37	62.03	137.71	0.9999	65.35	2.52×10^{6}	–124.73	68.63	118.22
	2	1.0	1.0000	29.71	482.62	–198.33	34.13	139.38	0.9999	38.66	11.10	–229.69	43.05	164.94
	3	1.0	1.0000	102.44	1652.87	–192.18	109.65	276.47	1.0000	117.13	29439.29	–168.24	124.31	270.34
5	1	2.0	0.9999	28.06	454.21	–196.43	31.36	109.42	1.0000	34.74	117.06	–207.70	38.02	120.56
	2	0.0	0.9990	51.59	833.72	–194.04	56.14	162.42	0.9997	60.77	1181.68	–191.14	65.30	169.99
	3	1.0	1.0000	90.97	1463.43	–190.93	96.46	222.67	0.9999	101.53	3.70×10^{5}	–144.91	107.00	202.79
	4	1.0	1.0000	266.18	4280.90	–182.62	272.10	402.03	0.9998	276.69	2.06×10^{18}	98.47	282.57	212.51
6	1	2.0	0.9995	178.34	2771.21	–182.18	181.97	261.54	0.9923	185.69	3.54×10^{20}	145.31	189.31	125.84
	2	2.0	0.9986	268.70	4316.30	–180.55	273.35	374.39	0.9981	278.43	2.58×10^{23}	198.06	283.06	172.22
	3	0.0	0.9863	93.38	1505.70	–192.24	100.00	253.12	0.9904	106.49	18225.42	–171.51	113.07	249.68
7	1	0.33	1.0000	17.13	555184.60	–138.27	20.83	82.38	1.0000	24.41	1.40	–245.41	28.09	137.33
	2	0.0	0.9984	35.86	581.46	–197.03	40.41	148.25	0.9995	44.84	23.76	–223.62	49.36	171.75
	3	2.0	0.9970	186.82	2965.89	–186.33	193.23	336.75	0.9967	199.69	2.30×10^{11}	–35.28	206.06	233.24
8	1	0.0	0.9914	42.69	688.84	–193.36	46.16	126.77	0.9953	49.72	4726.17	–177.35	53.17	127.10

Copyright © 2010 SciRes.

	2	0.5	1.0000	60.18	970.55	–192.84	64.77	171.16	0.9999	69.22	9083.61	–174.25	73.78	169.92
	3	2.0	0.9986	205.91	3316.03	–185.51	212.41	357.28	0.9984	218.87	1.19×10^{12}	–21.71	225.33	242.29
	4	2.0	0.9999	196.92	3172.60	–187.12	204.46	374.11	1.0000	212.76	1.03×10^{10}	–62.43	220.25	276.86
9	1	0.0	0.9999	58.40	934.77	–188.99	61.18	124.38	1.0000	64.07	1.86×10^{7}	–106.69	66.84	102.51
	2	0.0	0.9982	53.00	856.16	–193.50	57.38	159.346	0.9992	61.76	1959.32	–186.62	66.11	164.44
	3	2.0	0.9996	136.12	2170.36	–187.74	141.67	267.04	0.9994	146.75	2.00×10^{9}	–73.54	152.28	201.39
	4	0.0	0.9968	122.46	1965.60	–189.79	128.90	275.86	0.9977	135.86	3.05×10^{6}	–128.70	142.26	241.92
	1	0.33	0.9993	23.05	373.88	–198.97	26.74	115.11	0.9999	30.34	10.10	–228.99	34.01	135.72
10	2	2.0	0.9938	496.60	7928.71	–174.71	500.83	589.74	0.9951	506.27	1.48×10^{51}	730.26	510.48	138.86
	3	2.0	1.0000	261.18	4197.54	–181.55	266.29	377.74	0.9547	271.43	2.06×10^{21}	157.11	276.50	180.06
	1	0.0	0.9999	94.16	1516.85	–186.87	97.65	176.19	1.0000	101.22	1.31×10^{10}	–54.07	104.70	127.42
	2	1.0	1.0000	67.71	1088.20	71.70	–190.73	163.28	0.9998	75.49	7.75×10^{5}	–136.12	79.46	144.81
11	3	2.0	0.9957	194.96	3136.70	–183.48	199.77	305.84	0.9952	204.54	1.29×10^{16}	58.05	209.32	175.76
	4	0.5	1.0000	78.45	1265.17	–192.73	84.34	221.06	1.0000	89.88	12913.82	–173.41	95.74	218.75
	5	0.5	0.9997	193.02	3109.77	–186.37	199.77	351.11	0.9948	256.82	9.27×10^{13}	14.14	263.54	252.05
	1	2.0	0.9982	511.43	8173.13	–175.35	516.15	615.49	0.9988	522.15	1.12×10^{47}	650.47	526.84	158.30
12	2	1.0	0.9997	323.45	5192.46	–179.77	328.55	438.69	0.9995	333.73	6.93×10^{26}	262.93	338.79	177.70
	3	0.5	1.0000	205.84	3314.81	–185.32	212.18	353.47	1.0000	218.72	6.68×10^{12}	–7.20	225.02	230.51
	4	0.0	0.9944	62.35	1012.09	–196.88	70.13	254.30	0.9946	80.32	24.03	–227.98	88.05	301.31

3.6. Conclusions

Studying the TGA and DTA curves for the complexes indicates that there is a series of thermal changes on the DTA curves associate the weight loss in the TGA curves. This study leads to the following conclusions:

1) The presence of more than one exothermic peak in the DTA curves of all the complexes reveals that the pyrolysis occurs in several steps [49].

