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Synthesis and Structural Investigations of Copper Abietat Complexes

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The purpose of this study is to remove copper from wastewater by preparing copper abietat using abietic acid which exists in sunflower oil. For this, initially the abietic acid present in sunflower oil was obtained. Then copper abietat complex was obtained by extraction of these compounds at different pH values. The structure of copper abietat obtained at the appropriate pH range was studied using infrared spectroscopy, nuclear magnetic resonance and electron paramagnetic resonance techniques.

Key Words: Abietic acid, Copper abietat, Extraction, pH, EPR.

INTRODUCTION

The oil consists of a complex mixture of triglycerides with a variety of saturated and unsaturated compounds. The high iodine value (170-200) suggests the possibility of obtaining an appropriate drying oil that could compete with those of vegetable origin. The fatty acids are present with more than 22 carbons and up to six double bonds which oxidize easily, impairing the odor and colour of product.

Hixon and Bockelman[1,2] have studied the solubility of pure triglycerides and fatty acids in liquid propane by using vegetable oils. They determined CST for different components and studied the separation of such systems as propane-abietic acid-sunflower oil.

In coordination chemistry, complex compounds of carboxylic acids have important place[3-5]. In particular, the 3*d* metal carboxylates, creating a different type of metal-ligand bonds have attracted attention and mutual influence of spin-spin, ferrous and antiferromagnit complex is formed. Copper(II) coordination compounds, very important areas (especially bioanorganic and biomimetic) are used as a model[3-10].

The abietic acid has been found in sunflower oil. Because of having tricycle terpene abietic acid is different from the other acids. Its structure is the same as isoprene (Fig. 1). Generally, abietic acid shows the property of monocarboxylic acid[11].

Abietic acid is insoluble in water, but soluble in organic solvents. So the sodium salt of abietic acid is obtained from corresponding interaction of organic acid and aqeous solutions. First of all sodium abietate is synthesized. Later copper abietat has been obtained from reaction[12].

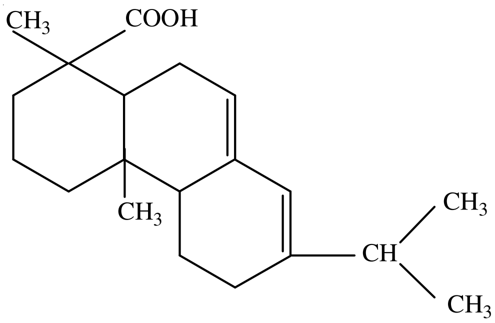

Fig. 1. Abietic acid

Copper, a commonly used heavy metal, which is found in many useful applications in our life is quite harmful discharged into natural water resources[14-16]. The toxicity of copper in humans has been comprehensively reviewed by some researchers. Acute copper poisoning after ingestion may show systemic effects such as hemolysis liver and kidney damage and fewer with influenza syndrome. Local effects reported irritation of upper respiratory tract, gastrointestinal disturbance with vomiting and diarrhea and a form of contact dermatitis[17]. Therefore, it is necessary to treat wastewater containing copper before being discharged into water streams[18].

Recent past has witnessed tremendous research work on sorption studies for removal of Cu(II) from aqueous solution using a wide range of different types of sorbent such as inorganic clay materials[19,20], natural polymers[21], synthetic polymers[22-25], lignocellulosic materials[26,27]. In addition, ion exchange resins have also been exploited for the removal of toxic metal ions[28,29]. However, these sorbents have only been confined to laboratory experiments due to classical problems related to plugging and fouling of packed column and membranes, *etc*. Moreover, the soft nature and the tendency to agglomerate are also major drawbacks associated with these sorbents[14].

Most unwanted wastes have adverse effects on human health and the environment, as they have in the structure of organic and inorganic pollutants. Heavy metals, dangerous for the environments are in large amounts and need to be removed from the environment. The purpose of this study is to remove copper from the environment by making complexes with abietic acid.

