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DIRECT ELECTROCHEMICAL SYNTHESIS OF MONO, BI AND POLYNUCLEAR COMPLEXES OF SOME HYDRAZIDE AND HYDRAZONE DERIVATIVES

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التحضير الكهروكيميائي المباشر لمتراكبات أحادي وثنائي وعديد الأنوية لبعض مشتقات الهيدرازايد والهيدرازون

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أقسام الكيمياء - كليات العلوم - جامعة المنصورة - بالإشتراك مع جامعات قطر وصنعاء وعين شمس

تم تحضير متراكبات بعض العناصر الانتقالية لأحادي وثنائي ورباعي الهيدرازايد والهيدرازون بالطريقة الكهروكيميائية باستخدام فلز آنودي مضحي به، تم فصل المتراكبات وبنسب جزيئية مختلفة من الفلز والمرتبط (٢:١، ١:١، ١:٢و١:٤) نتيجة لتفاعل فلزات كل من الكوبلت والنيكل والنحاس في محلول لامائي من الأسيتون مع مشتقات كل من حمض بنزويك الهيدرازايد ومالونيل ثنائي الهيدرازايد و١،١`، ٣،٣` - بروبان رباعي الكربوهيدرازايد واسيتيل وبنزويل سالسيل الهيدرازون و١،٣ - مالونيل ثنائي سالسيل الهيدرازون و١،١`، ٣،٣`- بروبان رباعي سالسيل رباعي الكربوهيدرازون، وكذلك فصلت نواتج إضافة من تفاعل بعض المتراكبات مع مرتبطات معطاءة متعادلة مثل ١، ١٠ - فينانثرولين وثلاثي فينيل الفوسفين، وبناءً على نتائج التحليل الكمي الميكروني للعناصر ودراسة التحليل الطيفي والقياسات المغناطيسية تم اثبات التراكيب الكيميائية للمرتبطات وللمتراكبات المحضرة، وحيث أن المركب المخلبي ١،١`، ٣،٣` - بروبان رباعي سالسيل رباعي الكربوهيدرازون يحتوي على أربع مجموعات هيدرازون لذلك تم اقتراح نموذج للمتراكب عديد الأنويه من خلال ترابط ذرات كل من الأكسجين الفينولية ونيتروجين الأزوميثين وأكسجين مجموعة الكاربونيل في الصورة الاينولية مع أيونات كل من النحاس والكوبلت.

Key words : Electrochemical synthesis, transition metal complexes, polynuclear complexes, hydrazides, hydrazones.

Running Title : Direct Electrochemical Synthesis.

ABSTRACT

Transition metal complexes of mono-, di- and tetrahydrazides and their hydrazones have been prepared by electrochemical techniques using the metal as a sacrifical anode. The electrochemical oxidation of Co, Ni and Cu in non-aqueous (acetone) solution of benzoic hydrazide (HBzH), malonic dihydrazide (H_2MH), 1,1,3,3` – propanetetracarbohydrazide ($H_4PTCH$), acetyl salisoylhydrazone ($H_2ASH$), benzolsalisolyhdrazone ($H_2BSH$), 1,3 – malonyldisalisoylhydrazone ($H_4MDSH$) and 1,1,3,3` - propanetetrasalisoyl - tetracarbohydrazone ($H_8PTSTCH$) gave 1:2, 1:1, 2:1 and 4:1 (metal : ligand) ratio in good yields. When a neutral donor ligand such as 1,10-phenanthroline or triphenylphosphine is present in solution, adducts were formed. Since the ligand (PTSTCH) has four hydrazone groups it may act in an ONO tridentate fashion from each side with one of the four metal ions forming a polynuclear complex coordinating through the phenolic oxygen, the azomethine nitrogen and the enolic oxygen of the carbonyl group. The complexes have been characterized by elemental analysis, infrared, electronic spectra, magnetic measurements and thermal (DTA, TG and DTG) studies.

INTRODUCTION

A large number of metal complexes formed by hydrazide and hydrazone derivatives have been reported.[1-6] Because of the intrinsic importance of hydrazide and hydrazone compounds as analytical reagents,[7] their applications in medical and pharmaceutical systems,[8] they have been intensively studied. The metal complexes of hydrazides and hydrazones have attracted a special attention due to their tuberculostatic activity.[9] We now report new complexes of Co(II), Ni(II), and Cu(II) complexes of benzoylhydrazine (BzH), malonylhydrazine (MH), 1,1,3,3-propane tetracarbohydrazide (PTCH), acetyl salisoylhydrazone (ASH), benzoyl salisoyhydrazone (BSH), 1,3-malonyl disalisoyl hydrazone (MDSH) and 1,1`,3,3`-propane tetrasalisoyltetra-carbohydrazone (PTSCH) by the electrochemical oxidation of metals in non-aqueous solutions for some hydrazides and hydrazones ligands. Adducts with 1,10-phenanthroline and triphenylphosphine were also prepared by the same technique. The complexes were characterized by conventional physical and chemical studies.[6]

