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EXTRACTION AND SPECTROTHERMAL STUDIES OF COPPER(II) DECANOATE COMPLEX

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Abstract: The extraction of copper (II) from 0.33 M Na_2SO_4 aqueous solutions with decanoic acid (HL) in chloroform at 25°C has been studied. The extracted species, when the decanoic acid compound was used alone, is $CuL_2.2(HL).2H_2O$. The complex of copper was synthesized and characterized by elemental analysis, infrared spectra, electronic spectra, X-ray diffraction (XRD), laser particle size analysis, and molar conductance measurements.

Keywords: Decanoic acid, metal carboxylate; extraction liquid; structural study.
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INTRODUCTION

The separation of copper in an industrial environment mainly uses the technique of liquid-liquid extraction with complexing agents. This method is used in many chemical processes for the production of inorganic salts such as chlorides of copper or cobalt. There are a wide variety of complexing agents and separation conditions to effect the liquid-liquid extraction of copper. These extractants are mostly organic phosphoric acids which have the ability to complex with nickel, copper or cobalt. The separation is performed using two phases; an organic that has a high affinity for complexing agent and an aqueous phase. The organic phase is the most commonly used jet fuel. It is necessary to adjust with high accuracy the parameters such as pH, the concentration of complexing agents, and the addition of salts to optimize the separation.

Carboxylic acids are organic molecules. The carboxylate of the higher fatty acids with the metal ions have many applications in different industrial areas such as driers in paints, the components of lubricating greases, stabilizers of plastics, catalysts, additives to fuels, as well as corrosion preventive materials (promoters of rubber–steel cord adhesion) [4], *etc*. Therefore, metal carboxylates have promising applications depending upon the metal used to make the complex.

EXPERIMENTAL SECTION

Reagents

Decanoic acid (98%, Fluka) was used as purchased. Chloroform was pre-equilibrated with an aqueous solution which did not contain copper(II). The ionic strength of the aqueous medium was assumed to be unity ($[Na_2SO_4]$= 0.33 M). The initial concentration of copper was 100 ppm.

Materials and measurements

Conductivity measurements were performed at 25±1°C on a DDSJ-308A conductivity meter with an electrode. The cell constant was determined by use of KCl standard aqueous solution. The molar conductivity (ΛM) of the complexes was measured using a $2.0 \cdot 10^{-3}$ mol.dm^{-3} solution in dimethyl formamide (DMF). X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer. An electron microscopy (SEM) coupled energy dispersive spectrometer-based (EDX) microanalysis was performed in chemical composition. Electronic spectra of complexes in chloroform ($CHCl_3$) were obtained using a SHIMADZU UV VISIBLE1240 spectrophotometer in the range of 1200–300 nm. Infrared spectra of the ligands and their metal complexes were measured using KBr discs with a Fourier transform infrared spectrometer (SHIMADZU FTIR 8400) covering the range 4000–400 cm^{-1}. Thermogravimetry (TG 70/217) Thristor-Power supply linse thermal analyzer was used to record simultaneous DTG and DTA curves in a static air atmosphere, at a heating rate 10°C min^{-1} in the temperature range 0-500°C using a platinum crucible.

Extraction and analytical procedures

An aqueous copper solution (30 mL, 1.57×10^{-3} M) was placed in a thermostated vessel at 25 ± 0,05 °C. The solution contained an equal volume of chloroform solutions containing 1×10^{-3}– 4×10^{-2} M of decanoic acid.

The time was sufficient since the equilibrium was reached rapidly. After equilibrium, both phases were allowed to stand for more than 20 min for a complete phase separation. The pH of the solution was adjusted to between 4 and 8 by adding a few drops of 0.2 M NaOH. The metal ion concentrations were determined in aqueous phase photometrically at 810 nm using a Philips UV-VIS SP6-36. The metal ion concentrations in the organic phase were calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction.

