بسم الله الرحمن الرحيم

Sudan University of Science & Technology

College of Graduate Studies

Synthesis and Characterization of Copper (II) Oxide Using Different Alkoxides

تحضير وتشخيص اوكسيد النحاس(II) باستخدام الكوكسيدات مختلفة

A Thesis Submitted in Partial Fulfillment for the Requirements of the Degree of M.Sc. in Chemistry

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May-2017

بسم الله الرحمن الرحيم

قـال تعـالي:

﴿يُرْسَلُ عَلَيْكُمَا شُوَاظٌ مِنْ نَارٍ وَنُحَاسٌ فَلَا تَنْتَصِرَانِ﴾

الرحمن((35))

صدق الله العظيم

Dedication

To

My parents,

My brothers

and sisters.

Acknowledgment

First of all thanks to Allah Almighty for helping me to complete this work.

It is a pleasure to record my deep appreciation, and thanks to Dr. Mohamed Sulieman Ali Eltoum for his wise guidance, which helped me to present this project in this shape. I am very grateful to the staff of the Department of Chemistry-Sudan University of Science and Technology.

Finlay Thanks to my family for their continual support.

Abstract

In this study a number of alkoxides of copper(II), $Cu(OR)_2$, (where R is a primary, secondary or tertiary alkyl group) were synthesized by the reactions of anhydrous copper(II) chloride with sodium alkoxides in 1: 2 molar, the process involved alcoholysis and trans-esterification techniques, finaly copper oxide was obtained by calcination of alkoxides in 600^0C . All the prepared alkoxides and copper oxide were characterized using different analytical techniques, such as, infra-red(IR), X-ray diffraction(XRD). The results obtained agreed well with prepared copper(II) alkoxide and oxide , it was shown that copper alkoxide preparation from primary alcohol is easier than secondary and tertiary one.

المستخــلص

في هذه الدراسه عدد من الالكوكسيدات النحاس (II) $Cu(OR)_2$ حيث ان R هي مجوعه الكيل اوليه او ثانويه او ثالثويه تم تحضيرها وذلك بتفاعل كلوريد النحاس (II) اللا مائي مع الكوكسيد الصوديوم بنسبه تفاعل 2:1 اخيراً حضر اوكسيد النحاس و ذلك بحرق هذه الالكوكسيدات الي درجه حراره تصل 600 درجه مئويه وتم تشخيص هذه المركبات بتقنيات مختلفه متل مطيافيه الاشعه التحت الحمراء ومطيافيه تشتت الاشعه السينيه وكانت النتائج مطابقه مع تحضير الكوكسيد واوكسيد النحاس (II) وشوهد ان تحضير الكوكسيد النحاس (II) من الكحول الاولي اسهل من الثانوي والثالثوي .

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1.1. Introduction

1.1.1.General Introduction of Metal Alkoxides

The chemistry of metal alkoxide dates back to 1840s when Liebig first time observed the reaction of alcohol with metal like sodium and potassium. In the same year the term alkoxides was used by Kuhlmann[1] for the alkaline derivatives of alcohols. Thereafter the chemistry of alkoxides has been the center of attraction for the researchers due to their tremendous applicability especially in the fields like catalysis, sol-gel and MOCVD methods (metal-organic chemical vapor-phase deposition) for synthesis of pure metal oxides, precursors for nano materials, ceramics etc. Alkoxides $M(OR)_n$ are compounds with one or more metal atoms or semi-metal atoms (M) with alkoxy groups (OR) as ligands. An alkoxy ligand is produced when hydrogen atom is stripped from an alcohol (ROH) or by dividing an ether (ROR) molecule in such way that oxygen is retained along with R group (i.e OR). In other words, alkoxides may be regarded similar to hydroxides (MOH) in which the H has been substituted by an alkyl or aryl group(R). The alkoxides are known for most of the elements in the periodic table. Most of the metallic elements are reactive towards oxygen because an oxide exists in stable single or mixed phases. Molecular precursors derived from alkoxide complexes can generate ceramic materials in a single step (thus-called single-source precursors – SSPs)[2] . Metal alkoxides are very good single source molecular precursor (SSP) for oxide synthesis. This is mainly due to their molecular structure and high reactivity, which depends on the electronegativity of the metal ion, ability to increase their coordination numbers and the steric hindrance in the alkoxy groups. This helps in the synthesis of corresponding colloidal metal oxides with high homogeneity. There has been a growing interest in the development of the chemistry of mixed-metal bi and polynuclear alkoxo and alkoxo-organometallic complexes for the last two decades. Motivation force for such interest derives from their fascinating structural chemistry, interesting catalytic properties, and high potential for industrial applications[3,4]. The important fact that most of the heterometallic alkoxo species can generate bimetallic or

multimetallic oxides has resulted in high research activity in the field. Their attractiveness lies in the fact that they are easily accessible and are inexpensive. Furthermore, alkoxide ligands are easily removable via thermal treatments. Finally, these compounds already have established metal-oxygen bonds. It is worth mentioning that their thermal deposition or decomposition processes can be performed at relatively low temperatures compared to conventional methods

  involving other inorganic salts. These features make the metal oxides derived from metal alkoxides, highly pure with specific properties like high hardness, chemical and mechanical resistance, and high temperature stability. The soft–chemical approach is a flexible, simple and novel synthesis for industrial production. Different types of precursor can lead to change in unique features of the structural framework that affects the physical and chemical properties in the final product by retaining the stoichiometric ratio under control. This will help to predict favorable morphology for its futuristic applications with high reliability, accuracy and reproducible results[4]. From above mention feature, it is evident that metal alkoxides play the key role for preparing materials of excellent functions and shapes. A range of catalytic applications of Group (IV) (i.e.Ti, Zr,and Hf) is mainly due to the Lewis acidic nature of M(IV) complexes. Group (IV) elements are important components of electro ceramics such as lead zirconium titanate (PZT) and barium titanate. Sol-gel processing of these and related materials is based upon hydrolysis of alkoxide solutions. It is found that the species produced when acetylacetone (acacH) is added to $Ti(OR)_4$ is 1:1 reaction product $[Ti(OR)_3(acac)]$ which is dimeric readily under-go ligand redistribution in solution to give $Ti(OR)_4$ and $[Ti(OR)_2(acac)_2]$. 17O NMR spectroscopy has been used to investigate the hydrolysis of the resulting mixture for R = Pri and the results were interpreted in terms of the hydrolysis behavior of the individual mononuclear components. Titanium complexes of alkoxide and aryloxide ligands exhibit a rich coordination chemistry and reactivity and find applications in various fields[5]. The interest in the development of non-metallocene complexes for the polymerization of α-olefins has created a new range of chelating dialkoxoligands for group IV transition metals. Complex formation may be

effected by the steric bulk on the ligands. Furthermore, the olefin polymerization reactivity by a possible catalyst may strongly depend on the crowding around the metal, as substantial bulk on one hand, may, hinder the approach of an incoming olefin and, on the other hand, decelerate termination processes[6]. Several types of amine bis (phenolate) titanium complexes, having different steric crowding around the metal have been synthesized. The [ONNO]-type ligands bind to the metal in a tetradentate fashion, leads to octahedral bis-(isopropoxide) complexes regardless of the steric bulk of the aromatic ring substituents. Various complexes involving ethylenediamine and metal alkoxides with particular reference to complexes involving titanium isopropoxide have been reported [6].

Since 1950 there has been an increase in the development of alkoxide chemistry. In 1950 there were only a dozen or so alkoxide compounds known but in the past 30 years the "alkoxide chemistry of almost all the metallic and metalloid elements has been investigated[1] . Ametal alkoxide is defined as $M(OR)_n$. These complexes can be viewed as derivatives of alcohols that have the general form ROH in which the hydrogen has been replaced by a metal or considering them derivatives of metal hydroxides $M(OH)_n$.

The metal alkoxide contains an M—O—C bond in which the M is slightly positively polarized and the O is slightly negatively polarized. The degree of polarization depends to a large extent on the electronegativity of the metal. The metal alkoxide compounds can range from covalent monomers (formed with silicon, germanium, phosphorus etc.) to electrovalent polymeric solids (formed with alkali earth metals or alkaline earth metals. The covalent character of the M—O bond increases with greater inductive effects from the alkyl groups. That is to say that the covalent character of the bond would be higher for the tertiary butoxide group than it would be for the regular butoxide group[1].

1.1.2.Preparation and Purification of Metal Alkoxldes

The methods for synthesizing metal alkoxides are well established and require only a brief review here. The simplest method involves the direct reaction between the metal M and the alcohol ROH[7] (eq 1-1).

$$M + xROH \rightarrow M(OR)_x + (x/2)H_2 \quad (1\text{-}1)$$

This reaction is limited to the more electropositive metals and occurs spontaneously with the alkali metals. The influence of the alkyl group in the alcohol on reactivity with the metal is exemplified by the rapid reaction of sodium and ethanol in contrast to the very slow reaction of sodium with tert-butyl alcohol. With the divalent and trivalent metals it is necessary to add a catalytic amount of iodine (Mg) or mercury(II) chloride (Al, lanthanides) to initiate the reaction by cleaning the metal surface. The easiest laboratory method for the synthesis of the alkoxides of higher valent metals utilizes the reaction between an alkali metal alkoxide and the halide (usually chloride) of the higher valency metal (eq 2-1). However

$$TiCI_4 + 4NaOEt \rightarrow Ti(OEt)_4 + 4NaCL \quad (2\text{-}1)$$
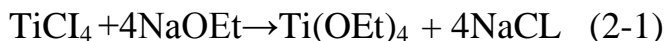
This method is unsuitable for metals (e.g., Zr, Hf, Nb, and Ta) whose alkoxides form stable heterometal alk oxides incorporating the alkali metal: viz., $NaZr2(OR)_9$ and $NaTa(OR)_6$. In such cases it is necessary to use anhydrous ammonia as the reagent for dechlorination of the metal (eq 3-1).

$$ZrCL_4 + 4NH_3 + 4ROH \rightarrow Zr(OR)_4 + 4NH_4CL \quad (3\text{-}1)$$
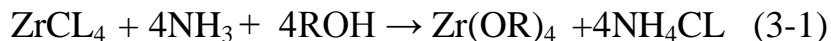
If a particular metal chloride is too unstable, e.g. Ce(1V) or Pu(IV), but a stable hexachlorometalate is accessible, then the latter may be used instead (eq 4-1).

$$(PyH)_2{}^+(MCL_6)^{2-} + 6ROH + 6NH_3 \rightarrow M(OR)_4 + 2Py + 6NH_4CL \quad (4\text{-}1)$$
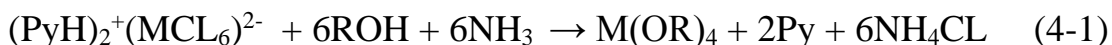
Even this method has its limitations because the hex- achlorometalate(1V) is sometimes (e.g., Sn or Pb) too inert to react with alcohol and ammonia. Miscellaneous other methods of synthesis are docu mented in ref 1, but it is noteworthy that more work has subsequently been carried out on the direct electrochemical synthesis of the alkoxides of Sc, Ti, Y, Zr, Nb, Ta, Ga, and Ge [7].