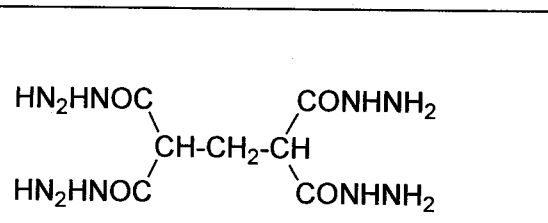
EXPERIMENTAL

Electrochemical Cell:

The cell used in the electrochemical technique consists of a tall-form 100 cm^3 Pyrex beaker containing 50 cm^3 of a solution phase. The cathode is a platinum wire approximately 1mm diameter. In most cases, the metal (2-5 g) was suspended and supported on a platinum wire.[6,10]

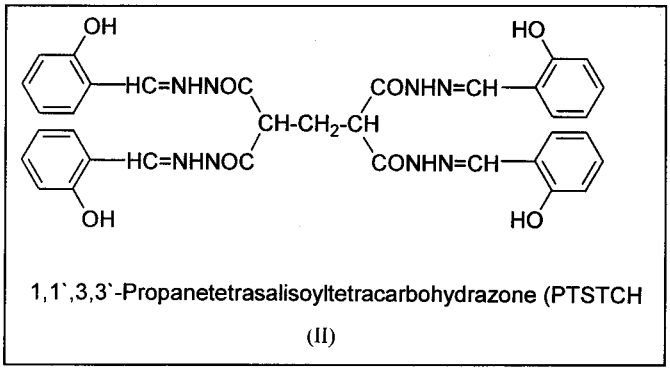
Organic Ligands:

The organic compounds, benzoylhydrazine (HBzH), malonylhydrazine (H_2MH), 1,1`,3,3`-propanetetracarbohydrazide (H_4PTCH),[2,6] acetyl salisoylhydrazone (H_2ASH), benzoylsalisoylhydrazone (H_2BSH), 1,3-malonyldisalisoylhydazone (H_4MDSH) and 1,1`,3,3`-propanetetrasalisoyltetra-carbohydrazone ($H_8PTSTCH$)[3,6] used in this technique were prepared and checked by elemental analysis (^1H-^{13}C-nmr) and IR spectral studies, [structures (I) and (II)].



1,1`,3,3`-Propane tetracarbohydrazide (PTCH)

(I)



1,1`,3,3`-Propanetetrasalisoyltetracarbohydrazone (PTSTCH

(II)

Metals:

Metals (Cu, Co and Ni) (Alfa) were supplied in the form of rods, approximately one cm diameter and two cm length or as sheets 2 x 2 cm^2.

Synthesis of Some Metal Complexes:

Preparation of [Co(BzH)z(HzOz]·3H2O

In a typical experiments, the electrochemical oxidation of a cobalt anode in a solution phase of acetone (50cm^3), benzoylhydrazine (0.27g) and tetraethylammomnium perchlorate (20 mg) was carried out for 2.5 h at 20 mA. As the electrolysis proceeded, hydrogen gas was evolved at the cathode where a faint pink product was formed, collected, washed several times with diethyl ether and dried. Essential identical procedures gave $[Ni(BzH)_2(ac)_2]\cdot H_2O$ and $[Cu(BzH)_2(ac)_2]$.

Preparation of $[Co(BzH)_2(phen)]\cdot 2H_2O$

To a stirred solution of $[Co(BzH)_2]\cdot 3H_2O$ (0.2 g, 0.5 mmol) in acetone solution (30cm^3) 0.09 g (0.5 mmol) of 1,10-phenanthroline was added and the solution immediately became brownish. After stirring for 1 hour, the solution was left overnight. The brown precipitate was washed with diethyl ether and analyzed as $[Co(BzH)_2(Phen)]\cdot 2H_2O$.

Preparation of $Cu_2(MDSH)\cdot 6H_2O$

To 0.68 g (0.002 mol) of the ligand, dissolved in a little DMSO and diluted by 60 cm^3 acetone, 20 mg Et_4NClO_4 was added. When the current is passed, a green colour was formed accompanied by a precipitate which increased by time. The reaction product was $Cu_2(MDSH)6H_2O$. An essentially iden-

tical procedure gave $Co_2(MDSH)\cdot 9H_2O$ in good yield.

RESULTS AND DISCUSSION

Electrochemical synthesis is based on the direct oxidation of a sacrificial anode (in our case the investigated metal) in non-aqueous solution containing the appropriate ligand precursor to produce metal complexes. Addition of a neutral ligand such as 1,10-phenanthroline (phen) or triphenyl phosphine (ph_3P) in solution allows the isolation of adduct compounds. The complexes isolated in this way gave analytical results which are in good agreement with 1:1, 1:2, 2:1 and 4:1 metal to ligand stoichiometries depending on the ligand used as well as the time of electrolysis. The electrochemical preparation followed essentially the same procedure in each case with the sacrificial metal forming the anode of a simple cell.

