

THERMAL ANALYSES (DTA AND TGA) OF LIGAND (H_6L) AND ITS METAL COMPLEXES Co(II), Fe(II), Cu(II) AND Ni(II).

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Abstract: In this article we study the thermal analysis (DTA and TGA) of ligand (H_6L) and its metal complexes: Co(II), Fe(II), Cu(II) and Ni(II), the thermal data of metal complexes were illustrated that the thermal curves in the 27-800 °C temperature range indicated that, the metal complexes are thermally stable up to 40 °C and the weight losses recorded in the 70-90 °C range is due to elimination of hydrated water molecules

Keywords: metal complexes, analytical, thermal analysis, DTA, TGA.

Introduction :

Cobalt oxide nano-particles were prepared by combustion method using urea as a combustion fuel. The effects of calcination temperature, 350–1000 C°, on the physicochemical, surface and catalytic properties of the prepared Co_3O_4 nano-particles were studied. The products were characterized by thermal analyses (TGA & DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques. Textural features of the obtained catalysts were investigated using nitrogen adsorption at 196C°. [1]

The iron manganese oxide nanocomposites were prepared by co-precipitation, sol-gel and mechanochemical methods by using iron(III) nitrate, iron(II) sulfate and manganese(II) nitrate as starting materials. These nanocomposites were prepared in the presence of various catalyst beds. The polyvinyl pyrrolidone (PVP) was used as a capping agent to control the agglomeration of the nanoparticles. Nano-catalysts were identified by FTIR, XRD, SEM and TEM. The sizes of nanoparticles were determined by XRD data and Scherer equation. The prepared nanocatalysts were tested for decomposition of hydrogen peroxide. [2]

The direct electrochemistry of horseradish peroxidase (HRP) on a novel sensing platform modified glassy carbon electrode (GCE) has been achieved. This sensing platform consists of Nafion, hydrophilic room-temperature ionic liquid (RTIL) and Au nanoparticles dotted titanate nanotubes (GNPs-TNTs). The composite of RTIL and GNPs-TNTs was immobilized on the electrode surface through the gelation of a small amount of HRP aqueous solution. The composite was characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD) and infrared spectroscopy (IR). UV-Vis and IR spectroscopy demonstrated that HRP in the composite could retain its native secondary structure and biochemical activity.[3]

$H_4PMO_{11}VO_{40}$, $H_5PMO_{10}V_2O_{40}$ and $H_9PMO_6V_6O_{40}$ acids and an acidic pyridinium salt of $H_4PMO_{11}VO_{40}$ were synthesized. They were characterized by FT-IR and the variations of their acid properties were determined by titration with n-butylamine. They proved to be highly active and selective catalysts for the hydrogen peroxide oxidation of methyl phenyl sulfide to the corresponding sulfoxide or sulfone.[4]

Experimental:

All chemical were of analytical grade and were employed with further purification. [5]

A. Preparation of the ligand (H₆L)

Hydrazine hydrate (1.43 g ,1mol) was added to 30 cm³ of ethyl alcohol containing sodium salt of p-hydroxy-methyl benzoate (5.0 g , 1mol). Stirring the suspension at 70C° for one hour, The product obtained is filtered off to give a starting material (hydrazide). Glucose in 20 cm³ dissolved in ethyl alcohol was added to the hydrazide heating to 60C° with stirring for an hour. The product obtained was filtered off the yellowish white to yield the ligand (H₆L) as shown below:

Sodium 4-((Z)-2 ((2R,3S,4S,5S),2,3,4,5,6 pentahydroxyhexylidene)hydrazine carbonyl)phenolate. Called (H₆L) .