RESULTS AND DISCUSSION

Extraction equilibrium of copper(II) with decanoic acid

Decanoic acid is known to exist as a dimer in the solvent of low polarity such as chloroform, hexane, toluene, and benzene [3]. The extraction of the metal, by a dimerized decanoic acid, $(HL)_2$, in chloroform can be represented by the general equation:

$$jM^{2+} + \frac{j(n+p)}{2}(HL)_{org} \overset{K_{ext}}{\longleftrightarrow} (ML_n p(HL))_{org} + jnH^+ \quad \textbf{(1)}$$

Where the subscript org corresponds to organic phases, and j is the degree of polymerization of the complex;
M : Metal
$(HL)_2$ extractant in dimeric form in the solvent of low polarity;
n: cationic charge;
org : organic phase
K_{ext} : constant of extraction
p : number of monomeric acid contained in the complex.
The extraction constant can be written as the following expression:

$$K_{ex1} = \frac{[(ML_n p(HL))_{org}][H^+]^{jn}}{[M^{+2}]^j\left[(HL)_{2org}\right]^{j(n+p)/2}} \quad \textbf{(2)}$$

The distribution coefficient D of the metal between the organic and aqueous phases may be expressed as follows:

$$D = \frac{C_{M,org}}{C_{M,aq}} = \sum_j \sum_a \frac{j[ML_n H_L p]_{org}}{[Cu^{2+}]\alpha_M} \quad \textbf{(3)}$$

$$= \sum_j \sum_p \left(jK_{ex(j\,ah)}[M^{n+}]_{aq}{}^{(j-1)}\alpha_M{}^{-1}[(HL)_2]_{org}{}^{n+p/2}[H^+]^{-nj} \right) \quad \textbf{(4)}$$

Where M_{org} and M_{aq} are the total concentrations of the metal in the organic and aqueous phases, respectively, and the side reaction coefficient allowing for metal complex in the aqueous phase. If only $(ML_n(HL)_p)j$ is responsible for the extraction system, equation (5) is derived from equation (4).

$$logD = (j-1)log[M^{n+}]_{aq} + \frac{n+p}{2}log[(HL)_2]_{org} - njlog[H^+] - log\alpha_M + logj + logK_{ex} \qquad (5)$$

Extraction of copper(II) with decanoic acid

The stoichiometry of the extracted species was determined by analyzing the experimental data. The conventional slope analysis method was used. The experimental results are arranged according to equation (5).

Figure 1 shows the results obtained for the extraction of copper(II) with solutions of various decanoic acid concentrations. The degree of extraction of copper(II) increases with increasing pH and decanoic acid concentration. The plots of logD versus pH for various concentration of decanoic acid are straight lines with slopes equal to two (n=2), This suggests full neutralization of copper(II) valence leading to release of two protons as given by equation (6). The data in Figure 1 also reveal no dependence of copper distribution upon the aqueous copper concentration, thereby confirming the monomeric nature of the extracted complex (j=1, $\alpha_{Cu}=1$).

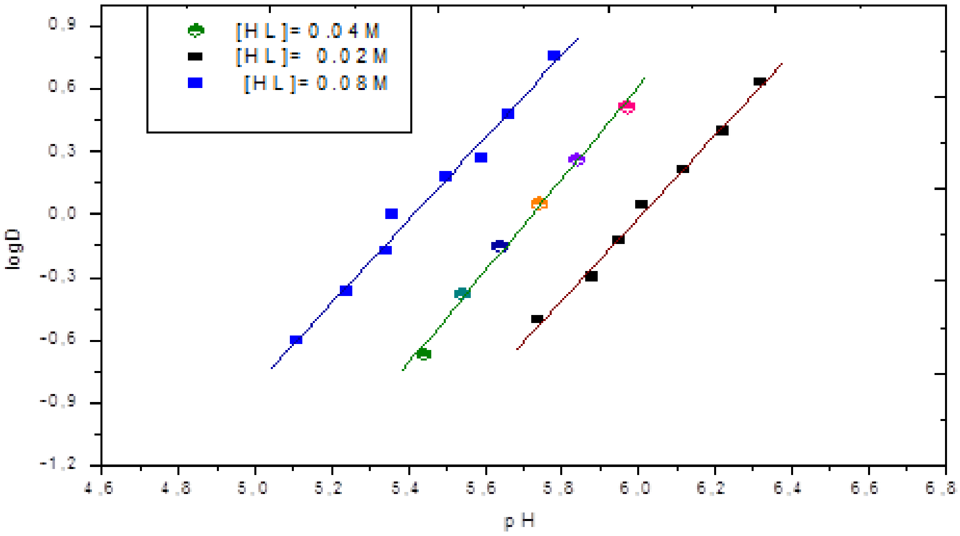


Figure 1. Extraction of copper (II) with decanoic acid.