Pt (-)/acetone + ligand/M(+)

The oxidation states of the metal ions in the complexes isolated by the electrochemical reaction are indicated by calculating the electrochemical efficiency which is defined as moles of metal dissolved per faraday of charge (E_f). The values listed in Tables (1 & 2) show that for the reaction of monoprotic ligands (benzhydrazide, HBzH) with copper, cobalt and nickel anodes, the E_f value is compatible with the following scheme.[7,14,16]

Cathode: $2HL + 2e \longrightarrow 2L^- + H_2(g)$

Anode: $2L^- + M \longrightarrow ML_2 + 2e$

For the reaction with biprotic ligands malnoyldihydrazide (H_2MH), acetyl (H_2ASH) and benzoyl salisoyl hydrazone (H_2BSH), the reaction product is 1:1 which can be explained by the following scheme:

Cathode: $H_2L + 2e \longrightarrow L^{2-} + H_2(g)$

Anode: $L^{2-} + M \longrightarrow ML + 2e$

The E_f values (Table 1) calculated for 1,1`,3,3`-propanetetracabohydrazide (H_4PTCH) complexes follows the scheme:

Cathode: $H_4L + 4e \longrightarrow L^{4-} + 2H_2(g)$

Anode: $L^{4-} + 2M \longrightarrow M_2L + 4e$

For 1,1`,3,3`-propanetetrasalisoyltetracarbohydrazone ($H_8PTSTCH$) the complexes have a 4:1 (M:L) ratio (Table 2) and are formed according to the following reactions:

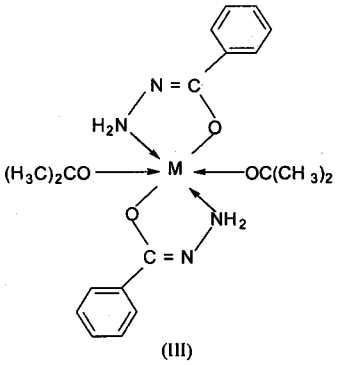
Cathode: $H_8L + 8e \longrightarrow L^{8-} + 4H_2(g)$

Anode: $L^{8-} + 4M \longrightarrow M_4L + 8e$

Analytical results together with some physical properties of the isolated complexes are listed in Tables (3 & 4). All the complexes are stable toward atmospheric conditions, soluble in DMSO or DMF. Their conductivity values (8.6 - 28.6 $ohm^{-1}\ cm^2\ mol^{-1}$) in 10^{-3} M solution agree well with those reported for non-electrolytes.[15]

The elemental analyses (Table 3) and IR spectra suggest that the ligands (HBzH & H_2MH) forms 1:1 complexes with the metal ions and ligates in the enol form. The IR spectra of complexes and adducts show: i) the lower shift (20-30 cm^{-1}) of NH_2 vibrations indicating the participation of amino group in bonding; ii) the amide I band disappears indicating the enolization of CONH group with subsequent coordination to the metal ions through the enolic C-O group; iii) the appearance of new bands in the 1614-1620 and 1068-1092 cm^{-1} regions assigned to ν(C=N) and ν(C-O) vibrations.[16-18] In the far-IR region, all the metal (II) complexes show bands at *ca* 415 and 370 cm^{-1} which are assigned to ν(O — M) and ν(N → M) vibrations, respectively.[19]

The electronic spectrum of $[Ni(BzH)_2(ac)_2]\cdot H_2O$), structure (III), shows a broad band centered at 16700 cm^{-1} attributed to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition (ν_2). The other transition band (ν_3) $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ is observed at 26490 cm^{-1}. These values are used to calculate ν_1, $^3A_{2g} \rightarrow {}^3T_{2g}$ by the d^8 equations reported for octahedral structure and is found to be at 9945 cm^{-1} [11-13,17,18].



(III)

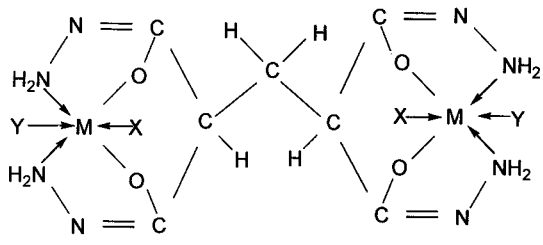
M = Co (II), Cu (II) or Ni (I I)

The parameters, B, β, 10Dq and ν_2/ν_1 values are calculated to be 768 cm^{-1} 0.74, 6652 cm^{-1} and 1.67, respectively. These data suggest an octahedral geometry for $[Ni(BzH)_2(ac)_2(H_2O)]$. The octahedral geometry is further supported by the ν_2/ν_1 ratio which lies in the range 1.65-1.72 previously reported for octahedral Ni(II) complexes.[17,18]

The electronic spectrum of $[Ni(BzH)_2\cdot phen]\cdot H_2O$ is consistent with an octahedral gemoetry showing two d-d transi-

tion bands at 16390 and 21276 cm^{-1} assignable to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively. The magnetic moment value (2.9 B.M.) measured for the complex supports the proposed octahedral structure. The B, β, 10Dq and ν_2/ν_1 values are calculated to be 680 cm^{-1}, 0.65, 6228 cm^{-1} and 1.7, respectively. The data are summarised in Table 5.