EXPERIMENTAL

All chemicals used in this study were of analytical purity. The solution of Cu(II) was prepared in 1 g/L concentration using $CuSO_45H_2O$. For pH adjustment 0.1 mol/L CH_3COOH and 0.1 mol/L NaOH were used. Extraction solutions of 10 % abietic acid ($C_{17}H_{13}O_2$) and 10 % NaOH were prepared by dissolving abietic acid in ether and NaOH in water.

IR spectra of copper abietat were recorded on a Shimadzu IR-470 spectrophometer. The NMR spectra were run in $CDCl_3$ on a Varian instrument at 300 MHz (Mercury plus) for ^1H NMR. In this study, EPR experiments were performed on powder sample of (Cu abietat) by using Bruker X band EMX-Model Elektron spin resonance spectrometer. The spectrometer parameters were adjusted as follows: microwave frequency- 9.78 GHz, microwave power - 20 mW, modulation amplitude - 10 Gauss and modulation frequency - 100 Hz. EPR parameters (tensor g and hyperfine splitting tensor A) were determined by computer analyzing of the experimental data by using a suitable model.

Preparation of the copper abietat: Thermometer, cooler and dropping funnel, containing NaOH solution (0.2 mol), were placed into 100 mL three necked flask, which contains abietic acid solution (0.2 mol). Copper complex was synthesized in the following way. Aqueous solution of NaOH was dropped into abietic acid in ether solution by running magnetic stirrer and heater. Sodium hydroxide was dropped for 1 h by mixing. The pH of the experimental conditions was made around 7-8. Then, $CuSO_4{\cdot}5H_2O$ (0.1 mol) solution for 1 h by mixing following this procedure, the mixure was waited for 24 h in room temperature. The solution was placed into extraction flask. Organic phase and water phase was separated. Copper abietat in organic phase, by removing ether, was crystallized and was obtained with 83.4 % yield.

$$4RH + 4NaOH \rightarrow 4RNa + 2CuSO_4 + 4H_2O$$

$$\rightarrow Cu_2R_4 2H_2O + 2Na_2SO_4 + 2H_2O$$

(where R = $C_{19}H_{19}CO_2$)

Synthesis of copper abietat in different pH values: In different ranges (3, 4, 5, 6, 7, 7.5, 8, 8.5, 9); nine samples were prepared by repeating the same experiment. Organic and water phases were seperated in solutions obtained from these samples. The amount of Cu^{2+} ions was determined by using atomic absorption spectroscopy (AAS).

RESULTS AND DISCUSSION

Formation of the copper abietat: Acoording to the result of spectral analysis, the following structure of copper abietat is proposed.

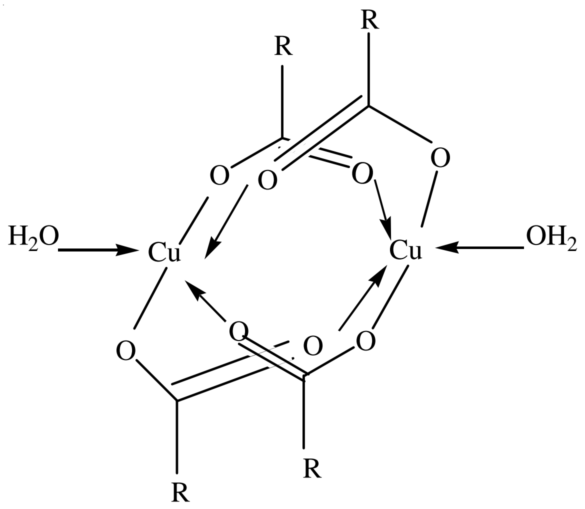

Fig. 2. Structure of copper abietat

Synthesis of copper abietat in different pH values: As a result of the experiment when the pH was 7.5 the transition of Cu^{2+} ions in the water phase into the organic phase was found to be at maximum level. The extraction percentage was 98.5 % in this pH value. After the pH value of 7.5, transition of Cu^{2+} ions from water phase into organic phase and also extraction percentage decreased. When pH was 7.5, sodium abietat was completely dissociated into carboxyl anions and sodium cations. When the solution is alkaline at pH 7.5, $Cu(OH)_2$ forms in lower yields in the reaction between NaOH and $CuSO_4$. The optimum pH very improtant in terms of reaction yield in obtaining copper abietat. Fort his purpose, the pH effect on share constant and extraction percentage were examined. Optimum pH value of products with the highest yield was found in the experiments. As seen from the following Table-1, the highest transition into organic phase was observed in the pH range of 7.5-8.5. The graphic of the share constants of copper abietat different pH values was shown in Fig. 3.

