

CHEMICAL AND PHYSICAL PROPERTIES OF COPPER (II) MIXED LIGAND COMPLEXES WITH SACCHARIN AND ASCORBIC ACID

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ABSTRACT

The novel mixed-ligand complexes of copper(II) with saccharin (Sac) and ascorbic acid (Asc) were synthesized and characterized by chemical and physical properties, UV-Vis spectrophotometry, FT-IR spectroscopy, X-ray powder diffraction, atomic absorption spectrophotometry and cyclic voltammetry. The $[\text{Cu}(\text{Asc})_m(\text{Sac})_n]$ complex was yellow polygonal crystals. The polygonal crystals dissolved in dimethylsulfoxide which present optimum absorbance at 271 nm. The IR spectrums showed functional groups at $\nu \text{ OH} = 3500 \text{ cm}^{-1}$, $\nu \text{ C=O} = 1612 \text{ cm}^{-1}$, $\nu \text{ C=C aromatic} = 1458 \text{ cm}^{-1}$, $\nu \text{ S=O} = 1300$ and 1145 cm^{-1} , $\nu \text{ C-O} = 1053 \text{ cm}^{-1}$, $\nu \text{ Cu-O} = 538 \text{ cm}^{-1}$ and $\nu \text{ Cu-N} = 424 \text{ cm}^{-1}$. The intensity and phase of X-ray powder diffraction of the complex corresponded with saccharin and ascorbic ligands phases. The complex showed electrical current at E_p is - 2.6650 V. Atomic absorption spectrophotometry indicated that the complex contains copper at 2.4 %w/w. Thermal decomposition of the complex was decomposed at higher temperatures, about 300 - 400 °C.

KEYWORDS: copper (II) complexes, saccharin, ascorbic acid, x-ray powder diffraction

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INTRODUCTION

Copper was the first metal to be widely used by humans. Humans have been using copper for nearly ten thousand years. Since ancient times, copper has been used by itself and in combination with other metals to make weapons, tools, and household items. Especially copper compound (such as copper sulfate) has been widely used. Copper sulfate is also used to preserve wood, electroplating, as leather tanning chemicals and mordant (fixative) in textile dyeing. Copper is still used today. In addition, it is used in agriculture, principally as a fungicide on crops (such as wheat), as a bactericide, as a pesticide to kill snails and slugs and as the water treatment to kill aquatic vegetation on swimming pool. Moreover, the copper sulfate solution mixed with calcium hydroxide to prevent mildew in vineyards. Since then, it has to use a formula called Bordeaux general distribution in agriculture.

During recent years, there has been increased interest in the general chemistry, structural

properties and reactivity of the metal complexes of saccharin. Saccharin ($\text{C}_7\text{H}_5\text{NO}_3\text{S}$), also called o-sulfobenzamide (Fig. 1a), is widely used as an artificial sweetening agent and its suspected carcinogenic nature [1, 2]. In particular, since it has been shown that it causes cancer in rats [3], saccharin joined the list of human potential cancer-causing substances the USA. After a long discussion, in 1997 saccharin was left on the list of potential human carcinogens [2]. However, the metal-saccharin compounds were suspected pathological effects. Therefore, a number of saccharine complexes with various metal ions have been extensively studied [1]. Structural and spectroscopic properties of saccharin in metal complexes with pyridine [4, 5] Cu (II) with saccharin and nicotinamide [6], imidazole and pyrazole [7, 2, 8] 2,2'-bipyridine [9] and 1,10-phenanthroline [10] have been reported.

Ascorbic acid is a naturally occurring organic compound with antioxidant properties. Ascorbic acid (Fig. 1b) has wide usage in medical practice for treatment some diseases caused by

degeneration of connective tissue. Investigated the complexation properties of ascorbic acid with components of biomembranes-bioligands [11]. They found that ascorbic acid has some complexation properties with different bioligands. From the above mentioned that copper (II) chloride is fungicide and bactericide, saccharine is an artificial sweetening agent and ascorbic acid is high antioxidant properties, therefore, the combine of three compounds are interesting. The complex of three substances may lead to an anti-microbial agent, antioxidant and compounds to treat diabetes. However, the copper (II) chloride, ascorbic acid and saccharin complex have not appeared in the chemical literature. The present paper reports the synthesis and chemical-physical properties of the new copper (II) complex with saccharin and ascorbic acid.

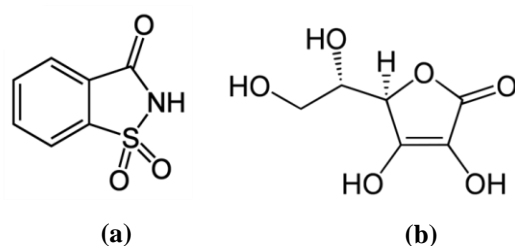


Fig. 1. The molecular structure of (a) saccharin and (b) ascorbic acid.