The cobalt complex, $[Co_2(PTCH)(ac)(H_2O)_3]\cdot 2H_2O$, structure (IV), has electronic spectral bands at 15750 and 19420 cm^{-1} due to the $^4T_{1g} \rightarrow {}^4A_{1g}$ (ν_2) and $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_3) transitions respectively, in an octahedral environment. The ν_2 and



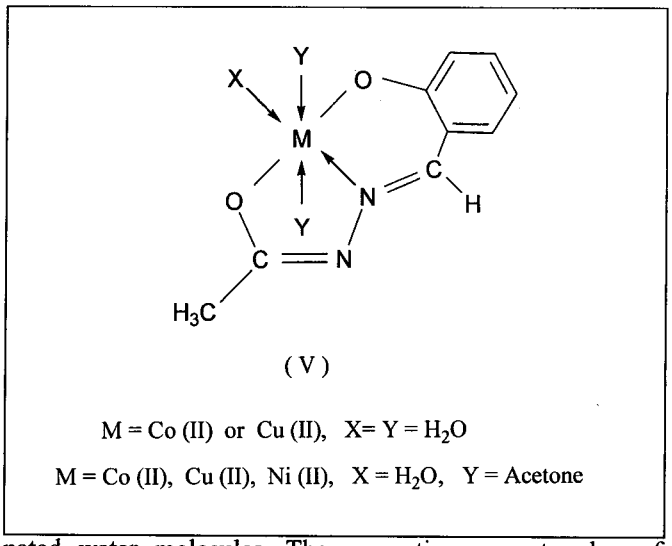
(IV)

M= Cu (II), Co (II) or Ni (II), X = H_2O & Y = $(Me)_2CO$

ν_3 values are used to calculate the third transition $^4T_{1g} \rightarrow {}^4T_{2g}$ (F) (ν_1), band by applying the d^7 equations.[11-13] These transition bands have been utilized to calculate 0 B, β, 10Dq and ν_2/ν_1 parameters; their values are 878 cm^{-1}, 0.9, 8410 cm^{-1} and 2.1 (Table 5). The overall magnetic moment value is 3.32 B.M.

Since Acetyl Salisoy Hydrazone (ASH) has four potential donor atoms, it may act as an ONO tridentate ligand. However, it is similar to BSH coordinating through the phenolic oxygen, the azomethine nitrogen and the enolic C-O oxygen. The Infrared spectra of ASH and BSH complexes show the disappearance of NH and carbonyl group bands with the appearance of new bands which could be attributed to the stretching vibrational mode of C = N-N = C group.

The electronic spectrum of the $[Co(ASH)(H_2O)_3]2H_2O$ complex has bands characteristic for an octahedral gemoetry.[17-18] The spectrum shows two bands at 15870 and 18860 assigned to the $^4T_{1g} \rightarrow {}^4A_{1g}$ (ν_2) and $^4T_{1g} \rightarrow {}^4T_{1g}$ (ν_3) transitions respectively, in an octahedral structure. The ν_2 and ν_3 values obtained from the electronic spectra were used to calculate the third transition band, $^4T_{1g} \rightarrow {}^4T_{2g}$ (F) (ν_1)[17-18]. The value of ν_1 was found to be at 8363 cm^{-1}. The IR spectrum shows a broad band at 3430 cm^{-1} due to ν(OH) of the coordi-

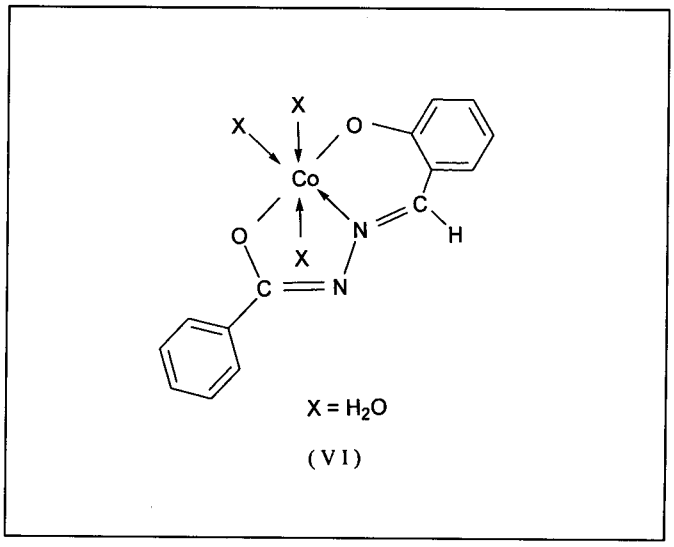


(V)

M = Co (II) or Cu (II), X= Y = H_2O

M = Co (II), Cu (II), Ni (II), X = H_2O, Y = Acetone

nated water molecules. The magnetic moment value of $[Co(ASH)(H_2O)_3]2H_2O$ (4.94 B.M.) lies in the range reported for high spin octahedral structures; the structure may be drawn as in (V).