1.1.3. Structure and Volatillty of Metal Alkoxldes

Volatility is of prime consideration in assessing the feasibility of a

metalloorganic compound as a precursor in chemical vapor deposition. Systematic studies on the alkoxides in the 1950s established that the steric effect of the alkyl group had a controlling influence on the volatility of the metal alkoxide. Thus the alkoxides containing less bulky alkyl groups (e.g., methyl and ethyl) proved to be oli- gomers (e.g., dimers, trimers, and tetramers) due to the bridging propensity of the alkoxide group, which may be bonded through its oxygen to two (b2) or three (g3) metals by means of conventional two-electron covalent bonds [1]. The driving force is of course the -
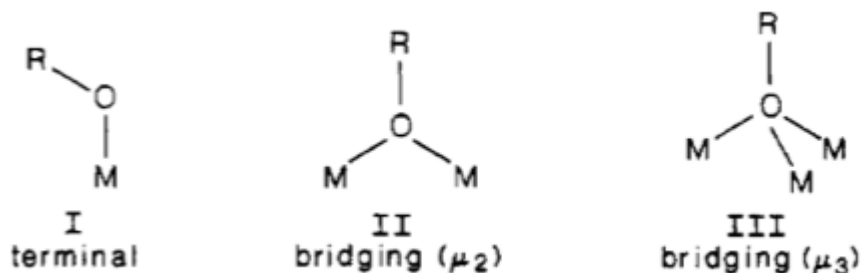
tendency of the metal to expand its coordination number from its covalency number to a higher value such as 6 in an octahedral complex. For most of the metal alkoxides the strength of the alkoxide bridges is sufficiently great to preclude the alternative mechanism for coordination expansion, namely the addition of another ligand L containing a donor atom[7].

Mass spectral evidence has shown that some oligo meric metal alkoxides retain their structural integrity in the vapor state, and clearly much more energy is required to vaporize a trimer or dimer than a monomer. Thus alkoxyboranes, which are monomeric $B(OR)$, are very much more volatile than aluminum alkoxides, which are oligomers [e.g., tetrameric $Al_4(OR)_{12}$], and alkoxysilanes, $Si(OR)_4$, are more volatile than the oli- gomeric titanium tetraalkoxides, $[Ti(OR)_4]_n$. Even when the alkoxide bridges are not very strong and monomers are formed on heating, extra energy is required to depolymerize the oligomers with consequent lowering of volatility. The monomeric metal alkoxides can be prevented by steric hindrance from intermolecular bond formation (bridging) by utilizing very bulky alkyl

groups, and a relatively volatile metal alkoxide can be obtained. The tert-alkyl groups are the ones par excellence for preventing bridging and promoting higher volatility. Besides coordination expansion of the metal, another significant factor is the metal's atomic radius since the larger the metal, the bulkier will be the alkoxide group necessary to prevent alkoxide bridging. Thus zirconium and hafnium form monomeric tetra-tert-butoxides but the larger thorium atom forms a less volatile oligomeric tert-butoxide and requires the larger tert-heptyl oxide (R = CMeEtPr') to produce a monomer[7].U nfortunately, the use of the very bulky tert-heptyl oxide groups to screen the thorium atom invokes a penalty in terms of volatility because the monomeric Th(0C- MeEtPn')4 is a very large polyatomic molecule with a much higher boiling point (139 ^{O}C/O.O5 mmHg) than the monomeric tert-butoxides of zirconium and hafnium (bp ca. 54 ^{0}C/O.l mmHg). In Table I are listed some volatility data on the tetraalkoxides of titanium, zirconium, and thorium. Examples of some representative transition-metal alkoxides exhibiting moderate volatility (i.e., readily distilled or sublimed in vacuo) are given in Table (1-1). Other limitations to the volatility of metal alkoxides are apparent in the alkoxides of monovalent and divalent metals. With only one alkoxide group per metal atom in the alkali metal alkoxides it is impossible even with tert-alkoxide groups to prevent alkoxides bridging,

$M(OR)_x$ as Precursors for Electronic Material

TABLE 1.1 Some Volatile Transition-Metal Alkoxides

$Cr(OBu^t)_4$	$V(OBu^t)_4$	$Ti(OBu^t)_4$
$Mo(OPr^i)_4$	$Nb(OPr^i)_5$	$Zr(OBu^t)_4$
$W(OPr^i)_6$	$Ta(OPr^i)_5$	$Hf(OBu^t)_4$
$U(OBu^t)_6$	-----	$Th(OHx^t)_4$

and lithium tert-butoxide for example is hexameric with a higher boiling point (110 OC/O.l mmHg)[7-8] than zirconium tert-butoxide. A similar case exists for the divalent metals where for example beryllium di- tert- butoxide is trimeric and relatively nonvolatile (sublimes at 100 0C/10-3 mmHg). The only appreciably volatile alkoxide of copper obtained to date is copper(I)

tert- butoxide, which, although tetrameric, can be sublimed (ca. 100 OC/1 mmHg)[10]. It is noteworthy that the volatility of the alkoxides of monovalent or divalent metals may be considerably enhanced by combination as a heterometal alkoxide with a higher valency metal alkoxide. Thus the non- volatile NaOPr' will combine with $Zr(OPri)_4$ to give $NaZr2(OPri)_9$, which can be distilled in vacuo.

1.1.4.Classification Based on Alkoxides Complexes Structure

Metal alkoxide complexes can have very complex structures due to formation of oligomeric and sometimes even polymeric aggregates. Formation of alkoxy bridges, M-(OR)-M, help the complexes to obtain maximal and preferred coordination even though the number of bonded ligands per metal atom are too few. Complexes are categorized, based on number of metal atoms in the complex. Optimal coordination is obtained by chelating ligand or by a shared (bridging) ligand atom.

Mononuclear complexes – Mononuclear complexes are highly charged metal ions where the coordination requirements are satisfied by the number of OR-ligands. The ligands are often large and branched with chelating abilities.
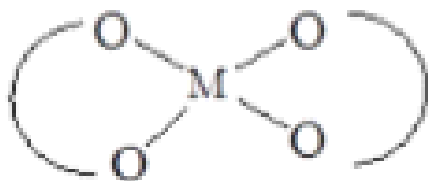
Binuclear complexes - In binuclear complexes, an oxygen atom in the ligand connect the two metal atoms. Usually at least two alkoxy bridges are connecting the metal atoms and thus stabilizes the complex
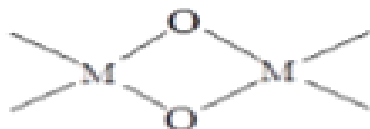
Mo and W complexes can have metal-metal bonds to stabilize the complex (without any bridging ligand), the multiplicity depends on the number and

nature of ligands.

$$(RO)_3MO \equiv MO(OR)_3$$
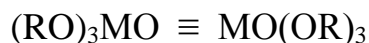
Trinuclear complexes – These complexes are often triangular structures, linear chains or non-linear chains with the same type of connections as in the binuclear complexes.

Tetranuclear complexes – These complexes have several different types of configuration. The tetrahedral configuration has a core of μ_4-O and four metal atoms connected by the oxo-ligand, but this is not a common configuration.

$Ti_4(OR)_{16}$ type is common and is built up by a M_4-rhomb with $2\mu_3$-O and 4μ-O. The R-groups are most often-primary alkyl groups for the 3d-metals.
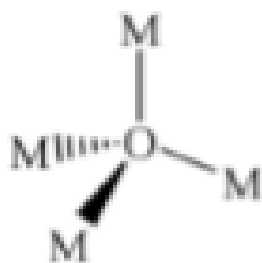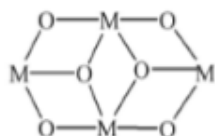
The cubane-like structure contains metal atoms in four opposite corners of a cube and oxygen atoms in the other corners ($4\mu_3$-O).
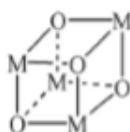
$Al4(\mu4-O)(\mu-OPri)_5$ complex and the $[Eu4(OPri)_{10}(HOPri)_3]\cdot2HOPri$ complex are some of the examples without a metal-metal bond . The $Al_4(OPri)_{12}$ type (the propeller type) has an octahedron (with Al in the center) in the center and three tetrahedra of Al connected by pairs of OR-bridges.
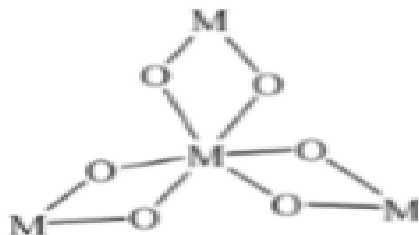
A heterometallic example is the Nd[Al(OPri)4]3 with the Nd atom in the center of the complex.

Pentanuclear complexes – These complexes belong most often to either of two different coordination.

First, the trigonal bipyramidand the square pyramid both with a $\mu5$-O in the center of

the M5O-cluster. Second, the structure with two triangles sharing a vertex. Many lanthanide oxo-isopropoxide complexes belong to the square pyramidal coordination, e.g. the [Eu4IIIEuIIO(OPri)12(HOPri)], HOPri complex and Ln5O(OPri)13, Ln = Nd, Gd or Er.

Hexanuclear complexes - Most common ones in hexanuclear complex are octahedral M6-arrangement with a $\mu6$-O in the center
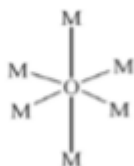
or a structure with two M3-triangles connected by the ligands, the double propellertype[11-12].
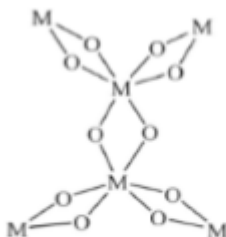
1.1.5. Physical Properties of Metal Alkoxides

Alkoxy derivatives involving M-O-C bonds could be expected to be highly polar in view of the strongly electronegative nature of oxygen (electro-negativity value 3.5 on the Pauling scale). How- ever, except for methoxides, most of the other alkoxides show a high degree of volatility and solubility in organic solvents. Two factors, which have been postulated for explaining the attenua- tion in the polarity of metal-oxygen bond, are the inductive effect

(which increases with the ramifi cation in the alkyl group) and the formation of oligomers through dative bonds of the type:
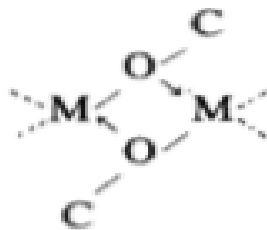
The latter tendency is also expected to decrease with the ramification of the alkyl group due to steric factors. Bradley et al[13]. as well as Mehrotra have tried to analyse these factors and from the similarity in the degree of association and volatility of neopentyloxides to secondary rather than primary amyloxides, it has been concluded that steric factors may be more effective[14]. The effects of various parameters like electro negativity and the size of the central metal atom and the ramification of the alkyl group are apparent from the data in table(1-2).