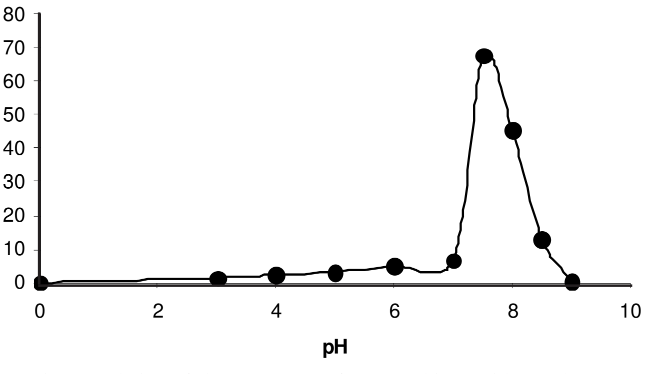

Fig. 3. Relation of share constant of copper abietat with pH change

$$E\ (\%) = \frac{\alpha}{(\alpha + V_{su}/V_{org})} \times 100$$

$$\alpha = \frac{C_{org}}{C_{su}}$$

E (%) = extraction percentage, α: share constant, V_{org}: The volume of organic phase (mL), V_{su}: the volume of water phase (mL), C_{org}: Cu^{2+} concentration in the organic phase (mg/mL), C_{su}: Cu^{2+} concentration in the water phase (mg/mL).

Characterisation of the copper abietat

FTIR spectral analysis: IR (KBr, ν_{max}, cm^{-1}): 1740 (C=O), 1605 and 3075 (C=C), 1380 and 1362 (isopropyl group), 1420 and 1550 (carboxylic group), 2985 ((-CH, $-CH_2$, $-CH_3$) (Fig. 4).

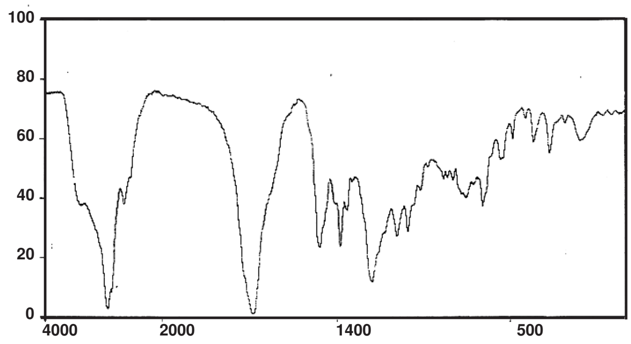

Fig. 4. IR spectrum of copper abieatat

^{1}H NMR spectral analysis: ^{1}H NMR ($CDCl_3$): δ ^{1}H NMR ($CDCl_3$) (300 MHz) δ 5.8 (1H, s), 5.4 (1H, br s), 1,2 (3H, δ, *J*: 6Hz), 1.0 (3H, s) 0.83 (3H, s) (Fig. 5).

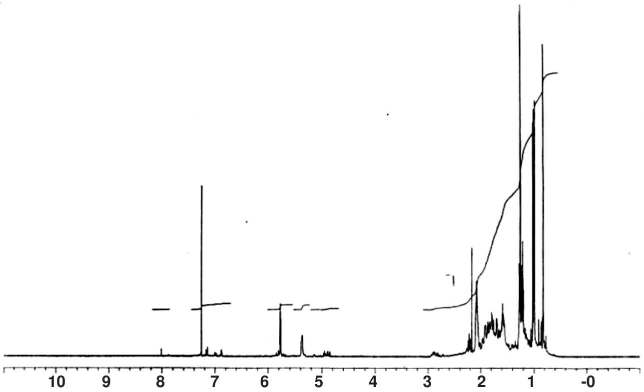

Fig. 5. ^{1}H NMR spectrum of copper abieatat

EPR spectral analysis: The EPR spectra recorded at the temperatures of 295 and 5 K are shown in Fig. 6. As can be seen from this figure, the spectrum at room temperature consists of three strong peaks and relatively broad and weak peak at 6 kG. Actually, the peak appeared at 3.25 kG contains unresolved small peaks. As it is also seen from the figure, considerable transformation of EPR spectrum takes place on decreasing the temperature and a single resonance line is observed at 3.25 kG at low temperatures. Additional broad peaks at 1.5 and 6.0 kG are cavity peaks at 5 K.

