

## Thermal behavior and thermodynamic parameters of some complexes of biologically active nucleic acid constituents

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World Journal of Advanced Research and Reviews, 2021, 12(02), 078–108

Publication history: Received on 22 September 2021; revised on 29 October 2021; accepted on 31 October 2021

Article DOI: <https://doi.org/10.30574/wjarr.2021.12.2.0556>

### Abstract

The thermal behavior of some complexes derived from biologically nucleic acid constituents has been studied applying differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques. Thermodynamic parameters, decompositions and thermal stabilities are calculated and explained. All the complexes gave exothermic peaks with -ve signs for change of entropy values,  $\Delta S$  which indicate that the activated transition states are more ordered, i.e. in a less random molecular configuration than the reacting complexes. TGA gives the mechanism of decomposition.

**Keywords:** Ligands; Complexes; DSC; Debye Model; Thermodynamic Parameters; Fragmentation Pathways

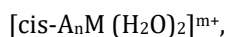
### 1. Introduction

Possibilities for research in the coming decade with new techniques, which follow the reactions of Pt complexes and nucleic acids and proteins, will allow the detection of otherwise invisible intermediate products. The need for new platinum antitumor drugs was underscored by the usefulness of cisplatin and carboplatin in chemotherapy and the resistance of many tumors to these compounds. Combinatorial chemistry could aid in the search for cisplatin analogs if fast, high-throughput assays were available. The goal is to develop rapid cell-based assays suitable for high-throughput screening that accurately predicts the cytotoxicity of platinum complexes. The next stage in drug design is likely to be the development of dedicated drugs that comprise the transport (through the membranes), survival in the cell, binding to the DNA, and eventually, excretion from the body with minimum side effects. In this process, both metal coordination and hydrogen bonding will be key factors at the molecular level. Recent advances in medicinal inorganic chemistry demonstrate significant prospects for the utilization of metal complexes as drugs, presenting a flourishing arena for inorganic chemistry. Significant progress in platinum based anticancer agents has been achieved, based in part on a mechanistic understanding of the DNA-binding and pharmacological effects of cisplatin.

DNAs are the target molecules for most of the metal anticancer agents in human body. The anticancer nature is the coordination of metal ions with DNA molecules. i.e. the direct chelation of the metal ions with certain nucleophilic groups in DNA (such as oxygen sites from phosphates and nitrogen as well as oxygen sites from bases), causing the DNAs' damage in cancer cells, the DNAs were hindered during the processes of replication or transcription, the growing and division of the cancer cells were stopped, and resulted in their death.

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When drug molecules (pre-anticancer molecules) enter into an organism, they will first undergo a series of processes including hydrolysis, transport and membrane-crossing, and then reach the nearby of the target DNA molecule and form active intermediates which interact with DNA molecules directly and exert the anticancer activity. These active intermediates have a general cis-form of two-water-binding transitional state:



where A is stably binding hydrophobic group,  $n=1, 2$  or more and M is metal ion.

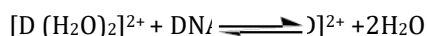
The number of water molecules binding to M must not be fewer than two and they must be lie in the ortho-position of the structure.

The functions of the hydrophobic ligand A are:

- caring the whole molecule to cross membranes (including cell membranes and nucleus membranes), go through the bilipid bilayers.
- making the metal ion to move to the nearby of the base's cyclic-nitrogen sites and form covalent bonding.

Metal anticancer complexes are often electrophilic and may react with many cellular components, such as simple ions and molecules like  $\text{Cl}^-$ ,  $(\text{HPO}_4)^{2-}$ ,  $\text{OH}^-$  and  $\text{H}_2\text{O}$ ; amino acids, peptides and polyphosphates like histidine (His), methionine (Met), cysteine (Cys), glutathione, metallothionein and ATP. From the view of the coordination chemistry, metal complexes (including those of Pt0 can bind to several types of possible biomolecules in the cell. But only the binding on DNA which lead to cell death is considered the most important. In the case of platinum complexes, it is quite clear that in the cells, after the relatively slow hydrolysis, cis-Pt have a preference for DNA over proteins and other molecules. L-methionine increases the rate of reaction of 5'-GMP with cisplatin and that S-bound L-HMet in the adduct  $[\text{Pt}(\text{dien})(\text{L-HMet-S})]^{2+}$  (dien= 1, 5-diamino-3-azapentane0 can be replaced by N7 of 5'GMP [1, 2]. A methionine-containing protein or peptide could transport and transfer some platinum to DNA [2].

Thus, in a very simple model, the action process of a metal anticancer agent in an organism may be briefly summarized into following equations:



$\text{DX}_2$  is the pre-anticancer molecule,

$[\text{D}(\text{H}_2\text{O})_2]^{2+}$  is the active intermediate produced by hydrolysis,

DNA-D is DNA-drug complex.

DNA molecule is a two-pole molecule, its surface is a negatively-charged backbone of phosphatepentose chains. In the inside of double helix there exist hydrophobic bases stacking layer by layer. For exerting its potency, the drug molecules must build with the phosphate groups of DNA at first, and then, with the help of DNA' conformational dynamic changes (partial unwinding of the double helix), the lipophilic groups of the drug molecule may be drawn by DNA's hydrophobic sections, the nitrogen sites on DNA molecules may be exposed, the metal atom could invade into the internal part of DNA and coordinates with the bases. Oxygen site on the phosphate group has a higher negative charge relatively, it is a good donor with high electronegativity; so its action with the metal atom was caused mainly by static electricity, forming electrovalency, belongs to charge-controlling reaction.

Through the study on hydrolysis mechanism and relationship between structure and activity of metal anticancer agents, the following three points are key if the metal anticancer agents have activities:

- (1) Appropriate hydrolysis rates of a complex.
- (2) Forming the active intermediate  $[\text{cis-A}_n\text{M}(\text{H}_2\text{O})_2]^{m+}$ .
- (3) Forming of the coordination both with the oxygen of phosphate groups and with nitrogen of bases.

The molecules with high anticancer activities should not only produce active intermediates by the proper hydrolysis rates, but also bind to both oxygen of phosphate groups and nitrogen of base in DNA, thus showing anticancer activity.

The two pole complementary principle (TPCP) has generalized the molecular structure, action modes and steric selectivity for metal anticancer agents. TPCP includes three aspects:

### 1.1. Two-pole complement in molecular structures

The drug molecules with anticancer activity always have two poles of hydrophilicity and hydrophobicity, positive and negative charges in their structures. Correspondingly, they will present easily-leaving groups and stable keeping groups in a solution. Such two-pole structures can lead the drug molecules not only to be dissolved in water and transported to the surface of the cell membranes, but also to cross the membranes by going through the lipid bilayers and arrive at the nearby of the target molecules.

### 1.2. Two-pole complement in the receptor-substrate action mode

The interaction between the drug molecule and its target molecule is always executed by forming an active intermediate which binds with oxygen sites (electrovalently) on phosphate groups and nitrogen sites (covalently) on purines, pyrimidines of DNA backbone through charge-controlling and orbital-controlling. That is a two-pole complement of electrovalent and covalent action modes.

### 1.3. Two-pole complement in the symmetry of the receptor-substrate system

The interaction characteristics of a chiral drug molecule with DNA behave as using the left hand enantiomer of the drug molecule binding with the right hand DNA, forming a two-pole complementary complex chirally.

## 2. Experimental

### 2.1. A- Synthesis of metal complexes in the solid state

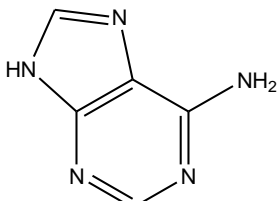
These were prepared by mixing metal chloride and acetylacetonate (acac) solutions with ligand solutions, Table (1), hence they were refluxed, filtered and dried for the separated products. The metal ions were determined by atomic absorption techniques and complexometric titrations using published procedures [3]. The complexes were digested by aqua regia several times to complete decomposition for the organic ligand compounds.

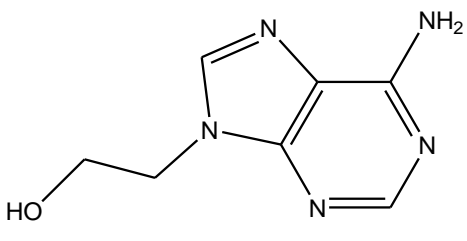
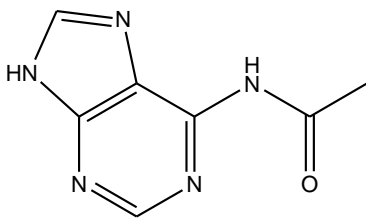
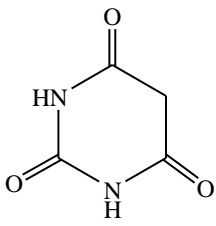
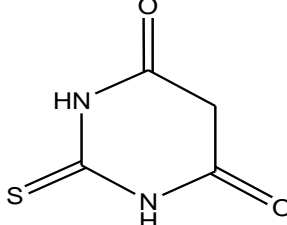
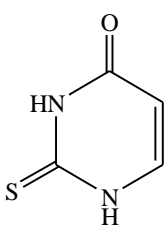
### 2.2. B- Instruments and working procedures

#### 2.2.1. Thermal analysis

The samples were measured using (TGA-50H detector, platinum cell, nitrogen atmosphere, 20 ml/min flow rate) and (DSC-60A detector, aluminum cell, nitrogen atmosphere, 50 ml/min flow rate).

**Table 1** Names, abbreviations, m.p. and structures of the ligands are given

Compound	Abbreviation	M.P.°C	Structures
Adenine	(AD)	360-365	

9-Hydroxyethyladenine	(HEAD)	244	
6-Acetyladenine	(ACAD)	216-217	
Barbituric acid	(BA)	248	
Thiobarbituric acid	(TBA)	245	
2-Thiouracil	(TU)	340	

### 3. Thermal analysis

Thermal analysis plays an important role in studying the structure and the properties of metal complexes in the solid state. A number of solid state reactions (e.g., thermal isomerization, conformational changes, polymorphic transformations, thermal phase transitions, thermochromism, etc...) can be explained using thermal analysis [4-14].

The thermal behavior of some complexes has been studied applying differential scanning calorimetry (DSC), Figures (1-10) and Thermogravimetric analysis (TGA) techniques. Thermodynamic parameters, decompositions and thermal stabilities are calculated and explained, Figures ( (11 (a, b)-20 (a, b)), (21-27)), Tables (2, 3) which can be correlated with their structures [14-19]. It's known that, in general, different polymorphs of some compounds exist as different structures and possess variable properties, e.g. density, hardness, crystal shape, optical and electrical properties, etc..). The compounds probably occur with different structures [20]. Some crystalline matter display the phenomenon of polymorphism which are crystal solvates containing solvents of crystallization. The nature of the interaction of the solvent with the host molecule can be used for explaining the behaviour of solvates [13]. Crystal solvates display polymorphic and pseudo-polymorphic transformations upon desolvation according to the nature of interaction [21].

DSC measurements are considered to be applied from both qualitative and quantitative views and provide information about physical and chemical changes involving endothermic, exothermic processes and changes in heat capacity.

DSC plot is used to determine the melting temperature through melting transition, where, the complex should absorb heat until all the crystals have melted, Table (2).

The Debye model [22] is used to describe capacity change over a large temperature range and  $C_p$  can be represented by the following empirical form:  $C_p = aT + b$ .

By plotting  $C_p$  versus  $T$ , a straight line is obtained, where  $a$  and  $b$  are parameters which can be determined from the slope and intercept of the line, respectively, Figures (11a-20a), Table (2).

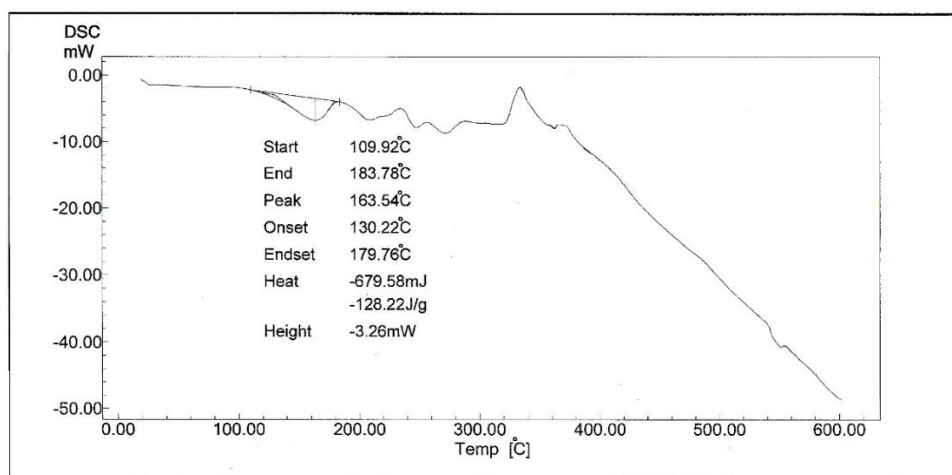
The applications based on Debye model for selected complexes are given from the following equations [23]:

$$C_p \approx C_v = \alpha T^3 + \gamma T, \quad \frac{C_p}{T} = \alpha T^2 + \gamma$$

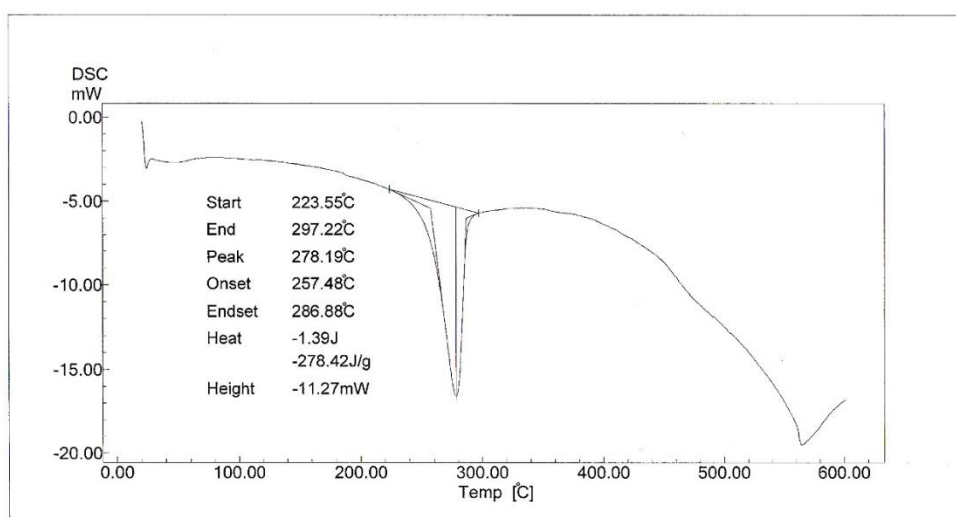
where  $\alpha$  and  $\gamma$  are the coefficients of the lattice and electronic heat capacities, respectively.  $C_v$  is the heat capacity at constant volume which is assumed to be equal to  $C_p$ .

The relationships of  $\frac{C_p}{T}$  versus  $T^2$  give straight lines with slopes  $\alpha$  and intercepts  $\gamma$ , Figures (11b-20b), Table (2).