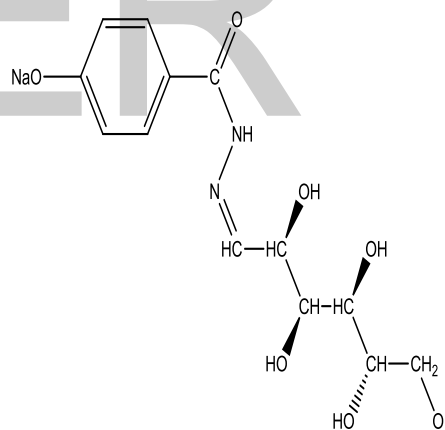


Figure (1) Ligand (H₆L)

B. Preparation of metal complexes:

A) Preparation of [H₅LFe₂(SO₄)₂.H₂O] complex :

iron(II) sulphate tetrahydrate (0.82 g, 1 mol) was added to (H₆L) (1.0 g, 1 mol) dissolved in ethanol 25 cm³. The mixture was warmed at 70 C° with stirring for 1 hour, cool at room temperature and filtered off the dark brown precipitate formed.

B) Preparation of [H₅LCo₂(SO₄)₂.H₂O]

complex :

Cobalt(II) sulphate heptahydrate (0.83 g, 1 mol) was added to (H₆L) (1.0 g, 1 mol) dissolved in ethanol 25cm³. The mixture was warmed at 70 C° with stirring for 1 hour, then cool the mixture at room temperature and then filtered off and the dark brown precipitate was obtained.

C) Preparation of [H₅LCu₂(SO₄)₂.H₂O].H₂O

complex :

Copper(II) sulfate pentahydrate (0.73 g, 1 mol) was added to H₆L (1.0 g, 1 mol) dissolved in ethanol 25cm³. The mixture was warmed at 60 C° with stirring for 1 hour, then the solution was cooled at room temperature filtered off and black precipitate was obtained.

D) Preparation of [H₅LNi₂(SO₄)₂.H₂O]

complex :

Nickel(II) sulfate hexahydrate (0.77 g, 1 mol) dissolved in ethanol 30 cm³ was added to (H₆L) (1.0 g, 1 mol) dissolved in ethanol 25 cm³. The

mixture was warmed at 60 C° with stirring for 1 hour, then the solution was cooled at room temperature filtered off and light brown precipitate was obtained.

E) Preparation of

[H₅LNi₂(OAc)₃.4H₂O].H₂O complex :

Nickle(II) acetate (0.73 g, 1 mol) dissolved in 25cm³ ethanol was added to (H₆L) (1.0 g, 1 mol) dissolved in ethanol 25cm³. The mixture was warmed at 60 C° with stirring for 1 hour, then the solution was cooled at room temperature filtered off and light green precipitate was obtained.

F) Preparation of

[H₅LCo₂(OAc)₃.4H₂O].H₂O complex :

Cobalt(II) acetate tetrahydrate (0.73 g, 1 mol) dissolved in 25 cm³ ethanol was added to (H₆L) (1.0 g, 1 mol) dissolved in ethanol 25 cm³. The mixture was warmed at 60 C° with stirring for 1 hour, then the solution was left at room temperature and when off and dried dark brown precipitate appeared. It was filtered off and at room temperature.

G) Preparation of

[H₅LCu₂(OAc)₃.4H₂O].H₂O complex :

Copper(II) acetate (0.59 g, 1 mol) dissolved in 25cm³ ethanol was added to (H₆L) (1.0 g, 1 mol) dissolved in ethanol 25cm³. The mixture was

warmed at 60 C° with stirring for 1 hour, then the solution was cooled at room temperature filtered off the black precipitate which was formed. Figure (8) showed Experimental setup preparation of the ligand and its metal complexes.

