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Journal homepage: <http://www.journalijar.com>**INTERNATIONAL JOURNAL  
OF ADVANCED RESEARCH****RESEARCH ARTICLE****COORDINATION COMPOUNDS OF BUTANE-1,1',4,4'- TETRACARBOXYLIC ACID  
TETRAKIS-(SALICYLALDEHYDENE HYDRAZIDE): THEIR PREPARATION,  
CHARACTERIZATION AND STRUCTURAL INVESTIGATION****Ragab R. Amin<sup>1</sup>, Taj Al-ansi<sup>2</sup>, Fathi Al-Azab<sup>3</sup> and Ahmed A.M. El-Reedy<sup>4</sup>****1,4** Basic-Applied Science Department, Faculty of Oral and Dental Medicine, Nahda University, Beni-Suef, Egypt**2,3** Chemistry department, Faculty of science, Sana'a university, Sana'a, Yemen**Manuscript Info****Manuscript History:**

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hydrazides; hydrazones; butane-1,1',4,4'-tetracarboxylic acid tetrakis(salicylaldehydenezhydrazide).

**\*Corresponding Author****Ragab R. Amin<sup>1</sup>****Abstract**

There has been increasing interest in the use of hydrazides, hydrazones and their metal derivatives for a wide range of applications. Transition metal complexes have been prepared by chemical and electrochemical techniques with butane-1,1',4,4'-tetracarboxylic acid tetrakis (salicylaldehydenezhydrazide) ( $H_8L$ ). Electrochemical preparations using the metals as sacrificial anodes in non-aqueous acetone solution of the ligand were carried out and it has been found that the ligand reacts with bivalent metal ions to form polynuclear complexes. Elemental analyses, magnetic measurements, IR as well as electronic spectral studies have been used to elucidate the stoichiometry and to investigate the structures of the prepared complexes. It was found that the ligand has four hydrazone moieties and coordinates with the metal ions as ONO system forming tetranuclear complexes. Coordination is through the phenolic oxygen, the azomethine nitrogen and the carbonyl groups of the ligand.

*Copy Right, IJAR, 2015.. All rights reserved***INTRODUCTION**

A large number of metal complexes formed with hydrazide and hydrazone derivatives have been reported.<sup>(1-7)</sup> The literature indicates that there is great interest in the synthesis of new hydrazides and hydrazones due to the complexing affinities towards various metal ions.<sup>(7-10)</sup> This paper reports the chemical and electrochemical synthesis of Cu(II), Co(II) and Ni(II) complexes with the novel ligand butane-1,1',4,4'-tetracarboxylic acid tetrakis-(salicylaldehydenezhydrazide) (Fig. 1).

**EXPERIMENTAL****Materials**

Metals (Cu, Co and Ni) (Alfa) were supplied in the form of rods of approximately 1 cm diameter and 2 cm length or as 2 x 2 cm<sup>2</sup> sheets.

## Synthesis of the Ligand Butane-1,1',4,4'-tetracarboxylic Acid

### Tetrakis(salicylaldehydenehydrazide)

1,1',4,4'-Tetracarboxylic acid tetraethylester was prepared by adding 0.1 mole (9.5 mL) of 1,2-dichloroethane to 0.2 mole of mono-sodium diethyl malonate (37.4 g dissolved in 40 mL ethanol) and the mixture was refluxed on a water bath with continuous stirring for 1 h. On pouring 300 mL water into the reaction mixture, the tetraester was separated and collected and dried over anhydrous  $\text{MgSO}_4$ ; the yield is 19 mL (54%).<sup>(5)</sup> The prepared butane-1,1',4,4'-tetracarboxylic acid tetraethylester (0.05 mole, 17.5 mL) was added drop-wise with constant stirring to a solution of hydrazine hydrate (0.2 mole, 11 mL) in 30 mL absolute ethanol. The reaction mixture was refluxed on a water bath for one hour. The white precipitate of butane-1,1',4,4'-tetracarboxylic acid tetrahydrazide formed, was separated by filtration, washed with a EtOH- $\text{H}_2\text{O}$  mixture (5 : 1) and dried in a vacuum desiccator over anhydrous  $\text{CaCl}_2$ ; the yield was 13 g (89 %).<sup>(5)</sup> A molar ratio of 4:1 of salicylaldehyde(3.3 mL, 2.5 mmol) and butane-1,1',4,4'-tetracarboxylic acid tetrahydrazide (2.9 g, 10.0 mmol) was mixed in ethanol at 45 °C (25 mL) with continuous stirring. A yellowish precipitate formed and the reaction mixture was refluxed on a water bath for two hours at 45 °C. The formed precipitate was filtered, washed with ethanol, diethyl ether and dried. The final product was butane-1,1',4,4'-tetracarboxylic acid tetrakis(salicylaldehydenehydrazide).