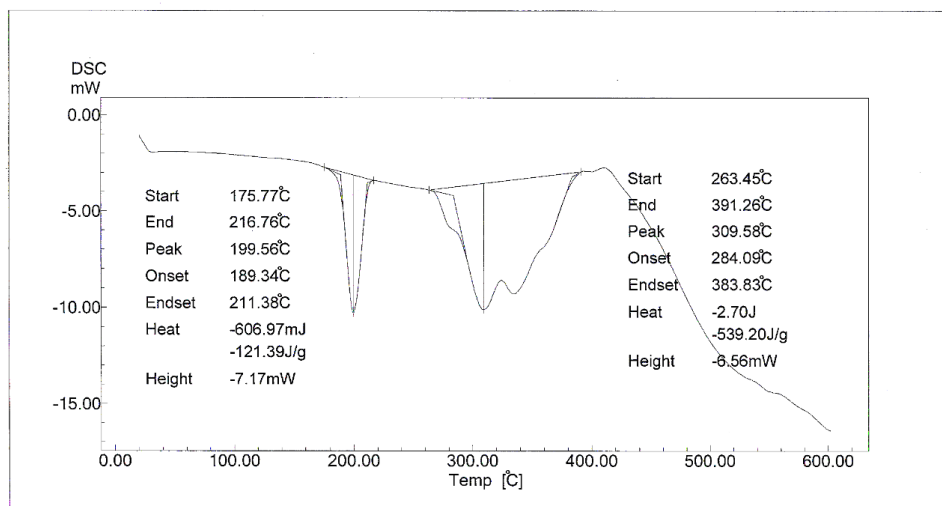
The straight lines are analyzed and the validity is calculated with  $R^2$  values for each line, Figures (11 (a, b)-20 (a, b)).



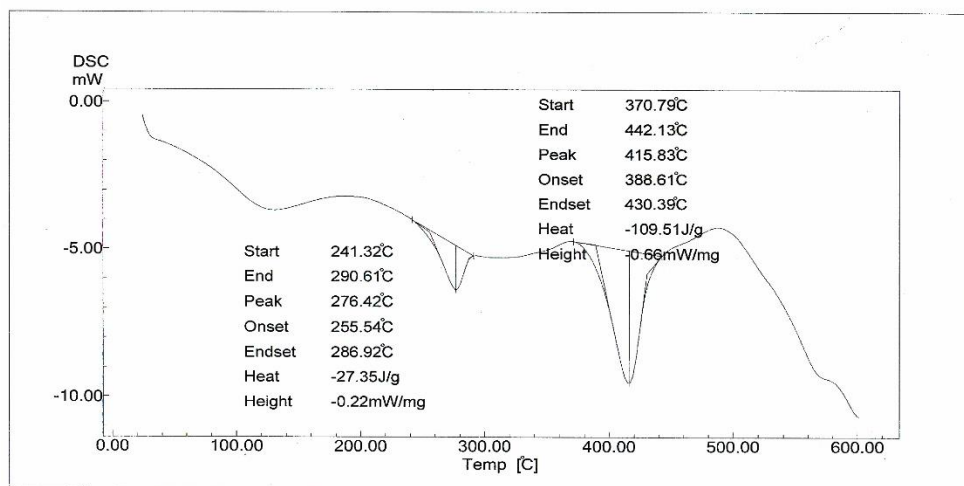
**Figure 1** DSC for Fe (adenine)<sub>3</sub>.



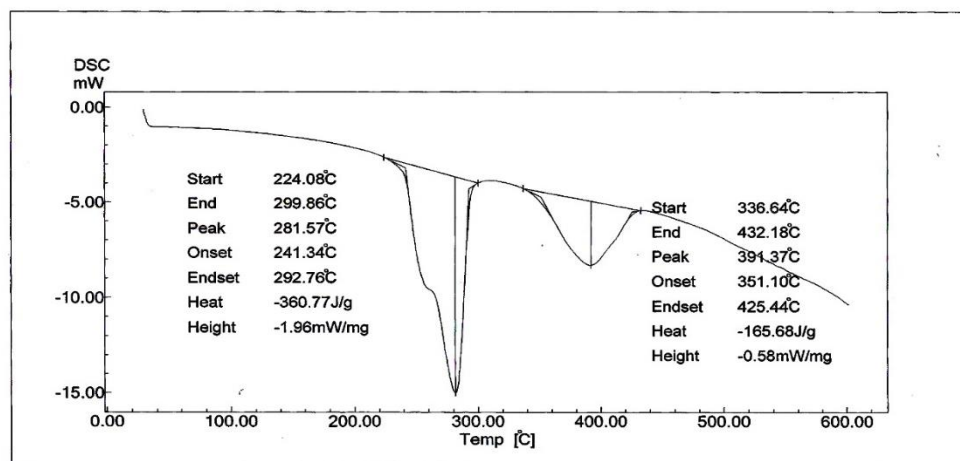
**Figure 2** DSC for Co (acac)<sub>2</sub> (adenine).



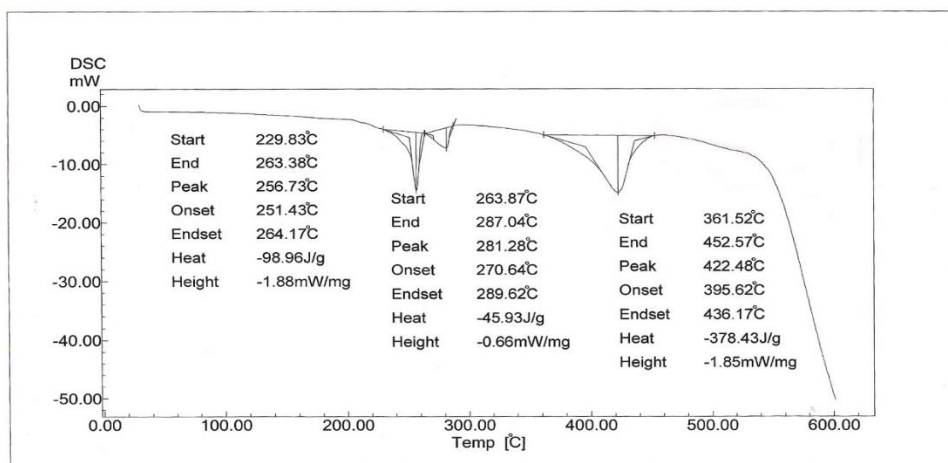
**Figure 3** DSC for Zn (hydroxyethyladenine)<sub>2</sub> (OH)<sub>2</sub>·2H<sub>2</sub>O.



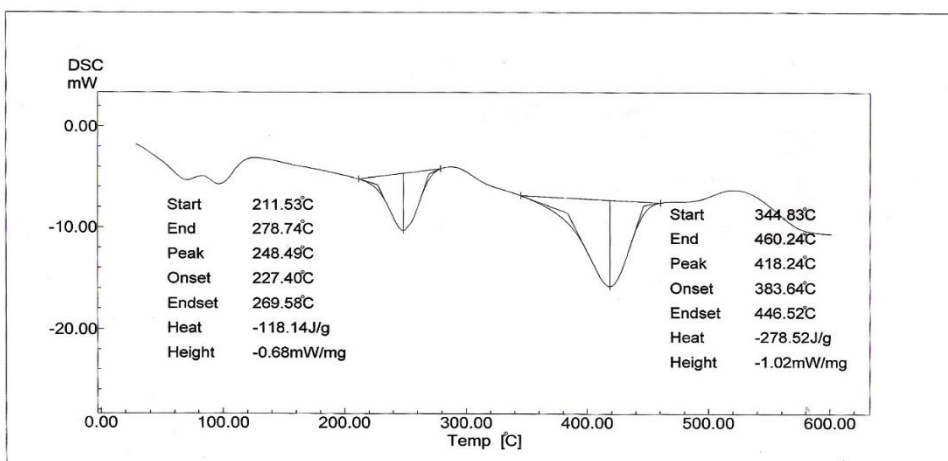
**Figure 4** DSC for Cr (BA) (OH)<sub>2</sub>·4H<sub>2</sub>O.



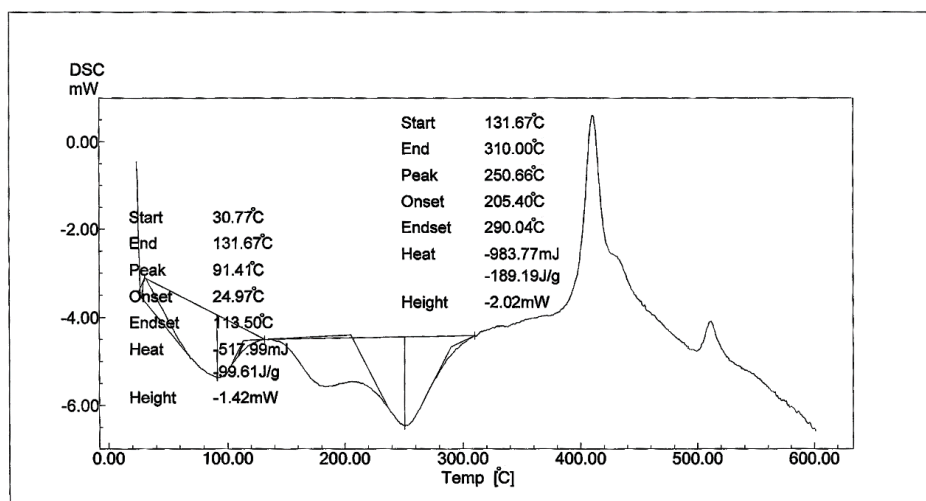
**Figure 5** DSC for Zn (BA)<sub>2</sub>.3H<sub>2</sub>O.



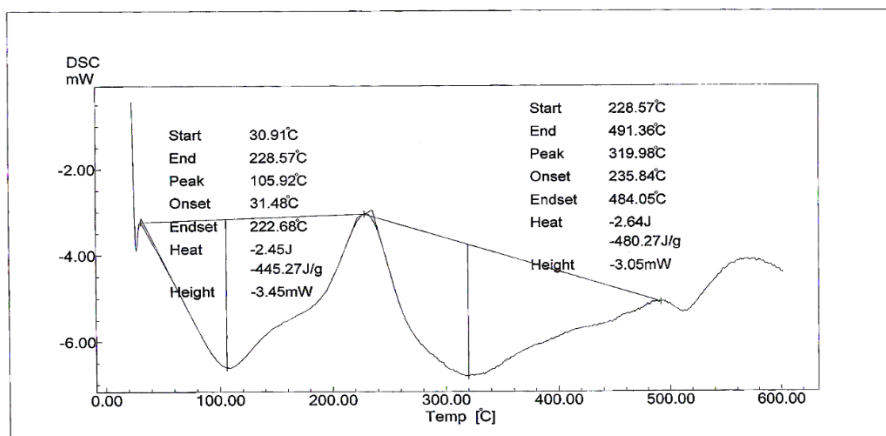
**Figure 6** DSC for Cd (BA)<sub>2</sub>.10H<sub>2</sub>O.



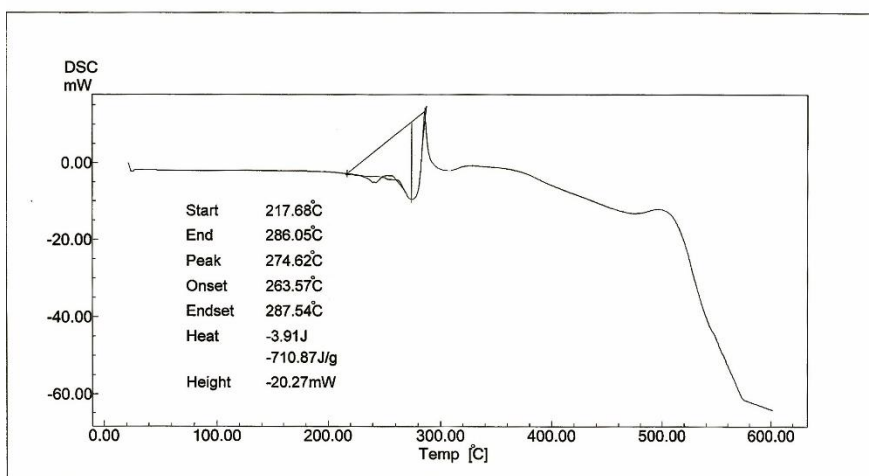
**Figure 7** DSC for Hg (BA)<sub>2</sub>.



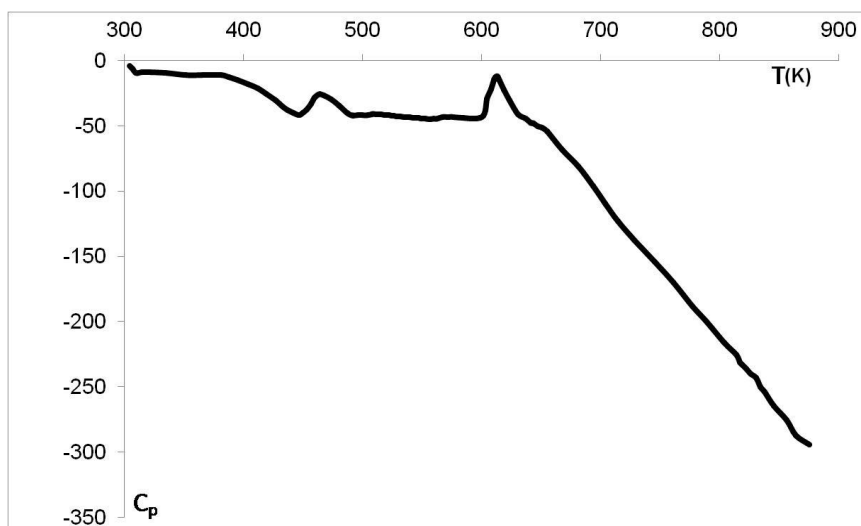
**Figure 8** DSC for Fe (TBA) (OH)·2H<sub>2</sub>O.



**Figure 9** DSC for Cr (TU) (OH)<sub>2</sub>·H<sub>2</sub>O.



**Figure 10** DSC for Hg (TU)<sub>2</sub>·4H<sub>2</sub>O.





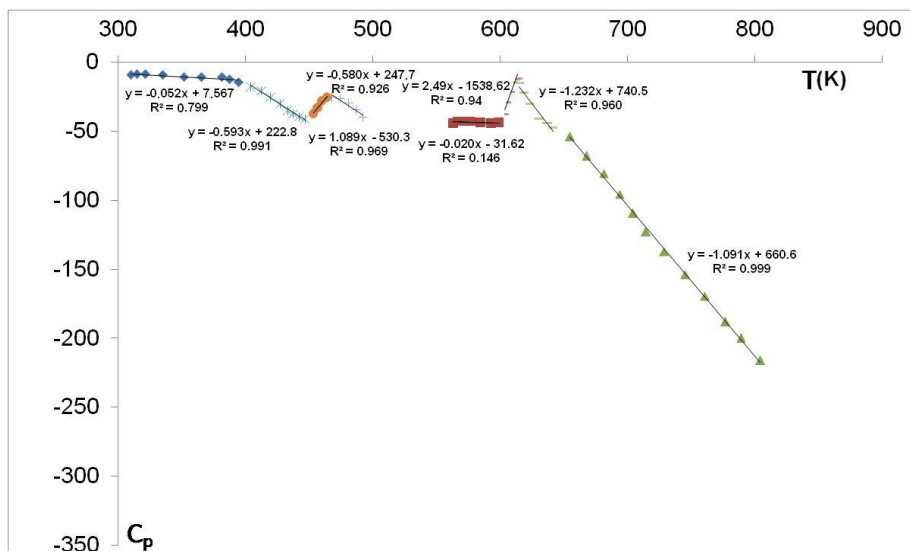


Figure 11a  $C_p$  - $T$  relationship for Fe (adenine)<sub>3</sub>.