MATERIALS AND METHODS

2.1 Chemicals

All chemicals used were purchased from a chemical supplier quality. Sodium saccharin was a product of Sigma. Copper(II) chloride dihydrate is AJAX and ascorbic acid is Fluka.

2.2 Synthesis of copper complex compound

The copper complex compound was prepared by addition of 0.01 mole copper(II) chloride, 0.01mole sodium saccharin and 0.01mole ascorbic acid to 50 mL of distilled water. The aqueous solution was stirred by a magnetic stirrer for 30 minutes. All conditions were performed at pH 1.97 and temperature at 25°C. The yellow crystals were obtained. The crystals were washed with water and filtrated and keep in desiccators. The crystals have tested the decomposition and solubility.

2.3 Spectroscopic characterization of the complexes

Electronic absorption spectra

The electronic absorption spectra of the compound in the 255-400 nm range were measured in DMSO on a Shimadzu 1800 UV-Vis spectrophotometer.

Infrared spectroscopy

The structures of complexes were determined after they were dried by FT-IR (Shimadzu 8900). The samples were prepared in solid form by using KBr-pellet technique. KBr was dried at 110 °C for 12 h and kept in desiccators. The complex was mashed and mixed with KBr in ratio 1:10. The mixed sample was extruded to pellet by Evacuable KBr die machine with 8 tons. The air was pumped out of the machine by appropriate compression to 13 mm dish by the hydraulic press for 3-4 min. Infrared spectra were measured on an FT-IR allowing in controlled atmospheres and temperatures system. The samples were measured at a spectral 400 – 4000 cm^{-1} resolution for evaluating the functional groups of complexes.

Atomic absorption spectroscopic studies

Atomic absorption spectroscopic studies of the Cu (II) complex were carried out using Shimadzu 6200 atomic absorption spectrophotometer (AAS). Solutions for the determination of metal contents were prepared by digesting 0.05 g of the copper complex by 4 ml of 70% HNO_3 and 4 ml of 70% HClO_4 then the volume were diluted to 100 ml with 2% HNO_3 . A number of metals were measured against the blank solution using AAS.

2.4 Cyclic voltammograms studies

The electrochemical redox behavior of a Cu (II) complex with saccharin and ascorbic acid were analyzed by means of voltammetric (cyclic voltammetry). The copper complex solution was prepared by concentration of 1.0 ppm in DMSO and 0.2 M TBAB was used as the electrolyte solution.

2.5 X-ray powder diffraction

Powder X-ray diffraction analysis of complexes was modified [12]. The powder X-ray diffraction was performed by the x-ray diffractometer (SHIMADZU 6100) instrument with Cu-K_α radiation (wavelength 0.154 nm) operating at 40 kV and 30 mA. Measurements were scanned for diffraction angles (2 θ) at 25° with a step size of 0.02 ° and a time per step of 1 sec.

RESULTS AND DISCUSSION

3.1 Synthesis and physical properties of the synthesis compounds

The $[\text{Cu}(\text{Asc})_m(\text{Sacc})_n]$ complex was prepared by the reaction of copper(II) chloride, sodium saccharin and ascorbic acid in distilled water. The reaction was occurred with mole ratio of copper (II) chloride, sodium saccharin and ascorbic acid 0.01:0.01:0.01 mole respectively. The synthesis of this compounds from three substances as follows. The reaction between Cu (II) chloride and ascorbic acid was shown precipitate blue at pH 2.01, the reaction between Cu (II) chloride and sodium saccharin do not occur at pH 4.92 and the reaction between sodium saccharin and ascorbic acid was no reaction at pH 3.08. However, the reaction was occurred when three substances to react. The reaction among Cu (II) chloride, ascorbic acid and sodium saccharin was occurred the precipitate of yellow at pH 1.97. The results show that the complex was yellow polygonal crystals (Fig. 2).

The physical properties of complex were study by melting point and dissolution properties. The solubility test was done by shaking 1 mg of crystal with 10 ml of each solvent for 2 h. The solubility test of the complex was found that the polygonal crystals dissolve in dimethylsulfoxide (DMSO) but not dissolve in distilled water and benzene. Copper (II) chloride, ascorbic acid and sodium saccharin are dissolves in water with melting point at 498 °C, 190 °C and 228 °C, respectively. However, when all three substances to react until the complex were set, the solubility properties were changed. The complex was soluble in DMSO which is an organosulfur compound that soluble both polar and nonpolar compounds. The melting point of complex was not appeared. However, the complex was decomposed at high temperatures, about 300 – 400 °C. The results showed that the complex stable at room temperature.

