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**SYNTHESIS, CHARACTERIZATION AND
CRYSTAL STRUCTURES OF
HOMONUCLEAR COPPER COMPLEXES WITH
1,3-Bis(dimethylamino)-2-Propanol as Ligand**

BY JIAN-CHUAN ZHENG

**A Thesis
Submitted to the
Faculty of Graduate Studies and Research
through the Department of Chemistry and Biochemistry
in Partial Fulfilment of the requirements for the Degree of
Master of Science at the University of Windsor**

Windsor, Ontario, Canada

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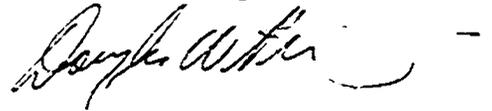


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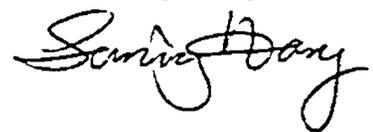
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Abstract

Reaction of 1,3-bis(dimethylamino)-2-propanol (bdmapH) with CuCl_2 in 1:1 ratio yielded a dimeric Cu(II) compound **1** with the formula of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$, which is a dizwitterion with two intramolecular ammonium groups. Its crystal structure was fully characterized by single-crystal X-ray diffraction analysis. Compound **1** crystallizes in the monoclinic space group $C2/c$ with $a = 18.619(3)\text{\AA}$, $b = 12.129(2)\text{\AA}$, $c = 13.822(2)\text{\AA}$, $\beta = 106.69(1)^\circ$, $V = 2989.8(7)\text{\AA}^3$ and $Z = 4$. The proton bonded to nitrogen was located directly from a difference Fourier map in the X-ray crystal structure analysis. The presence of a N-H bond was also confirmed by IR spectroscopy, $\nu(\text{N-H}) = 3420\text{cm}^{-1}$. Compound **1** has an effective magnetic moment, $\mu_{\text{eff}} = 1.56$ B.M. at 23°C , which indicates antiferromagnetic coupling of the unpaired electrons between two copper atoms. The proton on the ammonium group can be removed by a base through an intermolecular process. This has been demonstrated by the reaction of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ with $\text{Cu}(\text{OMe})_2$ in 1:1 ratio in CH_2Cl_2 to produce a trimeric Cu(II) compound **2** with the formula of $\text{Cu}_3(\text{bdmap})_2\text{Cl}_4$. Compound **2** crystallizes in the monoclinic space group $P2_1/a$ with $a = 16.45(2)\text{\AA}$, $b = 10.445(7)\text{\AA}$, $c = 16.47(1)\text{\AA}$, $\beta = 101.52(8)^\circ$, $V = 2793(5)\text{\AA}^3$, and $Z = 4$. Compound **2** also exhibits an antiferromagnetic exchange behaviour. Both dimer **1** and trimer **2** display irreversible redox behaviour.

A new class of tetranuclear copper complexes with planar cyclic structures has been synthesized by using 1,3-bis(dimethylamino)-2-propanolato and acetate ligands. Three members of this class of molecules have been characterized structurally. Compound **3** with the formula

$[\text{Cu}_4^{\text{II}}(\text{bdmap})_3(\text{OH})(\text{OAc})_2(\text{HOAc})(\text{H}_2\text{O})][\text{PF}_6]_2$ and compound 5 with the formula $[\text{Cu}_4^{\text{II}}(\text{bdmap})_2(\text{OAc})_4][\text{PF}_6]_2$ are discrete molecular complexes in the solid state. Compound 4 with the formula $[\text{Cu}_4^{\text{II}}(\text{bdmap})_2(\text{OAc})_3(\text{OH})_2(\text{H}_2\text{O})][\text{PF}_6]$ has one-dimensional structure in the solid state and the Cu_4 planar units are linked together through intermolecular hydrogen bonds and Cu-O bonds. Compound 3 crystallizes in the triclinic crystal system, space group $\text{P}\bar{1}$, $a=13.289(6)\text{\AA}$, $b=15.737(6)\text{\AA}$, $c=13.214(5)\text{\AA}$, $\alpha=97.29(4)^\circ$, $\beta=96.24(4)^\circ$, $\gamma=103.77(3)^\circ$, $Z=2$. Compound 4 crystallizes in the triclinic crystal system, space group $\text{P}\bar{1}$, $a=13.34(1)\text{\AA}$, $b=13.992(8)\text{\AA}$, $c=11.726(8)\text{\AA}$, $\alpha=113.59(4)^\circ$, $\beta=95.71(8)^\circ$, $\gamma=74.54(7)^\circ$, $Z=2$. Compound 5 crystallizes in the monoclinic crystal system, space group $\text{P}2_1/n$, $a=10.154(5)\text{\AA}$, $b=12.712(4)\text{\AA}$, $c=15.405(9)\text{\AA}$, $\beta=99.05(6)^\circ$, $Z=2$.

A hexanuclear Cu(II) compound 6 has been characterized structurally with the formula $[\text{Cu}_6(\text{bdmap})_2(\text{OAc})_3(\text{PyO})_2(\text{PyOH})][\text{PF}_6]_2$. Compound 6 has a one-dimensional structure in the solid state. There are one Cu_2 and one Cu_4 unit in the Cu_6 compound which are linked together through covalent copper-oxygen bonds.

Dedicated to the memories of my wife and my parents

Acknowledgements

I would like to express my deep and sincere appreciation to my supervisor Dr. Suning Wang for getting me started at this Department, and for the encouragement and understanding I have received throughout my work. I am especially thankful to the Chemistry Department of the University of Windsor which gave me this opportunity to come to Canada and to join this excellent research institution. I am indebted to the faculty for their kind attention and care over the years. I thank our technical staff, especially Mr. Mike Fuerth, for his kind and patient assistance.

Special thanks are due to Mr. David Hill who makes newcomers feel welcome. Finally I would like to acknowledge the Faculty of Graduate Studies for postgraduate awards and the Department of Chemistry for teaching assistantships.

Jian-chuan Zheng

Windsor Ontario

January, 1993

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List of Abbreviations

acmpzH:	1-(1-ethanoyl)-5-methylpyrazole
bdmap:	1,3-bis(dimethylamino)-2-propanol
bdmapH:	1,3-bis(dimethylamino)-2-propanolato
calcd.:	calculated
CV:	cyclic voltammogram
dbae:	2-dibutylaminoethanolato
dbaeH:	2-dibutylaminoethanol
deae:	2-diethylaminoethanolato
deaeH:	2-diethylaminoethanol
depo:	1,2-diphenyl-2-(methylamino)ethanone-1-oxime
DMF:	dimethylformamide
DPV:	differential pulse voltammetry
dec.:	decomposition
IR:	infrared
J_c :	critical current
MOCVD:	metal-organic chemical vapour-phase decomposition
m.p.:	melting point
mpzH:	3(5)-methylpyrazole
NMR:	nuclear magnetic resonance
T_c :	critical temperature
THF:	tetrahydrofuran

Chapter I

General Introduction

High-temperature superconductors, hetero-polymetallic oxide materials, have attracted considerable attention since the first group of high-temperature superconductors discovered¹⁻² by Bednorz and Mueller were oxides of the type $\text{La}_{2-x}(\text{Ca}, \text{Sr}, \text{Ba})_x\text{CuO}_4$ with T_c (critical temperature) values in the 25-40K range, soon followed by the so called 1-2-3 oxides of the general formula $\text{LnBa}_2\text{Cu}_3\text{O}_7$ ($\text{Ln}=\text{Y}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{or Yb}$) with T_c values in the 90K region.³⁻⁵ The discovery of materials with superconductivity above liquid nitrogen temperature has raised much hope and has promoted an intensive search for new classes of oxides with still higher superconducting transition temperatures. Two new series of layered oxides belonging to the Bi-Ca-Sr-Cu-O and Tl-Ca-Ba-Cu-O systems and possessing the general formula $\text{A}_2\text{Ca}_{n+1-x}\text{B}_x\text{Cu}_n\text{O}_{2n+4}$ where $\text{A}=\text{Bi}$ or Tl and $\text{B}=\text{Sr}$ or Ba have been found to exhibit superconductivity between 60 and 125K.⁷⁻²⁰ A few members of the series ($n=1-3$) of oxides have been characterized adequately, although there has been some difficulty in obtaining pure phase, especially in the bismuth cuprate system. Recently, superconducting lead cuprates of the type $\text{PbASr}_2\text{Cu}_3\text{O}_4$ ($\text{A}=\text{Ln}$ or $\text{Ln}+\text{Ca}$) have been discovered.²¹

Traditional ceramic methods require high-temperature processing, often in excess of 1000°C, in order to achieve intimate mixing of metal sources. High-temperature processing can be undesirable for many reasons, including (i) increased energy cost, (ii) inability to gain access to metastable phases present at milder temperatures and (iii) difficulty of control of the stoichiometry.²²⁻³⁰ In contrast, routes based on soluble precursors, which can be spun or dipped into films, appear attractive for a variety of reasons; low expense, the ability to coat large unusually shaped objects, and high homogeneity and purity.³¹ Recently MOCVD (metal organic

chemical vapour-phase deposition) and sol-gel methods have been used in the preparation of superconductors by chemical processes using soluble and volatile precursors. The sol-gel technique has been used for many years for producing oxide glasses and ceramics.³²⁻³⁶ The basic procedure of the sol-gel process is to form a solution of the elements of the desired compound in an organic solvent. The solution is then polymerized to form a gel. This gel is dried and fired to displace the organic components and form the final inorganic oxide.

There are essentially two different kinds of sol-gel technology. The first method involves the dispersion of colloidal particles in a liquid to form a sol to produce a gel. The second method involves the polymerization of organometallic compounds such as alkoxides. The chemical sol-gel process related to high T_c superconductors is based on organometallic precursors. Materials which are used in modern ceramic and device technology require high purity and precise control of composition and microstructure. Since the chemical reactants for sol-gel processing can be purified conveniently by distillation and crystallization, films of high purity can be fabricated by sol-gel processing.

In sol-gel processing, chemicals for preparing films are dissolved in a liquid to form a solution. Since all the starting materials are mixed at the molecular level, a high degree of homogeneity of film can be expected. The pores in properly dried gels are often extremely small and the components of a homogeneous gel are intimately mixed. This allows lower processing temperatures for sol-gel-derived ceramics. This can be important in compositions which undergo undesired phase transitions or have volatile components, or which exist in structures undergoing

undesired diffusion or compositional changes at higher temperature. Another advantage of sol-gel processing is that, because of the solution form of the raw materials, trace elements can be easily introduced into the solution by adding the elements in the form of organometallic compounds or soluble organic or inorganic salts. Such trace elements can improve the properties of oxide films. The viscosity, surface tension, and concentration of the organometallic polymeric solution can be easily adjusted. Large-area films or coatings of desired composition can be easily formed in a substrate of complex geometry. The methods of application of the film can be by dipping, spinning, spraying, or even painting. This allows for tailoring the process to specific requirements. Meanwhile volatile metal alkoxides offer several attractions as precursors for the deposition of metal oxides by MOCVD technique³⁷. MOCVD techniques present an alternative vapour phase approach to the preparation of thin metal-oxide films and, in principle, offer the advantages of simplified apparatus, excellent film uniformity, compositional control, high deposition rates, and the potential to develop large scale processing.⁴² The films and fibres of high temperature superconductors obtained by the two methods have been reported.^{22-23,38-41,43} A few papers described attempts to isolate and characterize intermediates. Studies have shown that properties of the rare earth superconductors are highly sensitive to processing conditions. Metal nonstoichiometry and some boundary impurities sharply decrease the critical temperature (T_c) and the critical current (J_c) of the materials.²²⁻²⁹ Clearly, chemical control of the species present in precursor solutions will enhance the ability to control the homogeneity and stoichiometry. Chemical processing makes it possible to obtain high T_c superconductors at much lower temperature than the conventional methods. At present, homonuclear or heteronuclear soluble aggregates incorporating metals relevant to superconductors (i.e. heavy alkali and/or alkaline-

earth metals, lanthanides and copper) constitute a synthetic challenge. Only a few examples have been reported recently.^{38,41,43} Furthermore, yttrium and lanthanide metal chemistry remains poorly developed.⁴²⁻⁴⁶ Three different metallic precursors are required for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ high Tc superconductor and even more source precursors are needed for systems such as the Tl-Ba-Ca-O or Bi(Pb)-Sr-Ca-O.^{30,38,47-56}

It has been well established that, for obtaining superconductors by MOCVD and sol-gel techniques, use of a "single-source" including homometallic and heterometallic precursors in which heavy elements are associated in an appropriate ratio increases the quality of the final material. Therefore, one of today's challenges is to build homonuclear or heteronuclear precursor sources to meet the requirements of MOCVD and sol-gel techniques. In addition, none of the superconducting theories have given satisfactory explanations of the superconducting mechanisms. The physical and chemical properties of superconductors could be understood by the study of molecular model complexes. The goal of this thesis is to synthesize new polynuclear copper(II) complexes with 1,3-bis(dimethylamino)-2-propanol ligand (bdmapH) and to study physical and chemical properties of these compounds.