$$Cu^{2+} + \frac{2+p}{2}(HL)_{2org} <=> CuL_2(HL)_{p\,org} + 2H^+ \qquad (6)$$

Under the present experimental conditions, the concentration of metal in organic phase is negligible when compared to the concentration of extractant, therefore, concentration of the dimer was calculated as $[(HL)_2] = [HL] / 2$. According to equation (4), the number of capric acid molecules involved in the monomeric species can be determined from the slope of the plots of (log D) against $\log[(HL)_2]_{org}$ at constant pH. The plots of log D versus $\log [(HL)_2]_{org}$ at constant pH values were also linear with a slope of $(2+p) / 2 = 2$, *i.e.*, $p = 2$, as shown in Figure 2. This suggests that two molecules of dimeric decanoic acid take part on the extraction of one ion of copper. This means that only the complex $CuL_2(HL)_2$ is extracted into chloroform [18].

The same type of extracted species was reported for the extraction of copper(II) with cyclopentylacetic acid [4] and α-bromostearic acid [5] in benzene. The complex formed has a structure of an adduct, in which particular places in the coordination sphere of copper ion is occupied in total by four molecules of the extractant.

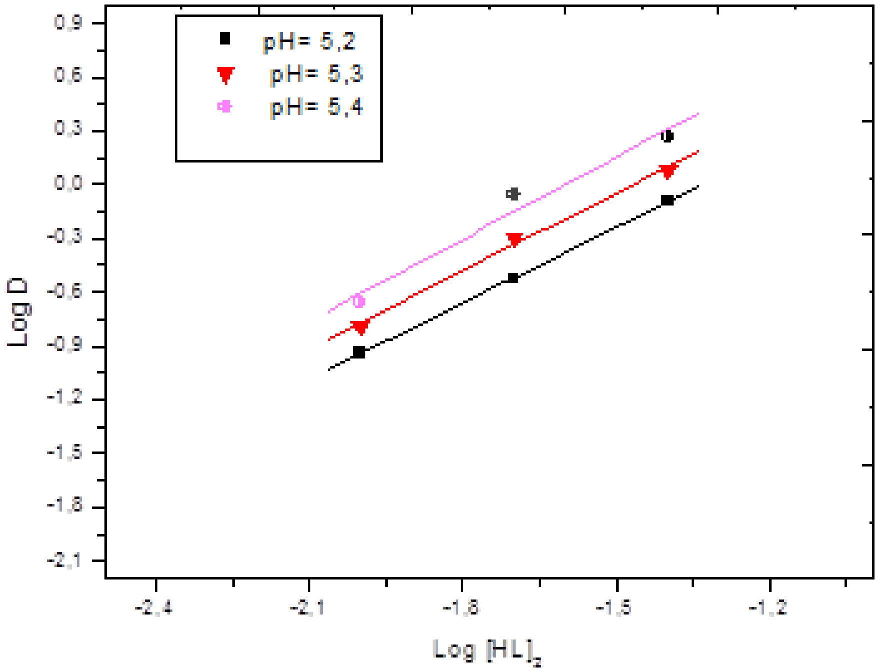


Figure 2. Effect of pH on the extraction of copper(II) with decanoic acid in chloroform.

The logarithmic value of K_{ex} of copper(II) can, therefore, be calculated for each experimental point ($\log K_{ex}=-7.2$).

Preparation of the complex

The organic solution of copper(II) carboxylate was prepared by solvent extraction from an aqueous $CuSO_4.5H_2O$ solution. During the extraction operation, the aqueous solution pH was adjusted at around pH 7 by the addition of dilute by a hydroxide solution. The initial concentration of copper(II) was 0.02 M. The initial concentration of free decanoic acid in the organic phase was 0.1 M. The single-metal carboxyl at solutions were washed with distilled water to remove residual anions and then passed through glass fiber paper and phase separating paper to remove physically entrained water. The precipitates were characterized by X-ray diffraction (XRD) analyses.