Table (1-2)

Boiling point and degree of association group IV alkoxides

Element M	Th	Hf	Zr	Ti	Si
Covalent radius (A)	1,55	1,44	1,45	1,32	1.11
Electronegativi-ty	1,11	1,23	1,22	1,32	1,74
Compound $M(OR)_4$	---------		Boiling point degree of association	Boiling point degree of association	--------
R=Et	0,5/300	0,2/178	0,1/190	0,1/130	760/166
	(6,0)	(3,6)	(3,6)	(2,4)	(1)
R=Me$_2$CH	0,1/210	0,1/157	0,1/160	0,1/49	------
	(3,8)	(3,0)	(3,0)	(1,4)	------
R=Me(CH$_2$)$_3$	----	0,1/240	0,1/243	0,2/142	0,1/98
	----	(3,6)	(3,6)	(2,4)	(1,0)
R=Me(Et)CH	----	---	0,1/164	0,2/127	---
			(2,5)	(1,4)	
R=Me$_3$C	,1/160	,1/44	,1/46	,1/50	
	(3,4)	(1,0)	(1,0)	(1,0)	
R=Me(Et)pr^{i}C	,1/145				
	(1,0)				

 On the basis of the molecular complexities of a number of metal alkoxides, Bradley in 1958 proposed a simple structural theory according to which alkoxide derivatives adopt the smallest possible structural unit (table 3-1) consistent with all atoms assuming a higher coordination number As an example of the significant conformity of the experimental data with the above simple formulation the structural findings for aluminum isopropoxide may be cited [15], which was shown by Mehrotra to show an "ageing" phenomenon from dimeric vapour to freshly distilled trimeric liquid to the fairly stable tetrameric crystalline form. This could be explained to be due to

the tendency of aluminum to change from "4" to "6" coordination state due to steric hindrance from

Table (1-3)

Stereochemistry and degree of association of metal alkoxides

Metal alkoxide	Coordination no of M	Stereo chemistry of M	Minimum degree of association	Observed degree of association
MOR	2	Linear	2	
	2	Bent	3	
	3	Pyramidal	4	4
$M(OR)_2$	6	Octahedral	Infinite three dimensional polymer	Infinite three dimensional polymer
$M(OR)_3$	4	Tetrahedral	2	2
	4 and 6	Octahedral and Tetrahedral	4	4
$M(OR)_4$	6	Octahedral	3	4-3
$M(OR)_5$	6	Octahedral	2	2
$M(OR)_6$	8	Cubic	2	2

the bulky tertiary butoxy groups. The structures for $[Al(OPri)_3]_4$ and $[Al(OBut)_3]_2$ are repre- sented below:
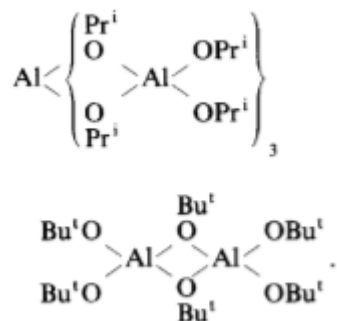
The former for instance has been confirmed by 1H and 27A1 NMR , mass spectrometry [16] and by X-ray crystallography. In spite of such isolated

cases of structural elucidation, applications of sophisticated instrumental techniques have so far been scanty in the field of metal alkoxides, which, therefore, provides a very attractive area for future investigations, not only on the structural details of individual alkoxides but the changes which these undergo in say, alcoholysis and hydrolytic reactions[17].

1.1.6.Reactions of Alkoxides

Metal alkoxides are generally very reactive species and the following section gives a summary of their more important reactions.
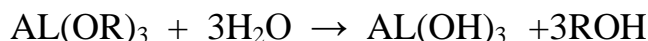
<a> Hydrolysis

Metal alkoxides are rapidly hydrolysed leading to the formation of hydroxides or hydrated oxides. e.g [18].

$$AL(OR)_3 + 3H_2O \rightarrow AL(OH)_3 + 3ROH$$

This means that when handling such materials great care must be taken to exclude moisture. However if a restricted amount of water is used then oxyalkoxides of definite stoichiometry may be formed. e.g.

$$2Ti(OBu^*)_4 + H_2O \rightarrow (OBu^*)_3Ti\text{-}O\text{-}Ti(OBu^*)_3 + 2Bu^*OH$$
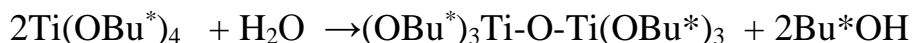
This limited hydrolysis of alkoxides has been exploited to make materials that are catalytically active. An example of this is the partial hydrolysis of zinc-aluminium alkoxides[19]:

$$(RO)_2AL(OR)_2Zn(OR)_2AL(OR)_2 + 2H_2O \rightarrow (RO)_2AL\text{-}O\text{-}Zn\text{-}O\text{-}AL(OR)_2 + 4ROH$$
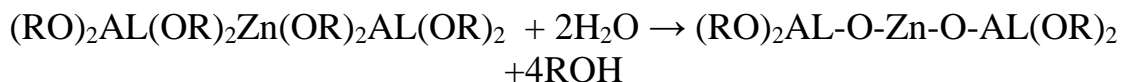
The μ-oxoalkoxide so formed is active for the ring opening polymerisation of lactones.

<b >Alcohol Exchange Reactions

Exchange of the alkoxy group of an alkoxide for a different alkoxy group is useful in the preparation of metal alkoxides and as such has been discussed in the section above.

<c> Reaction with Organic Acids

As can be expected from the relative acidities, organic acids react with metal alkoxides to form metal carboxylates. Indeed aluminium tri-carboxylates may be formed as long as all traces ofmoisture are removed. e.g[20].

$$AL(OPr^1)_3 + 3CH_3CO_2H \rightarrow AL(O_2CCH_3)_3 + 3Pr^1OH$$

<d> Meerwein-Ponndorf-Verley Reaction

The reduction of ketones by alcohols is catalysed by metal alkoxides of which aluminium alkoxides are the best. The reaction can be driven to completion by the removal of the volatile ketone formed

<often acetone>:

$$Me_2HC\text{-}OH + R''_2C\text{=}O \rightarrow Me_2C\text{=}O + R''_2HC\text{-}OH$$
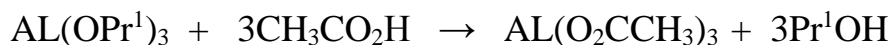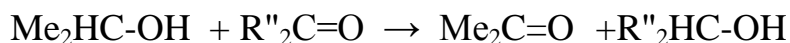
<e> Thermal Decomposition of Alkoxides

Metal alkoxides decompose on heating to the metal oxides, hydroxides or to the metal itself with the evolution of organic species. The mode of decomposition depends not only on the alkoxide but on the conditions of the pyrolysis. For example it is reported that copper<II> methoxide decomposes in air to form copper<II> oxide whereas in the course of the present study, decomposition under vacuum led to the formation of copper metal[21].

<f> Other Reactions

There are many more reactions of alkoxides: some react with hydrogen halides to form metal halides or mixed alkoxy-halides; some react with esters to form new alkoxides <see transesterification above>; some react with glycols to form glycolates which are often less moisture sensitive than alkoxides; some react with thiols to form thiolates[22].

1.1.7. Uses of Alkoxides :

Despite the fact that alkoxides are moisture-sensitive and thus require special handling techniques they have many industrial applications. A brief

summary of some of these is given below:

<a> Catalysts

The use of alkoxides as catalysts has already been alluded to in the above discussion in their role as catalysts in the MeerweinPonndorf-Verley reaction and in ring opening polymerisations. However there are other systems catalysed by alkoxides: Ziegler-Natta

polymerisations ; transesterifications and polyester formation•

<b> Polymer Cross-Linking Agents

The ability of certain alkoxides to promote cross-linking makes them useful in a variety of ways, for example titanium and zirconium alkoxides may be used in films where rapid drying is required whilst aluminium, titanium and zirconium alkoxides may be used in conjunction with silicones in the waterproofing of leather where it is believed that the alkoxides promote the curing of the silicone•

<c> As Precursors to Metal Oxides. Glasses and Ceramics

One of the major difficulties encountered when dealing with metal alkoxides is their susceptibility to hydrolysis. However it is this very property that has led to a major use of alkoxides: the formation of high purity metal oxides by the pyrolysis of the hydroxides formed on the controlled hydrolysis of alkoxides• The metal alkoxides are readily purified by distillation under reduced pressure or by recrystallisation so the oxides produced are free from impurity.

Glasses which can be formed at low temperatures <800 °C have been made from the products of the cohydrolysis of mixtures of silicon alkoxides and other metal alkoxides. These offer scope for the production of high-purity specialised glass films.

Similar, and perhaps more important is the preparation of superconductors via the pyrolysis of hydroxides formed on the hydrolysis of, for example, solutions of barium, yttrium and copper alkoxides• Again it is the high purity of the alkoxide precursors which is important in this

application.

Therefore it can be seen that alkoxides are useful industrial chemicals, and will certainly become more so if the final application described above can be exploited[23].

1.2.Literature review:

1.2.1.Prcursors for Sol-Gel preparations

Sol-gel processing for the synthesis of glasses, glass ceramics and ceramics had gained noticeable consideration both with regard to scientific and application purposes; all important meetings or conferences on ceramics deserve a section on this topic and many workshops and conferences deal exclusively with it. There are two important sol-gel processes, namely the alkoxide[24-25] and the colloidal methods; a third one, intermediate between the others but suitable only for silicate systems and based on the chemistry of amine-silicate solutions, has been reproposed [26-27]. The present paper will be limited to the alkoxide sol-gel method. As the method's title suggests, this process is based on the chemistry of alkoxides: they are indeed the most important and typical precursors; therefore their nature, properties, reactions, manufacture and availability will be considered in following in the endeavor to give a general picture of those proporties and reactions affecting the preparation process and determining the product features. An important part of the information was derived from the notable book by Bradley, Mehrotra and Gaur, "Metal Alkoxides"[28].

Precursors for sol-gel preparations are not only alkoxides. Inorganic and organic salts have also been used for introducing some oxides in multi component systems particularly when the use of alkoxides has proved to be difficult or unnecessary. These compounds will be considered and, when possible, a comparison with the corresponding alkoxides will be made. Organically modified silicates recently developed by Schmidt and coworkers [29] .