2) 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 [50].

3) The thermal behaviour of the complexes displays an observable difference with respect to each other. This difference indicates that the thermal behaviour of these complexes depends mainly on the type of the ligands rather than the type of the metal ion.

4) 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 [50].

5) The entropy values for all degradation steps of all degradation steps of all complexes were found to be negative, which indicates a more ordered activated state that may be possible through the chemisorption of some decomposition products [51-53].

6) The relatively low values of values of $\Delta H^{\#}$ for the prepared complexes confirm the M-S or M-N bond rupture [54,55]

7) 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 [48].

8) 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 [56,57].

9) 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 $\Delta H^{\#}$ [48].

10) Increasing the $\Delta G^{\#}$ values for the subsequent of a

Copyright © 2010 SciRes.

given complex reflects that the rate of removal of a given species will be lower than that of the precedent one [48]. This may be attributed to the structure rigidity of the remaining complex.

11) 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.

REFERENCES

[1] Arndt, F. (1955) *Org. Synth. Coll. II*, **231**.

[2] Rao, D.S., Ganorkar, M.C.D., Rao, L.S. and John, V.T. (1978) *Natl. Acad. Sci. Lett.*, **1**, 402.

[3] Bartels-Keith, J.R. (1960) *J. Chem. Soc.*, 1662.

[4] Miyakado, M., Inoue, S., Tanabe, Y., Watanabe, K., Ohno, N., Yoshioka, H. and Mabay, T.J. (1982) *Chem. Lett.*, 1539.

[5] Figueroa-Villar, J.D., Ayer, W.A. and Migaj, B. (1988) *Can. J. Chem.*, **66**, 506-512.

[6] Reddy, G.S.R. and Rao, N.R. (1994) *Indian J. Chem. B*, **33**, 113.

[7] Chalaca, M.Z., Figueroa-Villar, J.D., Ellena, J.A. and Castellano, E.E. (2002) *Inorg. Chim. Acta*, **328**, 45.

[8] Kureshy, R.I., Khan, N.H., Abdi, S.H.R., Iyer, P. and Patel, S.T. (1999) *Polyhedron*, **18**, 1773.

[9] Kureshy, R.I., Khan, N.H., Abdi, S.H.R. and Iyer, P. (1997) *J. Mol. Catal.*, **124**, 91.

[10] Rao, P.V. and Narasaiah, A.V. (2003) *Indian J. Chem. A*, **42**, 1896.

[11] Puerta, D.T. and Cohen, S.M. (2003) *Inorg. Chem.*, **42**, 3423.

[12] Battaini, G., Monzani, E., Casella, L., Santagostini, L. and Pagliarin, R. (2000) *J. Biol. Inorg. Chem.*, **5**, 262.

[13] Thaisrivongs, S., Romero, D.L., Tommasi, R.A., Janakiraman, M.N., Strohbach, J.W., Turner, S.R., Biles, C., Morge, R.R., Johnson, P.D., Aristoff, P.A., Tomich, P.K., Lynn, J.C., Horng, M.M., Chong, K.T., Hinshaw, R.R., Howe, W.J., Finzel, B.C. and Watenpaugh, K.D. (1996) *J. Med. Chem.* **39**, 4630.

[14] Eweiss, N., Bahajaj, A. and Elsherbini, E. (1986) *Heterocycl. Chem.*, **23**, 1451.

[15] Holla, B., Poojary, K., Kalluraya, B. and Gowda, P. (1996) *Farmaco*, **51**, 793.

[16] Jantova, S., Greif, G., Pavlovicova, R. and Cipak, L. (1998) *Folia Microbiol.*(*Prague*), **43**, 75.

[17] Awad, I., Abdel-Rahman, A. and Bakite, E. (1991) *J. Chem. Technol. Biotechnol.*, **51**, 483.

[18] Kucukguzel, I., Kucukguzel, S.G., Rollas, S. and Kiraz, M. (2001) *Bioorg.Chem. Lett.*, **11**, 1703.

[19] Bala, S., Gupta, R.P., Sachedeva, M.L., Lal, M., Singh, A.K. and Pujari, H.K. (1978) *Ind. J. Chem.*, **16B**, 481.

[20] Jantova, S., Greif, G., Pavlovicova, R. and Cipak, L. (1998) *Folia Microbiol.*, **43**, 75.

[21] Sadadudam, Y.S., Shetty, M.M. and Dlawan, P.V. (1992) *Eur. J. Med. Chem.*, **27**, 87.

[22] Bermejo, E., Carballo, R., Castineiras, A., Dominguez, R., Maichle-Mossmer, C., Strahle, J. and West, D. (1999) *Polyhedron*, **18**, 3695.