### Electrochemical Cell

The cell used in the electrochemical reaction consists of a tall-form 100 mL Pyrex beaker containing 50 mL of the appropriate amount of butane-1,1',4,4'-tetracarboxylic acid tetrakis(salicylaldehydenehydrazide) dissolved in acetone solution. The cathode is a platinum wire of approximately 1 mm diameter. In most cases, the metal (2-5 g) was suspended and supported on a platinum wire.<sup>(11-13)</sup>

### Electrochemical Synthesis of $[\text{Cu}_4(\text{L})(\text{H}_2\text{O})_8]$

The ligand (0.71 g, 1.00 mmol) was dissolved in the minimum amount of DMSO (0.5 mL) followed by the addition of 50 mL of acetone and 2.5 mg of  $\text{Et}_4\text{NClO}_4$ . When the current was passed through the cell for 4 hours, a green precipitate was formed. It was collected, washed with diethyl ether and dried.  $[\text{Co}_4(\text{L})(\text{H}_2\text{O})_{12}]$  and  $[\text{Ni}_4(\text{L})(\text{ac})_4(\text{H}_2\text{O})_4]$  were synthesised similarly.

### Chemical Synthesis of Metal Complexes

A hot ethanolic solution (30 mL) of the ligand, butane-1,1',4,4'-tetracarboxylic acid tetrakis(salicylaldehydenehydrazide) (0.71 g, 1.00 mmol) dissolved in 0.5 mL of DMSO was added to in the molar ratio 1:4 with to an 85 % aqueous ethanol solution (30 mL) of 4.0 mmol of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.8 g),  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (1.0 g) or  $\text{Ni}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.82 g). The reaction mixture was refluxed on a water bath for three hours and then concentrated to one third of its volume. The respective brown, orange or yellow precipitates were filtered, washed with ethanol and dried<sup>(10)</sup>.

### Physical Measurements

Carbon and hydrogen analyses were carried out by the Microanalytical Unit of Cairo University. Metal ions were determined complexometrically by standard methods.<sup>(15)</sup> Magnetic measurements were carried out by the Gouy method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as a calibrating agent. Infrared spectra in the range 4000-400  $\text{cm}^{-1}$  were recorded

on a Perkin-Elmer 1430 Ratio spectrometer with samples in KBr pellets. The  $^1\text{H}$  NMR spectra was recorded on an EM-390 (90 MHz) NMR spectrometer using deuterated acetone as solvent.