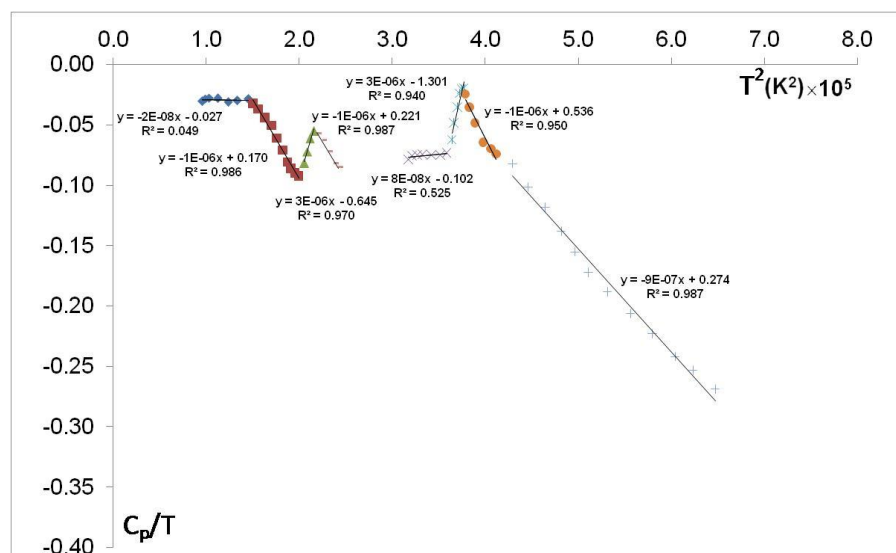
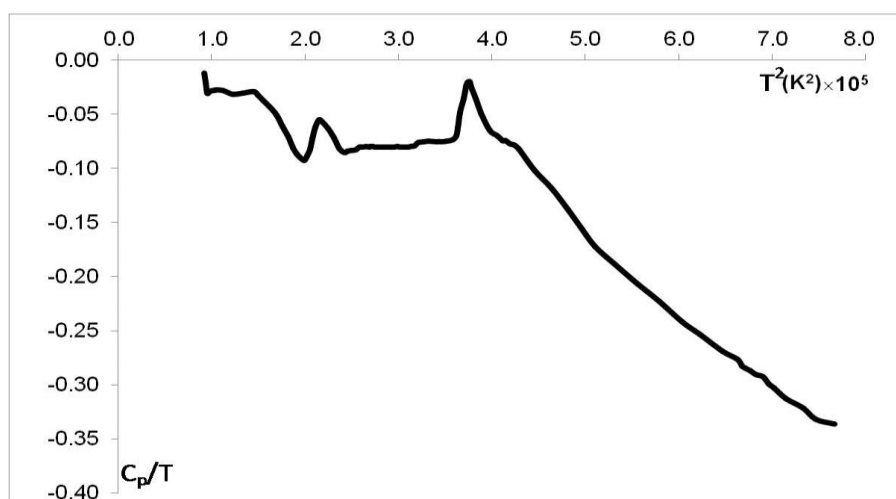


Figure 11b  $\frac{C_p}{T}$  - $T^2$  relationship for Fe (adenine)<sub>3</sub>.

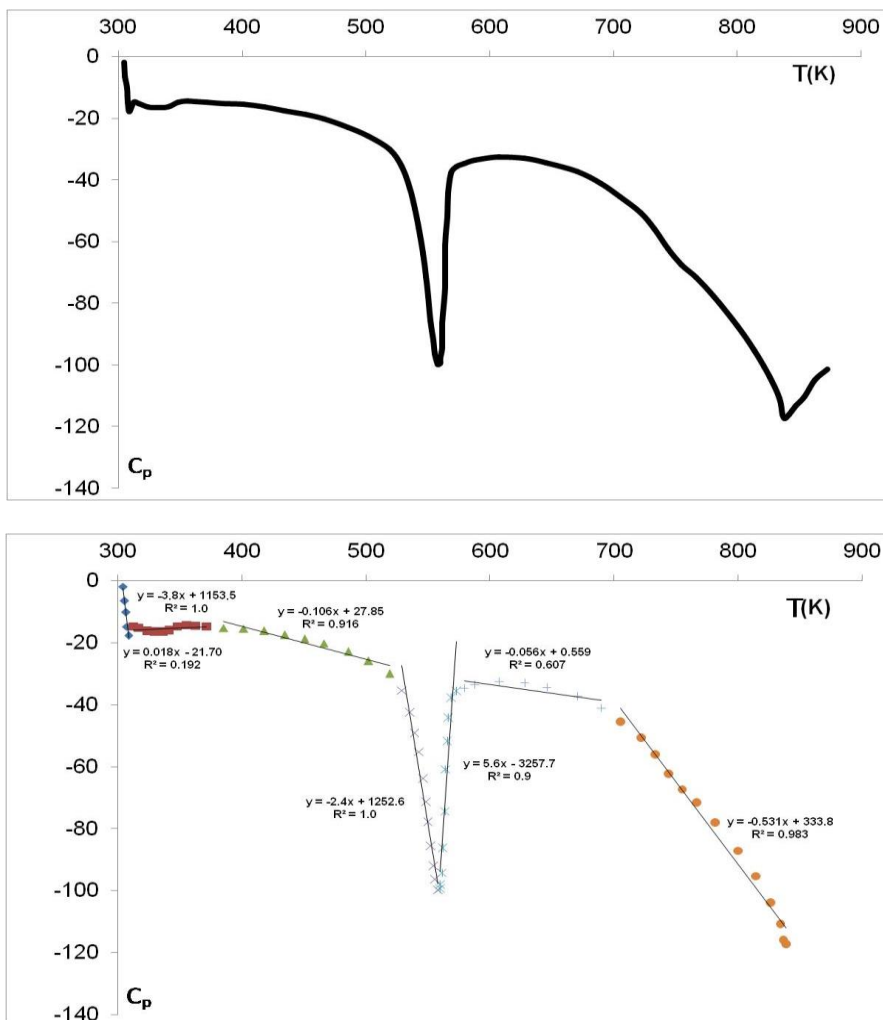
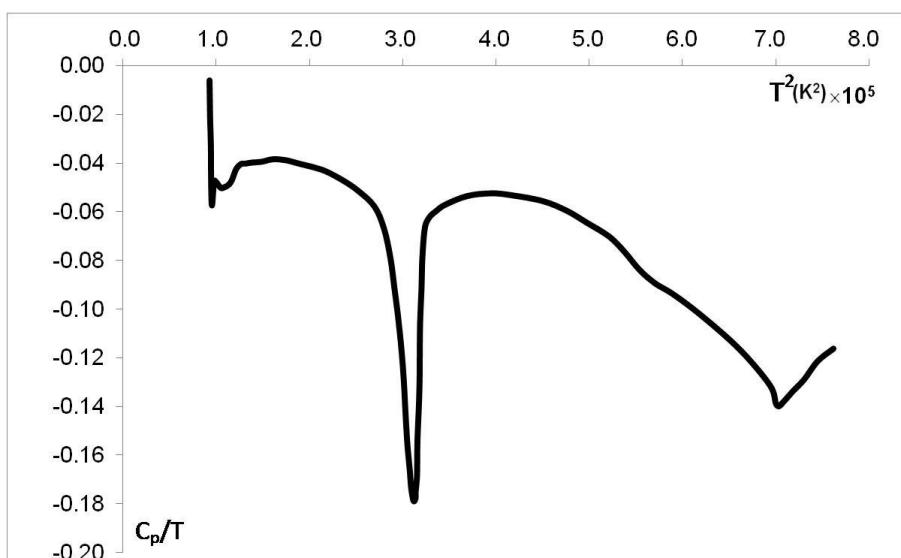


Figure 12a  $C_p$  - $T$  relationship for  $\text{Co}(\text{acac})_2$  (adenine).



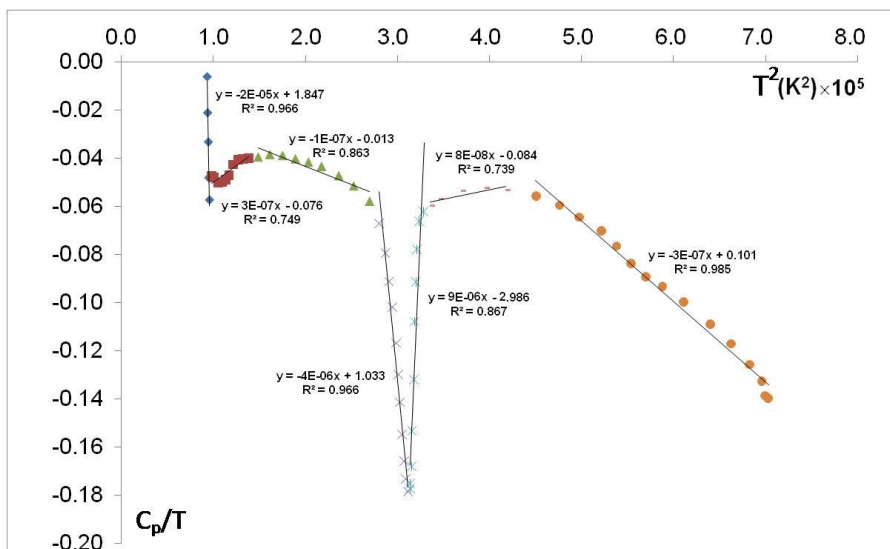


Figure 12b  $\frac{C_p}{T}$  -  $T^2$  relationship for Co (acac)<sub>2</sub> (adenine).

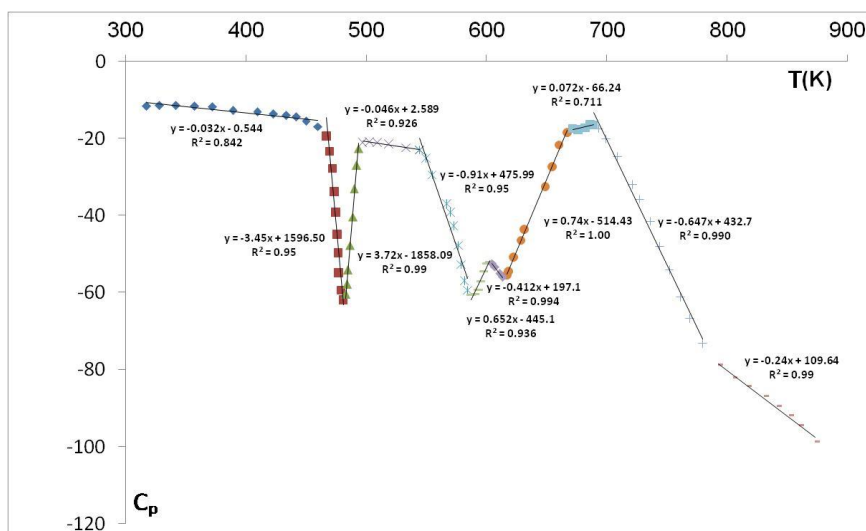
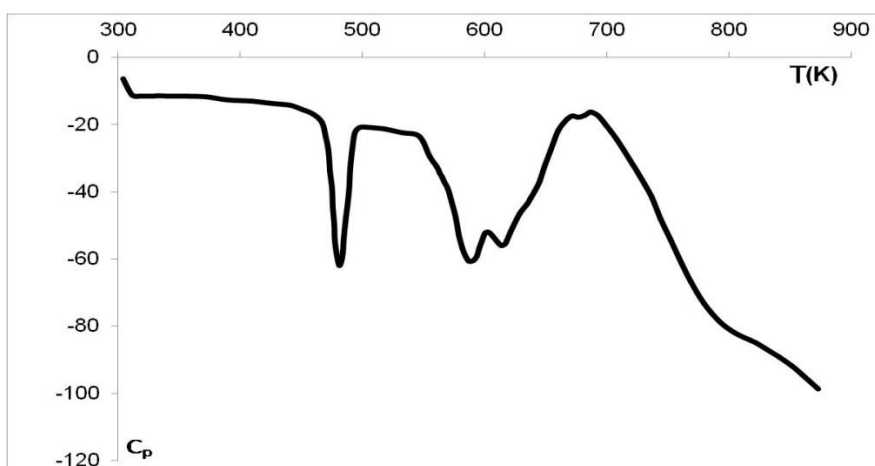
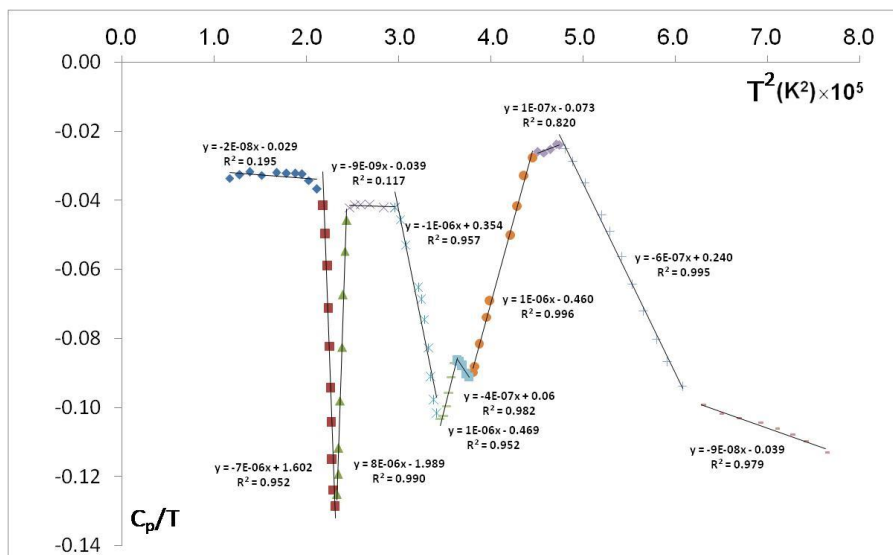
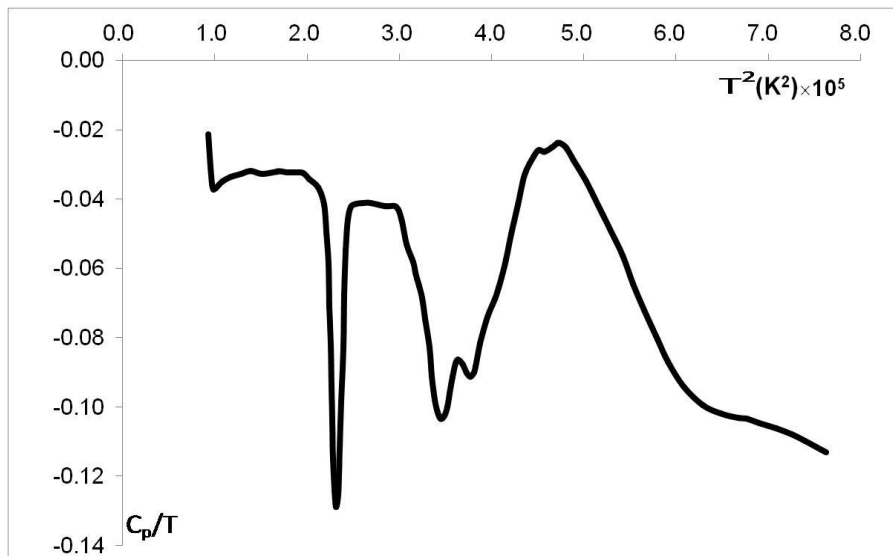
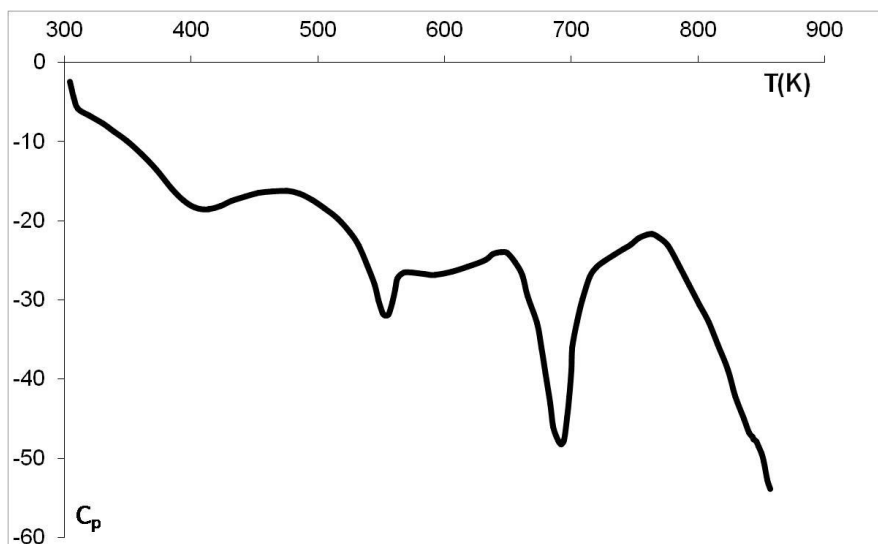


Figure 13a  $C_p$  -  $T$  relationship for Zn (hydroxyethyladenine)<sub>2</sub> (OH)<sub>2</sub>.2H<sub>2</sub>O.