[23] Almajan, G.L., Barbuceanu, S., Almajan, E., Draghici, C. and Saramet, G. (2008) *European Journal of Medicinal Chemistry*, 1-7.

[24] Joshi, S.D., Vagdevi, H.M., Vaidya, V.P. and Gadaginamath, G.S. (2008) *European Journal of Medicinal Chemistry*, **43**, 1989-1996.

[25] Akbar Ali, M. and Livingstone, S.E. (1974) *Coord. Chem. Rev.*, **13**, 101.

[26] Severin, K., Bergs, R. and Beck, W. (1998) *Angew. Chem., Int. Ed.*, **37**, 1722.

[27] Shikkargol, R.K., Angadi, S.D. and Kulkami, V.H. (1996) *Orient. J. Chem.*, 1172.

[28] Cansiz, A., Koparir, M. and Demitdag, A. (2004) *Molecules*, **9**, 204.

[29] Ragenovic, K.C., Dimova, V., Kakurinov, V., Molnar, D. G. and Buzarovska, A. (2001) *Molecules*, **6**, 815.

[30] Reid, J.R. and Heindel, D. (1976) *J. Heterocyclic Chem.*, **13**, 925.

[31] Geary, W.J. (1971) *Coord. Chem. Rev.*, **7**, 81.

[32] Macias, B., Villa, V.M. and Gallego, R.R. (1995) *Tran. Met. Chem.*, **20**, 347.

[33] Lever, A.B.P. (1984) Inorganic electronic spectroscopy. Elsevier Amsterdam, 4th Edition.

[34] Dubey, S.N. and Kaushik, B. (1985) *Indian J. Chem.*, **24A(11)**, 950-953.

[35] Kishita, M., Inoue, M. and Kubo, M. (1964) *Inorg. Chem.*, **3**, 237.

[36] Dubey, S., Handa, R. and Vaid, B. (1994) *Monatsh. Chem.*, **125**, 395-401.

[37] Earnshow, A. (1968) Introduction to magnetochemistry. Academic Press, London.

[38] Beena, K. and Dubey, S.N. (1989) *Indian. J. Chem.*, **28A(5)**, 425-427.

[39] Figgis, B.N. and Lewis, J. (1960) Modern coordination chemistry. In: Lewis, J. and Wilkins, R.G., Eds., Interscience, New York, 403-406.

[40] Chalaca, M. Z., Villar, J.D.F., Ellena, J.A., Castellano, E. E. (2002) *Inorg. Chim. Acta*, **328**, 45.

[41] Chitrapriya, N., Mahalingam, V., Zeller, M., Jayabalan, R., Swaminathan, K. and Natarajan, K. (2008) *Polyhedron*, **27**, 939-946.

[42] Gupta, B.K., Gupta, D.S., Dikshit, S.K. and Agarwala, V. *Ind. J. Chem.* (1977) **15A**, 624.

[43] Subramanian, M.S. and Viswanatha, A.J. (1969) *Inorg. Nucl. Chem.*, **31**, 2575.

[44] Issleib, K. and Batz, G.Z. (1969) *Anorg. Allg. Chem.*, **369**, 83.

[45] Nakamoto, K. (1978) Infrared spectra and raman spectra of inorganic and coordination compounds. 3rd Edition, John Wiley, New York.

[46] Coats, A.W. and Redfern, J.P. (1964) *Nature*, **20**, 68.

[47] Horwitz, H.H. and Metzger, G. (1963) *Anal. Chem.*, **35**, 1464.

[48] Kandil, S.S., El-Hefnawy, B.G. and Baker, A.E. (2004) *Thermochim. Acta*, **414**, 105.

[49] Ali, F.B., Al-Akramawi, S.W., Al-Obaidi, H.K. and Al-Karboli, H.A. (2004) *Thermchim. Acta*, **419**, 39.

[50] Said, A.A. and Hassan, M.R. (1993) *Poly. Degard. Stab.*, **39**, 393.

[51] Madhusudanan, M.P., Yusuff, M.K.K. and Nair, R.G.C. (1975) *J. Therm. Anal.*, **8**, 31.

[52] Gudasi, K.B., Maravalli, P.B. and Goudar, T.R. (2005) *J. Serb. Chem. Soc.*, **70**, 643.

Copyright © 2010 SciRes.

[53] Maravalli, P.B., Gudasi, K.B. and Goudar, T.R. (2000) *Transition Met. Chem.*, **25**, 411.
[54] Dakternieks, R.D. and Gradon, P.D. (1971) *Aust. J. Chem.*, **24**, 2509.
[55] Shetty, S.P. and Fernando, Q. (1970) *J. Am. Chem. Soc.*, **92**, 3964.
[56] Hill, O.J., Murrary, P.J. and Patil, C.K. (1994) *Rev. Inorg. Chem.*, **363**, 14.
[57] Roman, P., Beitia, I.J., Luque, A. and Miralles, G.C. (1994) *Polyhedron*, **13**, 2311.

Copyright © 2010 SciRes. **OPEN ACCESS**