Microanalysis of complex copper(II) decanoate (EDX)

Electron microscopy (SEM) coupled with energy dispersive spectrometer microanalysis (EDX) is used in the chemical composition was also performed. Figure 3 is the composition of the different complex.

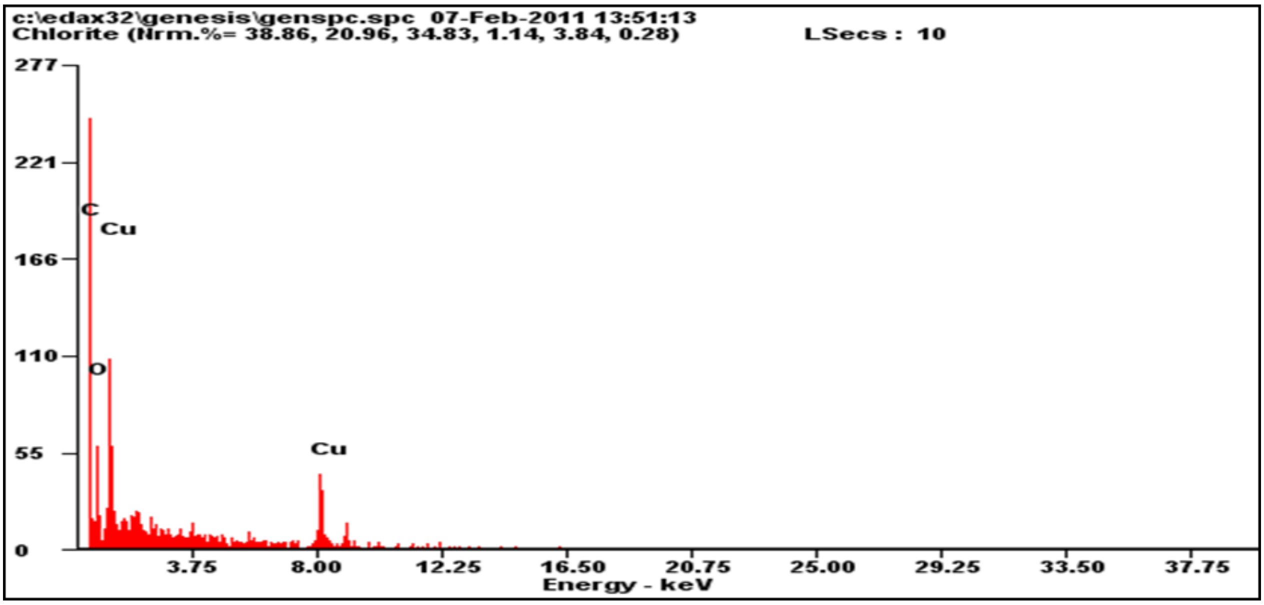


Figure 3. EDX pattern of copper (II) decanoate complex.

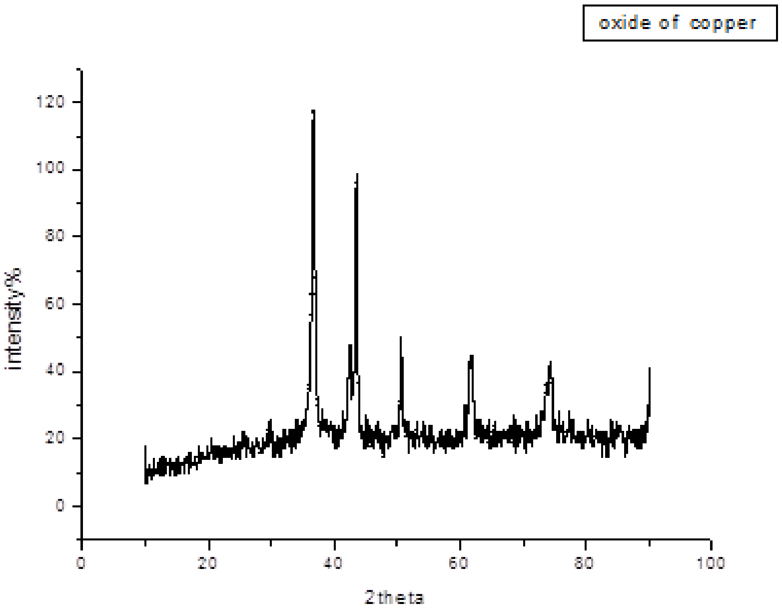
The contents of C, O, Cu(II) were determined by elemental analysis as shown in Table 1 [6].