**Figure 13b**  $\frac{C_p}{T}$  -  $T^2$  relationship for Zn (hydroxyethyladenine)<sub>2</sub> (OH)<sub>2</sub>.2H<sub>2</sub>O.



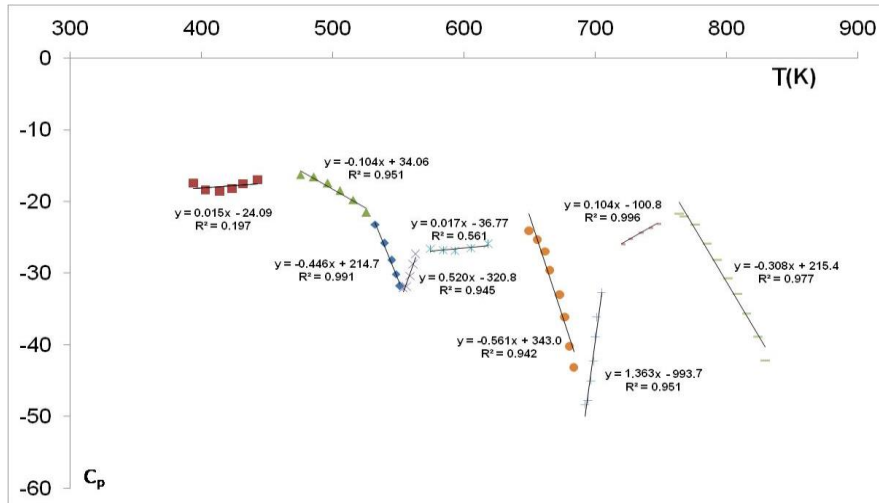


Figure 14a  $C_p$  - $T$  relationship for Cr (BA) (OH)·4H<sub>2</sub>O.

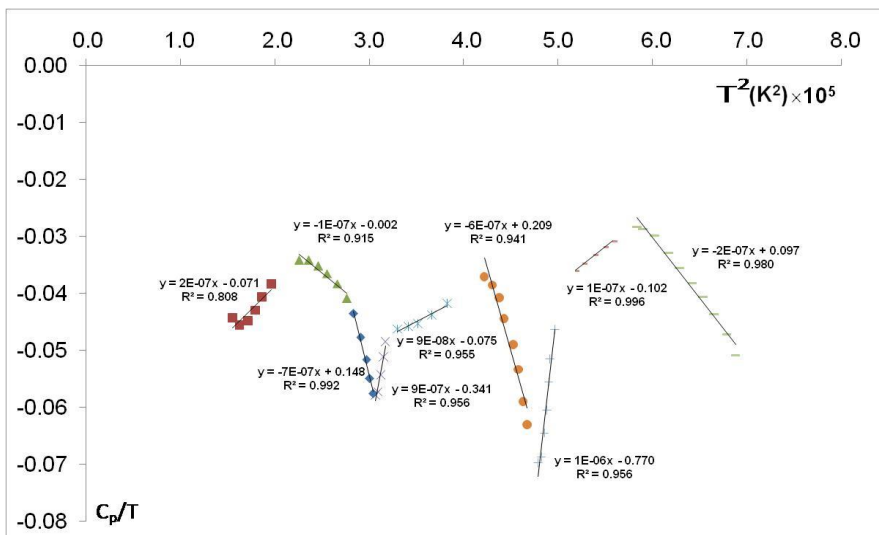
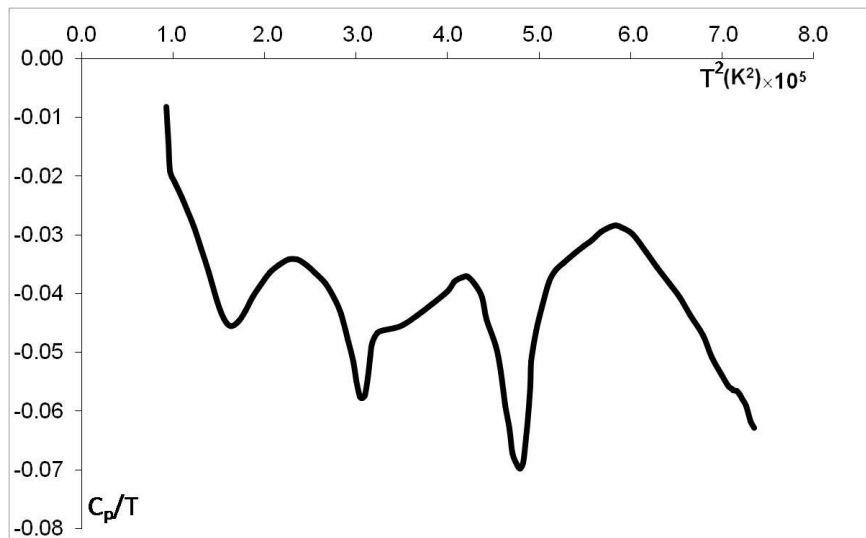


Figure 14b  $\frac{C_p}{T}$  - $T^2$  relationship for Cr (BA) (OH)·4H<sub>2</sub>O.

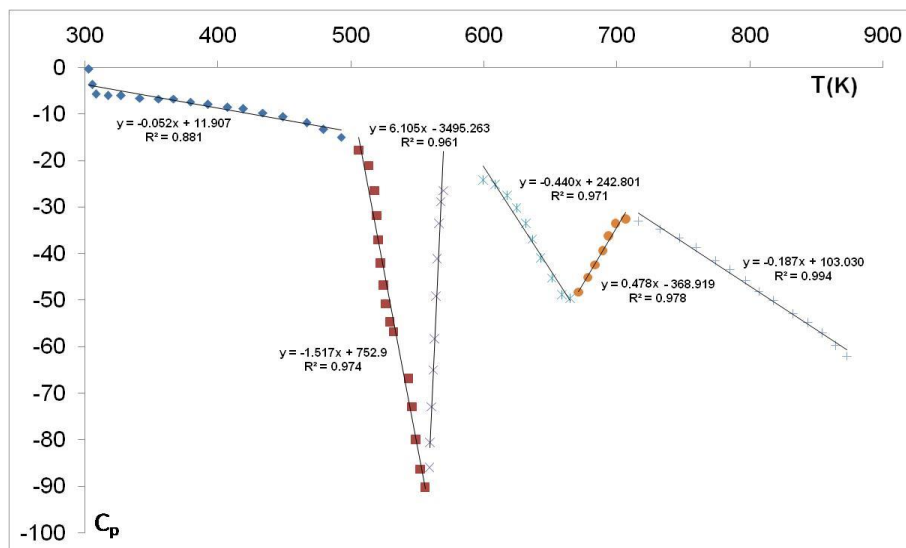
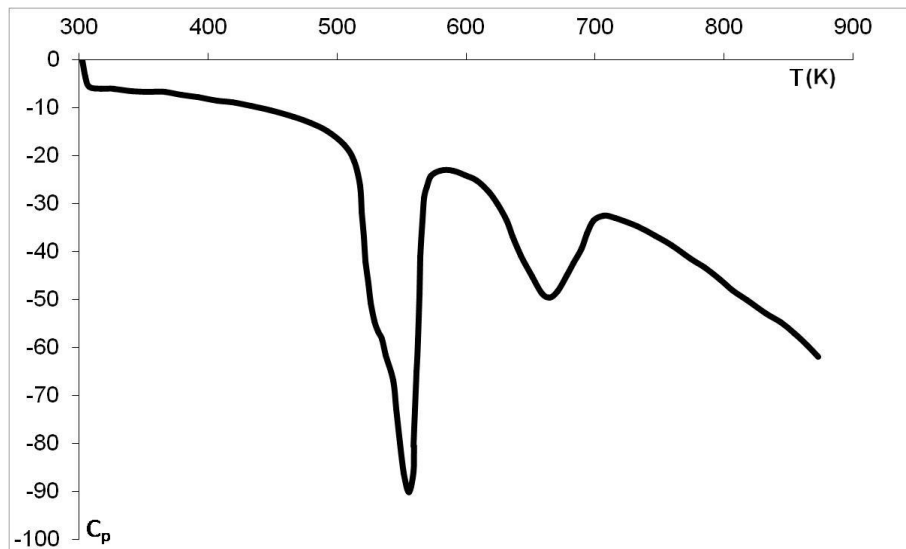
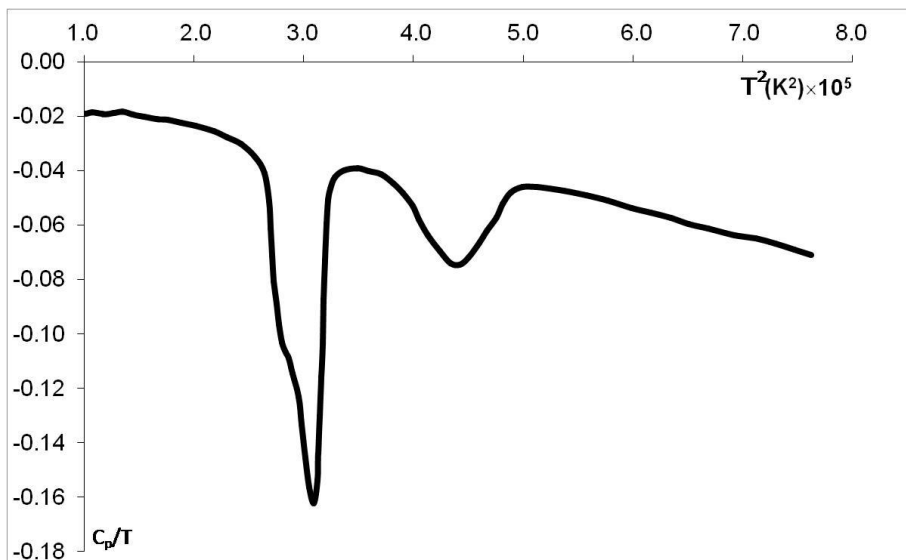


Figure 15a Cp - T relationship for Zn (BA)<sub>2</sub>.3H<sub>2</sub>O.



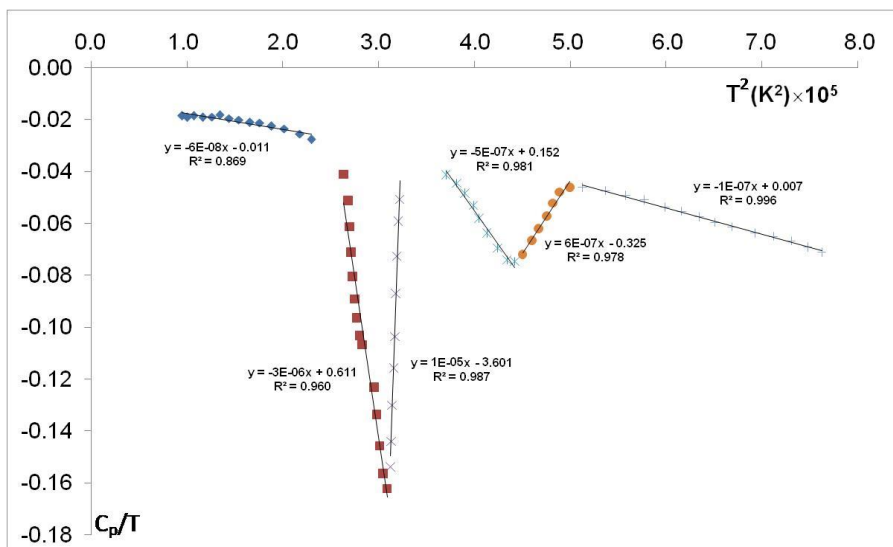


Figure 15b  $\frac{C_p}{T}$  -  $T^2$  relationship for Zn (BA)<sub>2</sub>.3H<sub>2</sub>O.

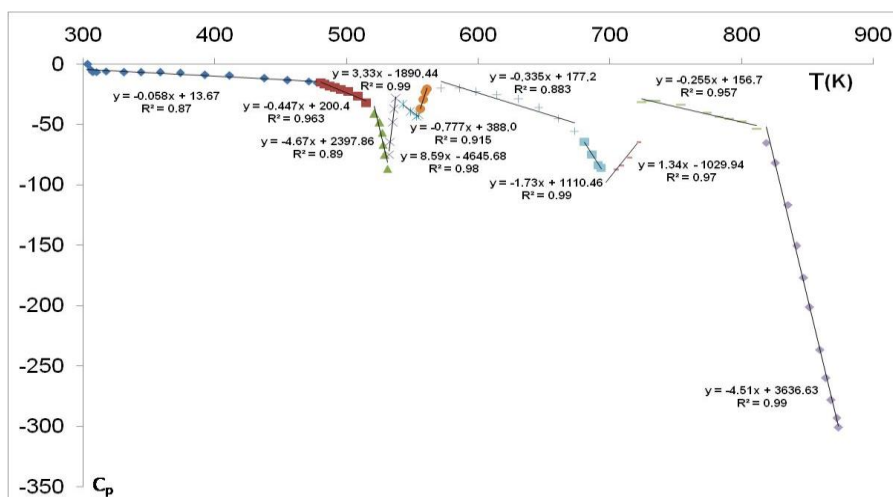
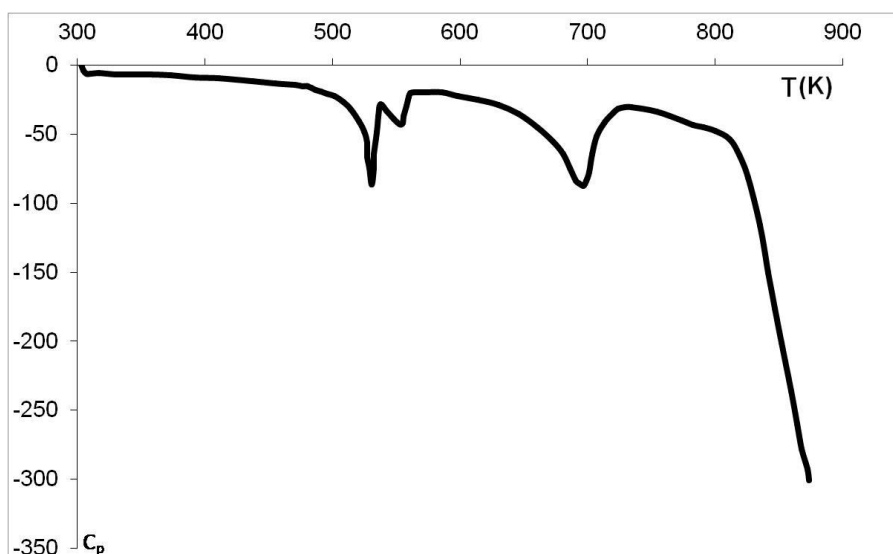


Figure 16a  $C_p$  -  $T$  relationship for Cd (BA)<sub>2</sub>.10H<sub>2</sub>O.