X = H_2O

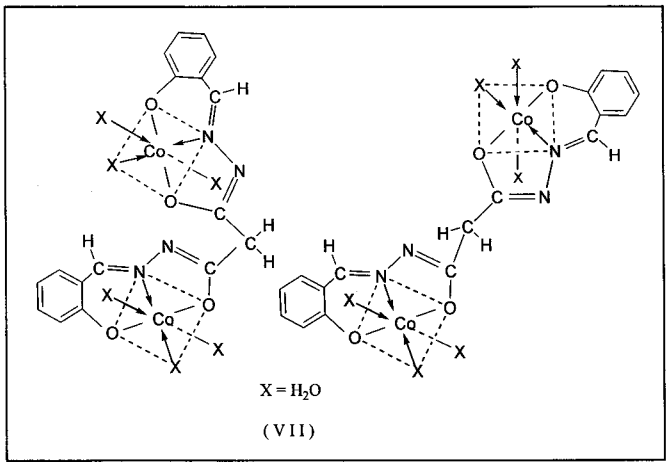
(VI)

The electronic spectrum of the $[Co(BSH)(H_2O)_3]\cdot 4H_2O$, has bands characteristic for octahedral gemoetry.[17, 18] The IR spectrum shows a broad band at 3440 cm^{-1} due to ν(OH) of the coordinated water molecules which complete the octahedral structure of $[Co(BSH)(H_2O)_3]\cdot 4H_2O$. The magnetic moment value (2.04 B.M.) lies in the range reported for a low spin octahedral structure (VI).

The IR spectral studies were used to elucidate the structure of 1,3-malonyl disalisoyl hydrazone (H_4MDSH) as well as its coordination sites. In the spectra of complexes the NH and C=O hands disappear with the appearance of a new band at 1604 cm^{-1} attributed to ν(C=N) vibration. The IR spectra of $[Cu_2(MDSH)(H_2O)_4]\cdot 2H_2O$ and $[Co_2(MDSH)(H_2O)_6]\cdot 3H_2O$ complexes show the disappearance of ν(C=O) with the appearance of a band at 1620 cm^{-1} which could be due to the

stretching vibration of the conjugated C=N-N=C group. The disappearance of ν(OH) with the appearance of ν(C-O) at 1152cm^{-1} suggest the involvement of the hydroxyl oxygen in bonding. Also, the vibrations of NH at 1492, 986 and 406 cm^{-1} in the free ligand have disappeared in the spectra of $[Cu_2(MDSH)(H_2O)_4]\cdot 2H_2O$ and $[Co_2(MDSH)(H_2O)_6]\cdot 3H_2O$. The magnetic moment of $[Cu_2(MDSH)(H_2O)_4]2H_2O$ is 2.3 B.M., less than the value expected for two unpaired electrons (one from each copper ion). The anomalous magnetic moment (1.15 B.M.) calculated for each one is due to metal – metal interactions.[20]

The DTA and TG curves, for $[Co_2(MDSH)(H_2O)_6]\cdot 3H_2O$,

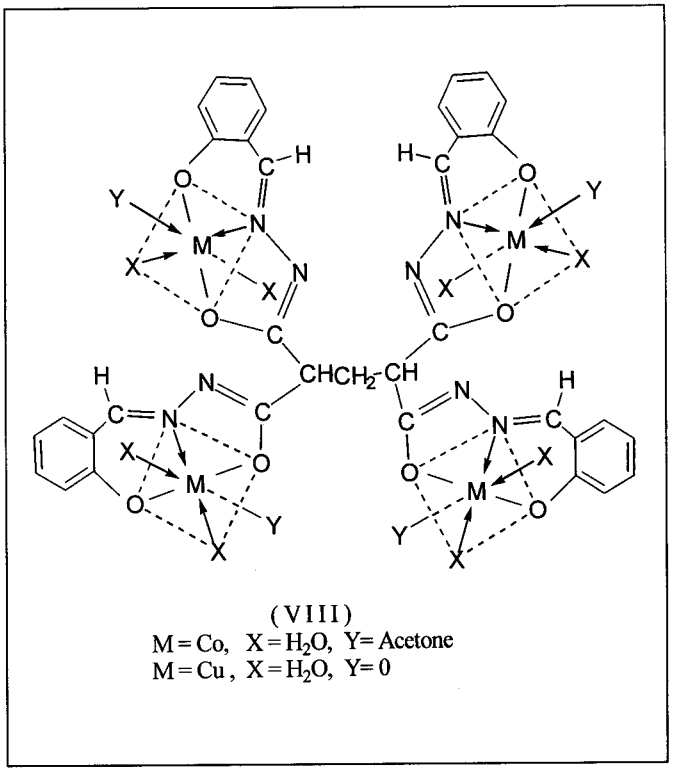


X = H_2O

(VII)

show an endothermic and exothermic peaks at 80 and 160°C corresponding to the hydrated (weight loss: cal. 8.7%; found 9.3%) and coordinated (Cal.17.4%; found 17.3%) water, respectively, which coincides with the proposed structure. The thermogram also shows exothermic peaks at 230, 320 and 420°C corresponding to the decomposition of the aliphatic and aromatic parts of the organic molecule. The remaining mass of cobalt oxide (calc: 24.1%, found: 24.0%) is in good agreement with the calculated value.[21-26] (structure VII).