Alkoxides are compounds in which elements are bonded to an hydrocarbon moiety through oxygen. They may be considered as either derivatives of

alcohols or derivatives of metal hydroxides or inorganic acids. According to the latter statement these compounds should be referred to as orthoes- ters: this is the case of silicon, boron, phosphorus and titanium alkoxides for example, tetraisopropyl titanate, $Ti(OPri)_4$. The term "metal alkoxide" (sodium methoxide, magnesium ethoxide

aluminum iso-propoxide) or "metal alcoholate" could be more properly used if alkoxides are considered products obtained from alcohols by the replacement of the hydroxyl hydrogen with a metal, as in $NaOCH_3$, $Mg(OC2HS)_2$ ' $Al(OC3H7)_3$ .i Both names were followed in the literature, often even for the same element. For example, the alkoxy derivatives of aluminum and titanium are named orthoaluminates and orthotitanates as well aluminum and titanium alkoxides. Furthermore, the different names for the same compound are widely used for commercial products. Obviously, the different nomenclature reflects the tendency to not use IUPAC recom-mended instructions: on the other hand, ordinary names appear more practical in the current language. Thus, for the sake of simplicity, the term "alkoxide" will be adopted in the following in all cases irrespective of electronegativity values and independently of proper scientific names[30].

1.3.Copper(II) Alkoxide:

 Although the alkoxide chemistry of earlier transition elements has been extensively explored during the last two to three decades a survey of the literature reveals that corresponding derivatives of later transition elements have received much less attention . This might be due to much stronger coordination tendency exhibited by the later transition elements, leading to highly polymerised derivatives which are insoluble in organic solvents and non- volatile. As part of a planned research programme on the chemistry of first row later transition elements, preliminary investigations alkoxides of chromium(III) and nickel(II) have shown them to be non-volatile and insoluble. In contrast to the general lability of the alkoxide groups in earlier transition metal alkoxides leading to facile alcoholysis reactions, sharp differences have been noticed in the alcoholysis tendencies of the above alkoxides. For example, nickel(II) primary alkoxides do not undergo alcoholysis with other alcohols even under forcing conditions. Secondary

and tertiary alkoxides of nickel(II) react with primary alcohols at the room temperature to give the corresponding alkoxides, but do not again react with other secondary and tertiary alcohols. Attempts have been made to explain the above differences due to the variation in the geometry of nickel primary (octahedral) and branched (tetrahedral) alkoxides. A survey of the literature revealed that only the methoxide and ethoxide of copper(II) had been prepared so far [31-32].

In the present , we report the preparation and properties of a number of primary, secondary, and tertiary alkoxides of copper(II). Alcoholysis reactions of these derivatives have been studied in detail for the first time. Plausible stereochemistries of thesederivatives have been proposed on the basis of spectraland magnetic measurements. These alkoxide derivatives of copper(II) are found to be polymeric in nature which provide interesting examples of antiferromagnetic interaction of paramagnetic ions in alkoxo-bridged lattices.

Soluble and volatile alkoxides of copper are precursors in sol-gel-like routes to cuprate-oxide superconductors' and in the CVD of copper and copper oxides: respectively. Copper(II) alkoxides are typically prepared by alcohol- interchange reactions with dimethoxycopper(II);however, most are insoluble , and nonvolatiee. Dimethoxycopper(II) has been prepared by the decomposi- tion of methylcopper(1) in MeOH in the presence of air," and by reaction of CuX, (X = CI, Br) and MOMe (M = Li, Na)[33].

1.4.Synthesis more Alkoxides of Copper by the Alcohol-interchange

The general applicability of the lithium alkoxides in the synthesis of copper(II) alkoxides has been shown [34]

$$CuCL_2 + 2LiOR + ROH \rightarrow Cu(OR)_2 + 2LiCL$$

R=Me,Et,iPr,tBu
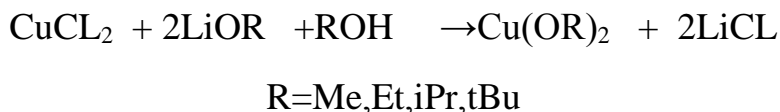
Synthesis of a few more alkoxides of copper has been described by the alcohol-interchange reactions

$$Cu(OR)_2 + 2R''OH \rightarrow Cu(OR'')_2 + 2ROH$$

$$R=Me.Et \ Or \ nBu$$

$$R''=Me. \ Et. \ iPt. \ nBu. \ sBu. \ tBu. \ or \ tAm$$
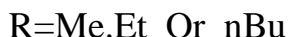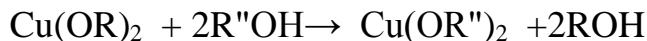
Alcohol-interchange reactions of copper(II) alkoxides reveal some novel features compared to those of alkoxides of chromium(III)(35) , cobalt(II(, and nickel(II) . Compared to the novel nature of alcoholysis reactions of these latter alkoxides, copper(II) alkoxides undergo facile alcohol-interchange reactions. Copper(II) alkoxides in this respect show resemblance to alkoxides of earlier transition metals like titanium and vanadium, which also undergo very facile alcoholy sis reactions. It has been observed that the primary alkoxides of copper(II) interchange their alkoxide groups quantitatively with tertiary, secondary, or other primary alcohols under refluxing conditions only, whereas the secondary and tertiary alkoxides undergo a more facile alcohol-interchange reaction with primary alcohols, even at room temperature with slight evolution of heat. It has been found that the secondary and tertiary alkoxides of copper(II) do not appear to undergo alcohol-interchange reactions with other secondary and tertiary alcohols. Although it is difficult to sort out the effects of various factors like thermodynamic and kinetic stabilities as well as the role of crystal field stability in different plausible geometries (apparently the main factor in alcoholysis trends of nickel alkoxides), the alcohol-interchange reactions of copper(II) alkoxides appear to be governed mainly by steric factors. As in a number of other metals, the alkoxy interchange reactions are sterically less hindered when esters are used in place of alcohols as reactants. For example, it has been reported that copper(II) isopro poxide, which hardly undergoes interchange with t-butanol can be converted to t-butoxide by treating with t-butyl acetate[36]:

$$Cu(O\text{-}iPr)_2 \quad + \quad 2CH3COO\text{-}tBu \quad \rightleftharpoons \quad Cu(O\text{-}tBu)_2 +2CH3COO\text{-}iPr$$
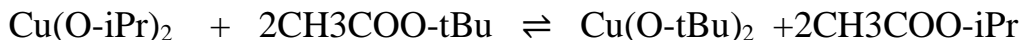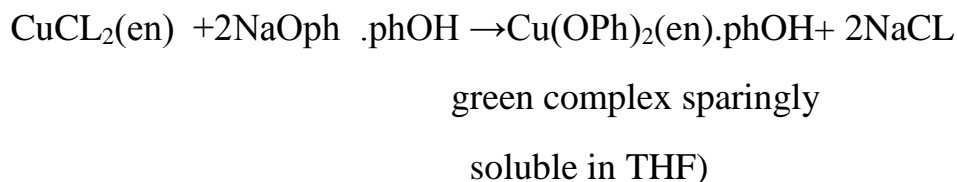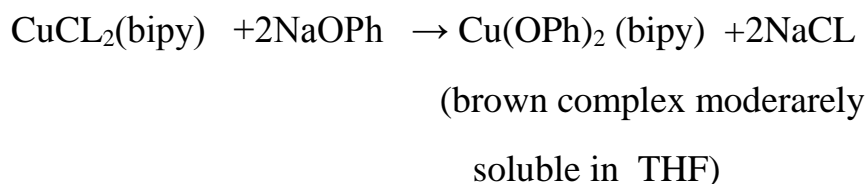
The alcoholysis reactions of copper(II) alkoxides thus follow the following order of relative lability, which is similar to that already reported in the alkoxides of a number of earlier transition metals : primary alkoxides =- secondary alkoxides - teritary alkoxides. Brubaker and Wicholas reported subnormal magnetic moments for $CU(OMe)_2$ (1.12 BM) and $Cu(OEt)_2$ (1.18 BM) and suggested a highly polymeric structure for these with tetragonally distorted copper atoms. Adams et al. measured the magnetic susceptibility of $Cu(OMe)_2$ over the range 80-350 K. They favored a linearchain model for polymeric $Cu(0Me)_z$ analogous to that of $CuC1_2$. Singh has measured the magnetic susceptibilities of typical primary, secondary, and tertiary alkoxides of copper and has found that **(a)** for $Cu(0Bu)_z$ it increases from 0.64 at 88.5 to 1.18 at 298.7 K; **(b)** for $Cu(O\text{-}iPr)_z$ it increases from 0.98 at 88.0 to 1.50 at 297.1 K; and **(c)** for $Cu(O\text{-}tAm)_2$ it increases from 1.37 at 87.5 to 1.83 at 297 K. These data indicate the presence of antiferromagnetic exchange interaction, which, as expected, decreases with increasing ramification of the alkyl group. The J values calculated employing the king model also follow a trend in the same direction as shown from the following values of J[37].

(J)Cu(O-nBu)₂	**(J)Cu(O-iPr)₂**	**(J)Cu(O-tAm)₂**
129 Cm⁻¹	**81Cm⁻¹**	**43 Cm⁻¹**

The visible spectra of $Cu(OMe)_z$, $Cu(OEt)_z$, and $Cu(O\text{-}nBu)_z$ are similar and show absorption bands at 15,500 + or- 75 and 19,100 + or 300 cm⁻ⁱ, which point to a distorted octahedral environment around copper. However, the spectra of branched alkoxides of copper, $Cu(O\text{-}iPr)_2$, $Cu(O\text{-}sBu)_2$, $Cu(O\text{-}tBu)Z$, and $Cu(O\text{-}tAm)_2$, are characterized by a very broad absorption in the visible region at approximately 15,000 cm⁻¹ that appears to tail in the nearinfrared region. This band may be assigned to a 2E--- 2T₂g, transition,

which would indicate a six-coordinated tetragonal geometry for copper in these branched alkoxides. Copper(II) complexes with unsubstituted phenoxide groups have not been reported as yet, and it may be that these have not been isolated because they would be unstable toward reductive elimination to phenoxy radicals, which would then couple to give diphenoquinone or 1,4-phenylene ethers in the presence of copper. In view of this, it is interesting to report that coordinated diphenoxo derivatives of copper(II) have been obtained by the reactions

$$CuCL_2(bipy) \ +2NaOPh \ \rightarrow Cu(OPh)_2 \ (bipy) \ +2NaCL$$

(brown complex moderarely

soluble in THF)

$$CuCL_2(en) \ +2NaOph \ .phOH \rightarrow Cu(OPh)_2(en).phOH+ 2NaCL$$

green complex sparingly

soluble in THF)

The bisphenoxo derivative of copper(II), $Cu(OPh)_2 \ (en)_2 \ . \ 2PhOH$ has been shown by X-ray diffraction to be a centrosymmetric phenoxo bridged dimer with terminal phenoxo and ethylenediamine groups and hydrogen bonded phenol molecules. The crystals are monoclinic (space group P2 I/n and the unit cell has dimensions a = 19.000, b = 10.930, c = 8.968A, p = 89.90, V = 1862.4 A3, and 2 = 4. The copper atoms are five coordinate, and the coordination geometry is that of a distorted square pyramid. The Cu-Cu distance is 3.215 A, and the compound has a nearly normal magnetic moment at roomtemperature. The X-ray crystal structure of CuO-tBu prepared by the reaction of CuCl with LiO-tBu in THF showed it to be a tetrameric compound, [CuO-tBu)_4 . The crystals are triclinic (space group Pi) with a = 11.890, b = 11.284, c = 10.047 A; a = 90.54, f3 = 106.39, and y =