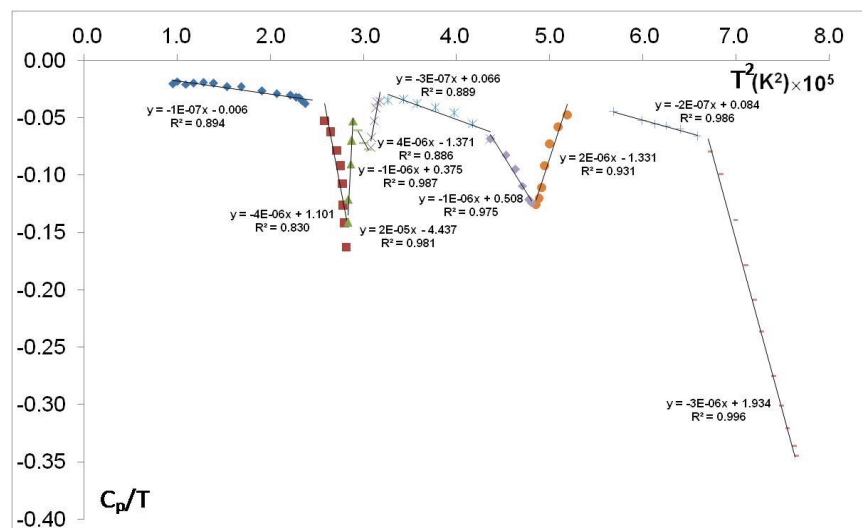
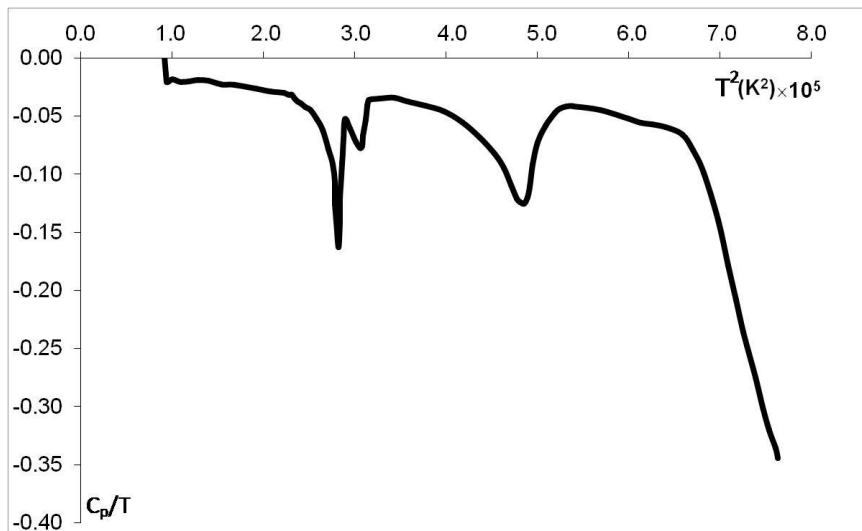
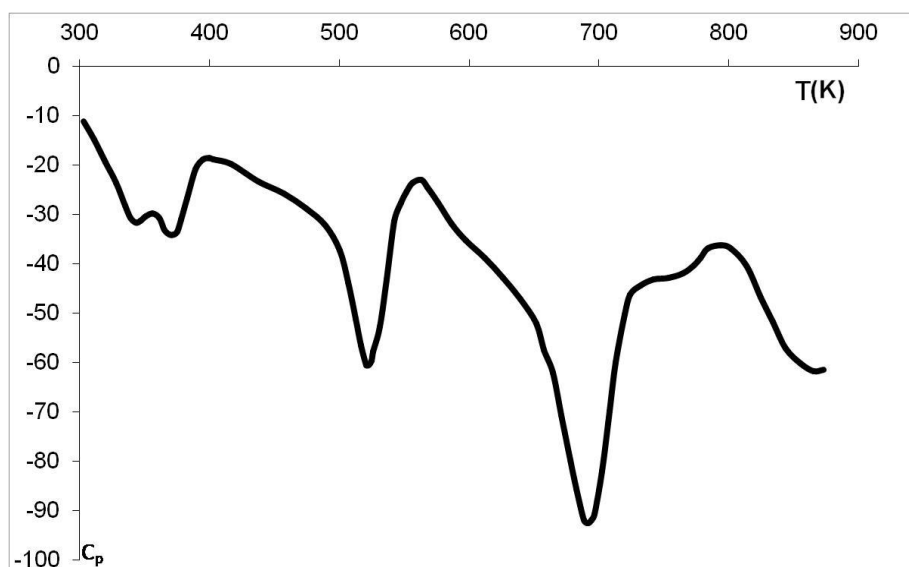


Figure 16b  $\frac{C_p}{T}$  -  $T^2$  relationship for Cd (BA)<sub>2</sub>.10H<sub>2</sub>O.





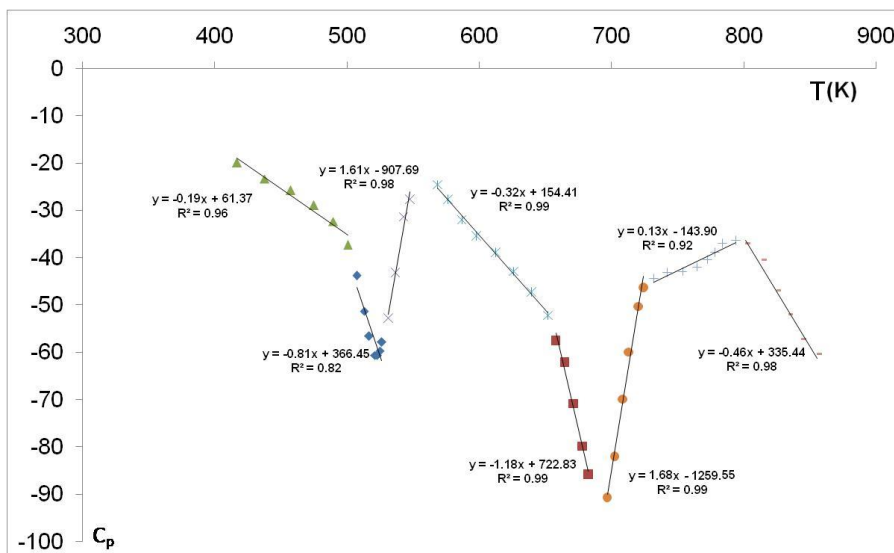


Figure 17a  $C_p - T$  relationship for  $Hg(BA)_2$ .

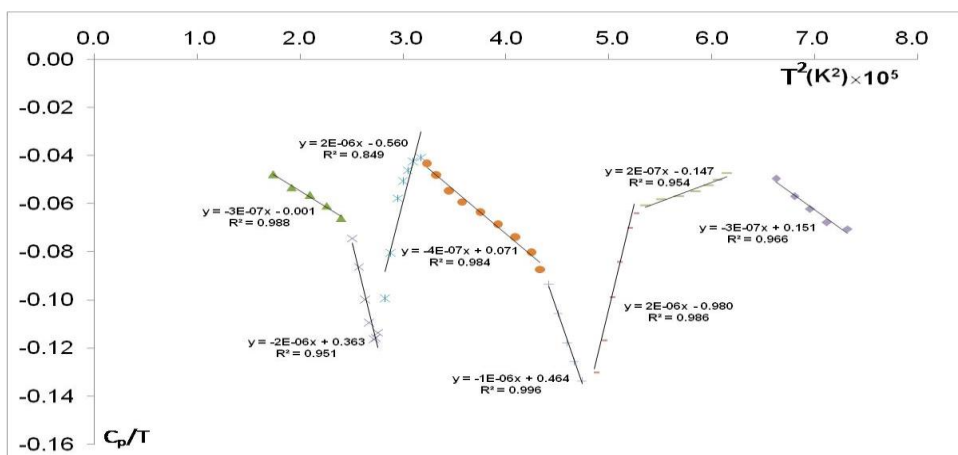
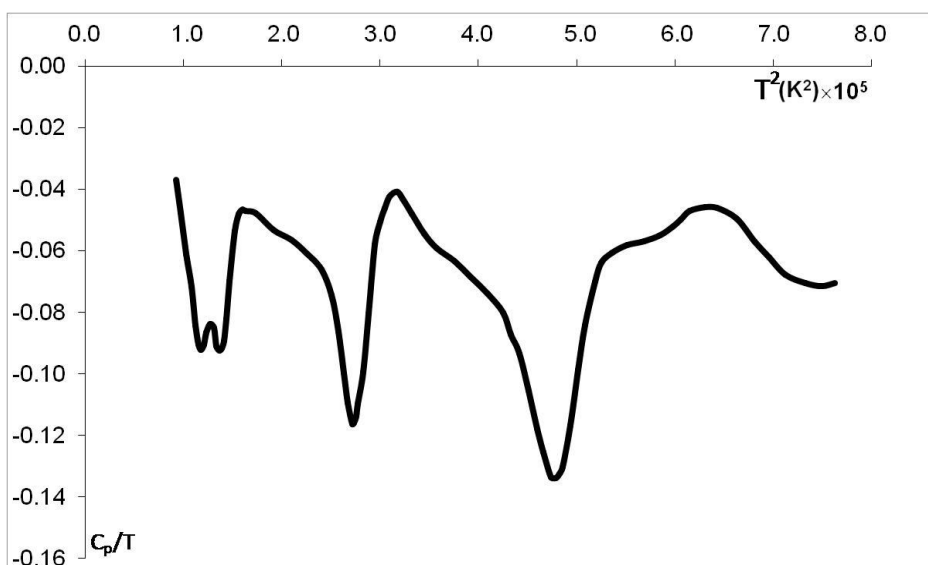


Figure 17b  $\frac{C_p}{T} - T^2$  relationship for  $Hg(BA)_2$ .

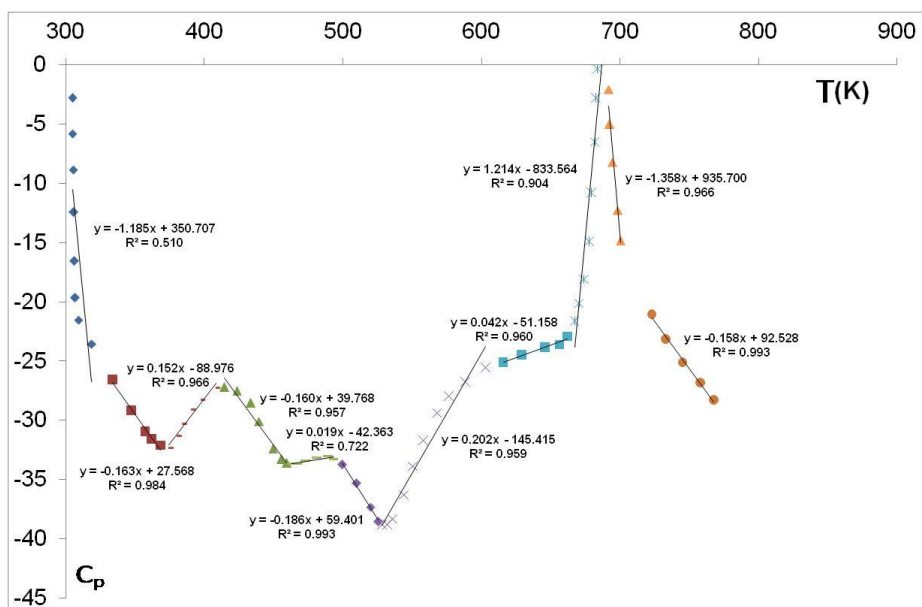
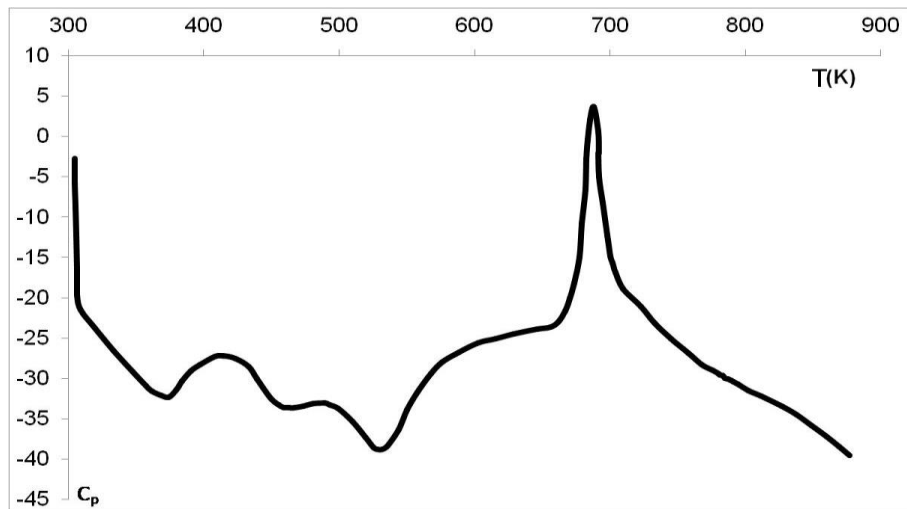
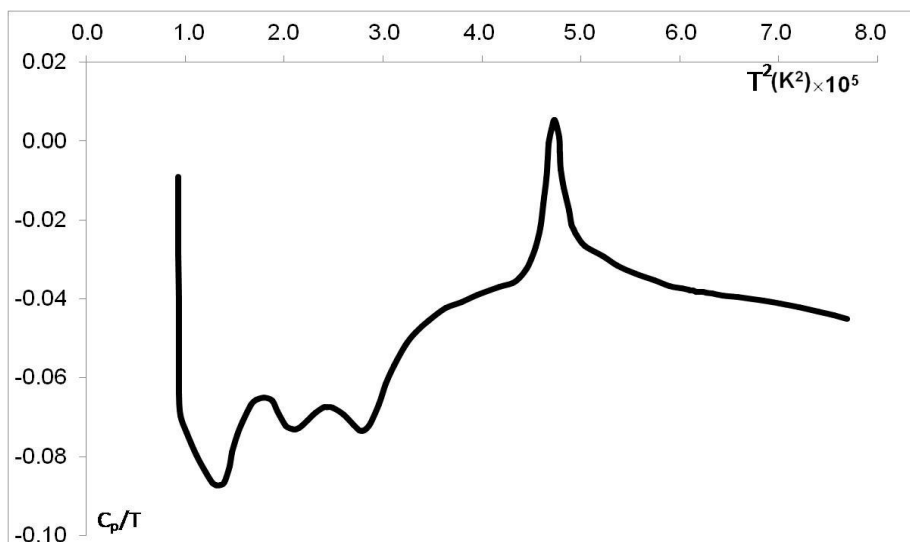


Figure 18a Cp -T relationship for Fe (TBA) (OH)·2H<sub>2</sub>O.



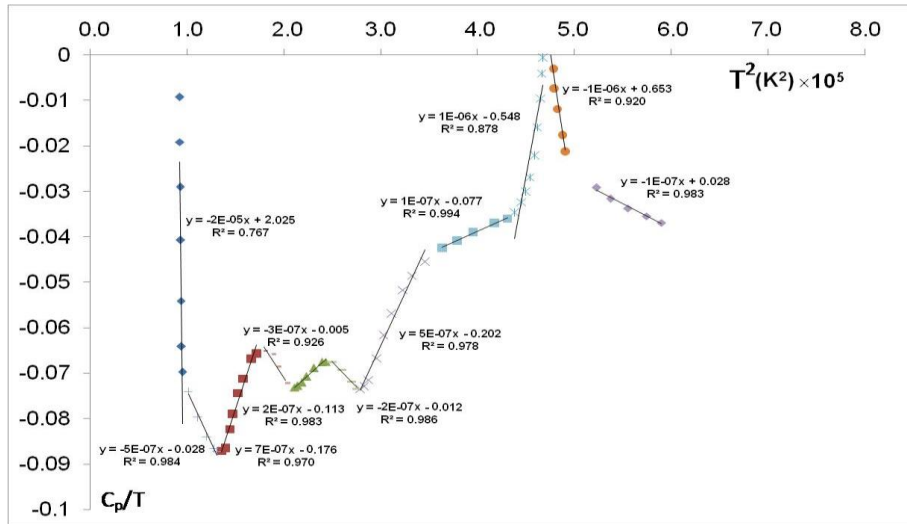


Figure 18b  $\frac{C_p}{T}$  -  $T^2$  relationship for Fe (TBA) (OH).2H<sub>2</sub>O.