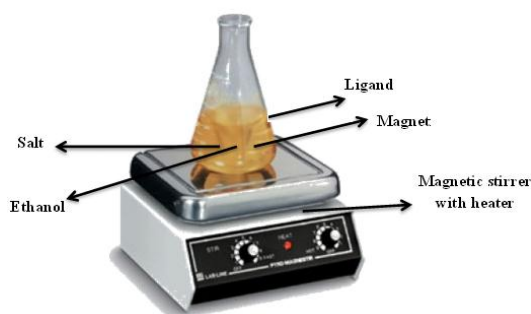


Figure (2) Experimental setup

Thermal analyses

DTA and TGA were carried out on a Shimadzu DT-30 thermal analyzer in nitrogen atmosphere, from room temperature to 800 C° at a heating rate of 10 C° per minute.

RESULTS AND

DISCUSSION

The thermal data of metal complexes (1), (2), (3), (4) and (5) were presented in Table 1. The thermal curves in the 27-800C° temperature range indicated that, the metal complexes are thermally stable up to 40 °C. The weight losses recorded in the 70-90°C range is due to elimination of hydrated water molecules. Fe(II) complex (1) thermogram

showed an endothermic peak at 50 C° due to break of the hydrogen bondings. An endothermic peak was observed at 75 C°, with 4.58% weight loss (Calc. 4.71%) corresponding to loss of two hydrated water molecules. The endothermic peak observed at 120 C°, with 12.91% weight loss (Calc. 12.36%) is due to loss of five coordinated water molecules [6].

The endothermic peak observed at 275 C°, with 15.41% weight loss (Calc. 15.04%) is due to loss of one terminal coordinated SO₄ group, whereas, the loss of the bridged SO₄ group was accompanied by an endothermic peak at 320 C° with 17.50% weight loss (Calc. 17.71 %). The endothermic peak observed at 350 C°, is corresponding to melting point of the complex [6].

Finally, the complex showed several exothermic peaks at 450, 520 and 640 C°, with total 35.50% weight loss (Calc. 35.87%) corresponding to thermal decomposition with eventually formation of Fe₂O₃ molecule. The thermogram of Cu(II) complex (2) showed an endothermic peak at 45 C° is due to broken of hydrogen bondings. The endothermic peak observed at 80 C°, with 1.82% weight loss (Calc. 1.66%) was assigned to loss of one hydrated water molecules. Whereas the endothermic peak observed at 135 C°, with 2.73% weight loss (Calc. 2.68%) was ascribed to loss of a coordinated water molecule[6].

Table (1):- Thermal analysis for metal (II) complexes.

Compound No. Molecular formula	Temp. (°C)	DTA (peak)		TGA (Wt.loss %)		Assignments
		Endo	Exo	Calc.	Found	
Complex 1 C ₁₃ H ₂₇ Fe ₂ O ₂₀ N ₂ S ₂ Na	50	Endo	-	-	-	Broken of H-bondings
	75	Endo	-	4.71	4.58	Loss of (2H ₂ O) hydrated water molecules
	120	Endo	-	12.36	12.91	Loss of (5H ₂ O) coordinated water molecules
	275	Endo	-	15.04	15.41	Loss of coordinated (SO ₄) group
	320	Endo	-	17.71	17.5	Loss of bridged (SO ₄) group
	350	Endo	-	11.26	11.18	Loss of coordinated SO ₄ group
	310	Endo	-	-	-	Melting point of the complex
450,520,640	-	Exo	35.87	35.5	Decomposition with formation of Fe ₂ O ₃	

Complex 2 C ₁₃ H ₁₉ Cu ₂ O ₁₆ N ₂ S ₂ Na	45	Endo	-	-	-	Broken of H-bondings
	75	Endo	-	3.49	3.49	Loss of 2(H ₂ O) hydrated water molecules
	145	Endo	-	8.7	8.4	Loss of (5H ₂ O) coordinated water molecules
	220	Endo	-	18.8	18.53	Loss of coordinated 3(OAc) group
	296	Endo	-	-	-	Melting Point
	430	-	Exo	20.7	20.27	Decomposition process with the formation of 2CuO