Table 1. The analytical data of complex copper decanoate at 25 °C.

Element	Wt %	At %
L = $C_{10}H_{19}O$		
C K	4.70	20.46
O K	0.46	1.49
Cu K	94.84	78.04

X-Ray Diffraction

The measurement of lattice parameters of the powders was carried out using a Bruker D8 model type diffractometer with copper anticathode $\lambda_{Cu\alpha k}$ = 1,54 Å. The recording condition and 0.04 ° / 5 s to 2θ taken between 10° and 90° is shown in Figure 4. The crystallographic data for the complex and oxide of copper are listed in Table 2.



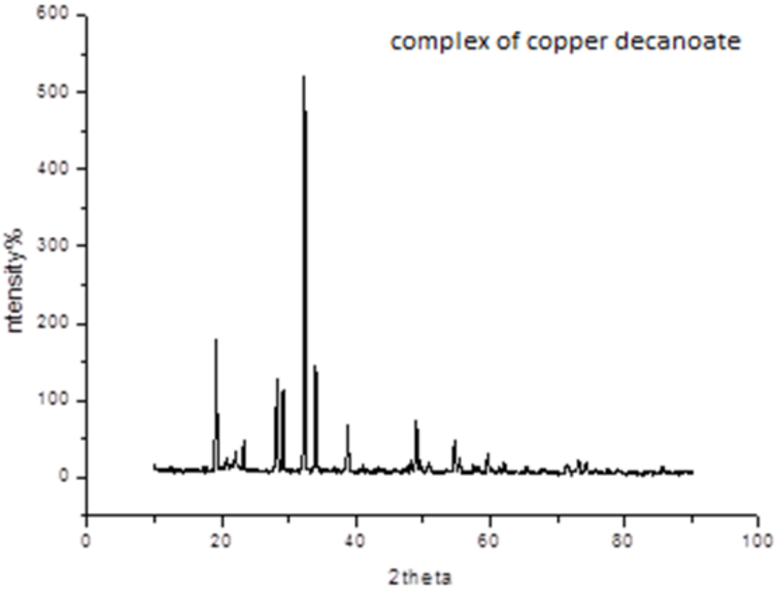


Figure 4. XRD patterns of complex copper(II) decanoate (top) and oxide of copper (bottom).

Table 2. Data of structure copper decanoate complex.

	Copper(II) decanoate complex	Cu_2O
Crystal system	monoclinic	Cubic
Space group	$P2_1/N$	PN3M
a (Å)	11.24	4.2494
b (Å)	4.68	4.2494
c (Å)	10.24	4.2494
α (°)	90	90
β (°)	92	90
γ (°)	90	90
V (A^3 °)	538	76.732
(h, k, l)	2≤h≤4 ,0≤K≤2 , 1≤h≤4	0≤h≤2 ,0≤K≤2 , 1≤h≤3

Molar conductivity measurements

Molar conductance value of the complex copper decanoate is found to be in the range 20.1-21.7 S. $cm^2.mol^{-1}$ in a dimethyl formamide (DMF) solution which proposes a non-electrolytic nature [7].

UV- Visible Spectra

The electronic absorption spectra of complexes were recorded in the range from 1200 to 400 nm at room temperature. The electronic absorption spectra are often very useful in the evaluation of results from other structural survey methods. Electronic spectral measurements were used to assign the stereochemistry of the metal ion in the complex based on the positions and the number of d-d transition peaks. Complexes' electronic absorption spectra were recorded in the range of 1100-400 nm, at room temperature. The electronic spectrum of the solid state of copper(II) has complex characteristics of Cu^{2+} ion octahedral environment of the strip is in the ranges from 690 to 680 [8, 9]. These transitions are characteristics of octahedral geometry of the metal atoms [10,11].