The main IR bands of the ligand (H_8L) and its complexes were studied (L = PTSTCH). The spectra of the isolated complexes differ from that of the free ligand. The IR spectra of the tetranuclear complexes, $[Cu_4(L)(H_2O)_8]\cdot 4H_2O$, and $[Co_4(L)(ac)_4(H_2O)_8]$, show the disappearance of NH and carbonyl groups with the appearance of new hands in the 1625-1605 cm-1 region which could be related to stretching vibrations of the conjugated C=N-N=C system. The DTA and TG curves show endothermic peaks at 90 and 170°C corresponding to the hydrated species (weight loss cal: 6.23%; found 12.5%) water molecules respectively[21,24], in agreements with the proposed structure $[Cu_4(L)(H_2O)_8]\cdot 4H_2O$. The DTA graph also shows exothermic peaks at 230, 280, 480 and 520°C corresponding to the decomposition of the organic moiety and the formation of Cu_2O[24-26]. The remaining mass of the copper oxide (calc. 27.55%, found 27.5%) is in agreement with the calculated one (structure VIII).



(VIII)

M = Co, X = H_2O, Y= Acetone

M = Cu, X = H_2O, Y= 0

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Table 1 : Experimental Conditions for the Direct Electrochemical Method for Preparation of Benzhydrazide (HBzH), Malonyldihydrazide (H_2MH) and 1,1`,3,3`-Propanetetracarbohydrazide (H_4PTCH) Complexes .

Compound	Colour	Weight (g)			Time of Elecrolysis (h)	Current (mA)	Metal Consumed (mg)	Mass of the Product (g)	% Yied	E_f
		Ligand	phen	ph_3P						
$Ni(BzH)_2(ac)_2.H_2O$	Green	0.27	-	-	2.5	20	60	0.45	95	0.54
$Ni(BzH)_2(phen)_2.H_2O$	Brown	0.27	0.2	-	2.5	20	56	0.48	96	0.51
$Ni(BzH)_2)(ph_3P).5/2H_2O$	Green	0.27	-	0.26	2.5	20	56	0.54	90	0.5
$Co(BzH)_2.5H_2O$	Pink	0.27	-	-	2.5	20	61	0.4	95	0.55
$Co(BzH)_2(ph_3P).5H_2O$	Brown	0.27	-	0.26	2.5	20	56	0.61	90	0.53
$Cu(BzH)_2(ac)_2$	Green	0.54	-	-	5.0	20	120	0.84	90	0.5
$Cu(BzH)_2(phen).1/2H_2O$	Brown	0.43	0.2	-	4.0	20	100	0.69	85	0.52
$Cu(BzH)_2(ph_3P)(H_2O).2H_2O$	Green	0.27	-	0.26	2.5	20	61	0.5	80	0.51
$Ni(MH)(H_2O)_2.2H_2O$	Pale blue	0.26	-	-	5.0	20	120	0.48	90	0.54
$Ni_2(MH)_2(phen)(H_2O)_3$	Brown	0.26	0.18	-	5.0	20	120	0.43	80	0.53
$Co(MH)(ac)_2.4H_2O$	Pink	0.21	-	-	4.0	20	90	0.38	90	0.5
$Cu(MH)(ac)_2.2H_2O$	Green	0.21	-	-	4.0	20	95	0.47	90	0.5
$Cu(MH)(phen).2H_2O$	Brown	0.21	0.15	-	4.0	20	96	0.56	90	0.5
$6Ni_2(PTCH)(ac)_4$	Pale green	0.28	-	-	5.0	20	107	0.32	70	0.49
$Co_2(PTCH)(ac)(H_2O)_3.2H_2O$	Pink	0.28	-	-	5.0	20	110	0.34	75	0.5
$Cu_2(PTCH)(ac)_2(H_2O)_2$	Dark green	0.28	-	-	5.0	20	120	0.49	96	0.5

ac = acetone, phen = 1,10-phenanthroline, ph_3P = triphenylphosphine

Table 2 : Experimental Conditions for the Direct Electrochemical Method for preparation of Acetylhydrazone (H_2ASH), Benzbenzylhydrazone (H_2BSH), 1,3-Malonyldisalisoylhydrazone (H_4MDSH) and 1,1`,3,3`,-Propanetetrasalisoyltetracarbohydrazone ($H_8PTSTCH$) Complexes.