113.86; d(calculated) = 1.55 for 2 = 8. Four of the formula units form a planar ring containing four Cu and four 0 atoms. The tertrameric units persist even in the vapor phase. Treatment of Cu(0-tBu) with di-t-butyl peroxide gave $Cu(O\text{-}tBu)_z$ as a yellow-green solid . Cu(0-tBu) has been shown to be an excellent metalation reagent, as illustrated by the following facile reaction at room temperature

$$PhCCH \ + \ Cu(O\text{-}tBu) \quad \rightarrow \quad PhCCCu \ + \ tBuOH$$

80 mmol   4mmol   97%   97%
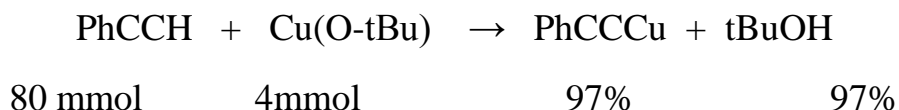
The coupling of 1,3-dinitrobenzene with aryl iodides by Cu(0-tBu) and pyridine provides a convenient route for 2,6-dinitrobiphenyls and is an improvement on the earlier methods . Secondary and primary alkoxides and the phenoxide of copper(I) have been synthesized by the heterogeneous reaction of alcohols with methylcopper(I). The reactions of copper(I) alkoxides with aryl halides yield alkyl aryl ethers under particularly mild conditions. Thermal decomposition of primary alkoxides of copper(I) generates intermediate alkoxy radicals, whereas that of secondary alkoxides appears to take place either by a free radical mechanism or through an intermediate formation of copper(I) hydride. Copper(I) alkoxides, $ROCu(PPh_3)_2$ (R = Et, $PhCH_2$), react with CO_2 to give products corresponding in composition to $ROCO_2CU(PPh_3)_2$. Hydrolysis or thermolysis of these (alkylcarbonato)copper(I) complexes gives a binuclear carbonatocopper(1) complex, $(Ph_3P)_2CuOCO_2\text{-} Cu(PPhs)_2$

Continuing their earlier investigations on the condensation of 5,5,5-trifluoro-4-hydroxy-4(trifluoromethyl)-2-pentanone (hexa- fluorodiacetone alcohol) with diamines in the presence of metal ions, Willis et al. have determined the structure of a dinuclear iminoalkoxy compound of copper(II)[38].

1.5.Copper(II) Oxide

Copper(II) oxide occurs in nature as the mineral tenorite. The structure (Fig. 1) shows Cu(II) with essentially square planar coordination of oxygen atoms

around the copper atoms. The space group is C2/c with unit cell dimensions a = 4.6837 A, b = 3.4226 A, c = 5.1288 A and 0 = 99.54. The structure is a distorted PdO type, and each copper atom has four 0' neighbors at 1.96 A and two apical oxygen atoms, at 2.78 A. In Cu(II) oxide, the Jahn-Teller distortion due to the stabilization of a single d-hole per atom, Cu(II) $3d^9$, results in the observed difference of its structure with the monoxides of the first row transition metals. The magnetic susceptibility of CuO shows an anomaly at 230 K which has been interpreted as an indication of antiferromagnetic ordering . Neutron diffraction studies have corroborated the magnetic ordering in CuO[39]. A reduced atomic moment (pc. = 0.65 f 0.10 pa) at the copper atoms is observed. The antiferromagnetic behavior of CuO is not typical, since the reported susceptibility does not show a maximum of x at the ordering temperature. The purpose of this work was to study the structural, electronic and magnetic properties of Cu(II) oxide and relate the electronic properties to small changes in the concentration of holes (Cu(III)[40].

1.5.1.Characterization of CuO

X-ray powder diffraction patterns were obtained with a Philips-Norelco diffractometer using monochromatic high-intensity Cu K*a*, radiation (h = 1.5405 A). For qualitative phase identification, patterns were taken with a scan rate of 1°2 $\ominus$ min^{-1}, while cell parameters were determined from scans taken at 0.25 ° 28 min^{-1}. Diffraction patterns were obtained over the range 12°< 2$\ominus$ < 72°, and the lattice parameters were determined by a least-squares refinement of the data using a computer program which corrected for the systematic errors in the measurement. A Cahn 113 thermal balance was used to determine the decomposition behavior of copper nitrate. The sample was purged at room temperature in a stream of oxygen for 2 h and then the temperature was increased to 600°C at a rate of 60 °C h^{-1} .In addition the thermal stability of Cu(II) oxide in flowing argon was determined. The temperature was increased to 1000°C at a rate of 60 °C h^{-1}. In all experiments, the flow rate of the gas was 60 std. cm^3 min. The total active oxygen content of the samples was determined by the procedure of Ward and

Struthers [6]. This method allows for the determination of total oxidation of copper, i.e. the amount of formal valent Cu(III) present in the samples. Magnetic susceptibility measurements were carried out using a Faraday balance at temperatures ranging from 77 to 300 K with a field strength of 10.4 kOe. At both 77 and 300 K, the field dependence was determined in the range 6.22 to 10.4 kOe. The van der Pauw method [7] was used to measure the electrical resistivity. Pellets were cold-pressed at 6 kbar and sintered at 650°C in flowing oxygen or argon. Contacts were made by ultrasonically soldering indium directly onto the sintered pellets. Ohmic behavior was established by measuring the currentvoltage characteristics. Qualitative Seebeck measurements were also made to characterize the carrier type of the samples [41].

1.5.2. Copper Oxygen Bonds

The chemical bonding between copper atom and oxygen is interesting both as a prototype system to understand the basic chemical bonding properties between transition metals and oxygen and due to the importance of copper in bioinorganic chemistry for dioxygen metabolism. It is known that at room temperature Cu atom can only form mono- and bis(dioxygen) complexes, $Cu(O_2)$ and $Cu(O_2)_2$, with O2 because the O atom transfer reaction is endothermic. It has been shown in low temperature matrix experiments that a copper dioxide molecule, OCuO, as well as a copper ozone complex, $Cu(O_3)$, can be formed upon UV photolysis. Among the Cu/O species, the copper monoxide (CuO) and $Cu(O_2)$ complex are perhaps the most studied and best understood molecules both experimentally and theoretically. Several matrix experiments have observed the copper dioxide molecule, but its structure and bonding are poorly characterized. We have previously reported on a photoelectron spectroscopy (PES) study of the $Cu(O_2)$ complex and copper dioxide, OCuO.11,12 In the current work, we present a complete study of all the CuOx (x) species produced from a laser vaporization cluster source using size-selected anion PES. Several new Cu/O molecules are observed for the first time, and their structure and bonding information is obtained from their PES spectra taken at various detachment photon energies. Both oxides and O2 complexes are observed for x > 1. We also observe wavelength-dependent photodissociations of the anions for the O2
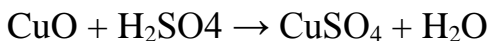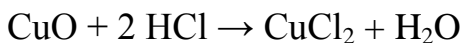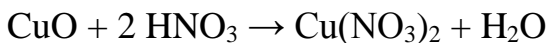
complexes, yielding direct structural information. The only previous PES study was on CuO- at 3.531 eV.13 We obtain the CuO- spectra at several photon energies (2.33, 3.49, 4.66, and 6.42 eV). Not only do we observe photon[42].

Energy dependent detachment cross sections of different transitions, but the high photon energies also allow transitions to higher excited states of CuO. The high excited states, representing essentially Cu 3d f O 2p charge transfer transitions, may be characterized as $Cu^{+2}+O^{2-}$. Interestingly, we also observe a metastable triplet excited state of the anion that allows a new transition to CuO excited state to be observed. For CuO_2, the new spectrum obtained at 6.42 eV yields two extra transitions at high electron binding energies (BEs) compared to the previous spectrum at 4.66 eV that revealed four transitions.11 The 6.42 eV spectrum represents essentially all the six valence molecular orbitals (MOs) of the linear copper dioxide molecule. A new CuO3- molecule is observed for the first time, which contains a CuO- bonded to an O2 molecule. Its spectrum can be understood as due to that of CuO- perturbed by an O2 ligand. The anion of this molecule dissociates at 3.49 eV photon energy into CuO- and O2. We also observe a minor isomer, Cu(O3)-, that dissociates into Cu- and O3 at 4.66 eV. The spectrum of CuO5- is observed to be quite similar to that of CuO3-, and the observed CuO5- species is suggested to be CuO_3^- solvated by an O_2 molecule. For both CuO4- and CuO6-, we observe two isomers. The dominant one is due to a copper dioxide, OCuO, solvated by one and two O_2 molecules, respectively. The second isomer in both cases can dissociate to Cu and is due to a Cu bonded to two and three O_2 molecules, respectively. The spectra of Cu , used as calibrations in our experiments, are obtained at several photon energies (3.49, 4.66, and 6.42 eV). Strong photon energy-dependent detachment cross sections are observed for the 4s and 3d electrons. Additionally, at 6.42 eV, a very strong two-electron transition is observed to the 2P excited state of Cu that is produced due to strong electron correlation effects[43].
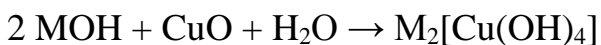
1.5.3.Reactions

Copper(II) oxide is an amphoteric oxide, so it dissolves in mineral acids such

as hydrochloric acid, sulfuric acid or nitric acid to give the corresponding copper(II) salts:

$CuO + 2\ HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$

$CuO + 2\ HCl \rightarrow CuCl_2 + H_2O$

$CuO + H_2SO4 \rightarrow CuSO_4 + H_2O$

It reacts with concentrated alkali to form the corresponding cuprate salts:

$2\ MOH + CuO + H_2O \rightarrow M_2[Cu(OH)_4]$

It can also be reduced to copper metal using hydrogen, carbon monoxide, or carbon:

$CuO + H_2 \rightarrow Cu + H_2O$

$CuO + CO \rightarrow Cu + CO_2$

$2CuO + C \rightarrow 2Cu + CO_2$
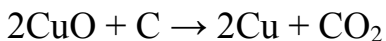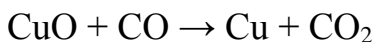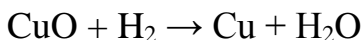
When cupric oxide is substituted for iron oxide in thermite the resulting mixture is a low explosive, not an incendiary[44].

1.5.4. Structure and Physical Properties

Copper(II) oxide belongs to the monoclinic crystal system. The copper atom is coordinated by 4 oxygen atoms in an approximately square planar configuration.

The work function of bulk CuO is 5.3eV

Copper(II) oxide is a p-type semiconductor, with a narrow band gap of 1.2 eV. Cupric oxide can be used to produce dry cell batteries.