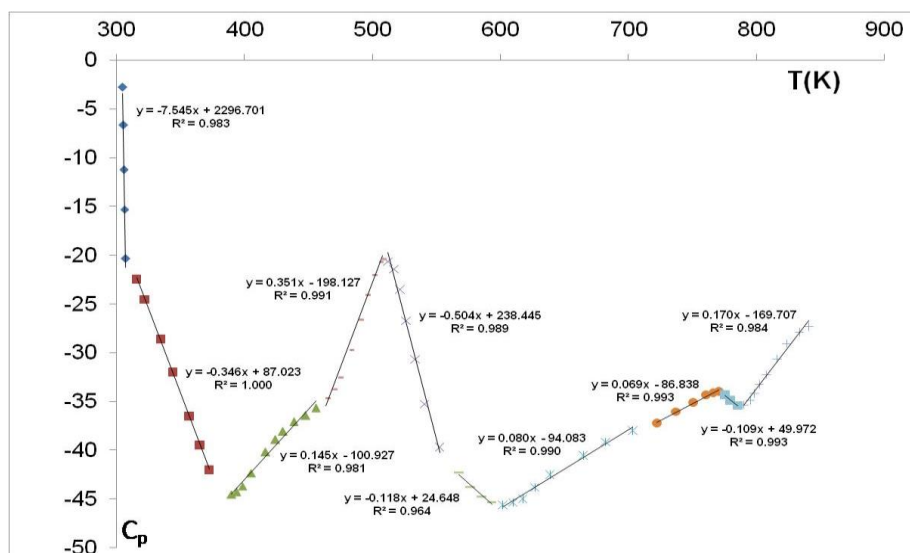
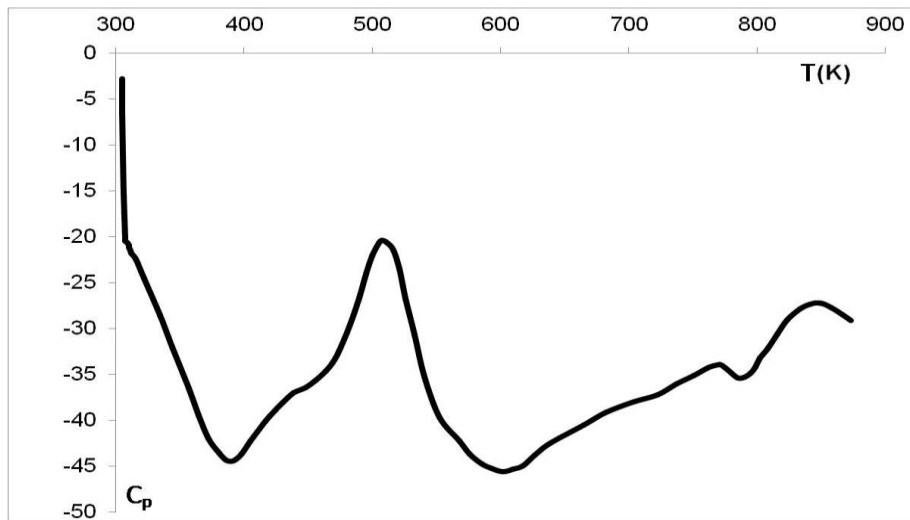
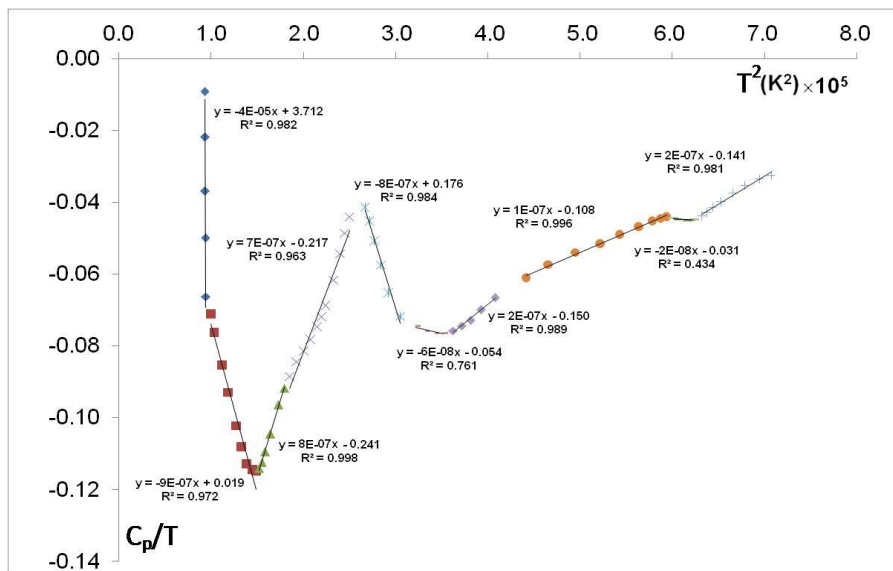
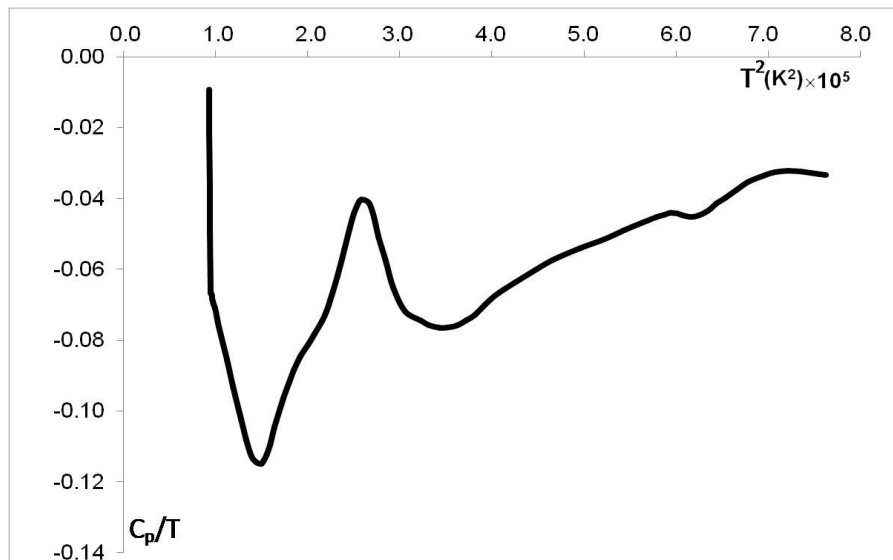
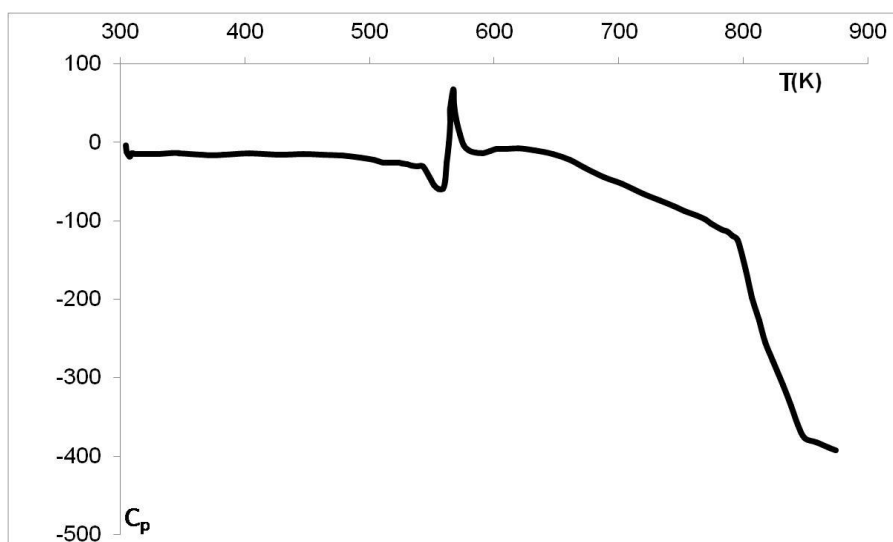


Figure 19a  $C_p$  -  $T$  relationship for Cr (TU) (OH)<sub>2</sub>.H<sub>2</sub>O.



**Figure 19b**  $\frac{C_p}{T}$  -  $T^2$  relationship for Cr (TU) (OH)<sub>2</sub>.H<sub>2</sub>O.



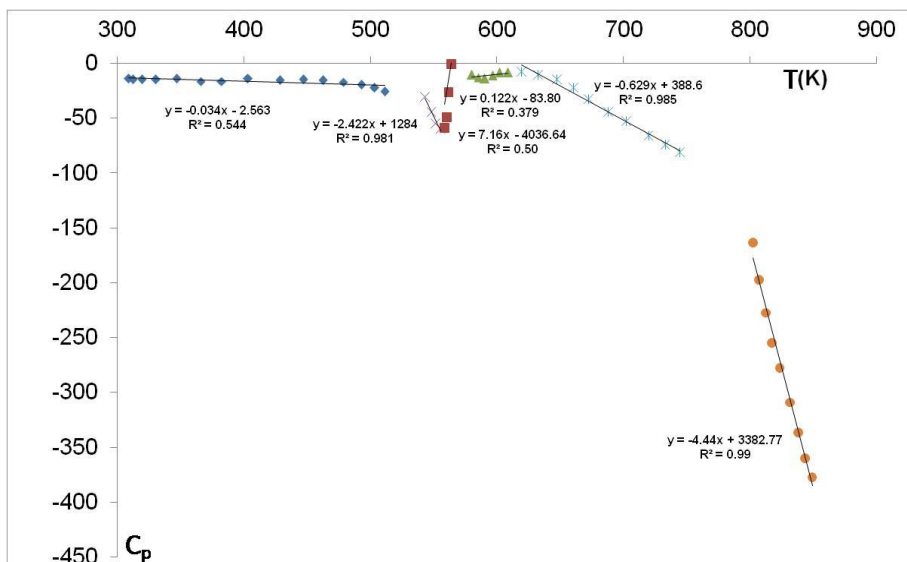


Figure 20a  $C_p - T$  relationship for  $\text{Hg}(\text{TU})_2 \cdot 4\text{H}_2\text{O}$ .

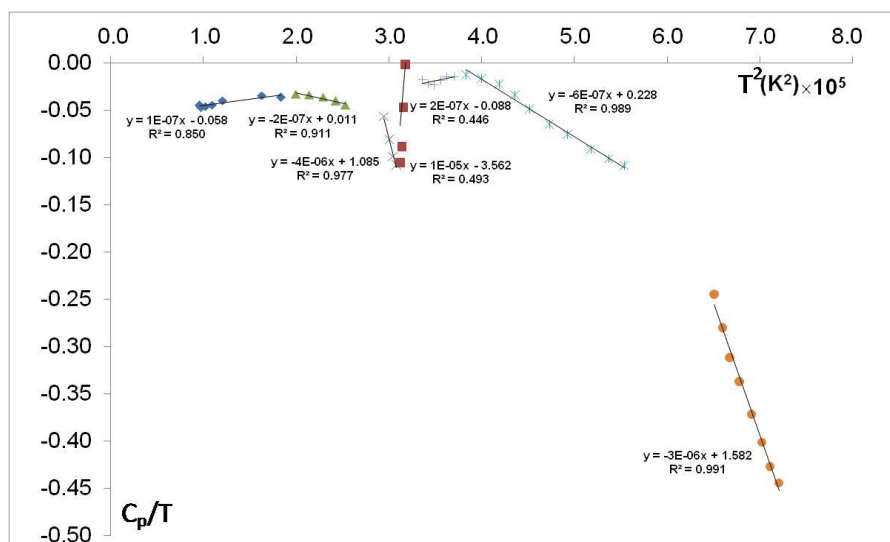
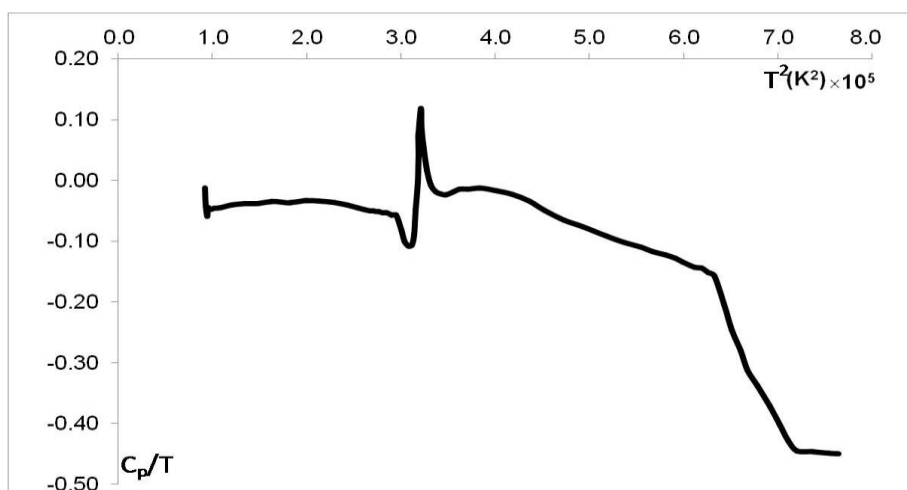


Figure 20b  $\frac{C_p}{T} - T^2$  relationship for  $\text{Hg}(\text{TU})_2 \cdot 4\text{H}_2\text{O}$ .

The change in enthalpy ( $\Delta H$ ) for any phase transformation [24] taking place at any peak temperature,  $T_m$ , can be given by the following equation:

$$\Delta S = \frac{\Delta H}{T_m} \quad (\text{at equilibrium, } \Delta G = 0)$$

The values of  $T_m$  (the peak temperature at which the peak is maximum or minimum),  $\Delta H$ ,  $\Delta S$ , (a, b) parameters of Debye model,  $\alpha$  and  $\gamma$  are given in Table (2).

**Table 2** DSC data and thermodynamic parameters of the complexes\*.

Compound	Heat range °C	$T_m$ °C	$\Delta H$ J/g	$\Delta S$ J/g.°C	a	b	$\alpha$	$\gamma$
Fe (adenine) <sub>3</sub>	109.92 – 183.78	163.54	-128.22	-0.784	-0.052	7.567	-2×10 <sup>-8</sup>	-0.027
					-0.593	222.842	-1×10 <sup>-6</sup>	0.170
					1.089	-530.338	3×10 <sup>-6</sup>	-0.645
					-0.580	247.741	-1×10 <sup>-6</sup>	0.221
					0.020	-31.629	8×10 <sup>-8</sup>	-0.102
					2.490	-1538.618	3×10 <sup>-6</sup>	-1.301
					-1.232	740.526	-1×10 <sup>-6</sup>	0.536
					-1.091	660.690	-9×10 <sup>-7</sup>	0.274
Co (acac) <sub>2</sub> (adenine)	223.55 – 297.22	278.19	-278.42	-1.001	-3.795	1153.536	-2×10 <sup>-5</sup>	1.847
					0.018	-21.704	3×10 <sup>-7</sup>	-0.076
					-0.106	27.857	-1×10 <sup>-7</sup>	-0.013
					-2.420	1252.625	-4×10 <sup>-6</sup>	1.033
					5.649	-3257.739	9×10 <sup>-6</sup>	-2.986
					-0.056	0.559	8×10 <sup>-8</sup>	-0.084
					0.531	333.876	-3×10 <sup>-7</sup>	0.101
Zn (hydroxyethyladenine) <sub>2</sub> (OH) <sub>2</sub> .2H <sub>2</sub> O	175.77 – 216.76 263.45 – 391.26	199.56 309.58	-121.39 -539.20	-0.608 -1.742	-0.032	-0.544	-2×10 <sup>-8</sup>	-0.029
					-3.450	1596.504	-7×10 <sup>-6</sup>	1.602
					3.721	-1858.094	8×10 <sup>-6</sup>	-1.989
					-0.046	2.589	-9×10 <sup>-9</sup>	-0.039
					-0.911	475.988	-1×10 <sup>-6</sup>	0.354
					0.653	-445.182	1×10 <sup>-6</sup>	-0.469
					-0.413	197.110	-4×10 <sup>-7</sup>	0.060
					0.744	-514.426	1×10 <sup>-6</sup>	-0.460
					0.072	-66.241	1×10 <sup>-7</sup>	-0.073
					-0.647	432.769	-6×10 <sup>-7</sup>	0.240
-0.237	109.642	-9×10 <sup>-8</sup>	-0.039					
Cr (BA) (OH).4H <sub>2</sub> O	241.32 – 290.61 370.79 – 442.13	276.42 415.83	-27.35 -109.51	-0.099 -0.263	0.015	-24.095	2×10 <sup>-7</sup>	-0.071
					-0.105	34.062	-1×10 <sup>-7</sup>	-0.002
					-0.447	214.790	-7×10 <sup>-7</sup>	0.148
					0.521	-320.860	9×10 <sup>-7</sup>	-0.341
					0.017	-36.773	9×10 <sup>-8</sup>	-0.075
					-0.562	343.006	-6×10 <sup>-7</sup>	0.209
					1.364	-993.696	1×10 <sup>-6</sup>	0.770
					0.104	-100.836	1×10 <sup>-7</sup>	-0.102
-0.308	215.479	-2×10 <sup>-7</sup>	0.097					