Compound	Colour	Weight (g)			Time of Elecrolysis (h)	Current (m A)	Metal Consumed (mg)	Mass of the Product (g)	% Yield	E_f
		Ligand	phen	ph_3P						
$Ni(ASH)(ac)_2$	Brown	0.18	-	-	2.5	20	59	0.35	95	0.53
$Co(ASH).5H_2O$	Brown	0.36	-	-	5.0	20	120	0.66	90	0.54
$Cu(ASH)\ 6H_2O$	Brown	0.18	-	-	2.5	20	65	0.35	90	0.54
$Ni(BSH)\ 4H_2O$	Brown	0.24	-	-	2.5	20	58	0.30	80	0.52
$Ni(BSH)(phen)H_2O$	Brown	0.24	0.18	-	2.5	20	57	0.38	80	0.51
$Co(BSH)(H_2O)_3.4H_2O$	Brown	0.24	-	-	2.5	20	60	0.33	75	0.54
$Co(BSH)(ph_3P).3H_2O$	Brown	0.24	-	0.26	2.5	20	60	0.57	95	0.54
$Cu(BSH)(ac)_2.H_2O$	Green	0.24	-	-	2.5	20	61	0.34	95	0.51
$Cu_2(MDSH).6H_2O$	Green	0.68	-	-	5.0	40	250	0.85	75	0.52
$Co_2(MDSH).9H_2O$	Orange	0.68	-	-	5.0	40	240	1.5	95	0.52
$Cu_4(PTSTCH).12H_2O$	Dark brown	0.69	-	-	5	40	230	0.9	75	0.53
$Cu_4(PTSTCH)\ (ac)_4$	Green	0.35	0.35	-	2.5	40	120	1.53	80	0.5
$Co_4(PTSTCH)(DMSO)_8 8H_2O$	Brown	0.69	-	-	5	40	215	1.3	95	0.51
$Co_4(PTSTCH)(ac)_4.8H_2O$	Pale brown	0.35	0.36	-	2.5	40	115	0.68	90	0.51

ac = acetone, phen = 1,10-phenanthroline, ph_3P = triphenylphosphine

Table 3. Analytical, Magnetic and Molar Conductivity Vaules of the Hydrazide Complexes.

Compound	M.P., °C	Λ_m	μ_{eff} (B.M.)	% Calc.			% Found		
				C	H	M	C	H	M
$[Ni(BzH)_2(ac)_2].H_2O$	198	21.0	3.00	51.8	5.6	12.6	51.9	5.1	12.3
$[Ni(BzH)_2(phen)].H_2O$	242	17.9	2.95	59.2	4.5	11.1	58.8	4.6	10.9
$[Ni(BzH)_2(ph_3P).H_2O].3/2H_2O$	248	19.0	2.81	60.4	4.8	9.2	60.3	4.6	9.4
$[Co(BzH)_2.(H_2O)_2].3H_2O$	196	12.1	4.9	40.1	5.7	14.1	40.1	5.6	13.9
$[Co(BzH)_2(ac)_2]$	230	10.4	5.2	53.9	5.8	13.2	54.0	5.4	13.4
$[Co(BzH)_2(phen)].2H_2O$	239	11.2	-	57.2	5.1	10.8	57.3	5.0	10.6
$[Co(BzH)_2(ph_3P).(H_2O)].3/2H_2O$	246	15.1	2.88	56.4	5.7	8.6	56.4	5.5	8.6
$[Cu(BzH)_2(ac)_2]$	202	14.9	1.77	53.4	5.7	14.1	53.4	5.4	13.8
$[Cu(BzH)_2(phen)].H_2O$	238	17.6	1.52	59.7	4.4	12.1	59.7	4.9	12.6
$[Cu(BzH)_2(ph_3P)(H_2O)].1/2H_2O$	212	15.6	1.65	59.1	5.2	9.8	59.0	5.1	10.1
$[Co(MH)(ac)_2].4H_2O$	234	10.1	1.47	28.7	5.3	15.7	28.2	4.9	15.9
$[Cu(MH)(ac)_2].2H_2O$	232	10.8	1.84	31.2	5.7	18.4	30.5	5.3	18.5
$[Cu(MH)(phen)].2H_2O$	>290	11.6	1.69	44.0	4.4	15.5	44.5	4.7	15.3
$[Ni(MH)(H_2O)_2].2H_2O$	200	12.8	2.61	13.8	4.6	22.5	13.9	4.2	22.2
$[Ni_2(MH)_2(phen)(H_2O)_2].H_2O$	218	18.7	3.51*	35.3	4.3	19.2	35.2	4.9	19.2
$[Ni_2(MH)_2(ph_3P)(H_2O)_3]$	212	17.9	3.44*	41.8	4.8	16.9	41.7	5.0	17.5
$[Cu_2(PTCH)(ac)_2(H_2O)_2]$	>300	-	1.35*	28.3	5.1	23.0	28.6	4.9	23.2
$[Co_2(PTCH)(ac)(H_2O)_3].2H_2O$	>300	-	1.66*	22.3	5.2	21.8	22.3	5.3	21.4
$[Ni_2(PTCH)(ac)_4]$	>300	17.1	3.1*	36.7	5.7	18.8	36.8	5.6	18.6

ac = acetone, phen = 1,10-phenanthroline, ph_3P = triphenylphosphine

*) per metal atom

Table 4. Analytical, Magnetic and Molar Conductivity Values of Hydrazone Complexes.