Complex 3 C ₁₃ H ₁₉ Ni ₂ O ₁₆ N ₂ S ₂ Na	60	Endo	-	-	-	Broken of H-bondings
	140	Endo	-	2.72	2.68	Loss of coordinated(H ₂ O) molecule
	235	Endo	-	14.93	14.29	Loss of terminal coordinated((SO ₄) group
	280	Endo	-	17.55	17.85	Loss of bridged (SO ₄) group
	310	Endo	-	-	-	Melting Point
	560	Endo	-	36.36	36.61	Loss of C ₈ H ₁₂ O ₆ moiety
	630	-	Exo	52.26	52.68	Formation of 2NiO

Compound No. Molecular formula	Temp. (°C)	DTA (peak)		TGA (Wt.loss %)		Assignments
		Endo	Exo	Calc.	Found	
Complex 4 C ₁₉ H ₃₆ Ni ₂ N ₂ O ₁₈ Na	45	Endo	-	-	-	Broken of H-bondings
	60	Endo	-	3.1	3.2	Loss of (H ₂ O) hydrated water molecules
	120	Endo	-	12.65	12.73	Loss of (4H ₂ O) coordinated water molecules
	230	Endo	-	23.74	23.64	Loss of coordinated 2(OAc) group
	265	Endo	-	15.57	15.45	Loss of bridged (OAc) group
	320	Endo	-	-	-	Melting point of the complex
	350,385,500,570	-	Exo	-	-	Loss with 2 NiO

Complex 5 C ₁₉ H ₃₆ Co ₂ N ₂ O ₁₈ Na	45	Endo	-	-	-	Broken of H-bondings
	80	Endo	-	2.5	2.7	Loss of (H ₂ O) hydrated water molecules
	115	Endo	-	10.25	10.45	Loss of (4H ₂ O) coordinated water molecules
	300	Endo	-	18.73	18.92	Loss of coordinated terminal 2(OAc) group
	320	Endo	-	11.52	11.71	Loss of bridged (OAc) group
	340	Endo	-	-	-	Melting point of the complex
	480,520,615	-	Exo	33.11	33.33	Decomposition process with the formation of 2CoO

Another endothermic peak was observed at 230 C°, with 15.0% weight loss (Calc. 14.70%), which is assigned to loss of coordinated terminal sulphate group. The endothermic peak observed at 285 C° which is assigned to loss of bridged coordinated sulphate group. The endothermic peak observed at 330C°, is corresponding to melting point of the complex. The complex showed several exothermic peaks at 520, 610 and 700

C°, with total 35.45% weight loss (Calc. 35.14%) corresponding to decomposition process with formation of 2CuO molecule [6].

The thermogram of Ni(II) complex (3) showed an endothermic peak at 60 C° due to broken of hydrogen bondings, whereas the loss of coordinated hydrated water molecule was accompanied with endothermic peak at 140 C° with 2.68% weight loss (Calc. 2.72%).The loss of terminal coordinated sulphate group was accompanied by

endothermic peaks at 235 C° with weight losses 14.29% (Calc. 14.93%)[6].

An endothermic peak was observed at 280 C° with 17.85% weight loss (Calc. 17.55%) which could be assigned to loss of a bridged sulphate group. The endothermic peak observed at 310 C° was assigned to the melting point of the complex. The endothermic peak observed at 560 C° was assigned to the loss of C₆H₁₂O₅ moiety with 36.61% weight loss (Calc. 36.36%). Complex was accompanied by exothermic peaks at 630 C° with total 52.68% weight loss (Calc. 52.26%) with final formation of 2NiO molecules[6].