Properties

chemical formula CuO

molar mass   79.545g/mol

appearance   black to brown powder

density   6.315g/cm3

boiling point   2,000 °C (3,630 °F; 2,270 K)

Melting point   1,326 °C (2,419 °F; 1,599 k)

Solubility in water   insoluble

Solubility   soluble in ammonium chloride, potassium cyanide

                     insoluble in alcohol, ammonium hydroxide,

                     ammonium carbonate

Band gap   1.2 eV

Refractive index   2.63
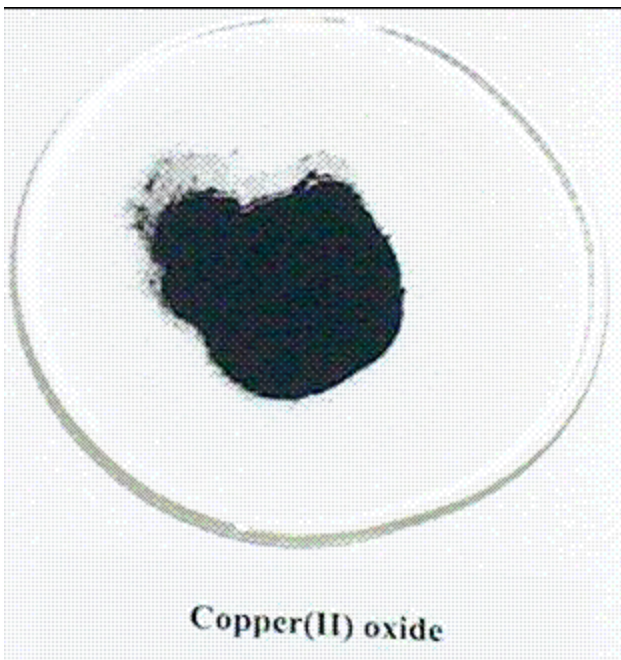
Fig (1-1) pic of CuO

1.5.5.Uses and Application

Cupric oxide is used as a pigment in ceramics to produce blue, red, and green (and sometimes gray, pink, or black) glazes. It is also used to produce cuprammonium hydroxide solutions, used to make rayon. It is also occasionally used as a dietary supplement in animals, against copper deficiency[11]. Copper(II) oxide has application as a p-type semiconductor, because it has a narrow band gap of 1.2 eV. It is an abrasive used to polish optical equipment. Cupric oxide can be used to produce dry cell batteries. It has also been used in wet cell batteries as the cathode, with lithium as an anode, and dioxalane mixed with lithium perchlorate as the electrolyte. Copper(II) oxide can be used to produce other copper salts. It is also used when welding with copper alloys.

Another use for cupric oxide is as a substitute for iron oxide in thermite. This can turn the thermite from an incendiary to a low explosive.

Throughout recorded history, copper (II) oxide has been used as a pigment to

color ceramics, enamels, porcelain glazes, and artificial gems, applications that continue to the present day. The oxide adds a bluish to greenish tint to such materials. Copper (II) oxide also finds use as an insecticide and fumigant. It is used primarily in the treatment of potato plants and as an antifouling agent on boat hulls. An antifouling agent is a material that prevents the formation of barnacles and other organisms on the bottom of a boat. When such organisms grow on a boat's hull, they increase the friction produced when the boat rides through the water, thus reducing its speed. The compound is also used as a wood preservative, to protect fence posts, pilings, decking, roofing, shingles, sea walls, and other freshwater and marine structures from insects and fungi [45].

Other uses to which copper (II) oxide is put including the following:

- In the preparation of superconducting materials, materials that have essentially no resistance to the flow of an electric current;

- In the manufacture of batteries and electrodes; As a welding flux for use with bronze objects and materials; For polishing of optical glass, glass used in telescopes, microscopes, and similar instruments;

- In the preparation of phosphors, materials that glow in the dark after being exposed to light; For the removal of sulfur and sulfur compounds for petroleum;

- In the manufacture of rayon; and as a catalyst in many industrial and commercial chemical reactions

1.5.6. Health effects

Copper (II) oxide is an irritant. It also can cause damage to the endocrine and central nervous system. Contact to the eyes or skin can cause irritation. Ingesting cupric oxide powder can result in a metallic taste, nausea, vomiting and stomach pain. In more severe cases, there may be blood in vomit or black or tarry stools, jaundice and enlarged liver. Blood cells rupture resulting in circulatory collapse and shock. Inhalation can lead to damage to

the lungs and septum. Inhalation of fumes during smelting of cupric oxide powder can lead to a disease called metal fume fever, which can result in flu like symptoms. Copper (II) oxide can cause a toxic build-up of copper in a small subset of the population with Wilson's disease. Handling copper (II) oxide powder should be done in well-ventilated area, and care should be taken to avoid contact with the skin or eyes. However copper is an essential trace element for the normal function of many tissues, including the nervous system, immune system, heart, skin and for the formation of capillaries as well as copper being extremely well metabolized by humans. Copper oxide is used in vitamins supplements as a safe source of copper and over the-counter treatments. Copper oxide is also used in consumer products such as pillowcases and socks, due to its cosmetic and anti-microbial properties. The risk of dermal sensitivity to copper is considered extremely minimal [46].

1.6. The aim of the study:

The objectives of the present study is :

- To prepare copper (II) alkoxides using (ethanol, 2-propanol, tert-butanol) and to characterise the formed copper alkoxides using IR spectro metar .

- To prepare copper (II) oxide from the obtained alkoxides and characterises the resulted copper oxides using IR, X-ray diffraction XRD spectro metars .

- To determine the concentration of copper (II) in the oxides.

2. Materials and Methods

2.1. Materials :

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- Absolute ethanol CH_3CH_2OH (HPLC-PLUS - Gradient , assay $\geq$99.8% (GC)   vapor density 1.59(vs air)

- Copper((II) chloride Anhydrous $CuCl_2$ (powder ,assay $\leq$ 99.995% trace metals basis ,density 3.386g/ml at 25°C,M.Wt= 134.45 g/mol)

- 2-propanol C_3H_8O (grade anhydrous, assay 99.5% M.Wt=60.1 g/mol, colorless , soluble in water completely ,density 0.785g/ml at 25 °C)

- Tert- butanol $C_4H_{10}O$ (grade anhydrous, assay $\leq$ 99.5 % M.Wt= 74.12 g/mol ,soluble in water miscible ,density 0.775g/ml at 25 °C)

- Sodium metal   Na   (sodium 25-35 wt % dispersion in paraffin)

- sodium thiocyanate   NaSCN (ACS reagent ,assay $\leq$98% ,soluble in water 1.000g/ml at25°C , M.Wt =81.07g/mol)

-   acetic acid (glacial) CH_3COOH (assay $\leq$99.85% ,density 1.049g/ml at 25°C , M.Wt =60.05 g/mol)

- potassium iodide KI M.Wt=166.003 g/mol

- sodium thiosulfate $Na_2S_2O_3.5H_2O$ (ACS reagent ,assay ≥99.5% , pH=6.0-8.4 at(25 C ,5%) , soluble in water ,M.Wt =248.18 g/mol)

- ammonia NH_3 (density 0.73 kg/m^3 ,M.Wt =17.031g/mol)

- starch solution

2.1.1. Instruments and Equipment:

- **Infra-Red Spectroscopy (IR):** JASCO, FT/IR-4100 LE Serial No. B18736106, protect: Class1, Made in Japan.

- **Water Bath:** Digital Water Bath, Daihan Labtech Co. L.T.D., Model; LWB-122 D, Serial No. 2014022849.

- **Sensitive Balance:** SHIMADZU, Electronic Balance, Type: AY120, NO. D432711233, Made in Japan.

- **X-ray Diffraction:** ADX-2700 X-ray Powder Diffraction Instrument

2.1.2. Glass wares:

All glass ware were of Pyrex type.

2.2. Methods:

2.2.1. Preparation of Sodium Ethoxide:

The sodium ethoxide was prepared by mixing 1:1 molar ratios of sodium metal and absolute ethanol.

About 100 ml of alcohol was taked in the reaction vessel and stirred continuously using a magnetic stirrer. Solid sodium pieces weighing 500–1000 mg were added to the alcohol. The reaction was initially carried out at room temperature and then the temperature was gradually raised to near boiling point of the respective alcohol to dissolve as much sodium as possible and the addition of sodium was stopped when the solution was saturated. Stirring and heating were stopped and the saturated sodium alkoxide solution was allowed to cool naturally for about 16 h to facilitate the formation of sodium alkoxide crystals and completion of the crystallization process. The crystalline sodium alkoxide was dried .

2.2.2.Preparation of Copper Alkoxides by using (ethanol,2-propanol,tert-butanol).

A solution of sodium alkoxide (2 moles) was added to a solution (or suspension) of copper(II) chloride in the parent alcohol(ethanol,2-propanol,tert-butanol). This caused an immediate change in color with the formation of an insoluble product. Contents were stirred for 5-6 hours at room temperature (35°C). The insoluble product obtained was filtered out and washed with parent alcohol(ethanol,2-propanol,tert-butanol) till the test of chlorine was negative in the washings as weel as in the product. Colored solids of the general formula, Cu(OR), were obtained after removing excess of the solvent under reduced pressure (0.5 mm).

2.2.3.preparation of copper(II) oxide :

Weighed 1 gram of the sample in a porcelain crucible and placed in an oven at a temperature above 600 °C for an hour.

2.2.4.Determination of Concentration of Copper (II).

2 grams of copper (II) oxide was weighted in to volumetric flask 250 mL then ammonia were added till become the color of the solution Blue 3 ml of acetic acid was added until the blue color disappeared, 2 g of potassium iodide was added and stired well-closed flask and put in a dark place for 5 minutes. The flask was titrated against   sodium thiosulfate solution of burette till it become a pale yellow color. Was add 5 ml of starch and 1 g of sodium thiocyanate   the titrational was continons till the blue color disappear.

2.2.5.Characterization of the Copper (II) Alkoxides and Copper (II) Oxide :

2.2.5.1. Fourier Transform Infrared Spectroscopy (FT-IR):

 2 mg of the (copper(II) alkoxide , copper(II)oxide) were triturated with 300 mg of dried potassium bromide. These quantities were usually sufficient to given a suitable intensity of spectrum when use a disc with diameter (10-15 mm). Carefully the mixture was grinded, spread uniformly in a suitable disc, and submitted to a pressure of about 800 MPa (8 t·cm^{-2}). For substances that were unstable under normal atmospheric conditions, the disc had been pressed in vacuum. Several factors might be caused the formation of faulty discs, such as insufficient or excessive grinding, humidity or other impurities in the dispersion medium or an insufficient reduction of particle size. A discwas rejected if visual examination had been show lack of uniform transparency or when transmittance at about 2000 cm^{-1} (5 µm) in the absence of a specific absorption band was less than 60 percent without compensation, unless otherwise prescribed.