Chapter II

Dimeric and Trimeric Copper Compounds with 1,3-Bis(dimethylamino)-2-Propanol Ligand

II.1. Introduction

There is much interest in the investigation of homonuclear copper alkoxide complexes stimulated by the possible applications in MOCVD and chemical sol-gel processes.^{37-38,43,57-63} Until recently, efforts to prepare cuprate-oxide superconductors from alkoxide-precursor solutions suffered from the lack of soluble copper(II) precursors.^{64-68,71} In order to synthesize new soluble Cu(II) precursor compounds for high temperature superconductors, the choice of ligand is very important. One of the largest and most important groups of ligands is that in which the coordination to the metal ion occurs through the oxygen atom. If the oxygen atom is bonded to carbon, the resulting complexes may be divided into two classes. In the first class are complexes such as metal carboxylates, carbonates etc., which are usually stable to air and moisture and can be obtained readily. In the second class are metal alkoxides which generally have low stability to moisture and air and require the use of oxygen-free and moisture-free synthetic techniques. This restricts the range of complexes which may be prepared.^{42,72} As reported in several reviews, alkoxides can be excellent precursors for the chemical vapour deposition (CVD) or sol-gel production of various metal oxide products.³⁷⁻³⁸ One successful approach to improving solubility and volatility of precursor compounds involves the use of multidentate alkoxy ligands. For example, $\text{Cu}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe})_2$ ⁶⁰, $\text{Cu}(\text{OCH}_2\text{CH}_2\text{OBu})_2$ ⁶¹, $\text{Ba}(\text{OCH}_2\text{CH}_2\text{OBu})_2$ ⁶³ are soluble in a range of organic solvents and $\text{Cu}(\text{OCHMeCH}_2\text{NMe}_2)_2$ ⁶² is one of the most volatile copper(II) alkoxides known, subliming at 60°C under vacuum. The multidentate alkoxy ligands containing -OBu, -NEt₂ or -CF₃ groups appear to improve the solubility and volatility of precursor molecules to meet MOCVD and sol-gel requirements. The ligand used in this work is a multidentate amino alcohol ligand, 1,3-bis(dimethylamino)-2-propanol (bdmapH). The

structure of this ligand is shown Figure 1. There are two different coordinating centres with the deprotonated bdmaph ligand (bdmap), a neutral site and an anionic site. The bdmap ligand could combine polynuclear metal centres together through both coordination sites. As multidentate alkoxy ligands, the two $-N(Me)_2$ groups of bdmap could increase the solubility of metal alkoxides. In fact, a very soluble dimeric copper(II) compound, $Cu_2(bdmap)(OAc)_3$ ¹²⁴, has been synthesized by our group. It has been used successfully in the preparation of 1-2-3 high T_c superconductors by the sol-gel method. The heteronuclear species of Y-Cu, Nd-Cu, Pr-Cu and Ba-Cu have been successfully synthesized with the bdmaph ligand in our laboratory.

A new dimeric and a new trimeric copper(II) compound with 1,3-bis(dimethylamino)-2-propanol ligand were prepared. The results are reported in this chapter.

II.2. Experimental Section

II.2.1. Chemicals and Solvents

All manipulations were carried out using standard Schlenk lines or a nitrogen-filled drybox. Tetrahydrofuran was distilled over sodium metal, and CH_2Cl_2 was distilled over P_2O_5 . They were stored under nitrogen prior to use. Anhydrous ethanol and diethyl ether were purchased from BDH. Cupric chloride was purchased from Fisher Scientific. Copper(II) methoxide and 1,3-bis(dimethylamino)-2-propanol were purchased from Aldrich Chemicals Co.. Copper(II) methoxide was stored in the drybox.

bdmapH \equiv **1,3-bis(dimethylamino)-2-Propanol**

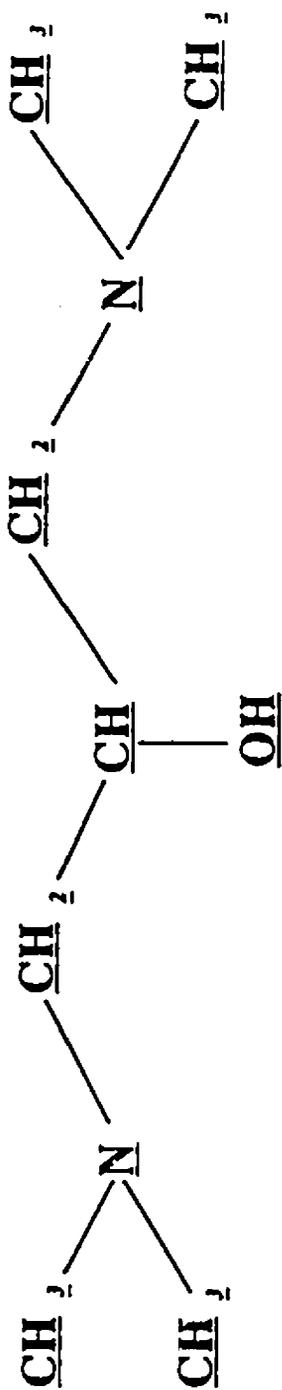


Figure 1. Structure of bdmapH Ligand

II.2.2. Synthesis of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ 1

A sample of CuCl_2 (500mg, 3.74mmol) was dissolved in THF (150ml) with stirring. Then 1,3-bis(dimethylamino)-2-propanol (540mg, 3.72mmol) was added dropwise to this solution. A light green crystalline solid formed immediately and precipitated from the solution. After being stirred for 1 h at room temperature, the solution was filtered. The bright green solid was washed with THF several times, collected and redissolved in ethanol. A clear green solution was obtained. Green crystals (620mg, 1.13mmol) were produced from a mixed solvent of ethanol and diethyl ether (60% yield, m.p. 137°C dec.). Elemental Analysis: calcd. $\text{C}_{14}\text{H}_{36}\text{Cu}_2\text{Cl}_4\text{O}_2\text{N}_4$; C%, 29.95; H%, 6.47; N%, 9.98. Found: C%, 29.82; H%, 6.70; N%, 9.67. IR (KBr, cm^{-1}): 3420 (m, N-H), 1150 (m, C-O).

II.2.3. Synthesis of $\text{Cu}_3(\text{bdmap})_2\text{Cl}_4$ 2

Method 1: A sample of the dimeric Cu(II) compound, $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ (50mg, 0.089mmol) was added into CH_2Cl_2 (10ml) and the solution was stirred. The sample was completely dissolved. A light green solution was obtained. Then $\text{Cu}(\text{OMe})_2$ (12mg, 0.096mmol) was added to this solution. After the mixture was stirred for 1 h at 23°C, the blue solid, $\text{Cu}(\text{OMe})_2$, disappeared completely and the colour of the clear solution became dark green. Then 10ml of diethyl ether was added to this solution to crystallize the product. After the mixture was allowed to stand at 23°C for 2-3 days, dark green crystals were obtained (dry weight 25mg, 0.0402mmol, 45% yield, m.p. 163-165°C dec.). Elemental Analysis: calcd. for $\text{C}_{14}\text{H}_{36}\text{Cu}_3\text{Cl}_4\text{O}_2\text{N}_4$, C%, 26.99; H%, 5.50; N%, 9.00. Found: C%, 27.07; H%, 5.48; N%, 8.72.

Method 2: CuCl_2 (135mg, 1mmol) was dissolved in THF (75ml). $\text{Na}(\text{bdmap})$ (168mg, 1mmol) was then added to this solution. The mixture was stirred overnight at 23°C . Dark green solid precipitated and was collected by filtration. After being washed with ethanol (20ml), the dark green solid was recrystallized from CH_2Cl_2 (25ml) and diethyl ether (10ml). A yield of 86mg (dry weight, 41%) of trimeric copper(II) compound was obtained.

II.2.4. Instruments

Elemental analyses were carried out at the Guelph Chemical Laboratories Ltd.. Infrared spectra were recorded as KBr pellets using a Nicolet 5DX FT-IR spectrometer, the range of wavelength was from 400cm^{-1} and 4000cm^{-1} . Melting points were determined on a Fisher-Johns melting point apparatus. Magnetic susceptibilities were measured on a SQUID device (S.H.F. variable-temperature susceptometer) at Michigan State University.

Electrochemical Analyses: A Potentiostat 273A electrochemical analyzer was used. Cyclic and differential pulse voltammograms (DPV) were obtained with a platinum working electrode and a platinum wire counter electrode. An Ag-AgCl electrode served as the reference electrode in all cases. The cyclic and differential pulse voltammograms of 0.7 M solution of **1** was recorded with 3.1 M NBu_4PF_6 in dimethylformamide (DMF) at scan rate of 0.05 vs^{-1} . The cyclic and differential pulse voltammograms of 0.6 M solution of **2** was recorded with 3.1 M NBu_4PF_6 in DMF at scan rate of 0.05 vs^{-1} .

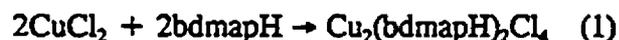
X-ray diffraction Analysis: Single crystals of **1** with rectangular shapes were grown by

slow diffusion of diethyl ether into the CH_2Cl_2 solution of **1** at 23°C . Dark green single crystals of **2** were obtained from the solution of CH_2Cl_2 and diethyl ether at 23°C . Both crystals were mounted on glass fibres and sealed with epoxy glue. Data were collected on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo K_α radiation and processed on a VAX workstation 3520 using the TEXSAN crystallographic (version 5.0). Data were corrected for Lorentz-polarization and absorption effects. The X-ray diffraction analyses were performed by Dr. Wang.

II.3. Results and Discussion

The Dimeric Copper(II) Compound $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ **1**

Synthesis: The dimeric copper(II) compound **1** was initially isolated from the reaction of $\text{Ba}(\text{bdmap})_2$, CuCl_2 and bdmapH in a 1:1:1 ratio. The reaction of CuCl_2 and bdmapH in a 1:1 ratio was subsequently designed for the direct synthesis of the dicopper compound **1**. The reaction is shown in equation (1).