Infrared spectra

Fourier Transform Infrared spectra of the ligand and complex were recorded on Perkin Elmer Spectrometer Model -UMCAM FT.IR- 8400s using KBr pellets. The studied wavelength range from 4000 - 400 cm^{-1}, corresponds to the mid-infrared region. The infrared spectrum of the ligand shows a band at 3411 cm^{-1} can be attributed to the OH group. This band is absent in copper complex's spectrum and there is a strong C = O band at 1710 cm^{-1}, the bands were allocated to the asymmetric and symmetric vibrations of OCH_3 groups occurring at 2920 and 2849 cm^{-1}, respectively (Figure. 5). In the FTIR spectra of copper decanoate, the band at 1711 cm^{-1} disappears, which indicates that C=O group is not present in the analyzed complex [14].

Absorptions in the range of 1688-1678 and 1394-1352 cm^{-1} correspond to asymmetric and symmetric v(COO^{-}) frequency bound to metal carboxylate. The great difference in frequency Δv(COO^{-}) (Δv > 200 cm^{-1}) is indicative of monodentate coordination via both carboxylate groups [11, 12]. The copper complex shows strong bands in the region of 3420 and 3450 cm^{-1} range assignable to v(O-H) stretching vibrations of coordinated water molecules [7, 14]. The small bands of copper(II) to 478 cm^{-1} result from vibration v(M-O) expansion.

Analyses by thermogravimetric and differential A.T.G - A.T.D) precursor

In order to estimate beforehand calcination temperature for obtaining a well-crystallized oxide, the complex precursor was analyzed by thermogravimetric (T.G.A.) and differential temperature analysis (D.T.A.) respectively. On a Linseis 1600 type apparatus, a stream of air and in a temperature range of from ambient temperature to a temperature of 500 °C, using a heating rate of 10 °C / min was analyzed for our sample. The result for the composed precursor developed in ethanol as the solvent is represented in Figure 5. The thermal data of the complex are listed in Table 3. The composition of the intermediates and final products are those which best fit with the mass loss observed in the TG studies. Thermogravimetric results are in good agreement with the corresponding DTA data. The curves TG / DTA suggest the presence of [$CuL_2(HL)_2.2H_2O$] complex. The weight loss observed between 20 and 200 °C, corresponding with an endothermic peak at 100 °C is due to dehydration with a loss of two molecules of water (3.3%). The thermal decomposition is produced in two stages between 200-500 °C and may be observed that three exotherms and endotherm to two (300, 340 and 420 °C), respectively. The final residue, found to be Cu_2O, had an observed mass of 89.9% [11, 19].