## RESULTS AND DISCUSSION

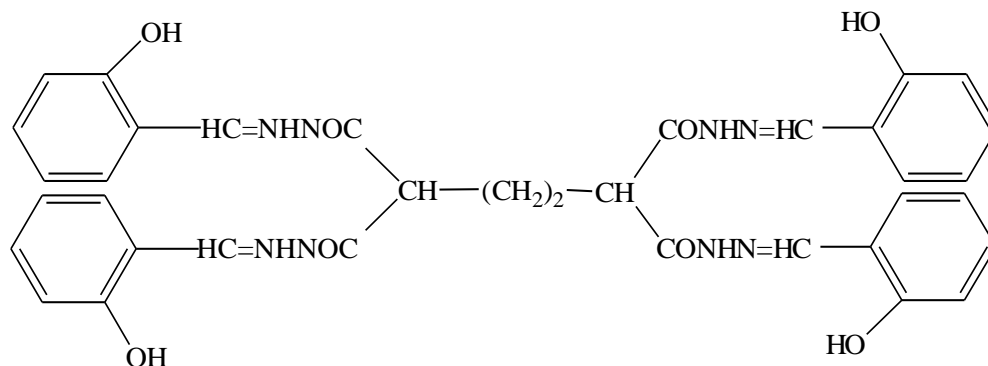
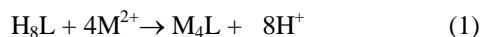


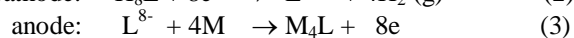
Fig. 1. Structure of the ligand butane-1,1',4,4'-tetracarboxylic acid tetrakis-(salicylaldehydehydrazide) ( $\text{H}_8\text{L}$ )

### Synthesis of the Complexes

Table I list the colors, elemental analyses and the magnetic measurements of the prepared metal(II) complexes as prepared by the chemical and electrochemical methods. All of the solid complexes are stable towards atmospheric conditions and are soluble in DMSO or DMF. The 4:1 complexes have been obtained by interaction of the ligand ( $\text{H}_8\text{L}$ ) with nickel(II), copper(II) or cobalt(II) acetate with subsequent precipitation, according to the following general equation,



where  $\text{M} = \text{Ni(II)}, \text{Cu(II)}$  or  $\text{Co(II)}$  and  $\text{H}_8\text{L}$  is the ligand. It is evident from the elemental analyses that butane-1,1',4,4'-tetracarboxylic acid tetrakis-(salicylaldehydehydrazide) forms complexes with 4:1 (metal-ligand) stoichiometry. The 4:1 complexes have also been prepared by the electrochemical method. The electrochemical synthesis is based on the direct oxidation of a sacrificial anode in non-aqueous solution containing the appropriate ligand to produce the metal complexes.<sup>(7, 11)</sup> The oxidation states of the metal ions in the isolated complexes by the electrochemical reaction are indicated by calculating the electrochemical efficiency,  $E_f$ , defined as moles of metal dissolved per Faraday of charge.<sup>(12,13)</sup> The  $E_f$  values listed in Table II show that the reactions of butane-1,1',4,4'-Tetracarboxylic acid tetrakis-(salicylaldehydehydrazide) with copper, cobalt and nickel are occurring as shown in equations (2) and (3).



Butane-1,1',4,4'-tetracarboxylic acid tetrakis-(salicylaldehydehydrazide) can coordinate metal ions as anionic species upon deprotonation and ligates in the enol form.<sup>(4,5)</sup> The analytical and spectral data indicate that the ligand  $\text{H}_8\text{L}$  has four hydrazone moieties and coordinates with the metal ions as ONO system through the phenolic oxygen, the azomethine nitrogen and the carbonyl groups forming tetranuclear complexes. The other coordination positions are occupied by water and/or acetone molecules in an octahedral structure.

**Table I. Analytical and Magnetic Values of Hydrazone Metal Complexes Synthesized by Chemical and Electrochemical Methods.**