Compound	Heat range °C	T <sub>m</sub> °C	ΔH J/g	ΔS J/g·°C	a	b	α	γ
Zn (BA) <sub>2</sub> .3H <sub>2</sub> O	224.08 – 299.86 336.64 – 432.18	281.57 391.37	-360.77 -165.68	-1.281 -0.423	-0.052	11.907	-6×10 <sup>-8</sup>	-0.011
					-1.517	752.913	-3×10 <sup>-6</sup>	0.611
					-1.930	980.786	-2×10 <sup>-6</sup>	0.600
					6.105	-3495.263	1×10 <sup>-5</sup>	-3.601
					-0.440	242.801	-5×10 <sup>-7</sup>	0.152
					0.478	-368.919	6×10 <sup>-7</sup>	-0.325
					-0.187	103.030	-1×10 <sup>-7</sup>	0.007
Cd (BA) <sub>2</sub> .10H <sub>2</sub> O	229.83 – 263.38 263.87 – 287.04 361.52 – 452.57	256.73 281.28 422.48	-98.96 -45.93 -378.43	-0.385 -0.163 -0.896	-0.059	13.671	-1×10 <sup>-7</sup>	-0.006
					-0.448	200.431	-4×10 <sup>-6</sup>	1.101
					-4.669	2397.860	2×10 <sup>-5</sup>	-4.437
					8.591	-4645.683	-1×10 <sup>-6</sup>	0.375
					-0.777	388.046	4×10 <sup>-6</sup>	-1.371
					3.333	-1890.435	-3×10 <sup>-7</sup>	0.066
					-0.335	177.283	-1×10 <sup>-6</sup>	0.508
					-1.726	1110.455	2×10 <sup>-6</sup>	-1.331
					-0.256	156.717	-2×10 <sup>-7</sup>	0.084
					-4.506	3636.635	-3×10 <sup>-6</sup>	1.934
Hg (BA) <sub>2</sub>	211.53 – 278.74 344.83 – 460.24	248.49 418.24	-118.14 -278.52	-0.475 -0.666	-0.193	61.372	-3×10 <sup>-7</sup>	-0.001
					-0.814	366.447	2×10 <sup>-6</sup>	0.363
					1.610	-907.689	2×10 <sup>-6</sup>	-0.560
					-0.316	154.413	-4×10 <sup>-7</sup>	0.071
					-1.184	722.833	-1×10 <sup>-6</sup>	0.464
					1.678	-1259.549	2×10 <sup>-6</sup>	-0.980
					0.135	-143.903	2×10 <sup>-7</sup>	-0.147
-0.464	335.441	-3×10 <sup>-7</sup>	0.151					

Compound	Heat range °C	T <sub>m</sub> °C	ΔH J/g	ΔS J/g·°C	a	b	α	γ
Fe (TBA) (OH)·2H <sub>2</sub> O	30.77 – 131.67 131.67 – 310.00	91.41 250.66	-99.61 -189.19	-1.090 -0.755	-1.185	350.707	-2×10 <sup>-5</sup>	2.025
					-0.163	27.568	-5×10 <sup>-7</sup>	-0.028
					0.152	-88.976	7×10 <sup>-7</sup>	-0.176
					-0.160	39.768	-3×10 <sup>-7</sup>	-0.005
					0.019	-42.363	2×10 <sup>-7</sup>	-0.113
					-0.168	59.401	-2×10 <sup>-7</sup>	-0.012
					0.202	-145.415	5×10 <sup>-7</sup>	-0.202
					0.042	-51.158	1×10 <sup>-7</sup>	-0.077
					1.214	-833.564	1×10 <sup>-6</sup>	-0.548
					-1.358	935.700	-1×10 <sup>-6</sup>	0.653
-0.158	92.528	-1×10 <sup>-7</sup>	0.028					
Cr (TU) (OH) <sub>2</sub> .H <sub>2</sub> O	30.91 – 228.57 228.57 – 491.57	105.57 319.98	-445.27 -480.27	-4.218 -1.501	-7.545	2296.701	-4×10 <sup>-5</sup>	3.712
					-0.346	87.023	-9×10 <sup>-7</sup>	0.019

					0.145	-100.927	$8 \times 10^{-7}$	-0.241
					0.351	-198.127	$7 \times 10^{-7}$	-0.217
					-0.504	238.445	$-8 \times 10^{-7}$	0.176
					-118	24.684	$-6 \times 10^{-8}$	-0.054
					0.080	-94.083	$2 \times 10^{-7}$	-0.150
					0.069	-86.838	$1 \times 10^{-7}$	-0.108
					-0.109	49.972	$-2 \times 10^{-8}$	-0.031
					0.170	-169.707	$2 \times 10^{-7}$	-0.141
Hg (TU) <sub>2</sub> .4H <sub>2</sub> O	217.68 – 286.05	274.62	-710.87	-2.589	-0.034	-2.563	$1 \times 10^{-7}$	-0.058
					-2.422	1284	$-2 \times 10^{-7}$	0.011
					7.158	-4036.643	$-4 \times 10^{-6}$	1.085
					0.123	-83.801	$1 \times 10^{-5}$	-3.562
					-0.630	388.615	$2 \times 10^{-7}$	-0.088
					-4.438	3382.770	$-6 \times 10^{-7}$	0.228
							$-3 \times 10^{-6}$	1.582

\* All are of exothermic behavior.

All the complexes gave exothermic peaks. All the change of entropy values,  $\Delta S$  have -ve signs which indicate that the activated transition states are more ordered, i.e. in a less random molecular configuration than the reacting complexes [25-30].

The decomposition pattern may be affected by stereochemistry of the metal complex and in some cases with the electronic character [31].

From TGA, Figures (21-27) Table (3) the mechanism of decomposition can be given.

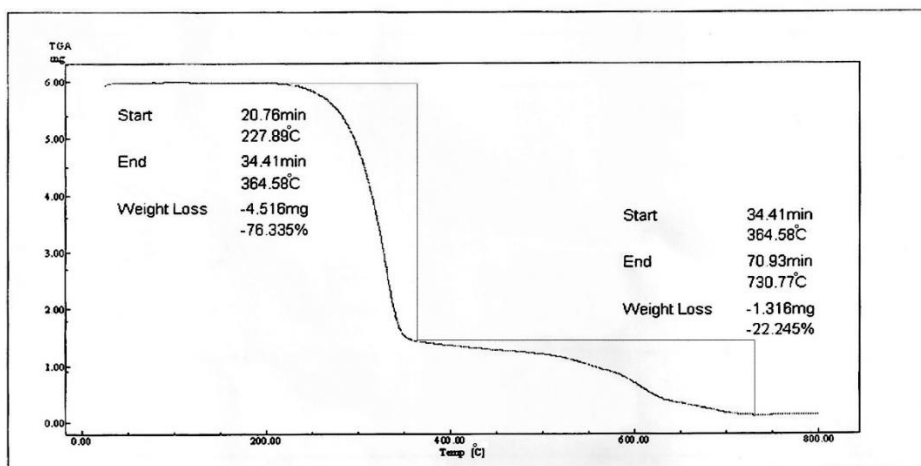


Figure 21 TGA for Hydroxyethyladenine.



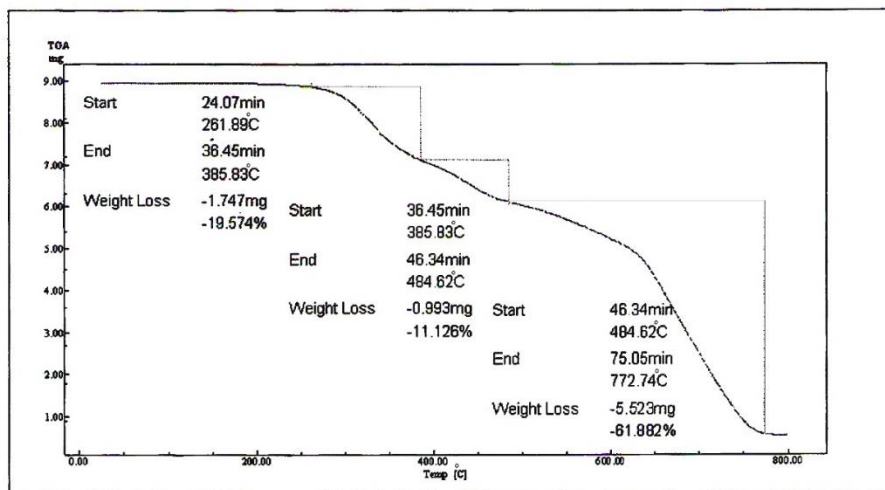


Figure 22 TGA for Zn (hydroxyethyladenine)<sub>2</sub> (OH)<sup>-</sup><sub>2</sub>·2H<sub>2</sub>O.

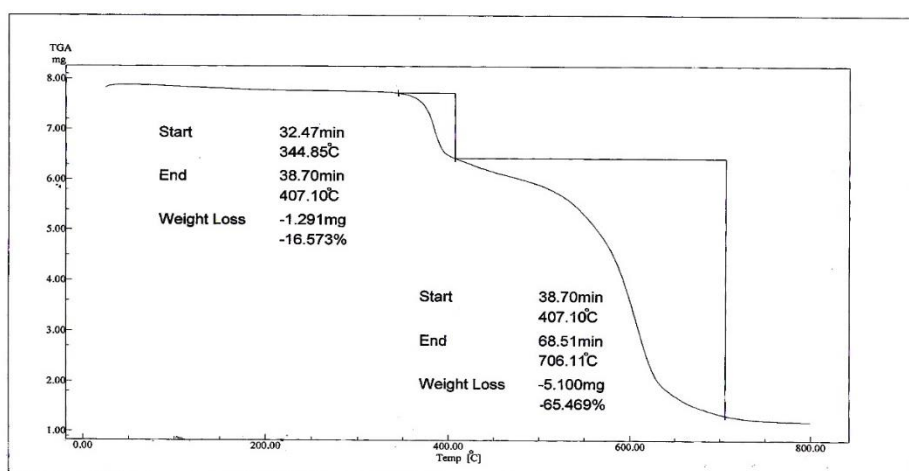


Figure 23 TGA for Cd (hydroxyethyladenine) (OH)<sup>-</sup><sub>2</sub>·3H<sub>2</sub>O.

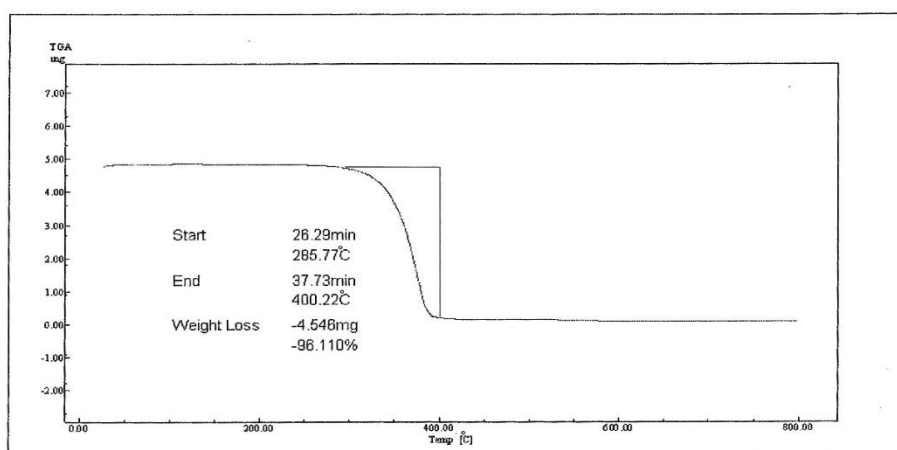


Figure 24 TGA for Acetyladenine.

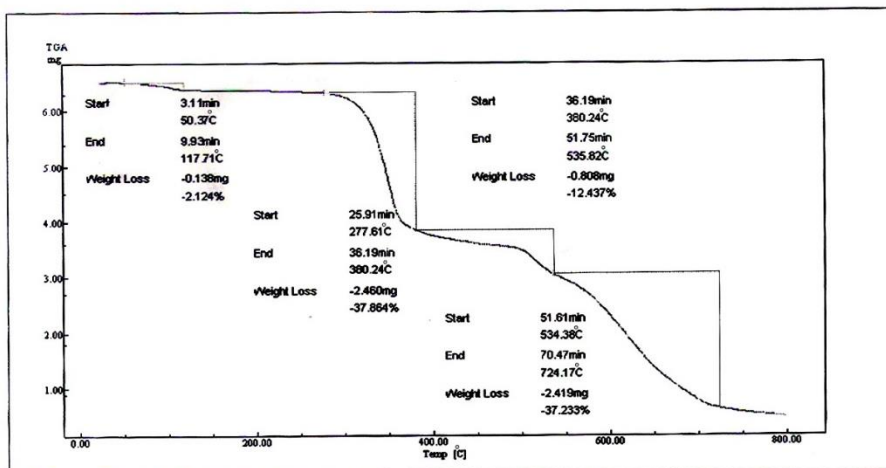


Figure 25 TGA for Cd (II) (<sup>6</sup>N-acetyl adenine)<sub>2</sub> (OH)<sub>2</sub>·2H<sub>2</sub>O.

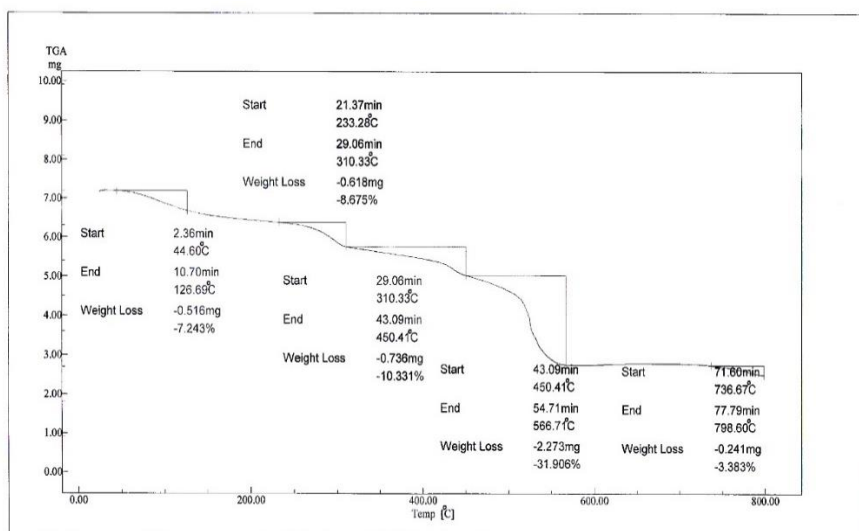


Figure 26 TGA for Co-Ni (TU)<sub>3</sub>·4H<sub>2</sub>O.