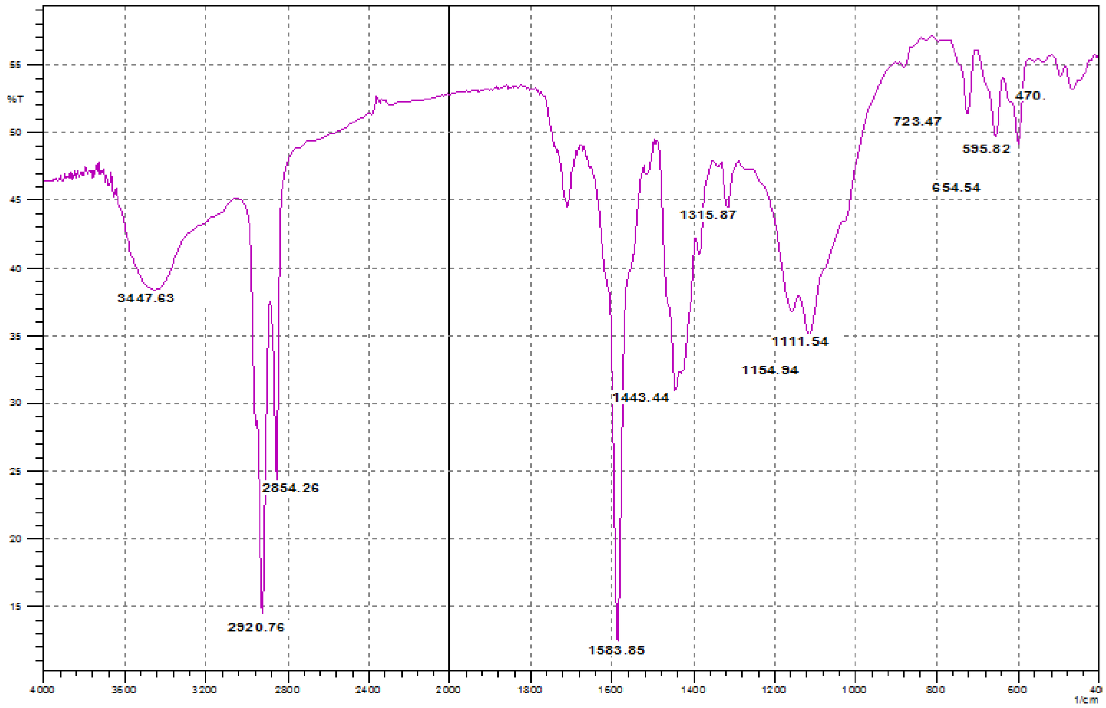


Figure 5. The infrared spectrum of copper decanoate complex.

Table 3. Thermal decomposition data of copper(II) complex with decanoic acid.

Complexes	T/°C	Mass loss / %	DTA / °C	intermediate product	color of the solid
[Cu(L2)(HL)$_2$].2H$_2$O	20-200	3.3	100	Cu(L$_2$)HL$_2$	blue
	200-500	89.9	exo / 420, 340, 300	Cu$_2$O	black

Particle size analysis

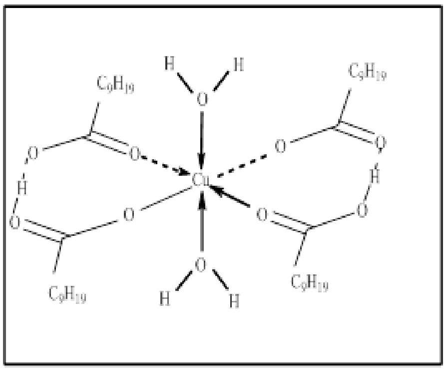
The particle size distribution depends on the diameter of the grains. They were chosen in order to show the influence of the complex on the particle size, made by laser granulometric method, showing the existence of two populations of medium sized complex copper decanoate, shown in Figure 6, representing a distribution of grain size in a range of sizes between 0.02 and 2000 µm (the first population of volume distribution of 2.83% and grain size 316.979 µm and second population is the volume of distribution of 3 to 84% and of size grains is 502.377178 µm. The main characteristics that can be extracted from analysis of the particle size complex are summarized in Table 4.

Table 4. Analysis of complex copper decanoate size distributions.

Average complex volume (µm)	d (0.1 µm)	d (0.5 µm)	d (0.9 µm)
[Cu(HL)$_2$L$_2$].2H$_2$O 230.134	6.465	77.891	168.468

Conclusion

Thus on the basis of above mentioned studies, it is proposed that the ligand is decanoic acid. The geometry of copper decanoate complex is proposed to be octahedral on nature as given of structure present (see Scheme 1).



Scheme 1. Structure of the copper decanoate complex.

REFERENCES

[1] Ensafi A. Simultaneous determination of trace amounts of cadmium, nickel and cobalt in water samples by adsorptive voltammetry using ammonium 2-amino-cyclopentene dithiocarboxylate as a chelating agent. Talanta. 2000 Jun 30;52(3):435–40. DOI: 10.1016/S0039-9140(00)00334-9.

[2] W.Lauo, Y. Hos, J Anal Chem Acta. 280: 893,(1993).

[3] Yamada H, Tanaka M. Solvent effects on extraction of copper with capric acid. Journal of Inorganic and Nuclear Chemistry. 1976 Jan;38(8):1501–4. DOI: 10.1016/0022-1902(76)90016-6.

[4] Aidi A, Barkat D. Solvent extraction of copper(II) from sulfate medium with N -(2-hydroxybenzylidene)aniline. Journal of Coordination Chemistry. 2010 Dec 10;63(23):4136–44. DOI: 10.1080/00958972.2010.530662.

[5] Bold L, Bluescu A Rev Roum Chim 23: 1631 (1978).

[6] 1. Hou H, Wei Y, Song Y, Mi L, Tang M, Li L, et al. Metal Ions Play Different Roles in the Third-Order Nonlinear Optical Properties of d10 Metal-Organic Clusters. Angewandte Chemie International Edition. 2005 Sep 19;44(37):6067–74.