	Compound	Color	M.p.	Empirical Formula	Formula Weight	$\mu_{\text{eff}}$ (B.M.) <sup>a</sup>	Yields, in %	Analytical data Found (calc.) %		
								C	H	M
-	H <sub>8</sub> L	<b>Yellow</b>	248	C <sub>36</sub> H <sub>34</sub> O <sub>8</sub> N <sub>8</sub>	706.732	-	97	60.9 (61.2)	5.1 (4.85)	-
(1)	[Cu <sub>4</sub> (L)(H <sub>2</sub> O) <sub>8</sub> ] $\cdot$ 2H <sub>2</sub> O <sup>b</sup>	Brown	>300	C <sub>36</sub> H <sub>46</sub> Cu <sub>4</sub> N <sub>8</sub> O <sub>18</sub>	1132.998	1.1	85	38.4 (38.2)	4.3 (4.1)	22.0 (22.4)
(2)	[Cu <sub>4</sub> (L)(ac) <sub>4</sub> ] <sup>b</sup>	Green	>300	C <sub>48</sub> H <sub>50</sub> Cu <sub>4</sub> N <sub>8</sub> O <sub>12</sub>	1185.152	0.75	90	48.3 (48.6)	4.2 (4.3)	21.6 (21.5)
(3)	[Co <sub>4</sub> (L)(ac) <sub>4</sub> (H <sub>2</sub> O) <sub>8</sub> ] <sup>b</sup>	Paige	>300	C <sub>48</sub> H <sub>66</sub> Co <sub>4</sub> N <sub>8</sub> O <sub>20</sub>	1311.092	3.85	92	43.8 (44.0)	5.0 (5.1)	17.9 (18.0)
(4)	[Cu <sub>4</sub> (L)(H <sub>2</sub> O) <sub>8</sub> ]	Green	>300	C <sub>36</sub> H <sub>42</sub> Cu <sub>4</sub> N <sub>8</sub> O <sub>16</sub>	1096.956	1.3	84	40.0 (39.4)	3.7 (3.9)	22.7 (23.2)
(5)	[Co <sub>4</sub> (L)(H <sub>2</sub> O) <sub>12</sub> ]	Brown	>300	C <sub>36</sub> H <sub>50</sub> Co <sub>4</sub> N <sub>8</sub> O <sub>20</sub>	1150.832	3.9	81	37.3 (37.6)	4.1 (4.4)	19.8 (20.5)
(6)	[Ni <sub>4</sub> (L)(H <sub>2</sub> O) <sub>4</sub> ]	Yellow	>300	C <sub>36</sub> H <sub>34</sub> Ni <sub>4</sub> N <sub>8</sub> O <sub>12</sub>	1005.664	2.8	75	42.8 (43.0)	3.3 (3.4)	23.0 (23.4)

<sup>a</sup>For every metal ion, <sup>b</sup>Complexes synthesized by the Electrochemical method; ac = acetone

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								C	H	M
-	H <sub>8</sub> L	Yellow	248	C <sub>36</sub> H <sub>34</sub> O <sub>8</sub> N <sub>8</sub>	706.732	-	97	60.9 (61.2)	5.1 (4.85)	-
(1)	[Cu <sub>4</sub> (L)(H <sub>2</sub> O) <sub>8</sub> ] $\cdot$ 2H <sub>2</sub> O <sup>b</sup>	Brown	>300	C <sub>36</sub> H <sub>46</sub> Cu <sub>4</sub> N <sub>8</sub> O <sub>18</sub>	1132.998	1.1	85	38.4 (38.2)	4.3 (4.1)	22.0 (22.4)
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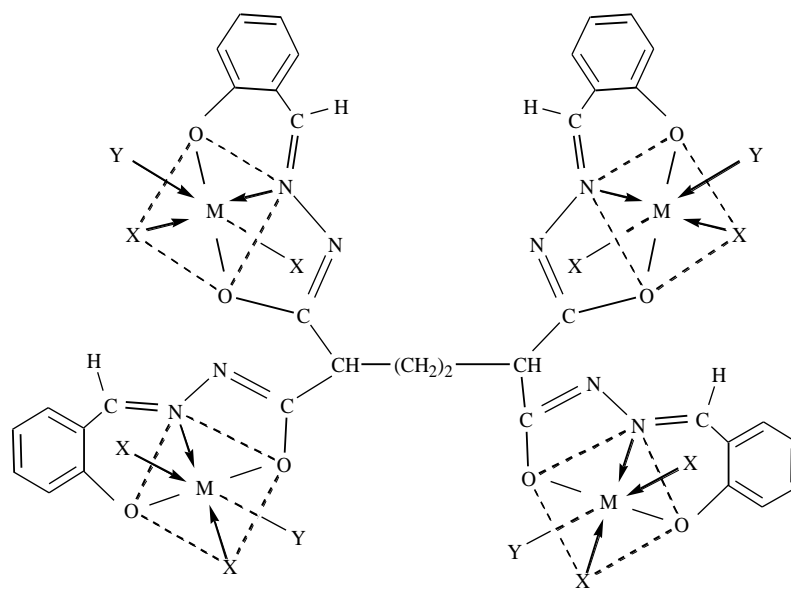
<sup>a</sup>For every metal ion, <sup>b</sup>Complexes synthesized by the Electrochemical method; ac = acetone