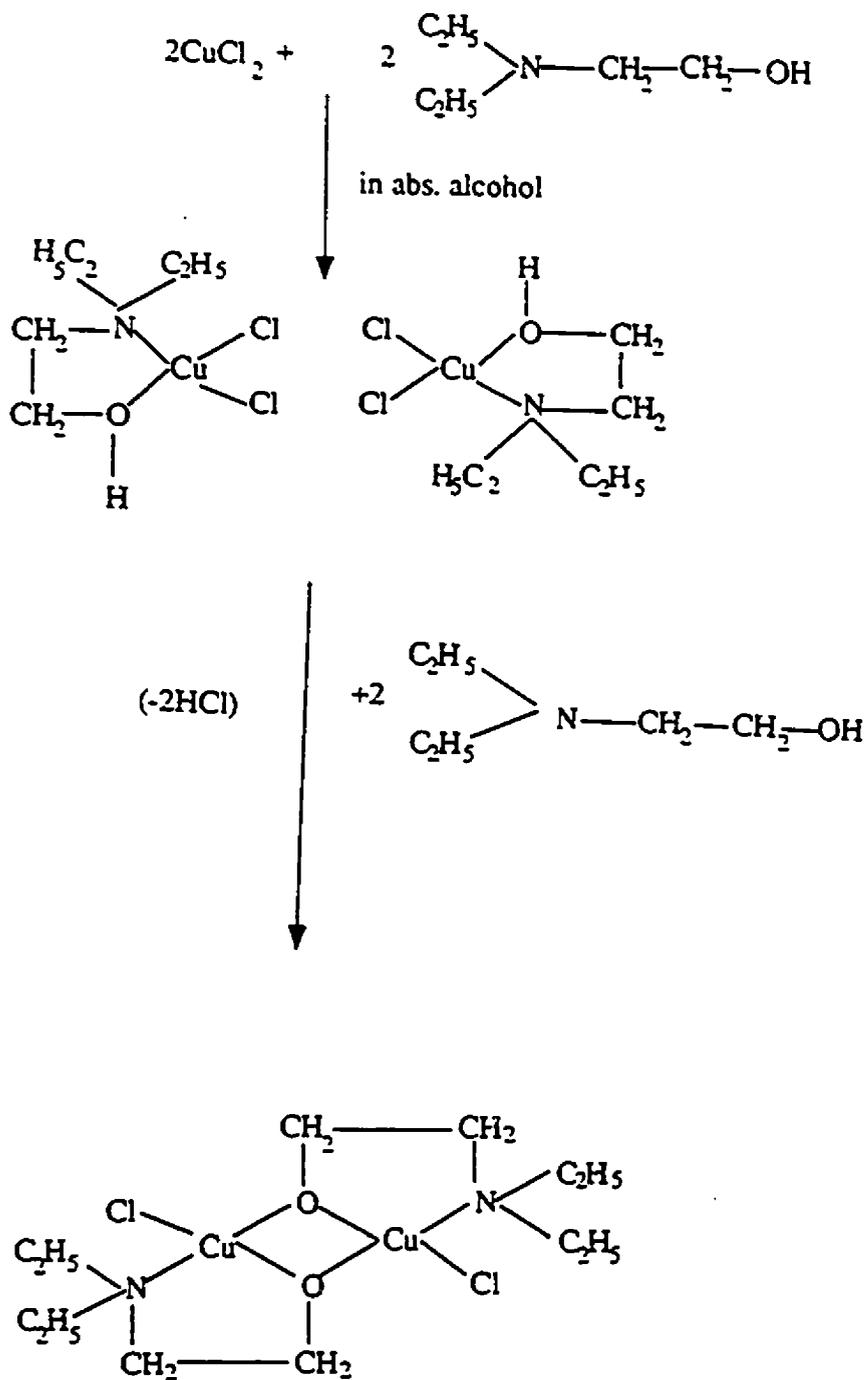
The starting materials in equation (1) were directly dissolved in $\text{C}_2\text{H}_5\text{OH}$ or CH_2Cl_2 for the synthesis of compound **1**. In order to increase the yield in equation (1), a slightly excess of bdmapH was added to the solution of CuCl_2 in THF. The CuCl_2 then reacted completely with bdmapH to produce the compound **1** in THF. The excess bdmapH was removed by filtration.

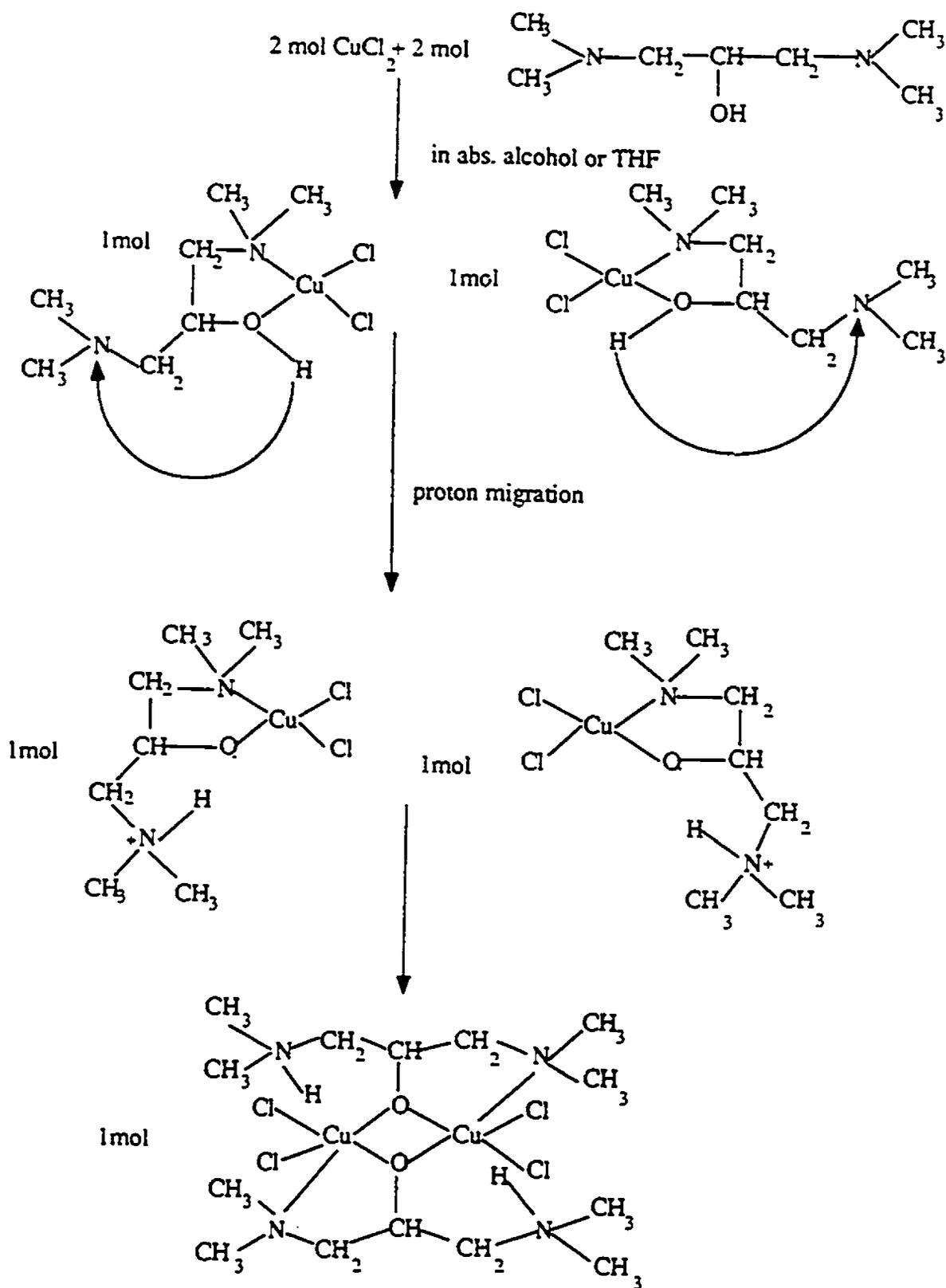
The syntheses of a wide variety of compounds of the types $\text{CuCl}(\text{OR})$ and $\text{CuBr}(\text{OR})$, where ROH is an amino alcohol, have been reported by Hein and coworkers.⁸⁹⁻⁹⁰ They postulated that the complexes should be formulated as dimers in which the amino alcohol ligands ($\text{HOCH}_2\text{CH}_2\text{NR}_2$) act as a chelating bridge, and this had been confirmed by the report⁹¹ of the structure of bromo-(2-diethylaminoethanolato) copper(II). In addition, Hein also proposed the mechanism of the dimer formation as shown in scheme 1.

In the synthesis of $\text{Cu}_2(\text{deae})_2\text{Cl}_2$ ¹³⁴ (deae = 2-diethylaminoethanolato), CuCl_2 was dissolved in absolute alcohol and then 2 equivalents of deaeH was added to the solution. It was proposed that the intermediate mononuclear copper(II) complex, $\text{Cu}(\text{deaeH})\text{Cl}_2$, formed initially. The HCl in $\text{Cu}(\text{deaeH})\text{Cl}_2$ was subsequently eliminated by an intermolecular elimination reaction. The HCl formed an adduct with the excess amino alcohol ligand to produce an ammonium salt. Finally, the two mononuclear copper(II) molecules combine together to form a dimeric copper(II) molecule.

In this case, the bdmaph ligand is different from the deae ligand mentioned above. There is one more nitrogen coordination centre in bdmaph than in the deae ligand which is capable of accepting one proton. The formation mechanism of compound 1 (dizwitterion) was proposed as shown in scheme 2. Reaction of 1,3-bis(dimethylamino)-2-propanol (bdmaph) with CuCl_2 in 1:1 ratio in pure THF or ethanol could yield a monomeric Cu(II) compound first. Because there is no additional bdmaph ligand in the solution to remove HCl by an intermolecular elimination reaction and the second nitrogen group in bdmaph may have a steric chemical effect preventing

Scheme 1





HCl elimination through the intermolecular process, the proton of the hydroxy group on the bdmaph ligand could shift to the nitrogen atom in the same bdmaph ligand by intramolecular process to produce a zwitterion monomer Cu(II) unit. The negative charge is located on the oxygen atom and the positive charge is on the Cu atom in the monomer. The two monomers could then be combined together to yield the dimer by Coulomb attraction and the formation of additional Cu-O bonds. It is apparent that if the protons in **1** could be removed by adding another base to the solution, an additional coordination site would be created which might be used to incorporate the third metal centre. This has been demonstrated by the formation of a trinuclear copper compound from the reaction of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ with $\text{Cu}(\text{OMe})_2$ in a 1:1 ratio. Although this dimeric Cu(II) compound **1** has not been used as a precursor in the preparation of high T_c superconductors by MOCVD or sol-gel methods. It can be shown that the dimeric Cu(II) compound is a very good starting material in the syntheses of homonuclear copper(II) complexes.

X-ray Crystal Structure: Dinuclear complexes form a major group of Cu(II) complexes for the following reasons:³¹ (i) they can be prepared readily by the usual methods used in preparing monomeric complexes; (ii) they provide useful simple models for the study of magnetic interaction of two unpaired d electrons;³⁴⁻³⁶ and (iii) they are useful models of the biological copper systems.³⁷⁻³⁸

Different types of structures of Cu(II) complexes with amino alcohol ligand have been found. The structures of $[\text{CuX}(\text{OCH}_2\text{CH}_2\text{NR}_2)]_n$ ⁷⁵ ($\text{X}=\text{Cl}, \text{Br}, \text{NCS}, \text{or NCO}$; $\text{R}=\text{Me}, \text{Et}, \text{Pr}^t$,

or Buⁿ) compounds are comparable. A summary of all investigated crystal structures of halogeno- and pseudohalogeno-(2-dialkylaminoethanolato) copper(II) complexes is presented in Table 1. For convenience in comparison, two complexes in Table 1 are chosen. They are $[\text{Cu}_2(\text{deae})_2\text{Cl}_2]_2$ ¹³⁴ and $\text{Cu}_2(\text{dbae})_2\text{Br}_2$ ¹³⁸ (dbae = 2-dibutylaminoethanolato). These compounds were obtained by the reaction of CuX_2 with two moles of deaeH or dbaeH ligands.

The molecular structure of dimeric copper compound 1 is shown in Figure 2. The molecular bond distances and angles are given in Table 2 and Table 3, respectively. Compound 1 has a two fold axis (C_2) and consists of two copper atoms, four chlorine ligands, and two bdmapH ligands. The two protons are shifted to two nitrogen atoms in two bdmap ligands by an intramolecular chemical process, and the protons remain in the molecule. In contrast, the protons in amino alcohol ligands (deaeH and dbaeH) migrated to the solution by an intermolecular chemical process. Each Cu atom in 1 is coordinated by two chlorine atoms, one nitrogen atom and is bridged to the other Cu atom by two oxygen atoms. The coordination geometry around Cu atom is, therefore, a distorted square pyramid with Cl(1) as a weakly coordinated axial ligand. Cu-Cl(1) of 2.530(1)Å is much longer than the Cu-Cl distances of 2.235(2)Å and 2.225(3)Å in $[\text{CuCl}(\text{deae})]_4$. Cu-Cl(2) distance of 2.288(1)Å in 1 is normal.⁶⁹ Such distorted square-pyramidal geometry has been observed in $[\text{CuCl}(\text{deae})]_4$. The Cu geometry in $[\text{CuBr}(\text{dbae})]_2$ is approximately tetrahedral. Cu-O and Cu-O' distances of 1.980(3)Å, 1.959(3)Å in 1 are normal, similar to Cu-O distance in $[\text{Cu}(\text{dbae})\text{Br}]_2$ and $[\text{Cu}(\text{deae})\text{Cl}]_4$. The Cu-Cu distance, 2.847(1)Å, is shorter than Cu-Cu distances of 2.931(1)Å, 2.940(2)Å in $[\text{Cu}(\text{deae})\text{Cl}_2]_2$. The Cu-O-Cu angle is 92.6(1)° in the dimeric $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ but 97.6(3)° and

Table 1. Summary of all known crystal structures of $\text{Cu}[(\text{OC}_2\text{H}_4\text{NR}_2)\text{X}]$ complexes ($\text{R}=\text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$; $\text{X}=\text{Cl}$, Br , NCO and NCS)