The thermogram of Ni(II) complex (4) showed an endothermic peak at 45°C due to broken of hydrogen bondings, whereas the loss of hydrated water molecule was accompanied with endothermic peak at 60 C° with 3.2% weight loss (Calc. 3.1%). The loss of coordinated four water molecules was accompanied by endothermic peaks at 120 C° with weight losses 12.73% (Calc. 12.65%) . An endothermic peak was observed at 230 C° with 23.64% weight loss (Calc. 23.74%) which could be assigned to loss of a coordinated two acetate group. The endothermic peak observed at 265 C° was assigned to the melting point of the complex. An endothermic peak was observed at 265 C° with 15.45% weight loss (Calc. 15.57%) which could be assigned to loss of a bridged acetate group. The endothermic

peak observed at 320 C° was assigned to the melting point of the complex[6].

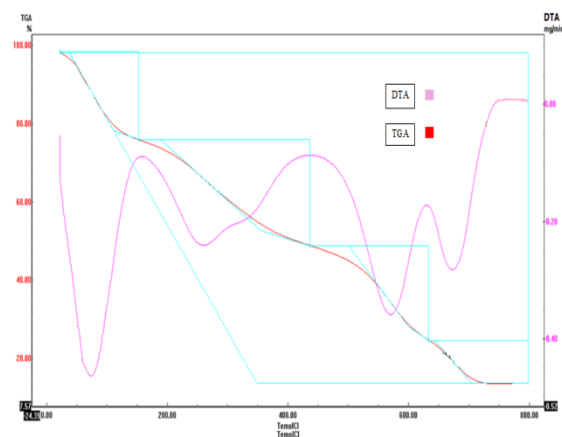


Figure (3):- Thermogram of [H₅LFe₂(II)(SO₄)₂.H₂O] complex (1)

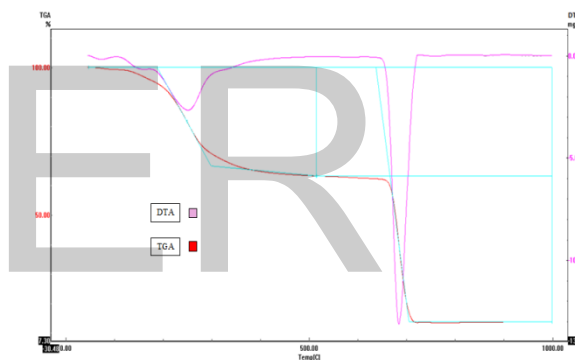


Figure (4):- Thermogram of [H₅LCu₂(II)(SO₄)₂.H₂O].H₂O of complex (2)

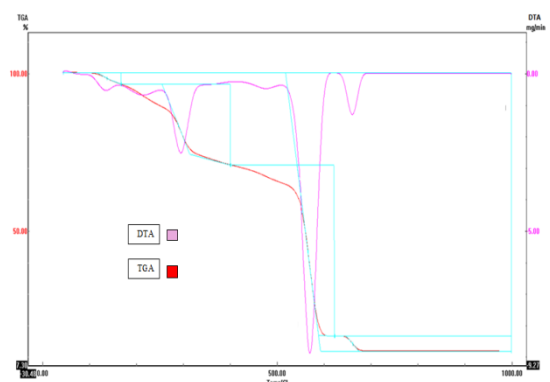


Figure (5):- Thermogram of [H₅LNi₂(II)(SO₄)₂.H₂O] complex (3)

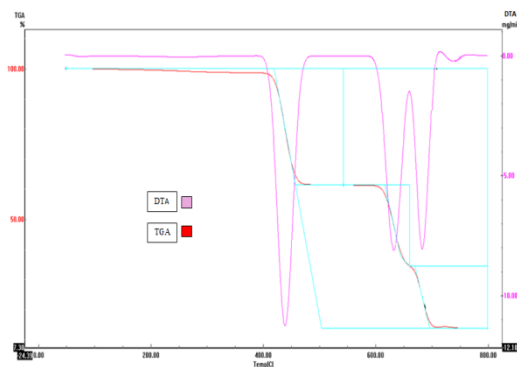


Figure (6):- Thermogram of $[H_5LNi_2(II)(OAc)_3.4H_2O].H_2O$ complex (4)

Thermal decomposition of the complex was accompanied by multiple exothermic peaks at 350, 385, 500, and 570 C° with total 47.3% weight loss (Calc. 46.8%) with loss of 2NiO molecules. The thermogram of Co(II) complex (5) showed an endothermic peak at 45°C due to broken of hydrogen bondings, whereas the loss of hydrated water molecule was accompanied with endothermic peak at 80 C° with 2.7% weight loss (Calc. 2.5%) [6].