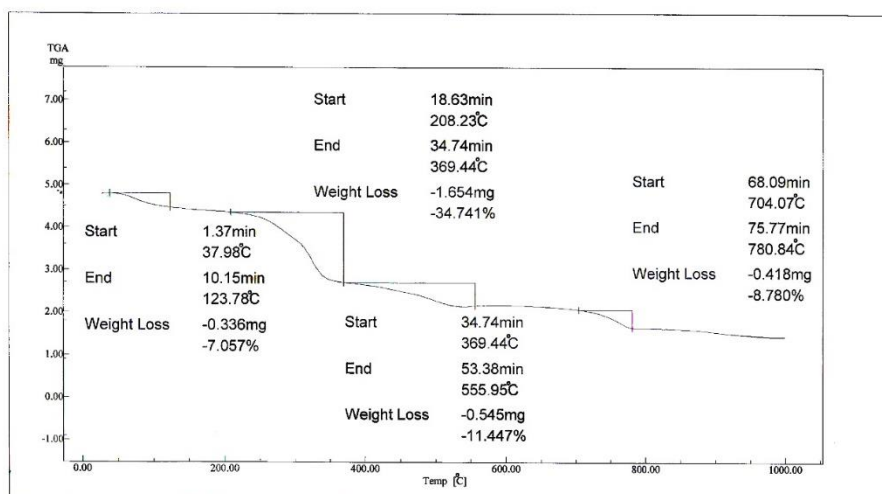


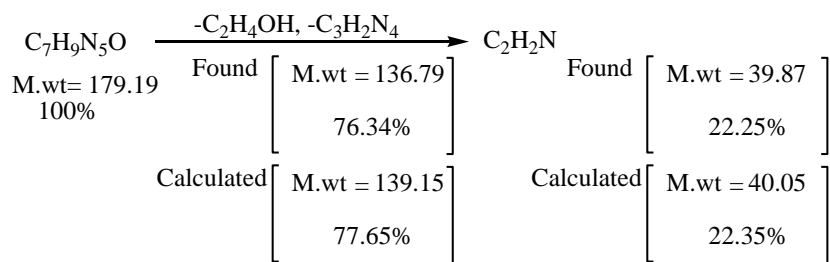
Figure 27 TGA for Ni-Cu (TU)<sub>3</sub>·4H<sub>2</sub>O.

**Table 3** TGA analyses of some compounds.

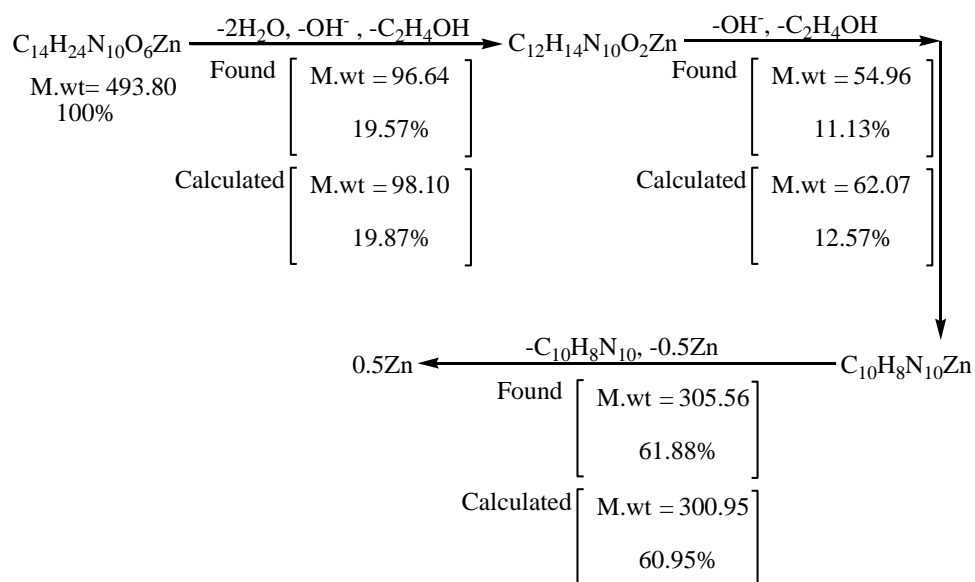
Compound	Weight loss % (calculated)	Weight loss % (found)	Assignments
Hydroxyethyladenine	77.65 22.35	76.34 22.25	C <sub>2</sub> H <sub>4</sub> OH, C <sub>3</sub> H <sub>2</sub> N <sub>4</sub> C <sub>2</sub> H <sub>2</sub> N
Zn (hydroxyethyladenine) <sub>2</sub> (OH <sup>-</sup> ) <sub>2</sub> .2H <sub>2</sub> O	19.87 12.57 60.95	19.57 11.13 61.88	2H <sub>2</sub> O, OH <sup>-</sup> , C <sub>2</sub> H <sub>4</sub> OH OH <sup>-</sup> , C <sub>2</sub> H <sub>4</sub> OH C <sub>10</sub> H <sub>8</sub> N <sub>10</sub> , 0.5Zn Remains: 0.5Zn
Cd (hydroxyethyladenine) (OH <sup>-</sup> ) <sub>2</sub> .3H <sub>2</sub> O	18.72 66.48	16.57 65.47	3H <sub>2</sub> O, OH <sup>-</sup> OH <sup>-</sup> , C <sub>2</sub> H <sub>4</sub> OH, C <sub>5</sub> H <sub>4</sub> N <sub>5</sub> , 0.5Cd Remains: 0.5Cd
Acetyladenine	100	96.11	C <sub>7</sub> H <sub>7</sub> N <sub>5</sub> O
Cd (acetyladenine) <sub>2</sub> (OH <sup>-</sup> ) <sub>2</sub> .2H <sub>2</sub> O	3.36 37.66 38.04 10.47	2.12 37.86 37.23 12.44	H <sub>2</sub> O H <sub>2</sub> O, 2 (OH <sup>-</sup> ), C <sub>6</sub> H <sub>6</sub> N <sub>4</sub> O C <sub>8</sub> H <sub>8</sub> N <sub>6</sub> O 0.5Cd Remains: 0.5Cd
Co-Ni (TU) <sub>3</sub> .4H <sub>2</sub> O	6.32 9.30 10.19 31.43 4.57	7.24 8.68 10.33 31.91 3.38	2H <sub>2</sub> O 2H <sub>2</sub> O, OH CNS C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> OS, C <sub>3</sub> H <sub>2</sub> N C <sub>2</sub> H <sub>2</sub> Remains: C <sub>2</sub> N <sub>2</sub> OSCoNi
Ni-Cu (TU) <sub>3</sub> .4H <sub>2</sub> O	6.27 35.88 12.20 9.06	7.06 34.74 11.45 8.78	2H <sub>2</sub> O 2H <sub>2</sub> O, OH, C <sub>2</sub> H <sub>2</sub> , C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> OS C <sub>2</sub> NS C <sub>2</sub> H <sub>2</sub> N Remains: CN <sub>2</sub> OSNiCu

The fragmentation pathways of the compounds can be represented as follows:

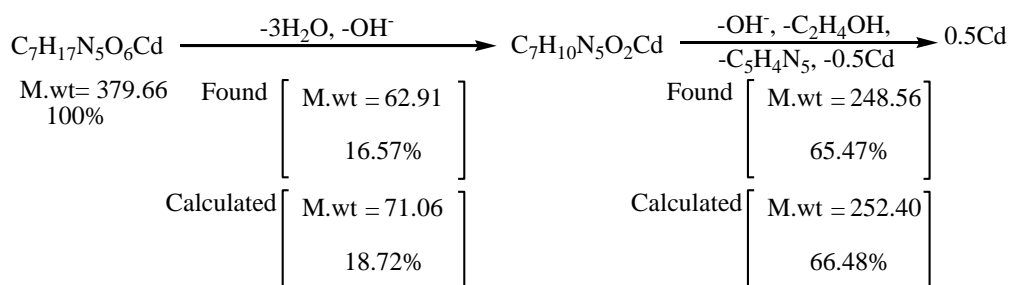
### 1-Hydroxyethyladenine



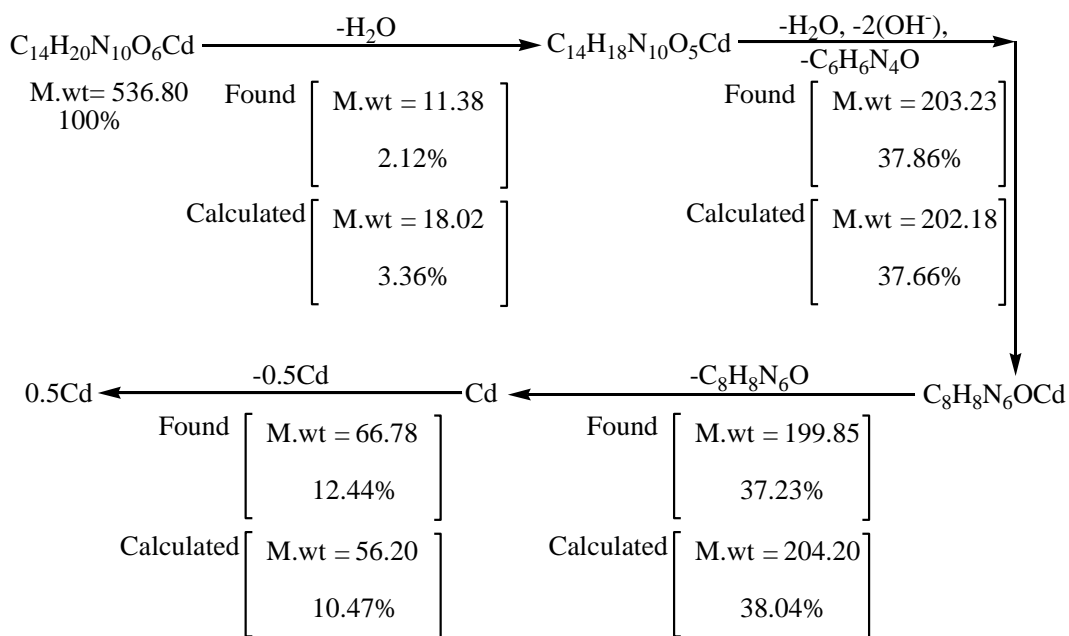
### 2-Zn(hydroxyethyladenine)<sub>2</sub>(OH)<sub>2</sub>·2H<sub>2</sub>O



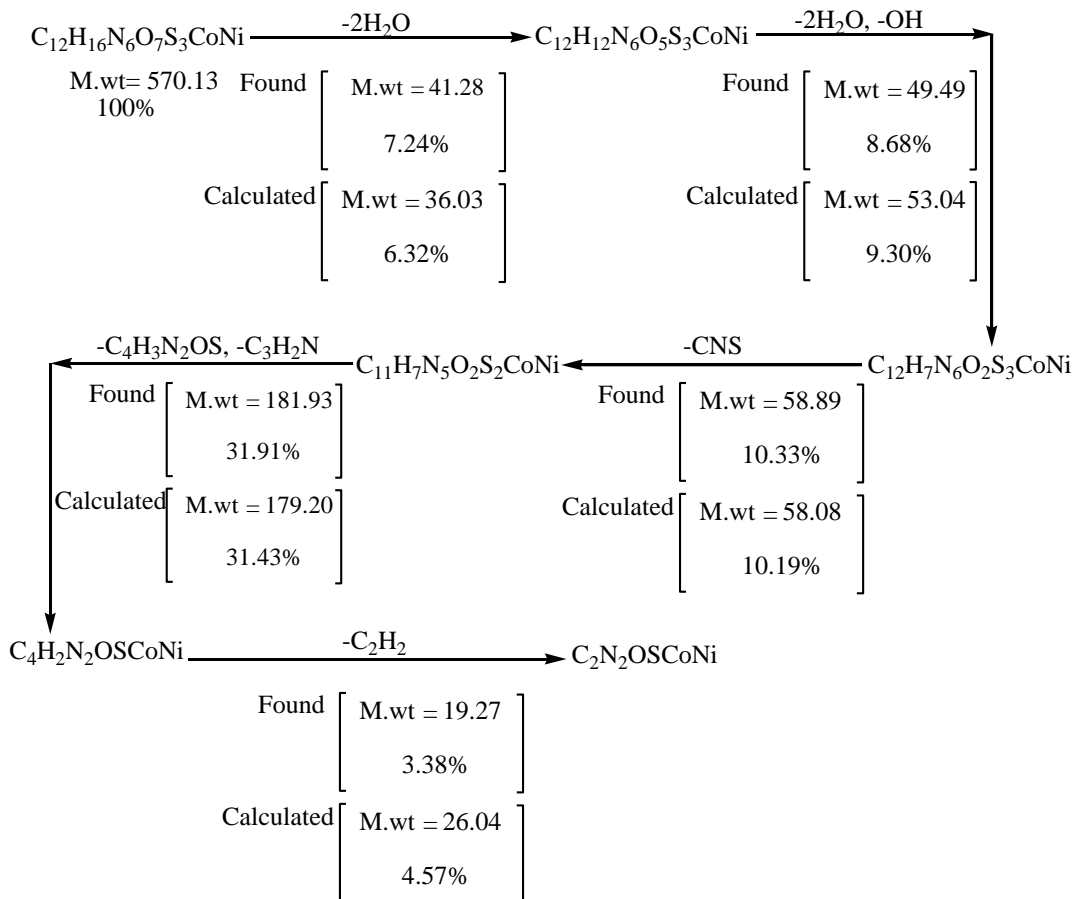
### 3-Cd(hydroxyethyladenine)(OH)<sub>2</sub>·3H<sub>2</sub>O

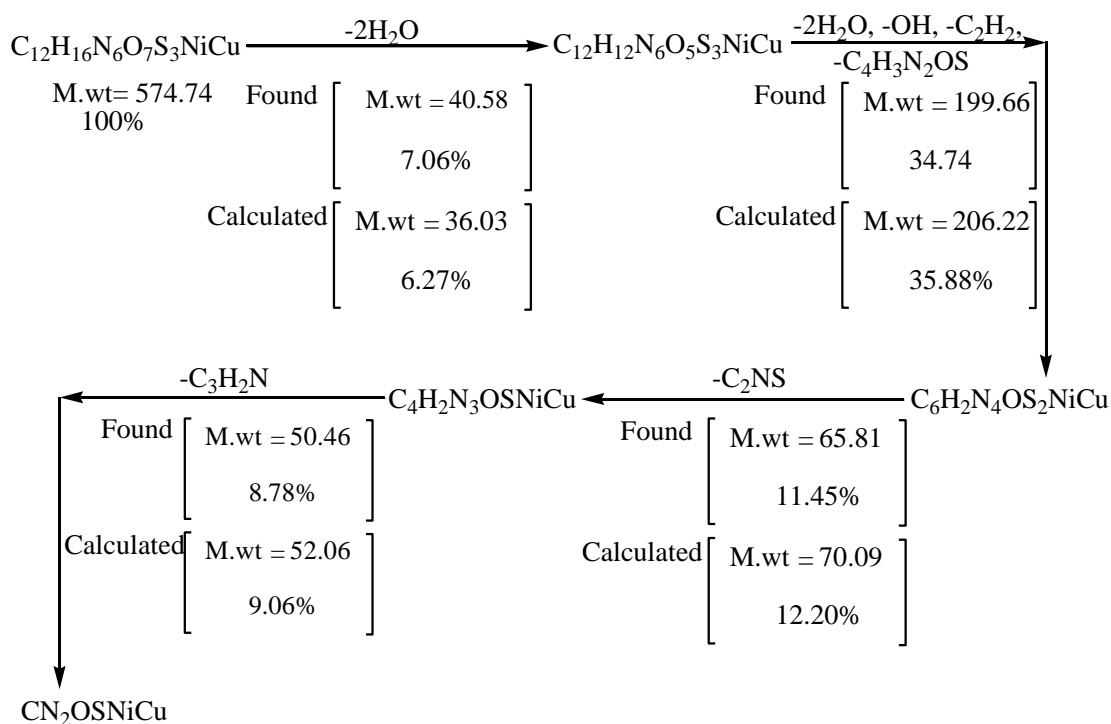


**4-Cd(acetyladenine)<sub>2</sub>(OH<sup>-</sup>)<sub>2</sub>·2H<sub>2</sub>O**



**5-Co-Ni(TU)<sub>3</sub>·4H<sub>2</sub>O**



**6-Ni-Cu(TU)<sub>3</sub>·4H<sub>2</sub>O****4. Conclusion**

DSC and TGA of some nucleic acid compounds are given. The mechanism of thermodynamic parameters is explained.

**Compliance with ethical standards***Acknowledgments*

We would like to thank our committee for providing chemicals and all the facilities for measuring the data.

*Disclosure of conflict of interest*

All the authors are satisfied to the data.

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