R	X	Molecular Type	References	
CH_3	NCO	Tetrameric	131	
	NCS	Polymeric	133	
C_2H_5	Cl	Tetrameric	134	
	Br	Dimeric	135	
		Polymeric	136	
$n\text{-C}_3\text{H}_7$	NCO	Tetrameric	130	
	NCS	Polymeric	129	
$n\text{-C}_4\text{H}_9$	Cl	Tetrameric	128	
$n\text{-C}_4\text{H}_9$	Cl	Tetrameric	137	
		Tetrameric	137	
	Br	Dimeric	138	
		NCO	Tetrameric	132
		NCS	Tetrameric	132

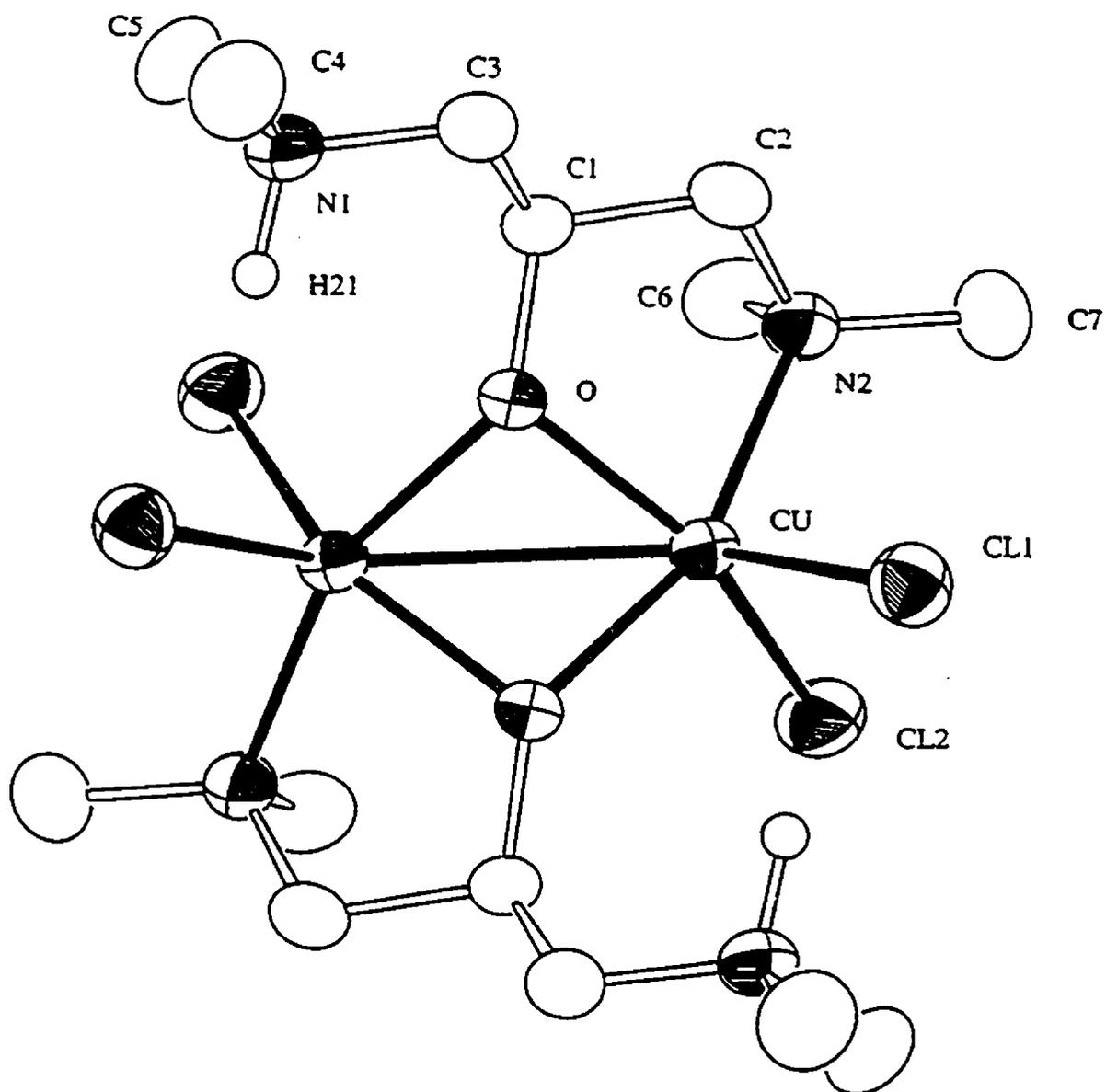


Figure 2 Structure of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$

Table 2 Bond Distances of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_2$

atom	atom	distance	atom	atom	distance
Cu	Cu	2.847 (1)	N(2)	C(2)	1.476 (6)
Cu	Cl(1)	2.530 (1)	N(2)	C(6)	1.470 (6)
Cu	Cl(2)	2.288 (1)	N(2)	C(7)	1.476 (6)
Cu	O	1.980 (3)	C(1)	C(2)	1.524 (6)
Cu	O	1.959 (3)	C(1)	C(3)	1.516 (6)
Cu	N(2)	2.041 (4)	C(8)	C(9)	1.386 (8)
O	C(1)	1.398 (5)	C(8)	C(9)	1.386 (8)
N(1)	C(3)	1.494 (6)	C(9)	C(10)	1.41 (1)
N(1)	C(4)	1.488 (6)	C(9)	C(12)	1.39 (1)
N(1)	C(5)	1.483 (6)	C(10)	C(11)	1.25 (2)
N(1)	H(21)	1.001			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 3 Bond Angles of Cu₂(bdmapH)₂Cl₂

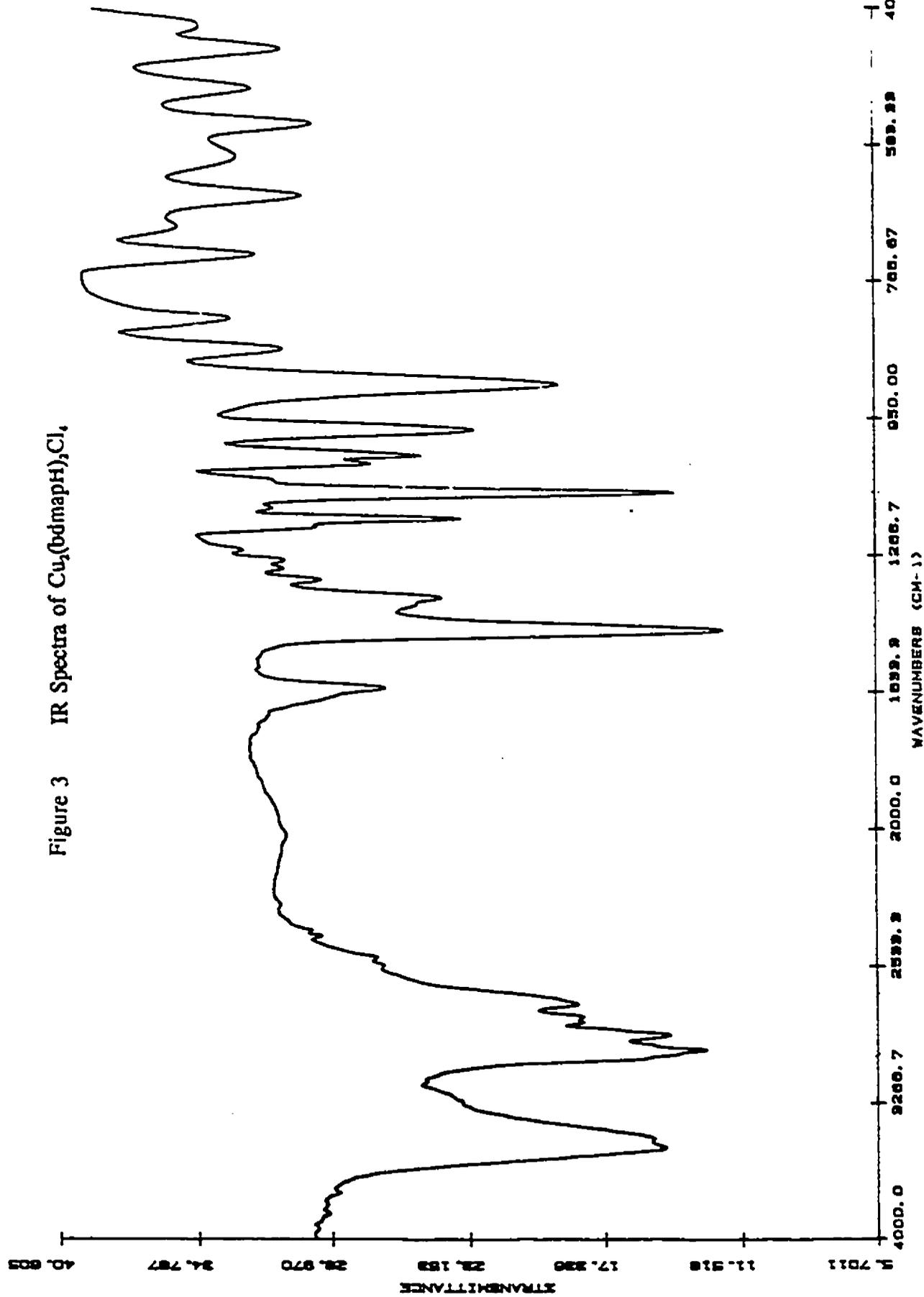
atom	atom	atom	angle	atom	atom	atom	angle
Cu	Cu	Cl (1)	126.93 (3)	C (3)	N (1)	C (5)	113.7 (4)
Cu	Cu	Cl (2)	112.05 (4)	C (4)	N (1)	C (5)	110.2 (4)
Cu	Cu	O	43.42 (8)	Cu	N (2)	C (2)	103.4 (3)
Cu	Cu	O	44.02 (8)	Cu	N (2)	C (6)	109.5 (3)
Cu	Cu	N (2)	113.6 (1)	Cu	N (2)	C (7)	114.9 (3)
Cl (1)	Cu	Cl (2)	104.76 (5)	C (2)	N (2)	C (6)	110.3 (4)
Cl (1)	Cu	O	105.59 (9)	C (2)	N (2)	C (7)	109.5 (4)
Cl (1)	Cu	O	95.74 (9)	C (6)	N (2)	C (7)	109.1 (4)
Cl (1)	Cu	N (2)	98.5 (1)	O	C (1)	C (2)	108.0 (3)
Cl (2)	Cu	O	149.4 (1)	O	C (1)	C (3)	108.5 (4)
Cl (2)	Cu	O	97.27 (9)	C (2)	C (1)	C (3)	109.8 (4)
Cl (2)	Cu	N (2)	96.1 (1)	N (2)	C (2)	C (1)	110.3 (4)
O	Cu	O	75.8 (1)	N (1)	C (3)	C (1)	112.6 (4)
O	Cu	N (2)	83.3 (1)	C (9)	C (8)	C (9)	117.3 (9)
O	Cu	N (2)	157.3 (1)	C (8)	C (9)	C (10)	117.9 (8)
Cu	O	Cu	92.6 (1)	C (8)	C (9)	C (12)	133.2 (9)
Cu	O	C (1)	115.2 (2)	C (10)	C (9)	C (12)	109 (1)
Cu	O	C (1)	132.8 (3)	C (9)	C (10)	C (11)	122 (2)
C (3)	N (1)	C (4)	111.0 (4)	C (10)	C (11)	C (10)	123 (2)
C (3)	N (1)	H (21)	108.03	C (4)	N (1)	H (21)	105.08
C (5)	N (1)	H (21)	108.50				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

95.7(2)° in the bottom and top halves of the tetrameric [Cu(deae)Cl]₄ and 104.5(4)° in dimeric of [Cu(dbae)Br]₂. The Cu-N(2) distance of 2.041(4)Å is similar to the Cu-N distances of 2.057(7)Å and 2.072(7)Å in [CuCl(deae)]₄ and the value of 2.036Å in [Cu(dbae)Br]₂. The Cu₂O₂ unit in **1** is nonplanar. The dihedral angle between the planes of Cu-O-Cu and Cu-O-Cu is 125.5°. However, the Cu₂O₂ unit of [Cu(deae)Cl]₄ and [Cu(dbae)Br]₂ is approximately planar. The two bdmaph ligands in compound **1** have a cis configuration with respect to the Cu-Cu' vector.

The most interesting feature of this dimeric molecule, Cu₂(bdmaph)₂Cl₄, is the dizwitterion form. The hydrogen atom H(21) bonded to N(1) is located directly from a difference Fourier map in the X-ray crystal structure analysis. The H(21) atom is more than 4Å from the Cl(1) and Cl(2) atoms. Therefore, no hydrogen bonds are present between H(21) and the chlorine atoms. Although the distance of N(1) to O, 2.908Å, is close to the sum of the Van der Waals radii⁷⁶ of O and N atoms (2.945Å), H(21) is 2.51Å from O, and the N(1)-H(2)-O angle 103.0° is nonlinear. Therefore, no intramolecular hydrogen bonds are present.⁷⁷⁻⁷⁹ Crystallographic data also indicates that there are no intermolecular hydrogen bonds. The proton bonded originally to the oxygen atom is apparently shifted to the nitrogen atom, and an intramolecular ammonium ion, zwitterion, is formed.