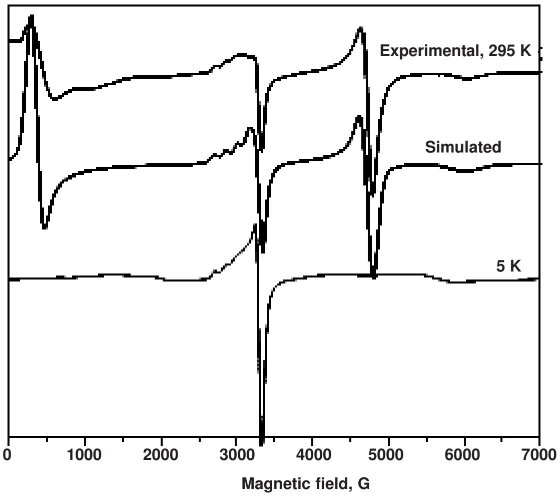

Fig. 6. Experimental and fitted EPR spectra recorded at various temperatures

It is known that for uncoupled Cu^{+2} ion $\left(S = \frac{1}{2}, I = \frac{3}{2}\right)$ one can normally expect one electronic transition (between the states $m_s = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$) to be splitted into four hyperfine structure peaks for a particular direction of external magnetic field with respect to the sample. If the sample is anisotropic, then the resonance field shifts as the direction of the external field is varied with respect to the sample axes. Therefore, for powdered samples one observes superposition of the spectra coming from individual particles that angularly distributed with respect to the experimental field. Thus, the resultant spectrum exhibits multi-component structure. The amount of the shifts will be limited by the anisotropy parameters. In present case the splitting of the main peaks from each others is unexpectedly very high that can not be attributed to the anisotropy of

TABLE-1
Cu^{2+} ION EXTRACTION FROM AQUEOUS SOLUTION

Volume off NaOH (mL)	Volume of abietic acid (mL)	Volume of $CuSO_4$ containing 1 mg/mL Cu^{2+}	pH	At the end of the extraction of Cu^{2+} volume		α	E (%)
				Water phase (mg/mL)	Organic phase (mg/mL)		
5	10	10	3.0	0.144	0.206	1.43	58.8
5	10	10	4.0	0.288	0.686	2.38	70.4
5	10	10	5.0	0.230	0.719	3.13	75.8
5	10	10	6.0	0.170	0.860	5.06	83.5
5	10	10	7.0	0.120	0.806	6.72	87.0
5	10	10	7.5	0.013	0.880	67.69	98.5
5	10	10	8.0	0.019	0.862	45.37	97.8
5	10	10	8.5	0.063	0.830	13.17	92.9
5	10	10	9.0	0.725	0.320	0.441	30.6

g-factor only. So, there should be additional effects at room temperature.

It is suggested that the observed peculiarities of EPR spectra at room temperature can be attributed to triplet state of binuclear copper compound. Similar EPR spectra for binuclear copper complexes are reported[30,31]. The resonance line at 3.25 G was shown to arise from the mononuclear impurities which can be found from similar system[32,33].

The spectrum at room temperature was analyzed by using fine structure term in addition to Zeeman and hyperfine interactions. Thus, the Hamiltonian describing Cu(II)-Cu(II) coupled system can be written as[34].

$$\begin{aligned} H = \beta_e(g_{xx}H_xS_x + g_{yy}H_yS_y + g_{zz}H_{zz}S_z) \\ +(A_{zz}I_zS_z + A_{yy}I_yS_y + A_{xx}I_xS_x) \\ + D\left\{S_z^2 - \frac{1}{3}S(S+1)\right\} \end{aligned} \tag{2}$$

Here, the first parenthesis is electronic Zeeman Hamiltonian, the second parenthesis is hyperfine interaction term between electronic spin S and nuclear spin I and the third term is axially symmetric zero field splitting Hamiltonian, where D is the zero field splitting parameter. The remaining symbols have been used with their usual meaning.