3.2 Electronic spectra

The electronic spectra of the $[\text{Cu}(\text{Asc})_m(\text{Sacc})_n]$ complex and its ligands were recorded in DMSO between 255 and 400 nm. The compared dates of the UV-Vis spectra for the $[\text{Cu}(\text{Asc})_m(\text{Sacc})_n]$ complex and its ligands are shown in Fig. 3. The electronic spectra of the $[\text{Cu}(\text{Asc})_m(\text{Sacc})_n]$ complex is 271 nm which is a complete difference from its ligands demonstrating the formation of coordination compounds. The maximum absorption of copper (II) chloride, ascorbic acid and sodium saccharin are 295 nm, 261 nm and 273 nm, respectively. Copper (II)

chloride have the maximum absorbance 295 nm, but when new ligand's the absorbance was reduced to 271 nm. Moreover, the energy was higher to 7.34×10^{-20} kJ from 6.74×10^{-20} kJ (Table 1). The result shown that copper (II) ion was reacted by new ligands which are ascorbic acid and sodium saccharin.

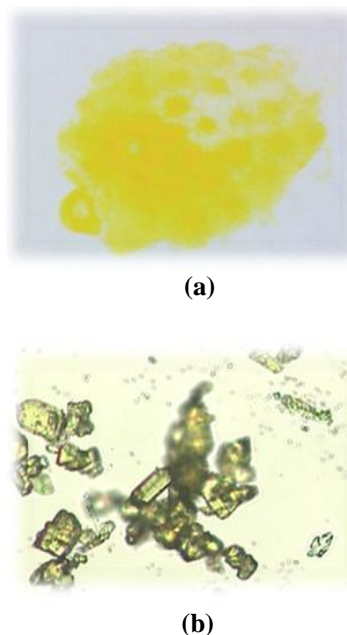


Fig. 2. The polygonal crystals of copper complex under microscope with 400x magnification.

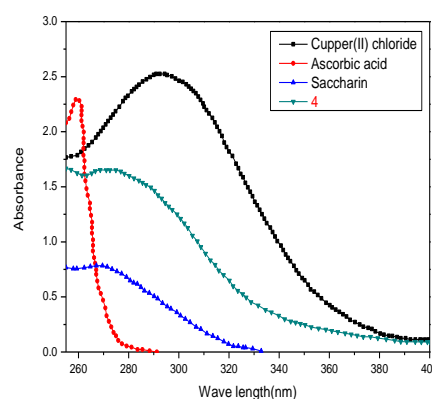


Fig. 3. The UV-Vis spectra of the $[\text{Cu}(\text{Asc})_m(\text{Sacc})_n]$ complex and its ligands (Copper (II) chloride, Ascorbic acid and Saccharin) in DMSO.

Table 1. The maximum wavelength (λ_{max}) and the energy (E) of the central atom, ligands and complexes synthesized.

Samples	λ_{max}	E (kJ)
CuCl ₂ .2H ₂ O	295	6.74 x 10 ⁻²⁰
Ascorbic acid	261	7.62 x 10 ⁻²⁰
Sodium saccharin	273	7.28 x 10 ⁻²⁰
[Cu(Asc) _m (Sacc) _n]	271	7.34 x 10 ⁻²⁰