Samples have been prepared by the same procedure and the spectrum was recorded between 4000- 400 cm^{-1} (2.5-15.4µm) under the same operational conditions. The transmission minima (absorption maxima) in the spectrum was obtained with the substance to be examined correspond in position and

relative size to those in the spectrum obtained with the reference substance[47].

2.2.5.2.X-ray Diffraction Analysis

Single crystals were finely ground between glass plates, and a thin layer of the resulting powder was dispersed with acetone on a glass slide. Powder diffraction patterns were obtained with a Philips-Norelco diffractometer using monochromatic high intensity CuKá1, radiation (X = 1.5405A). For qualitative identification of the phases present, the patterns were taken from 12 ° < 2e < 72 ¢ with a scan rate of 1 ° 2e/min and a chart speed of 30 in/hr. Cell parameters were determined by a least squares refinement of the reflections using a computer program which corrects for the systematic errors of the measurement [39].

2.3. Percentage yield of Copper (II) and Formula Weight of a Copper Compound

$$\%Copper \ = \ \frac{mass\ of\ copper}{mass\ of\ sample}\ X\ \ 100\%$$

This first equation will allow you to determine the percent copper in the sample. Another way of expressing this relationship is:

$$\%Copper \ = \ \frac{n(63.55)}{f.\ w.}\ X\ \ 100\%$$

Where:　　　　　　　n = the number of copper atoms in the compound
　　　　　　63.55   =the atomic weight of copper
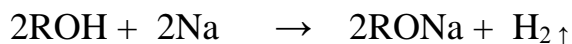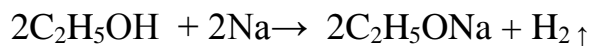　　　　　　f. w. = the formula weight of the compound
Since all of the unknown compounds used in this experiment contain only one copper atom, the second equation gives an easy way of calculating the
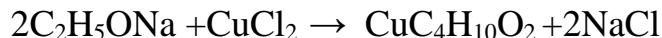
formula weight of the compound.

3. Results and Discussion

The copper(II) alkoxides and copper(II) oxide were synthesized and characterized, The percentage yield of copper (II) in copper(II) oxide was Found to be 78.4 %.
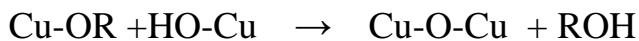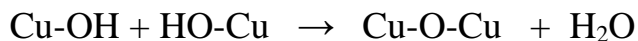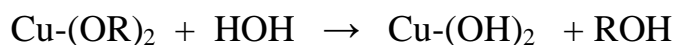
The Preparation of cooper (II) alkoxides and copper (II) oxide can be presented by the following equation:

$$2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2 \uparrow$$

$$2ROH + 2Na \rightarrow 2RONa + H_2 \uparrow$$

$$R= C_2H_5OH, C_3H_8OH, C_4H_{10}OH$$

Preparation of Sodium Alkoxides

$$2C_2H_5ONa + CuCl_2 \rightarrow CuC_4H_{10}O_2 + 2NaCl$$

$$2RONa + CuCl_2 \rightarrow Cu (OR)_2 + 2NaCl$$

$$R= C_2H_5OH, C_3H_8OH, C_4H_{10}OH$$

Preparation of Copper (II) Alkoxides

$$Cu\text{-}(OR)_2 + HOH \rightarrow Cu\text{-}(OH)_2 + ROH$$

$$Cu\text{-}OH + HO\text{-}Cu \rightarrow Cu\text{-}O\text{-}Cu + H_2O$$

$$Cu\text{-}OR + HO\text{-}Cu \rightarrow Cu\text{-}O\text{-}Cu + ROH$$
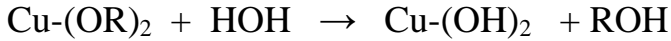
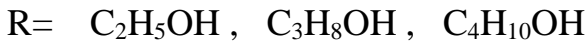$$R= C_2H_5OH, C_3H_8OH, C_4H_{10}OH$$

Preparation of Copper (II) Oxide

3.1. The full sol gel mechanism in such preparation can be represented as follow:

•Hydrolysis

$Cu\text{-}(OR)_2 + HOH \rightarrow Cu\text{-}(OH)_2 + ROH$

•Condensation

$Cu\text{-}OH + HO\text{-}Cu \rightarrow Cu\text{-}O\text{-}Cu + H_2O$

$Cu\text{-}OR + HO\text{-}Cu \rightarrow Cu\text{-}O\text{-}Cu + ROH$

$R = C_2H_5OH , C_3H_8OH , C_4H_{10}OH$
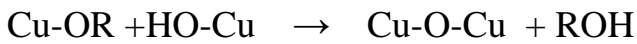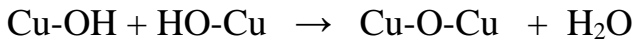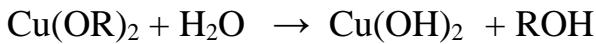
based on the growth of metal oxo polymers in a solvent

- inorganic step polymerization reactions through hydrolysis and condensation of metal alkoxide $Cu(OR)_2$ ....OR is an alkoxy group

- first step hydroxylation upon the hydrolysis of alkoxy groups

$Cu(OR)_2 + H_2O \rightarrow Cu(OH)_2 + ROH$

- second step polycondensation process leading to the formation of branched oligomers with a metal oxo based skeleton and reactive residual hydroxo and alkoxy groups

competitive mechanisms

- oxolation ; formation of oxygen bridges

$Cu(OH)_2 + XO\text{-}Cu \rightarrow Cu\text{-}O\text{-}Cu + XOH$
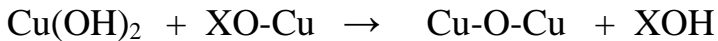
where $X=H$,generally when hydrolysis ratio $h=H_2O/M \gg 2$

or $X=R$ when $h= H_2O/M < 2$

3.2. IR spectra:

The result show in spectra of ethanol isopropanol tert butanol they showed features around 3500-1600, 3000-1450, 1050, and 540 and 440 cm-l

The 3500 and 1600 Cm-1 due to OH stretching and bending vibration.

The 3000-1450 peaks due to CH stretching and bending vibration of alkoxide .

The feature around 1050 due to C-O vibration

The band around 540 and 440 cm-l due to CuO

The peake of copper alkoxide shifted by the influence of copper oxide

Table (3-4) Characteristic bands of copper alkoxides and oxide

Compound	C-O Cm^{-1}	C-H Cm^{-1}	OH cm^{-1}	Cu-O cm^{-1}
CuOC$_2$H$_5$	1050	2850	3000	890
CuOC$_3$H$_8$	1028.81	2927.87 s 1450-37 b	3369.87 s	865.77
CuOC$_4$H$_{10}$	1030.03	2922.15 s 1451.05 b	3389.7 s	868.70
CuO	-	-	3434	-437.14 600.78
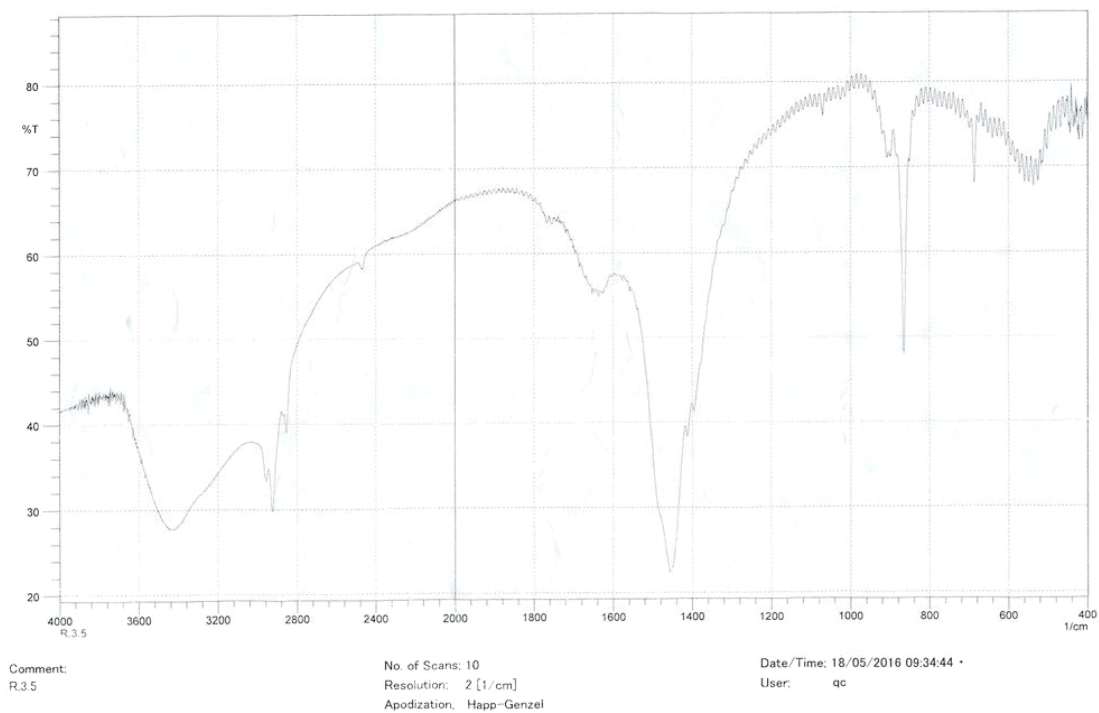
Figure (3-2). FTIR spectrum of Copper di ethoxide
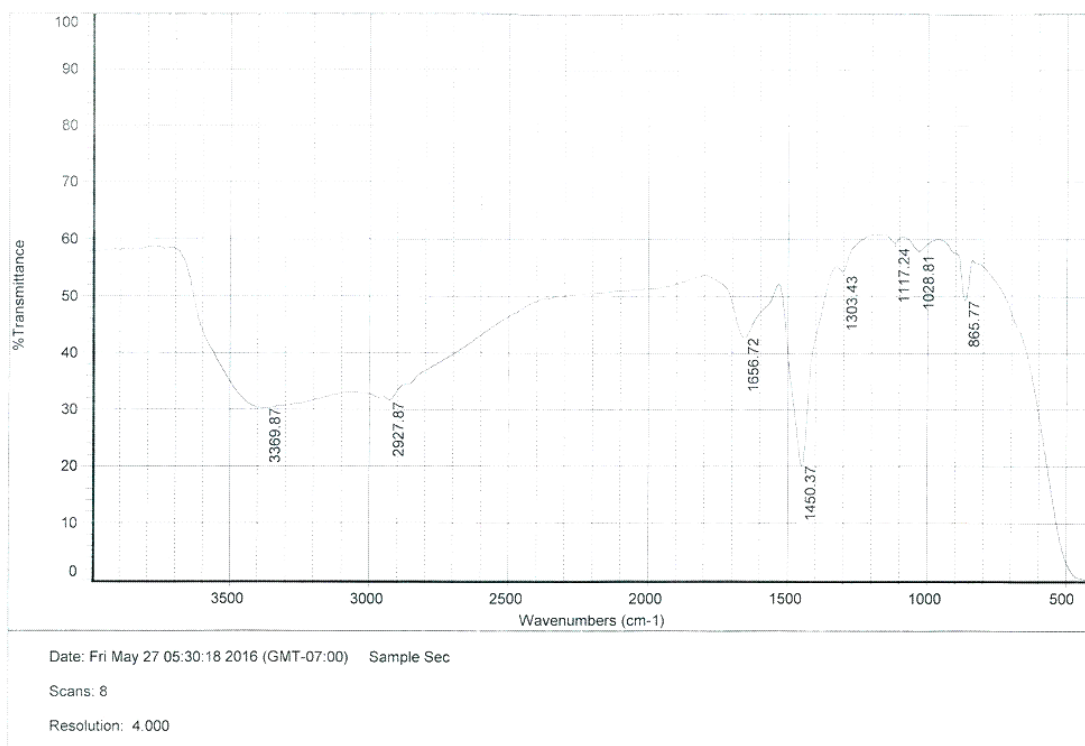
Figure (3-3). FTIR spectrum of Copper di propoxide