EPR parameters of the observed mononuclear part (there is no fine structure) of the spectrum were determined by simulation of the spectra using fitting parameters: $g_\perp = 2.35$, $g_\parallel = 2.065$ ($g_{xx} = g_{yy}$) and $A_\perp = 150$, $A_\parallel = 17$ Gauss ($A_{xx} = A_{yy}$). The simulated spectrum was given in the same figure with experimental ones (Fig. 7). These principle values of g tensor are comparable with the previous studies on the same kinds of Cu^{2+} complexes[35-38].

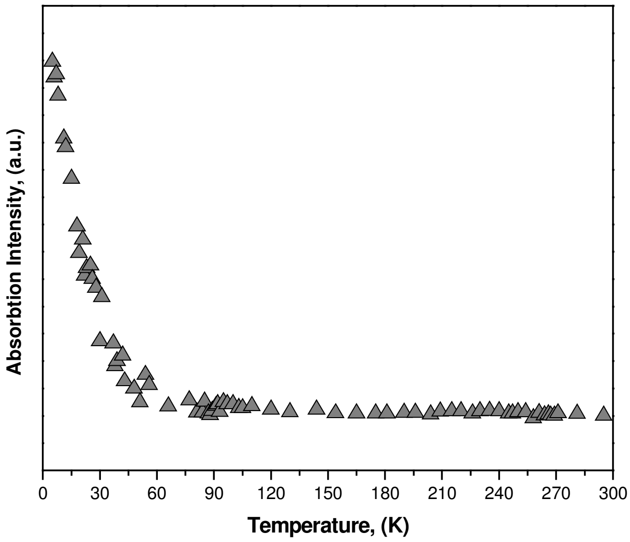

Fig. 7. Absorption intensity of powdered sample of copper abietat

From the computer analysis of the spectra the parameters for exchange coupled Cu(II)-Cu(II) pairs are obtained as $g_\perp = 2.65$, $g_\parallel = 2.07$ and $D = 0.427$ cm^{-1}. The exchange coupling parameter should be large enough in order to couple two electrons to form a triplet (S = 1) state and give ESR spectra even at high temperatures. The singlet-triplet energy gap was estimated from the following expression[39] as approximately 310 cm^{-1} by assuming r = 2.5 Å.

$$D = \frac{-J}{8}\left[\frac{1}{4}(g_\parallel - 2)^2 - (g_\perp - 2)^2\right] - \left[g_\parallel^2 + \frac{g_\perp^2}{2}\right]\frac{\beta^2}{r^3}$$

As it is seen from Fig. 7, only mononuclear Cu^{2+} transitions was observed in EPR spectrum at low temperatures. This means that the ground state of Cu center at low temperature is singlet. Additional broad peaks at 1500 and 5600 Oe are cavity peaks at 5K. The absorption intensity of the spectra at different temperature is shown in Fig. 7.

Conclusion

In present studies, the compound was identified as copper abieatat by comparison of its spectroscopic data. Its ^{1}H NMR revealed the presence of two unsaturated proton at δ 5.8 and 5.4 ppm with singlet and broaden singlet. The identical methyl protons attached to isoproyl carbon were observed 1.2 ppm with dublet (*J* = 6 Hz). Also protons signal at δ 1.0 was attributed to methyl protons at near to carbonyl carbon. In the IR spectrum of copper abieatat, it was realized a carbonyl group (1740 cm^{-1}), isoproyl group (1380 and 1362 cm^{-1}), an diene (1605 and 3075), carboxylic acid salt (copper abietat) (1420 and 1550 cm^{-1}) and aliphatic methyl, methine and methylene groups (2985 cm^{-1}). When looking for the EPR analysis of these compounds, copper abietat structure is clearly observed. In this way of metallic copper in wastewater from the environment can be removed by binding with abietic acid.

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