Compound	M.P., °C	Λ_m	μ_{eff} (B.M.)	% Calc.			% Found		
				C	H	M	C	H	M
$[Co(ASH).(H_2O)_3].2H_2O$	>280	12.8	4.94	33.2	4.3	18.1	33.7	4.0	17.9
$[Co(ASH)(ac)_2(H_2O)].2H_2O$	>280	-	1.7	44.5	5.0	14.5	45.0	4.6	14.2
$[Cu(ASH)(H_2O)_3].3H_2O$	>280	10.2	1.6	31.0	4.0	18.2	30.8	3.7	17.8
$[Cu(ASH)(ac)_2.(H_2O)]$	>280	11.9	1.69	48.1	5.1	16.9	48.1	4.9	16.6
$[Ni(ASH)(ac)_2.H_2O]$	>280	12.4	2.61	48.8	5.4	16.1	49.0	4.8	16.2
$[Co(BSH)(H_2O)_3].4H_2O$	>300	-	2.04	39.6	5.2	13.9	38.8	4.7	13.8
$[Co(BSH)(ph_3P).(H_2O)_2].H_2O$	270	-	1.94	62.6	4.8	9.6	62.2	4.7	9.4
$[Cu(BSH)(ac)_2.H_2O]$	>300	11.5	1.74	54.9	4.5	14.5	54.9	4.6	14.2
$[Ni(BSH).(H_2O)_3].H_2O$	>300	11.9	2.44	45.5	4.8	15.9	45.4	4.5	16.0
$[Ni(BSH)(phen)\ H_2O]$	>300	11.6	2.56	58.8	3.8	11.0	59.2	4.3	10.9
$[Cu_2(MDSH)(H_2O)_4].2H_2O$	>300	-	1.15*	35.5	4.2	22.1	35.5	3.9	21.9
$[Co_2(MDSH)(H_2O)_6].3H_2O$	>300	-	1.77*	32.4	4.8	19.2	32.5	5.0	19.1
$[Cu_4(PTSTCH)(H_2O)_8].4H_2O$	>300	-	0.95*	36.4	4.2	22.0	36.4	4.6	21.8
$[Cu_4(PTSTCH)(ac)_4]$	>300	-	0.71*	48.2	4.1	21.7	48.3	4.2	21.6
$[Co_4(PTSTCH)(DMSO)_8(H_2O)_8]$	>300	-	1.33*	36.2	.5.3	13.9	35.8	.5.6	13.6
$[Co_4(PTSTCH)(ac)_4(H_2O)_8]$	>300	28.1	3.72*	43.5	5..0	18.1	43.5	50	17.9

ac = acetone, phen = 1,10-phenanthroline, ph_3P = triphenylphosphine

*) per metal atom .

Table 5 : Electronic and Ligand Field Parameters for Nickel(II) and Cobalt(II) Complexes.

Compound	V_1 (Calculated)	V_2	V_3	V_2 / V_1	Dq (cm^{-1})	B (cm^{-1})	β
$[Ni(BzH)_2(ac)_2].H_2O$	9945	16660	24690	1.67	6652	768	0.74
$[Ni(BzH)_2(phen)].H_2O$	9135	16390	21276	1.70	6228	680	0.65
$[Ni_2(MAH)_2(phen).(H_2O)_3]$	11365	18518	24390	1.62	7308	793	0.76
$[Ni_2(MAH)_2(ph_3P).(H_2O)_3]$	9411	16130	23800	1.71	7180	780	0.75
$[Ni_2(PTCH)(ac)_4]$	9315	16390	23250	1.75	7185	779	0.75
$[Co(BzH)_2(ac)_2]$	6740	14500	18500	2.15	776	852	0.88
$[Co(MH)(ac)_2].4H_2O$	7345	15750	18870	2.14	840	839	0.86
$[Co_2(PTCH)(ac)(H_2O)_3].2H_2O$	7330	15750	19420	2.15	841	878	0.91
$[Co(ASH)(H_2O)_3].2H_2O$	8463	15870	18860	1.87	840	834	0.86
$[Co(ASH)(ac)_2(H_2O)].2H_2O$	8350	15620	19600	1.87	835	894	0.92
$[Co(BSH)(H_2O)_3].4H_2O$	7703	14390	18870	1.87	780	880	0.91
$[Co(BSH)(ph_3P)(H_2O)_2].4H_2O$	8270	15500	18200	1.90	820	800	0.82

ac = acetone, phen = 1,10-phenanthroline, ph_3P = triphenylphosphine.