[7] Rigin V. Simultaneous atomic fluorescence spectrometric determination of traces of iron, cobalt and nickel after conversion to their carbonyls and gas-phase atomization by microwave-induced plasma. Analytica Chimica Acta. 1993 Nov;283(2):895–901. DOI: 10.1016/0003-2670(93)85303-2.

[8] Geary WJ. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. Coordination Chemistry Reviews. 1971 Oct;7(1):81–122. DOI: 10.1016/S0010-8545(00)80009-0.

[9] Kumar G, Kumar A, Shishodia N, Garg YP, Yadav BP. Synthesis, Spectral Characterization and Antimicrobial Evaluation of Schiff Base Cu(II), Ni(II) and Co(II) Novel Macrocyclic Complexes. E-Journal of Chemistry. 2011;8(4):1872–80. DOI: 10.1155/2011/497279.

[10] Kurdekar GS, Sathisha MP, Budagumpi S, Kulkarni NV, Revankar VK, Suresh DK. 4-Aminoantipyrine-based Schiff-base transition metal complexes as potent anticonvulsant agents. Medicinal Chemistry Research. 2012 Sep;21(9):2273–9. DOI: 10.1007/s00044-011-9749-3.

[11] Lever ABP. Inorganic electronic spectroscopy. 2nd ed. Amsterdam ; New York: Elsevier; 1984. 863 p. (Studies in physical and theoretical chemistry). ISBN: 978-0-444-42389-4.

[12] Olmez H, Arslan F, Icbudak H. Spectrothermal studies on Co(II), Ni(II), Cu(II) and Zn(II) salicylato (1,10-phenanthroline) complexes. Journal of Thermal Analysis and Calorimetry. 2004;76(3):793–800. DOI: 10.1023/B:JTAN.0000032264.74742.27.

[13] Konstantinović S, Radovanović B, Krkljes A. Thermal Behaviour of Co(II), Ni(II), Cu(II), Zn(II), Hg(II) and Pd(II) complexes with isatin-β-thiosemicarbazone. J Therm Anal Calorimet. 2007;90(2):525–31.

[14] Kumar G, Kumar A, Shishodia N, Garg YP, Yadav BP. Synthesis, Spectral Characterization and Antimicrobial Evaluation of Schiff Base Cu(II), Ni(II) and Co(II) Novel Macrocyclic Complexes. E-Journal of Chemistry. 2011;8(4):1872–80. DOI: 10.1155/2011/497279.

[15] Premkumar T, Govindarajan S. Divalent transition metal complexes of 3,5-pyrazoledicarboxylate. Journal of Thermal Analysis and Calorimetry. 2006 May;84(2):395–9. DOI: 10.1007/s10973-005-6932-0.

[16] Lever ABP. Inorganic Electronic Spectroscopy. Amsterdam: Elsevier; 1968. ISBN: 978-0-444-40675-0.

[17] Nakamoto K. Infrared and Raman spectra of inorganic and coordination compounds. 3d ed. New York: Wiley; 1978. 448 p. ISBN: 978-0-471-62979-5.

[18] Adjel F, Barkat D. Synergistic extraction of copper(II) from sulfate medium with capric acid and tri- n -octylphosphine oxide in chloroform. Journal of Coordination Chemistry. 2011 Feb 20;64(4):574–82. DOI: 10.1080/00958972.2010.551400.

[19] Rozyckia C. Chemical Analysis (Warsaw) 26: 37 (1981).

BAKIR(II) DEKANOAT KOMPLEKSİNİN EKSTRAKSİYONU VE SPEKTROTERMAL ÇALIŞMALARI

Öz: Bakır(II) iyonunun 0,33 M Na_2SO_4 sulu çözeltilerinden dekanoik asit (HL) ile kloroform içinde ve 25 °C'de ekstraksiyonu çalışılmıştır. Dekanoik asit tek başına kullanıldığı zaman ekstrakte olan tür $CuL_2.2(HL).2H_2O$'dur. Bakır kompleksi sentezlenmiş ve elementel analiz, kızılötesi spektrumları, elektronik spektrumlar, X-ışını saçılması (XRD), laser parçacık boyutu analizi ve molar iletkenlik ölçümleri ile karakterize edilmiştir.

Anahtar kelimeler: Dekanoik asit, metal karboksilat, ekstraksiyon sıvısı, yapısal çalışma.
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