IR Spectrum Analysis: The IR spectrum of compound **1** is given in Figure 3. It is known from X-ray crystal structure analysis that there are N-H bonds in compound **1**. The IR spectrum of the complex displayed a medium-intensity sharp band at 3420cm⁻¹, which is assigned



to the N-H stretching vibration. The frequency of the N-H stretching vibration, 3420cm^{-1} , is higher than the normal value range $3350\text{-}3300\text{cm}^{-1}$.⁹³(secondary-RHN). Because the ammonium group is positively charged, it increases the N-H bond strength and hence shifts the band to a higher frequency in comparison with the secondary amine. It is also evident that hydrogen bond is not present. The absorption band at around 1150cm^{-1} is assigned to the C-O stretching vibration. Some absorption bands observed in the $900\text{-}400\text{cm}^{-1}$ region could be caused by metal-oxygen vibrations.⁹⁶ The similar absorptions resulting from metal-oxygen vibrations in copper(II) acetylacetonates have been observed at $700\text{-}400\text{cm}^{-1}$ (three bands 684cm^{-1} , 654cm^{-1} , 455cm^{-1}) by Morgan⁹⁵ and Lecomte.⁹⁶

Magnetic Susceptibility: The summary shown in Table 1 indicates that different types of structures of $[\text{CuX}(\text{OCH}_2\text{CH}_2\text{NR}_2)]_n$ in the solid state have been confirmed. All of these molecular structures contain an oxygen-bridged dimeric unit. However, different molecules exhibit different intra- and inter- molecular magnetic interactions between the individual copper(II) ions. Uhlig and Staiger have studied the room-temperature magnetic properties of a number of compounds of this type¹²²⁻¹²³ and deduced that they may be divided into three distinct groups according to their magnetic moments: (1) compounds with greatly reduced moments at 20°C (less than 1 BM); assumed to be oxygen-bridged dimer; (2) compounds with normal magnetic moments; in this case the copper atom probably has a coordination number greater than 4; (3) compounds with only slightly reduced moment at 20°C (about 1.5 BM); it was suggested that these complexes might be tetrameric.⁷⁴

The molar susceptibility (χ_m) and the reciprocal molar susceptibility (χ_m^{-1}) of the dimer $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ as a function of temperature is shown in Figure 4. The susceptibility decreases with increasing temperature and it decreases rapidly at low temperature range of 5-20K. No maximum in the investigated temperature range was observed. This may be caused by the small energy gap between the singlet ground state and the triplet excited state. The magnetic moment ($\propto \sqrt{\chi_m T}$) of compound 1 increases with increasing temperature as is demonstrated by the plot of $\chi_m T$ vs T for compound 1 shown in Figure 5. The magnetic moment is 1.56 BM at room temperature. This may be caused by the change from a ground singlet state to an excited triplet state. This behaviour is in accordance with an antiferromagnetic exchange interaction. Many dicopper(II) compounds display antiferromagnetic coupling behaviour.⁶⁹ The magnetic moment of compound 1 at room temperature belongs to type III mentioned above, but the structure of compound 1 does not match type III.

Electrochemistry: The dimeric compound 1 was studied by the technique of cyclic voltammetry. The cyclic voltammogram (CV) of 0.7 M solution of 1 was recorded with 3.1 M NBu_4PF_6 in DMF at a scan rate of 0.05 vs^{-1} . The diagram of the CV of compound 1 is shown in Figure 6, which displayed an irreversible feature. The reduction of $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$ appeared to occur at about -0.35V, because the standard electrode potentials (V) of the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ have been reported in the range of -0.35-1.12.⁶⁹ The reduction of $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{0}}$ usually occur at a more negative potential than -0.35V, and the oxidation of $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{III}}$ usually occur at a more positive potential than zero.¹³⁹

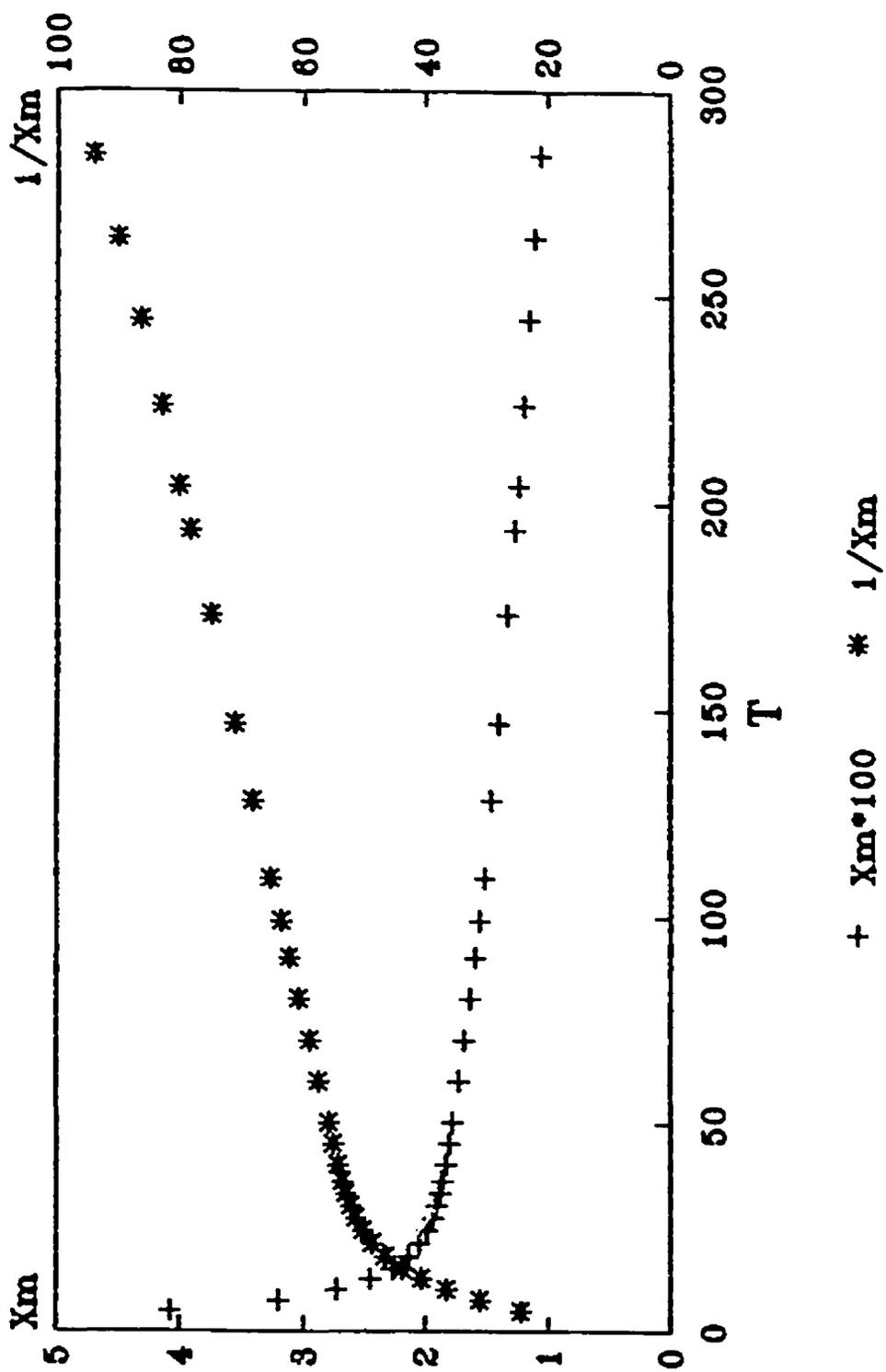


Figure 4 Magnetic Susceptibility of X_m vs T, X_m^{-1} vs T

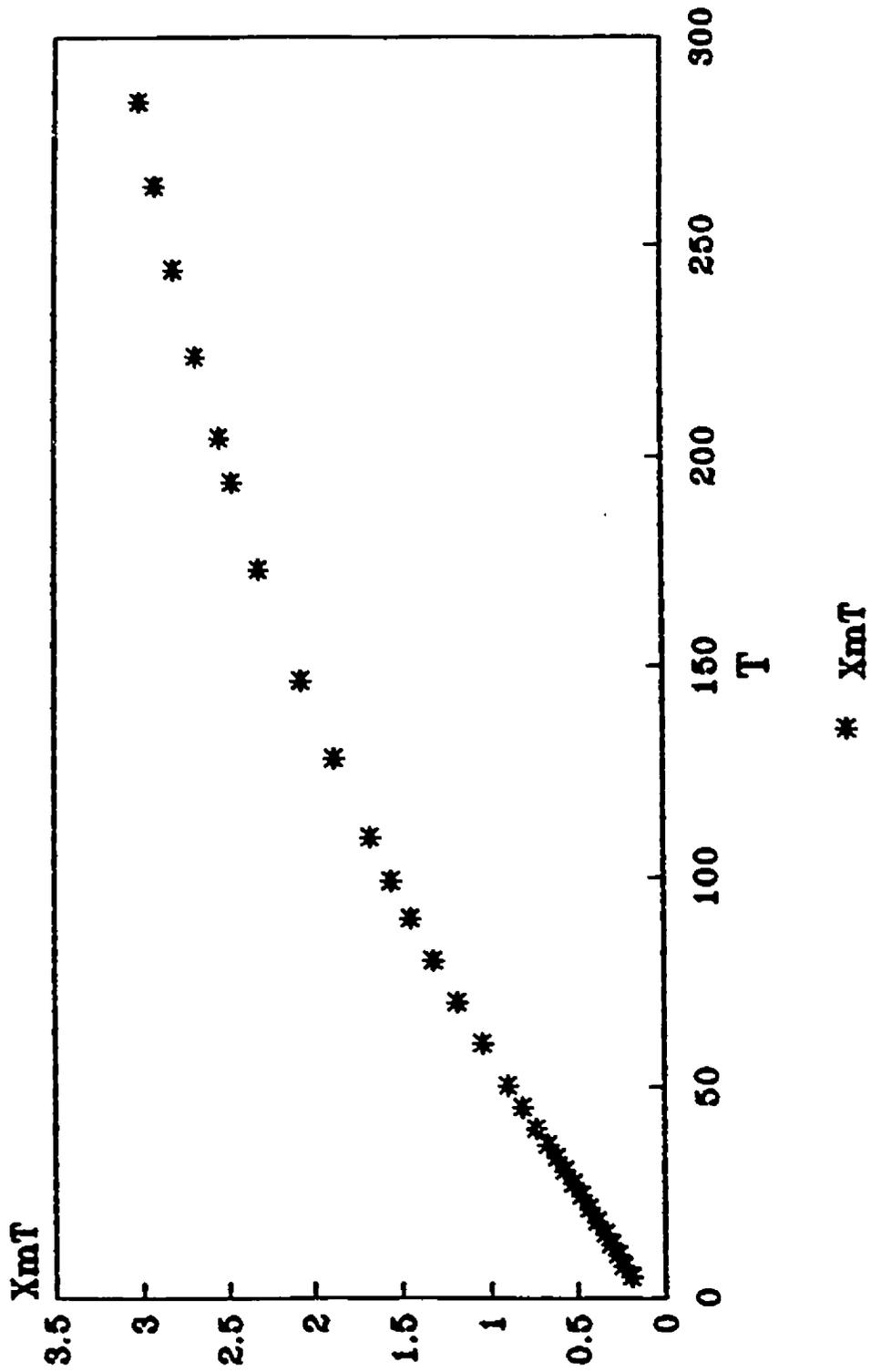
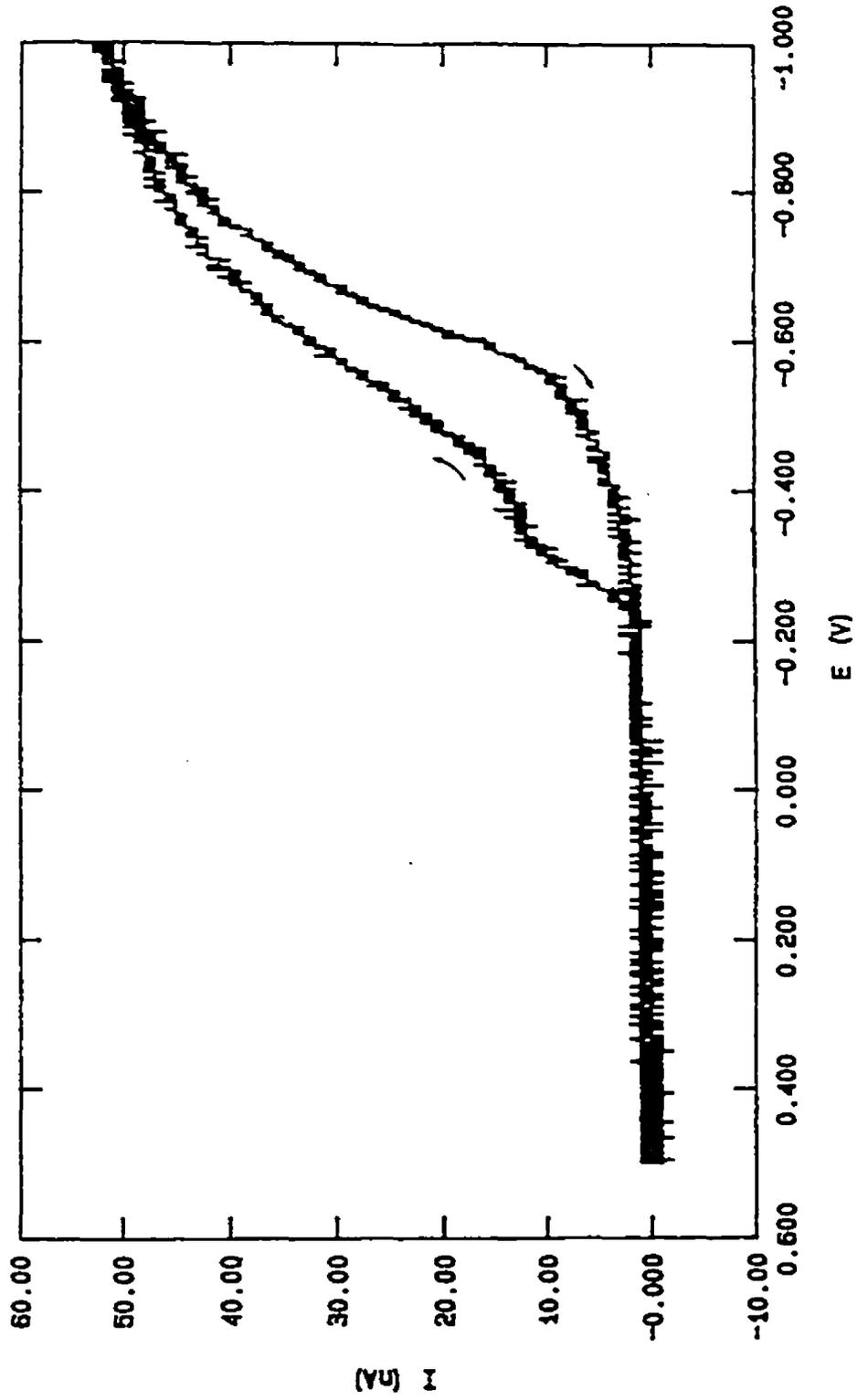