The loss of coordinated four water molecules was accompanied by endothermic peaks at 115 C° with weight losses 10.45% (Calc. 10.25%) . An endothermic peak was observed at 300 C° with 18.92% weight loss (Calc. 18.73%) which could be assigned to loss of a coordinated terminal two acetate group. The endothermic peak observed at 320 C° with 11.71% weight loss (Calc. 11.52%) which could be assigned to loss of a bridged acetate group. The endothermic peak observed at 340 C° was

assigned to the melting point of the complex. Thermal decomposition of the complex was accompanied by multiple exothermic peaks at 480, 520, 500, and 615 C° with total 33.33% weight loss (Calc. 33.11%) with formation of 2CoO. The thermograms of complexes (1), (2), (3), (4) and (5) are shown in Figures (3-7) and summarized the data in Table (1)

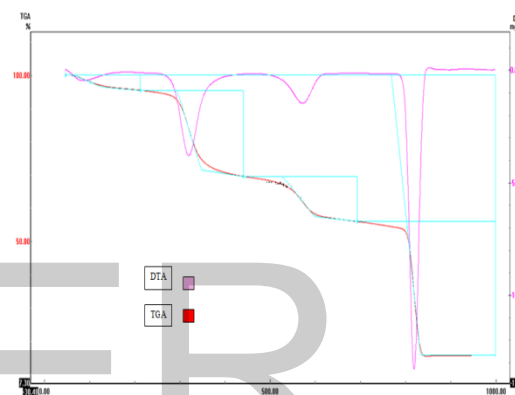


Figure (7):- Thermogram of $[H_5LCo_2(II)(OAc)_3.4H_2O].H_2O$ complex (5)

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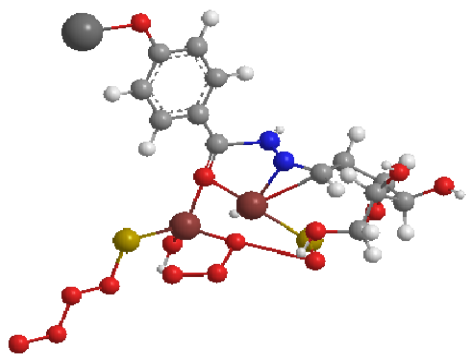
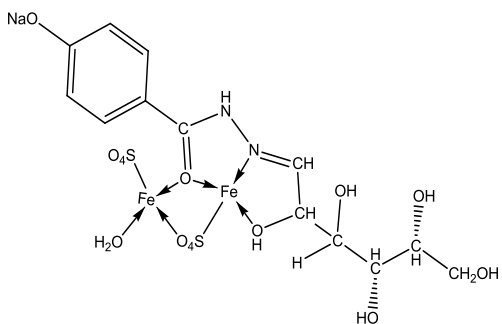


Figure (8) $[H_5LFe_2(SO_4)_2 \cdot H_2O]$ complex and 3D structure

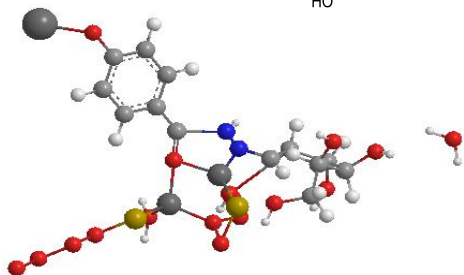
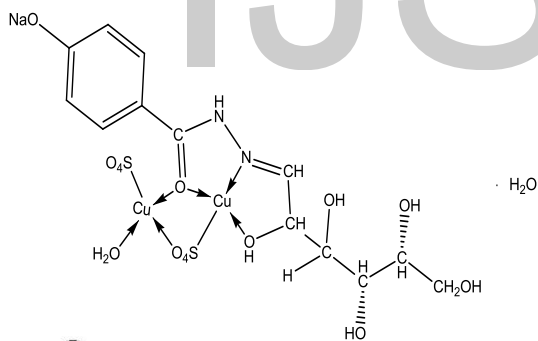