Figure labels visible on spectrum: 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0 (%Transmittance axis); 3500, 3000, 2500, 2000, 1500, 1000, 500 (Wavenumbers cm-1 axis); peaks: 3389.70, 2922.15, 1655.75, 1451.05, 1030.09, 868.70

Date: Fri May 27 05:16:11 2016 (GMT-07:00)   Sample Ter

Scans: 8

Resolution: 4.000
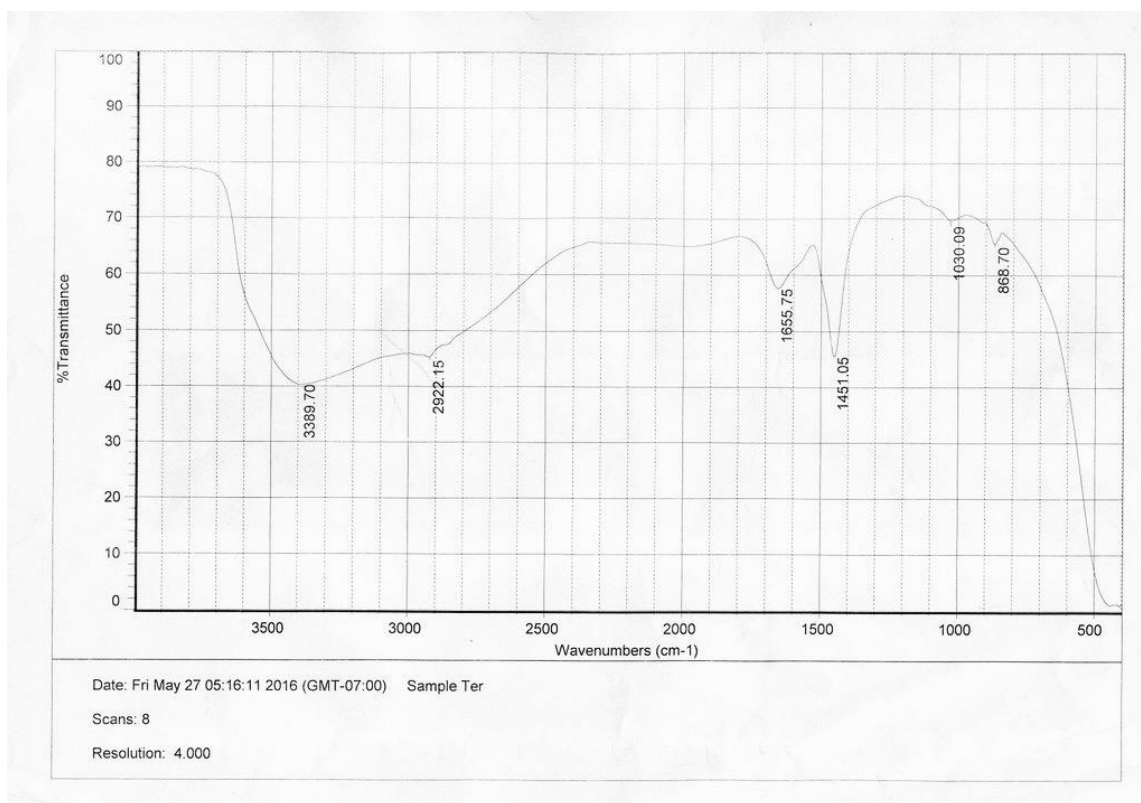
Figure (3-4). FTIR spectrum of copper di butoxide

The FTIR spectrum of the oxide was shown in figure (3-5). The spectrum shows the following characteristics: the peaks 437.14 cm-1 (Cu-O symmetric stretching), and 522.08 cm-1 (Cu-O asymmetric stretching) and 600.78 cm-1 (Cu-O wagging) imply the presence of metal-oxide group in the sample. The vibration peak 3434 cm-1 indicates the presence of hydroxide group in the sample. This may be due to the water attached to the surface of the CuO , which is also one of the byproducts of the reaction and can be removed by further heating. The metal–oxygen bond is observed at 1383 cm-1 (M-O rocking in plane) and at 1634 cm-1 (M-O rocking out of plane) indicates the formation of CuO from copper chloride.

43
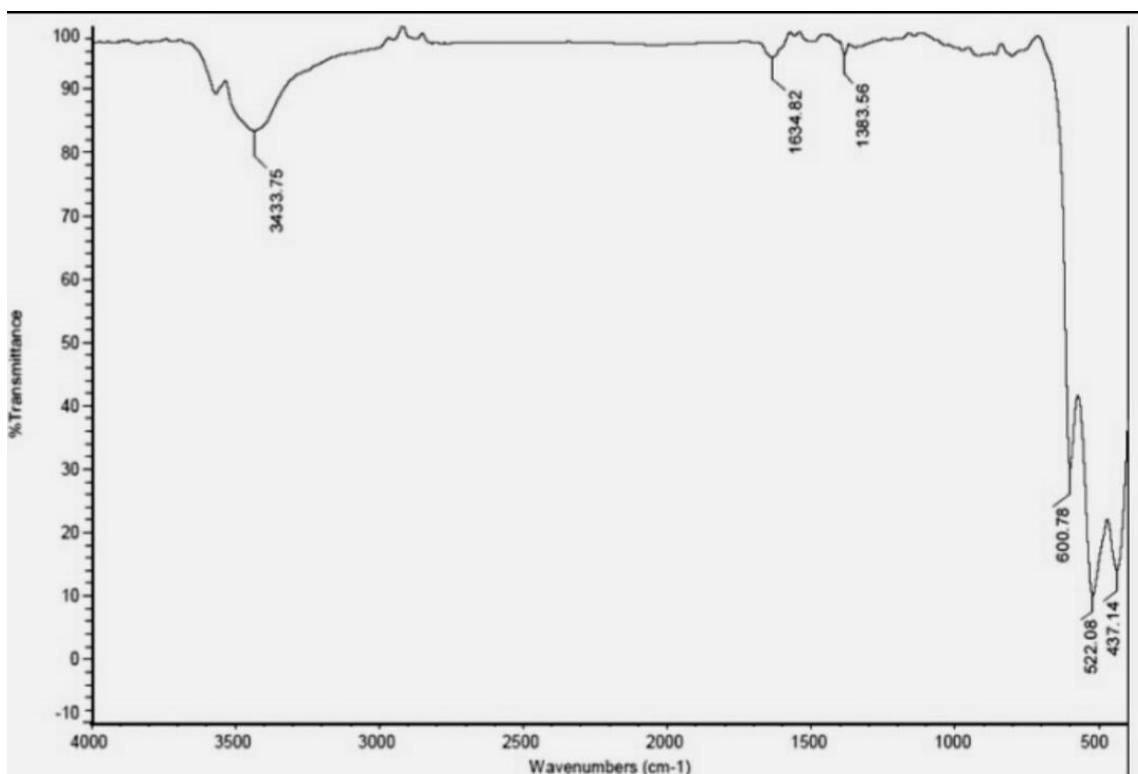
Figure (3-5). FTIR spectrum of CuO

3.3.X-rey diffraction:

the XRD pattern of the prepared CuO was shown in figure (3-6)All the peaks in diffraction pattern indicate the monoclinic structure of CuO, and the average grain size calculated using Debay-Scherrer formula is approximately 20.4054 nm these values are in agreement with the literature values [72-0269].
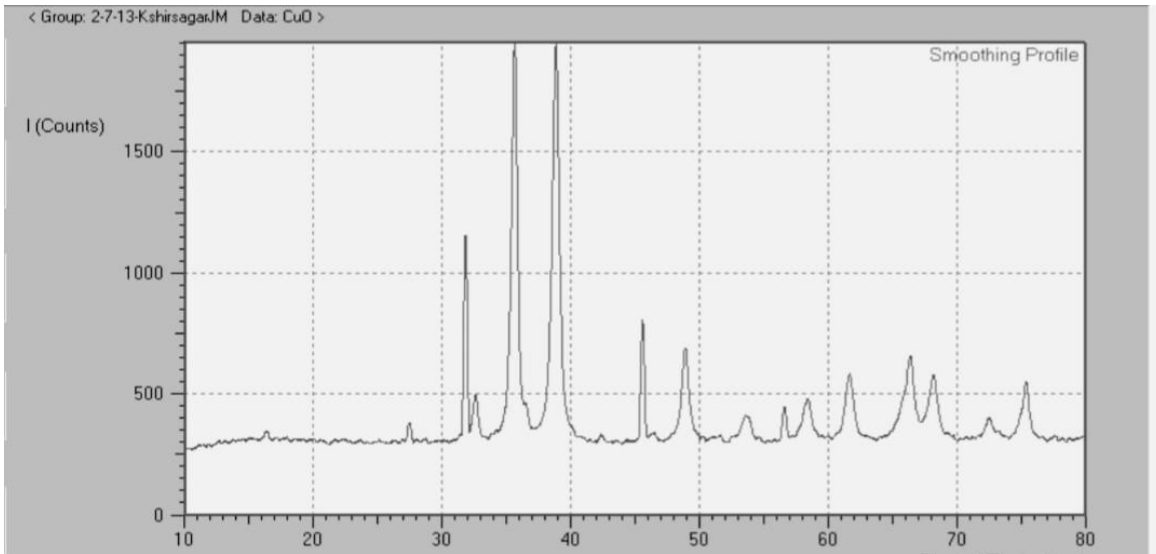
Figure(3-6). X ray diffractogram of CuO

3.4. Conclusion:

In the present study:

The first part of the study include the preparation of different copper (II) alkoxides and copper(II) oxide complexs .

Characterization of the formed different alkoxides and copper (II) oxide using IR, and X-ray diffraction.

 Ethanol react with sodium matel to form sodium ethoxide (NaOCH$_2$CH3) astrong base commanly used for elimination reactions.

  more hindered alcohols like 2-propanol and tert- butanol react faster with potassium than with sodium .

  sol-gel processing has been used as a new approach for the preparation of several metal oxides.

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