Figure 5 Magnetic Susceptibility of $X_m T$ vs T

Figure 6 Diagram of CV of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$



The Trimeric Copper(II) compound, $\text{Cu}_3(\text{bdmap})_2\text{Cl}_4$ 2

Synthesis: By comparing the structures of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ 1 and $\text{Cu}_2(\text{deae})_2\text{Cl}_2$, it has been proposed that the protons in the bdmapH ligand of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ 1 could be removed by certain bases by an intermolecular process. To test this proposal, the reaction of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ 1 and $\text{Cu}(\text{OMe})_2$ in a 1:1 ratio in method 1 was designed. $\text{Cu}(\text{OMe})_2$ can remove 2 moles of proton to form 2 moles of HOME. An additional coordination site is presumably created to incorporate the third Cu(II) centre. As a result, the trimer, $\text{Cu}_3(\text{bdmap})_2\text{Cl}_4$ 2, was isolated from the reaction shown in equation (2).



The compound 2 was also obtained by the reaction of CuCl_2 and $\text{Na}(\text{bdmap})$ in a 3:2 ratio in method 2. The equation is shown in (3).



Since the salt of NaCl was coprecipitated with $\text{Cu}_3(\text{bdmap})_2\text{Cl}_4$ in THF, the yield in method 2 was slightly lower than the yield in method 1.

X-ray Crystal Structure: Trinuclear copper(II) complexes are far less common than dinuclear copper(II) systems and limited to only three types,⁴¹ which are shown in Figure 7. The three types are 1) non-linear, 2) triangle, 3) linear. Compound 2 was crystallized from CH_2Cl_2 solvent and contains 1 equivalent of CH_2Cl_2 per molecule. The CH_2Cl_2 molecule was very readily lost in air. Despite the poor quality of the crystal of 2, the crystal structure of 2 was still determined by X-ray diffraction. The molecular structure is given in Figure 8 and the bond

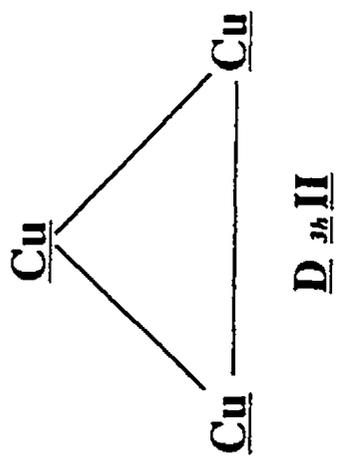
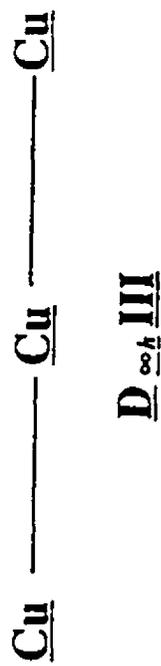
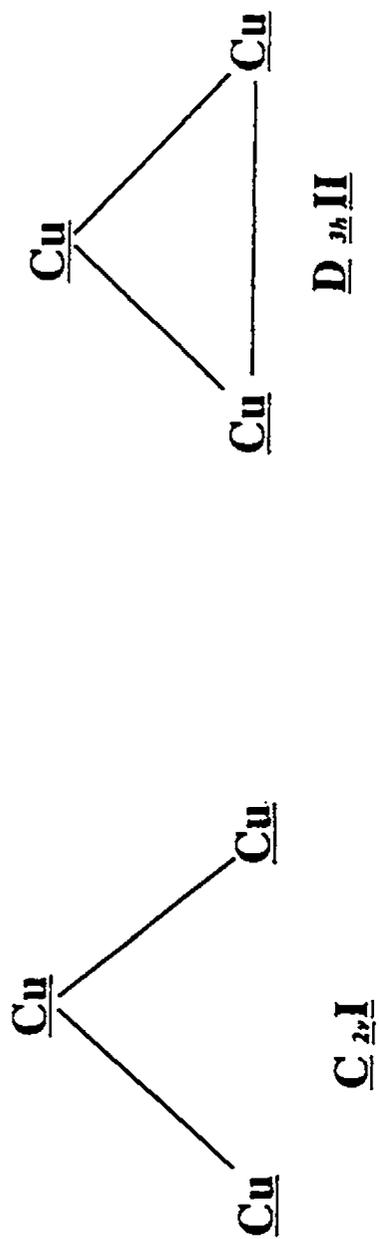
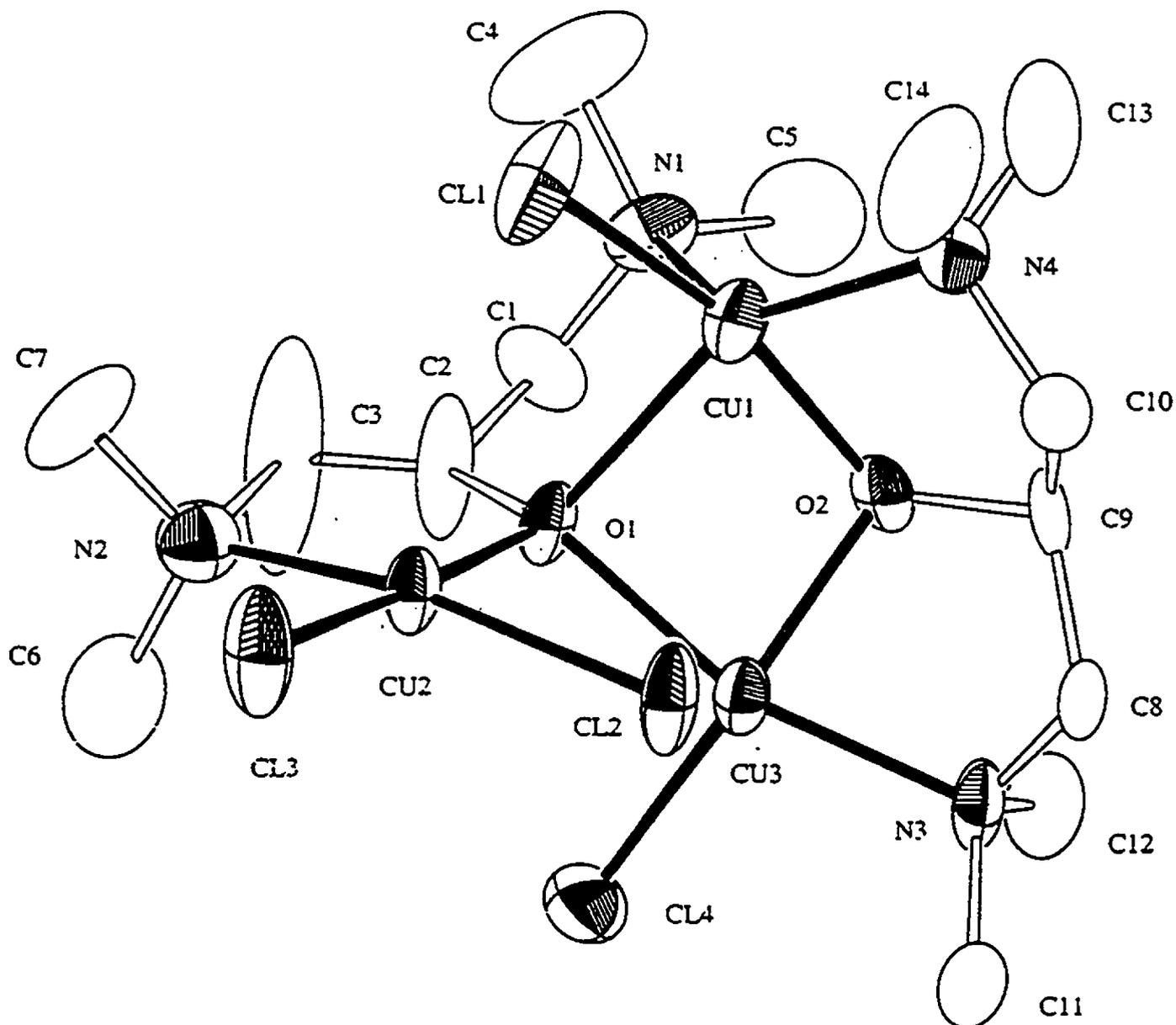


Figure 7 Types of Trinuclear Copper(II) Complexes

Figure 8 Structure of $\text{Cu}_3(\text{bdmap})_2\text{Cl}_4$ 

distances and angles are given in Table 4 and Table 5, respectively. As shown in Figure 8, the trinuclear copper(II) compound **2** contains a triangular Cu₃ unit. An oxygen atom is located in the triangular Cu₃ centre and bonded to three copper(II) atoms.