skeletal vibrations at 1278 and 785  $\text{cm}^{-1}$  are absent in the IR spectra of the complexes. The aromatic ring vibrations shift to lower frequency, to 1540 for the 1572  $\text{cm}^{-1}$  band and to 1472  $\text{cm}^{-1}$  for the 1488  $\text{cm}^{-1}$  band. The band intensity of the ring vibrations also increases upon complexation, particularly the band at 1448  $\text{cm}^{-1}$ , probably because of the polarization induced by the  $L \rightarrow M$   $\sigma$ -bonding. Intensification and broadening of H-bonded O-H modes near 3400  $\text{cm}^{-1}$  for  $\nu(\text{O-H})$  and the multiplicity observed in the vicinity of 1300  $\text{cm}^{-1}$  may be assigned to participation of water molecules in the coordination. <sup>(17-24)</sup> The value of magnetic susceptibility (2.8 B. M.) support the octahedral structure for  $[\text{Ni}_4(\text{L})(\text{H}_2\text{O})_4]$ . <sup>(14)</sup> In effect, intensification and broadening of the  $\nu(\text{C-O})$  at  $1017 \pm 3 \text{ cm}^{-1}$  might be taken as evidence for strong H-bonding between coordinated water and the salicyl oxygen involved in the complexation. Unfortunately, the limited frequency range of our instrument limited further interpretation of structural shifts, particularly for the L-M bonding, which is of importance for distinguishing between the various transition metal complexes. The non-ligand bands occurring in the 410–420  $\text{cm}^{-1}$  range in the spectra of all complexes may be tentatively assigned to  $\nu(\text{M-N})$  vibrations. <sup>(18-24)</sup> The respective magnetic moment values (3.85 and 3.9 B.M.) for  $[\text{Co}_4(\text{L})(\text{ac})_4(\text{H}_2\text{O})_8]$  and  $[\text{Co}_4(\text{L})(\text{H}_2\text{O})_{12}]$  are near the values for high-spin octahedral cobalt(II) complexes.

## Conclusion

On comparing the solid complexes of butane-1,1',4,4'-tetracarboxylic acid tetrakis-(salicylaldehydenezhydrazide) obtained by either the chemical or electrochemical method, we found that there is a similarity in the structure between the isolated complexes. The ligand reacts in the enol form either by a chemical reaction with metal(II) acetate or by anodic oxidation of the metal in non aqueous solution. The suggested structures of the complexes are shown in Fig. 5



- 1):  $M = \text{Cu}$ ,  $X = \text{H}_2\text{O}$  &  $Y = 0$ , (2):  $M = \text{Cu}$ ,  $X = 0$  &  $Y = \text{acetone}$ , (3):  $M = \text{Co}$ ,  $X = \text{H}_2\text{O}$  &  $Y = \text{acetone}$   
 (4):  $M = \text{Cu}$ ,  $X = \text{H}_2\text{O}$  &  $Y = 0$ , (5):  $M = \text{Co}$ ,  $X = Y = \text{H}_2\text{O}$ , (6):  $M = \text{Ni}$ ,  $X = 0$  &  $Y = \text{H}_2\text{O}$

Fig. 5. Suggested Structures of the Complexes

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