3.3 FT-IR spectroscopic analysis

The existence of the complexes of the [Cu(Asc)_m(Sacc)_n] has been investigated by FT-IR spectroscopy. The key FT-IR spectral features of the [Cu(Asc)_m(Sacc)_n] are ν OH band at 3500 cm⁻¹, ν C=O band at 1612 cm⁻¹, ν C=C aromatic = 1458 cm⁻¹, ν S=O band at 1300-1145 cm⁻¹, ν C-O band at 1053 cm⁻¹ ν Cu-O = 538 cm⁻¹ [13] and ν Cu-N band at 424 cm⁻¹. The existence of these complexes was difference from the existence of sodium saccharin and ascorbic acid. The existence of sodium saccharin are ν C=O 1723 cm⁻¹, ν C-N 1337 cm⁻¹ and ν O=S=O 1055 cm⁻¹. Functional group of ascorbic acid is COOH and OH groups. Therefore, the existence of ascorbic acid are ν OH 3725, 3408, 3316, 220 cm⁻¹, ν CH 3040 cm⁻¹, ν C=O 1750 cm⁻¹, ν C=C 1665 cm⁻¹, ν C-O-C 1125 cm⁻¹, ν C-O 1046 cm⁻¹, and ν C-OH 1030 cm⁻¹. The wave number of functional group on the complex were differ with ligand such as ν OH band (3500 cm⁻¹: 3725, 3408, 3316, 220 cm⁻¹ (ascorbic acid ligand)), C=O (1612 cm⁻¹: 1750 cm⁻¹(ascorbic acid): 1723 cm⁻¹(sodium saccharin)), ν C=C (1458 cm⁻¹: 1665 cm⁻¹(ascorbic acid)) and ν C-O (1053 cm⁻¹: 1046(ascorbic acid)). Moreover, The existence of [Cu(Asc)_m(Sacc)_n] is clearly revealed by the typical Cu-O and Cu-N vibrations (Fig. 4). In the low frequency region, it can be observed a band centered at 424 cm⁻¹ and 538 cm⁻¹ attributed to the Cu-O and Cu-N stretching frequency, respectively [14,15]. The result shows that copper is a central ion with saccharin and ascorbic acid ligands. The FT-IR spectra of the [Cu(Asc)_m(Sacc)_n] complex is shown in Fig. 5. The proposed structure of the [Cu(Asc)_m(Sacc)_n] complex is shown in Fig. 4.

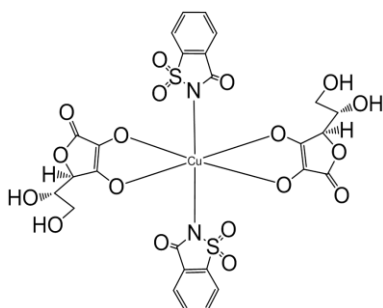


Fig. 4. The proposed structure of the [Cu(Asc)_m(Sacc)_n] complex

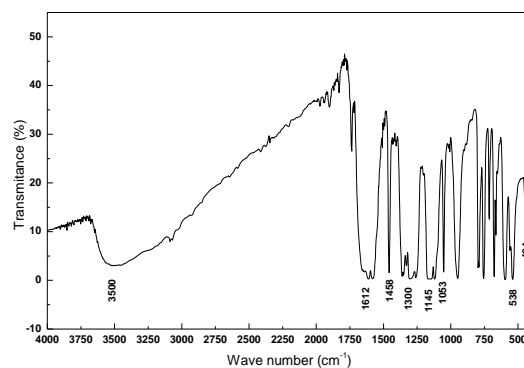


Fig. 5. The FT-IR spectrum of copper complex in the region of 400 - 4000 cm⁻¹.

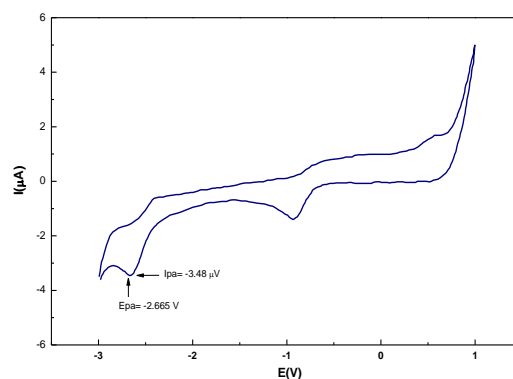


Fig. 6. The electrochemical curves of copper complex in DMSO solution (1.0 ppm).

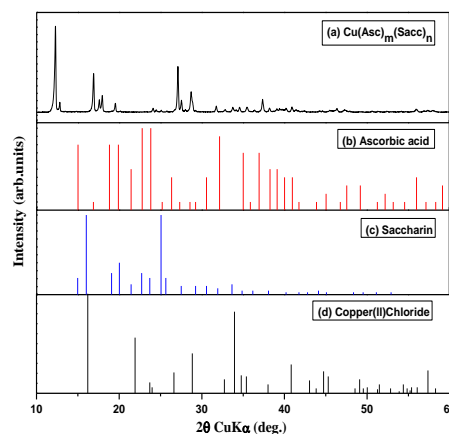


Fig. 7. The X-ray powder diffraction patterns of (a) [Cu(Asc)_m(Sacc)_n], (b) Ascorbic acid, (c) Saccharin and (d) Copper (II) Chloride.

CONCLUSION

The synthesis and chemical-physical properties of copper (II) ligand complexes with saccharin and ascorbic acid were presented for the first time. The existence of these complexes has been confirmed by FT-IR spectroscopy, which revealed that formation of these complexes by spectral region of Cu-N and Cu-O bond. Further, the formed complexes have been analyzed by AAS and X-ray powder diffraction. The X-ray powder diffraction of copper complex is corresponding to ascorbic acid and saccharin compounds.

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