In accord with the three types of trinuclear copper(II) complexes (Figure 7), the compound **2** belongs to type II. Trinuclear copper(II) compounds of type II with the general formulation of $[\text{Cu}_3\text{O}_p(\text{OH})_{1-p}(\text{ligand})_3]\text{X}_{2-p}$ ($p=0$ or 1 ; $\text{X}=\text{ClO}_4^-$ or SO_4^{2-} ; $\text{ligand}=\text{RNC}(\text{R}')\text{C}(\text{R}')\text{NO}^-$; $\text{R}=\text{Et}$, $n\text{-Pr}$, $n\text{-Bu}$, Ph ; $\text{R}'=\text{Me}$, Ph) have been reported.⁹⁸⁻¹⁰³ In general, the complexes isolated contain both Cu₃O and Cu₃OH cores held by three peripheral oximate bridges of the ligand. Their crystal structures were fully characterized by X-ray structure analyses as shown in Figure 9a and coordinated ligands are shown in Figure 9b, 9c and 9d. Furthermore, a μ_3 -carbonate-bridged trinuclear copper(II) cluster has also been reported,¹⁰⁴ and it belongs to type II. However, the structure of compound **2** is very different from the structures of Cu₃ species shown in Figure 9a. For example, in the trinuclear copper(II) specie $[\text{Cu}_3\text{OH}(\text{PL})_3]\text{SO}_4$, HPL = the bidentate pyridine-2-carbaldehyde ligand,¹⁰⁵ the three copper atoms are held together by the oximate group (=N-O) as three bridges between two copper ions through the imino nitrogen and the deprotonated oxygen. The molecule of $[\text{Cu}_3(\text{OH})(\text{PL})_3]\text{SO}_4$ has C_{3v} symmetry. The oxygen atom of the hydroxy group is situated on the three-fold axis about which the trinuclear unit is centred and bonded to three Cu atoms, so that it is 1.98(1)Å from each of the copper atoms and 0.697(15)Å above the plane passing through the three metal atoms. The geometry of each copper atom is an approximate tetragonal pyramid. In contrast, the O(1) atom in one bdmep ligand in **2** is bonded to three Cu ions. The Cu(1) and

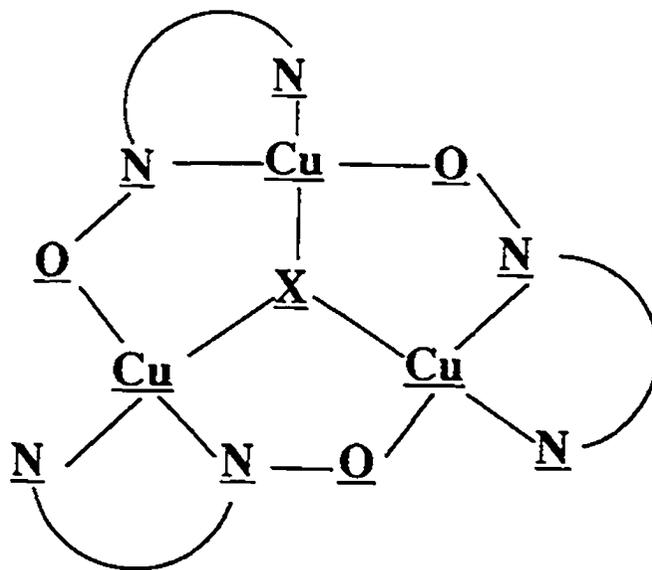
Table 4 Bond Distances of $\text{Cu}_3(\text{bdmapH})_2\text{Cl}_4$

atom	atom	distance	atom	atom	distance
Cu(1)	Cl(1)	2.214(6)	N(1)	C(1)	1.47(2)
Cu(1)	O(1)	2.20(1)	N(1)	C(4)	1.43(3)
Cu(1)	O(2)	1.90(1)	N(1)	C(5)	1.48(3)
Cu(1)	N(1)	2.28(1)	N(2)	C(3)	1.47(3)
Cu(1)	N(4)	2.03(2)	N(2)	C(6)	1.39(3)
Cu(2)	Cl(2)	2.276(5)	N(2)	C(7)	1.44(3)
Cu(2)	Cl(3)	2.197(5)	N(3)	C(8)	1.45(2)
Cu(2)	O(1)	1.93(1)	N(3)	C(11)	1.47(2)
Cu(2)	N(2)	2.08(2)	N(3)	C(12)	1.48(2)
Cu(3)	Cl(4)	2.211(6)	N(4)	C(10)	1.46(2)
Cu(3)	O(1)	2.02(1)	N(4)	C(13)	1.47(3)
Cu(3)	O(2)	1.91(1)	N(4)	C(14)	1.46(3)
Cu(3)	N(3)	2.01(1)	C(1)	C(2)	1.44(2)
Cl(5)	C(15)	1.72(3)	C(2)	C(3)	1.28(3)
Cl(6)	C(15)	1.69(3)	C(8)	C(9)	1.49(3)
O(1)	C(2)	1.42(2)	C(9)	C(10)	1.54(3)
O(2)	C(9)	1.42(2)			

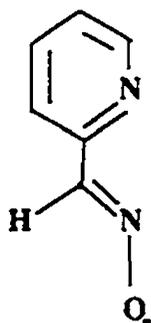
Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

atom	atom	atom	angle	atom	atom	atom	angle
Cl (1)	Cu (1)	O (1)	92.0 (3)	Cu (2)	O (1)	C (2)	115 (1)
Cl (1)	Cu (1)	O (2)	163.4 (4)	Cu (3)	O (1)	C (2)	120 (1)
Cl (1)	Cu (1)	N (1)	98.9 (5)	Cu (1)	O (2)	Cu (3)	105.3 (5)
Cl (1)	Cu (1)	N (4)	99.8 (5)	Cu (1)	O (2)	C (9)	117 (1)
O (1)	Cu (1)	O (2)	77.5 (5)	Cu (3)	O (2)	C (9)	116 (1)
O (1)	Cu (1)	N (1)	78.1 (5)	Cu (1)	N (1)	C (1)	108 (1)
O (1)	Cu (1)	N (4)	148.0 (6)	Cu (1)	N (1)	C (4)	112 (1)
O (2)	Cu (1)	N (1)	91.5 (6)	Cu (1)	N (1)	C (5)	111 (1)
O (2)	Cu (1)	N (4)	83.5 (6)	C (1)	N (1)	C (4)	114 (2)
N (1)	Cu (1)	N (4)	128.3 (7)	C (1)	N (1)	C (5)	106 (2)
Cl (2)	Cu (2)	Cl (3)	95.4 (2)	C (4)	N (1)	C (5)	107 (2)
Cl (2)	Cu (2)	O (1)	86.3 (3)	Cu (2)	N (2)	C (3)	100 (1)
Cl (2)	Cu (2)	N (2)	163.0 (5)	Cu (2)	N (2)	C (6)	109 (1)
Cl (3)	Cu (2)	O (1)	176.6 (4)	Cu (2)	N (2)	C (7)	111 (1)
Cl (3)	Cu (2)	N (2)	94.6 (5)	C (3)	N (2)	C (6)	115 (3)
O (1)	Cu (2)	N (2)	84.4 (5)	C (3)	N (2)	C (7)	107 (2)
Cl (4)	Cu (3)	O (1)	97.7 (4)	C (6)	N (2)	C (7)	113 (2)
Cl (4)	Cu (3)	O (2)	158.4 (4)	Cu (3)	N (3)	C (8)	105 (1)
Cl (4)	Cu (3)	N (3)	101.1 (6)	Cu (3)	N (3)	C (11)	112 (1)
O (1)	Cu (3)	O (2)	82.1 (5)	Cu (3)	N (3)	C (12)	108 (1)
O (1)	Cu (3)	N (3)	161.3 (6)	C (8)	N (3)	C (11)	111 (2)
O (2)	Cu (3)	N (3)	80.5 (6)	C (8)	N (3)	C (12)	113 (1)
Cu (1)	O (1)	Cu (2)	109.4 (5)	C (11)	N (3)	C (12)	108 (2)
Cu (1)	O (1)	Cu (3)	91.6 (4)	Cu (1)	N (4)	C (10)	106 (1)
Cu (1)	O (1)	C (2)	110 (1)	Cu (1)	N (4)	C (13)	106 (1)
Cu (2)	O (1)	Cu (3)	108.4 (5)	Cu (1)	N (4)	C (14)	117 (1)

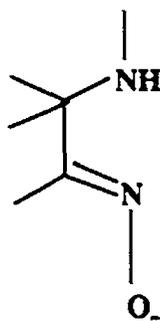
Figure 9 Structures of Trinuclear Cu(II) complexes with General Formula $[\text{Cu}_3\text{O}(\text{ligand})_6]^{+}$ or $[\text{Cu}_3(\text{OH})(\text{ligand})_6]^{2+}$



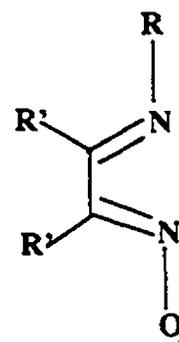
9a



9b



9c



9d

Cu(3) ions are bridged by one additional oxygen atom O(2) from the second bdmmap ligand. The molecule of compound **2** lacks symmetry, because the coordination environments of the three copper atoms are different. Cu(1) is coordinated by one chlorine atom, two nitrogen atoms and two oxygen atoms. Its geometry could be described as a distorted square pyramid with a weakly bonded axial ligand N(1): N(1)-Cu(1)=2.28(1)Å. The Cu(2) atom is coordinated by two chlorine atoms, one nitrogen atom and one oxygen atom. The geometry of Cu(2) is square planar: N(2)-Cu(2)-Cl(2)=163.0(5)° and O(1)-Cu(2)-Cl(3)=176.6(4)°. The Cu(3) atom is coordinated by one chlorine atom, one nitrogen atom and two oxygen atoms. The geometry around Cu(3) is approximate square-planar: O(1)-Cu(3)-N(3)=161.3° and O(2)-Cu(3)-Cl(4)=158.4(4)°. The distances of the central O(1) from the three Cu atoms are different because the coordination environment of each copper atom is different. The Cl(2) atom is 2.694(4)Å from Cu(3), which may be responsible for the small degree of distortion from square-planar geometry. The Cu(1)-Cu(3) distance of 3.027(4)Å is relatively shorter than the Cu(1)-Cu(2) distance of 3.378(4)Å and the Cu(2)-Cu(3) distance of 3.200(3)Å. It is also shorter than distances of 3.220(3)Å between two of the copper atoms in [Cu₃(OH)(PL)₃]SO₄. This is probably caused by the double bridges of oxygen atoms. Although each pair of Cu atoms are linked by double bridges in [Cu₃(OH)(PL)₃]SO₄, one of the bridges is through the imino nitrogen and the deprotonated oxygen. The oxygen atoms in the two bdmmap ligands in **2** bridge two Cu atoms, Cu(1) and Cu(3), in a similar fashion as found in **1**. However, the Cu-Cu distance of 2.847(1)Å is much shorter than the Cu(1)-Cu(3) distance of 3.027(4)Å and the Cu(1)-O(2)-Cu(3) angle of 105.3(5)° in **2** is much larger than the angle of 92.6(1)° in **1**, apparently as a result of the increased crowding. Cu(1), O(1), Cu(3) and O(2) are approximately in the same plane. The dihedral angle

between planes of Cu(1)-O(1)-Cu(3) and Cu(1)-O(2)-Cu(3) is 21.8°. This plane is nearly perpendicular to the plane of N(2)-O(1)-Cl(2)-Cl(3); dihedral angle = 80°. The Cu-N distances, except for Cu(1)-N(1), are in the range of 2.08-2.01Å, which are normal for Cu-N bond distances. The Cu(1)-O(2) distance of 1.90(1)Å and Cu(3)-O(2) distance of 1.91(1)Å are also normal. The Cu-Cl distances are 2.276-2.197Å in normal range of Cu-Cl bond distance.⁸¹

Magnetic Susceptibility: As mentioned above, trinuclear Cu(II) complexes are far less known than those of dinuclear Cu(II) systems and only three types have been identified (Figure 7). Trinuclear Cu(II) compounds in type II are dominated by the compounds of type $[\text{Cu}_3\text{O}(\text{ligand})_3]\text{X}$ and $[\text{Cu}_3(\text{OH})(\text{ligand})_3]\text{X}_2$, the ligands are as shown in Figure 9b, 9c and 9d). It has been found that the oximate group ($=\text{N}-\text{O}^-$) in these complexes generally mediates a strong antiferromagnetic spin exchange and a complete or nearly complete spin coupling has been observed in some cases even at room temperature. Compound 2, $\text{Cu}_2(\text{bdmap})_2\text{Cl}_4$, is not a symmetric molecule, and the central oxygen atom in the bdmap ligand bridges three copper(II) atoms. The plots of the molar susceptibility (χ_m) and the reciprocal molar susceptibility ($1/\chi_m$) of compound 2 vs temperature (K) are shown in Figure 10. The curve of χ_m vs T(K) exhibits features associated paramagnetism.

The paramagnetic contribution to the susceptibility arises from the spin and orbital angular moment of the electrons interaction with the field. The paramagnetic behaviour obeys the Curie Law;

$$\chi_m = \frac{Ng^2\beta^2}{4KT}$$

where N is Avogadro's number, $g = 2.0023$ for a free electron, and β is the Bohr magneton of the electron. If compound 2 is paramagnetic, the plot of χ_m^{-1} vs T in Figure 10 should be a straight line, which obeys the Curie-Weiss law.

$$\chi_m = \frac{C}{T + \theta}$$

where $C = Ng_2\beta^2/4K$, θ corrects the T for the non-zero intercept.