Figure (9) $[H_5LCu_2(SO_4)_2 \cdot H_2O] \cdot H_2O$ complex and 3D structure

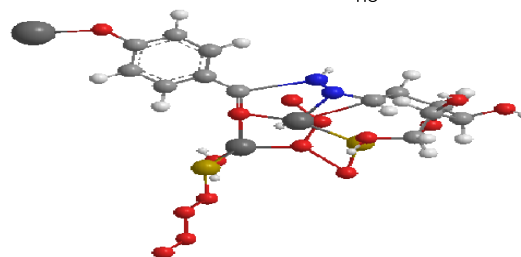
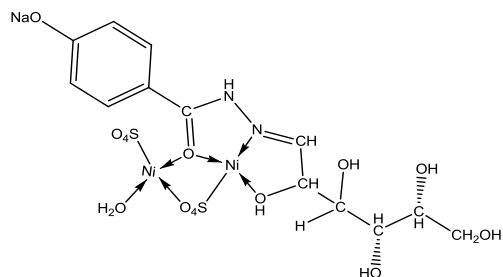


Figure (10) $[H_5LNi_2(SO_4)_2 \cdot H_2O]$ complex and 3D structure

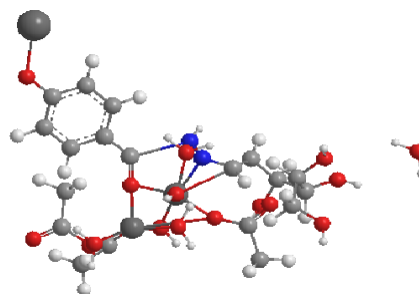
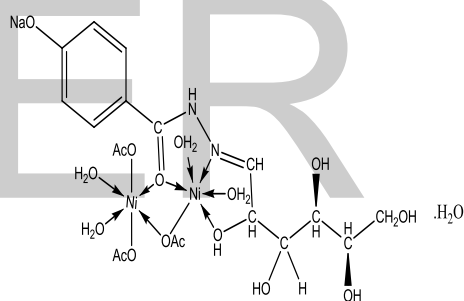


Figure (11) $[H_5LNi_2(OAc)_3 \cdot 4H_2O] \cdot H_2O$ complex and 3D structure

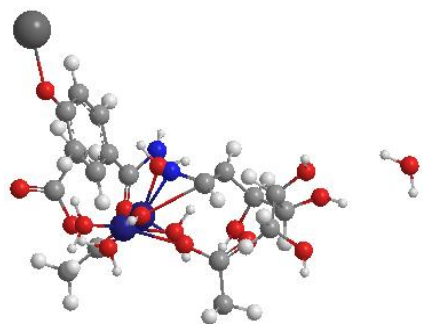
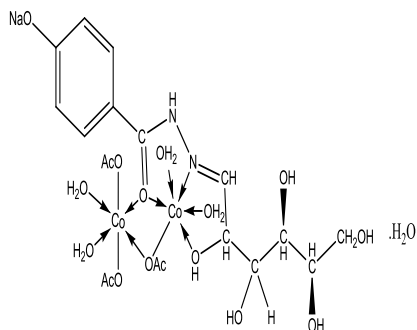


Figure (12) $[H_5LCo_2(OAc)_3 \cdot 4H_2O] \cdot H_2O$
complex and 3D structure

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