In fact, the plot of χ_m^{-1} vs T is a curve as shown in Figure 10. In the low temperature range of 5-70K, the plot is almost a straight line, which follows the Curie-Weiss law. As the increase of the plot, the curve is no longer straight, which may be the result of an antiferromagnetic exchange interaction. The room temperature effective magnetic moment per trimeric unit of complex ($\mu_{\text{eff}} = 1.97$ BM at 297K), which clearly indicates antiferromagnetic coupling, since the value expected for uncorrelated spins should be at least 3. The effective magnetic moment is also temperature dependent as indicated in Figure 11. The $\chi_m T$ value decreases with the decrease of temperature. This is also in agreement with antiferromagnetic coupling.

Electrochemistry: The redox property of compound 2 was studied by using the cyclic voltammetry technique. The CV diagram of compound 2, which is shown in Figure 12, displayed an irreversible feature. The CV diagram showed one cathodic process of a large broad peak at an E_p value of -0.6V, which is probably caused by $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$ reduction. Compound 2

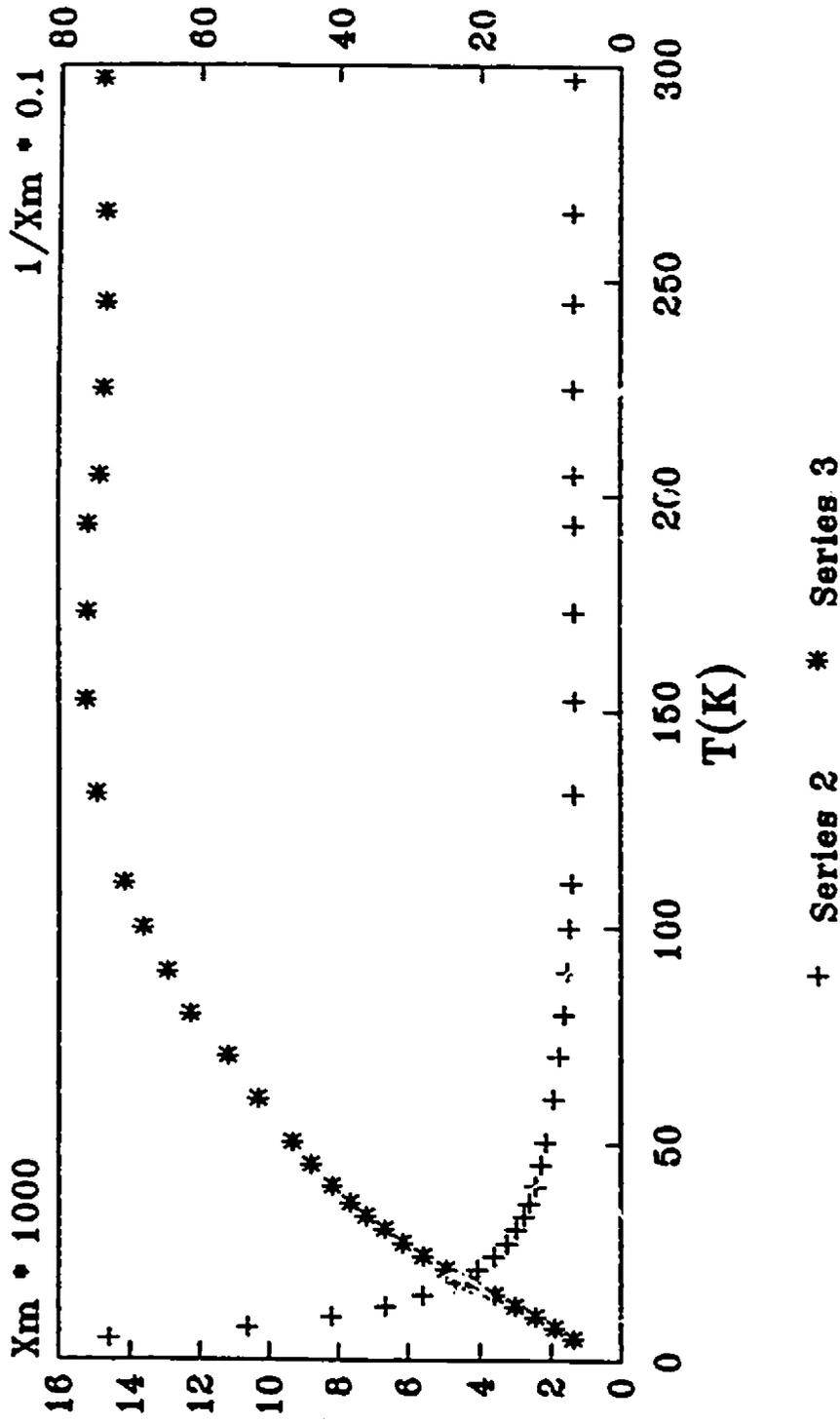


Figure 10 Magnetic Susceptibility of X_m vs T , X_m^{-1} vs T

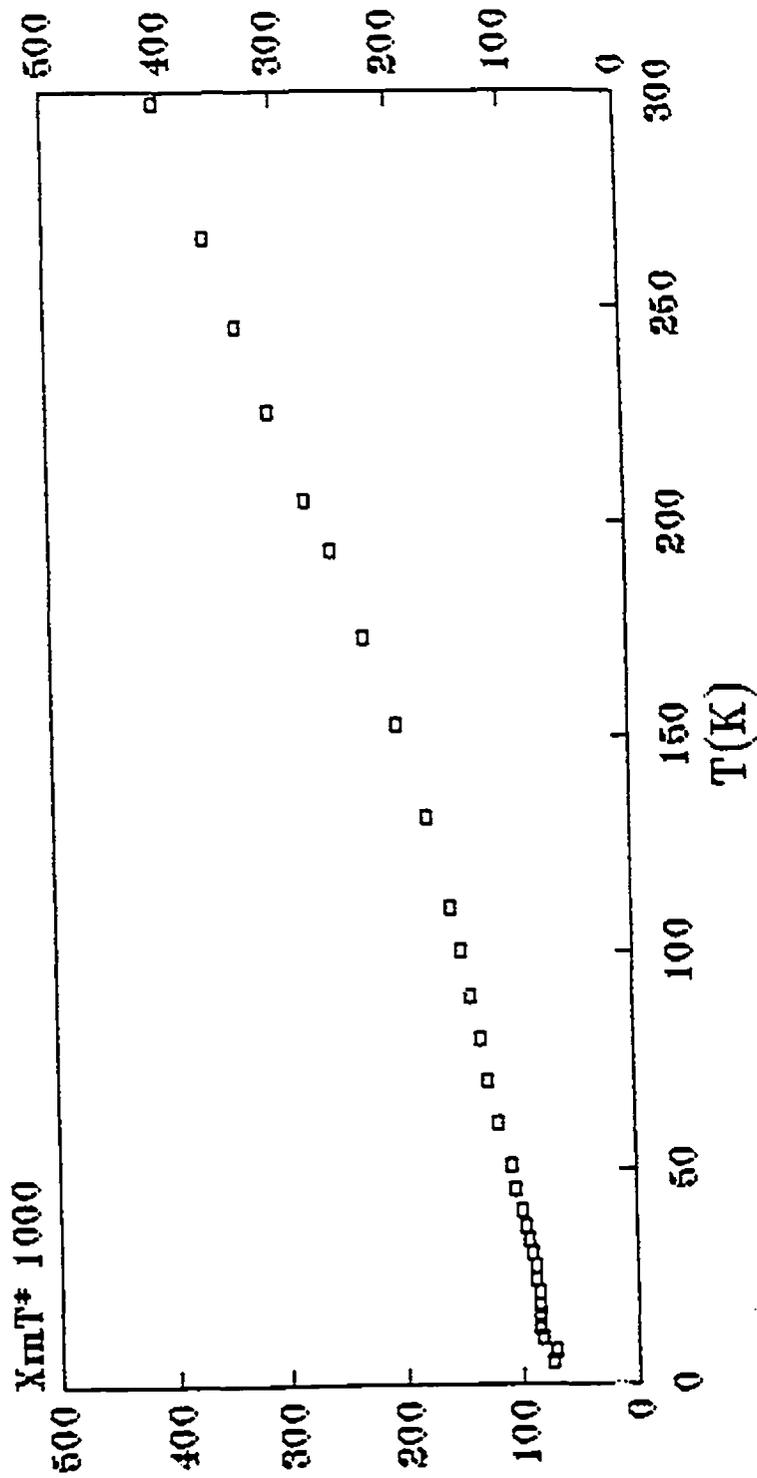
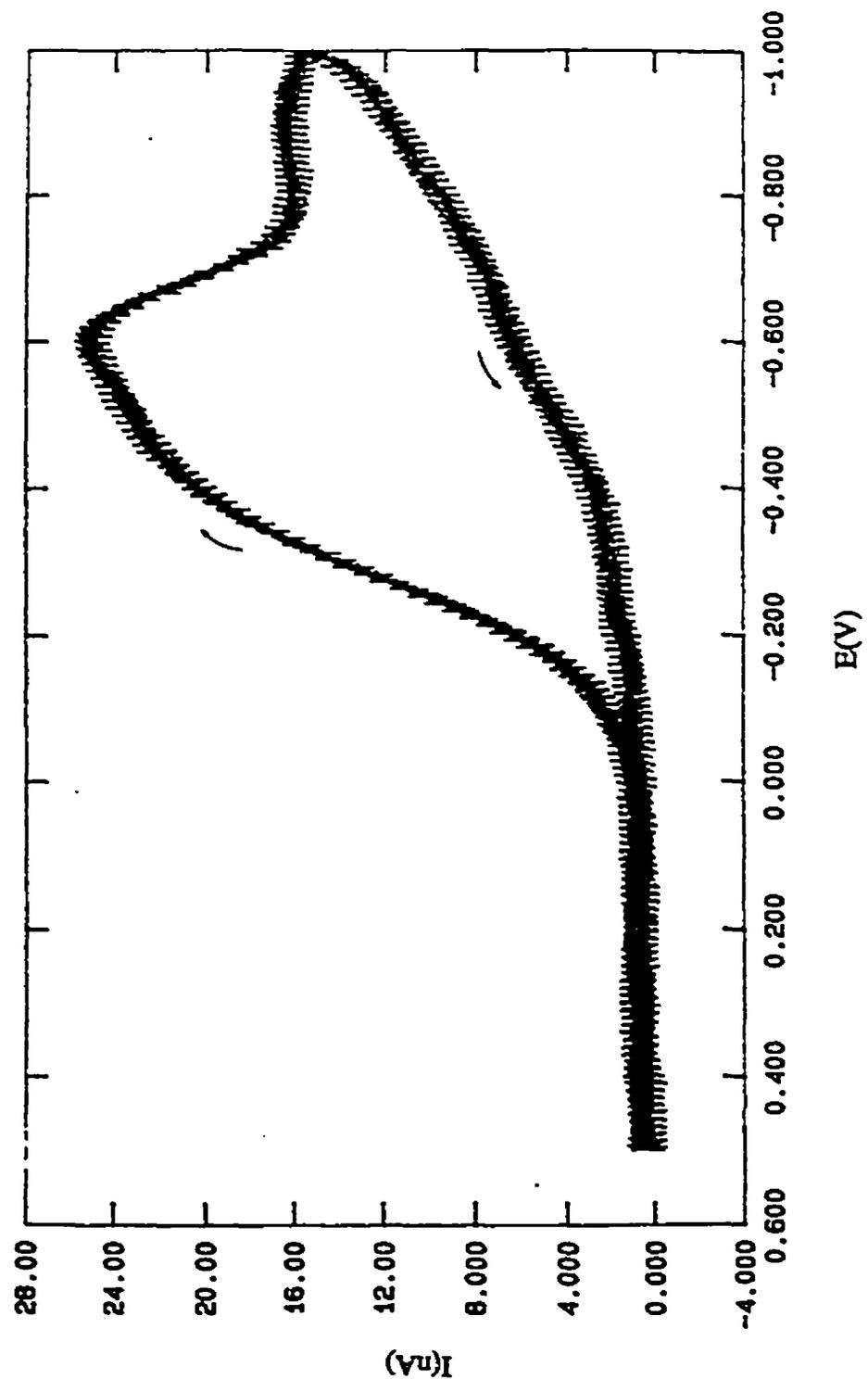


Figure 11 Magnetic Susceptibility of $X_m T$ vs T

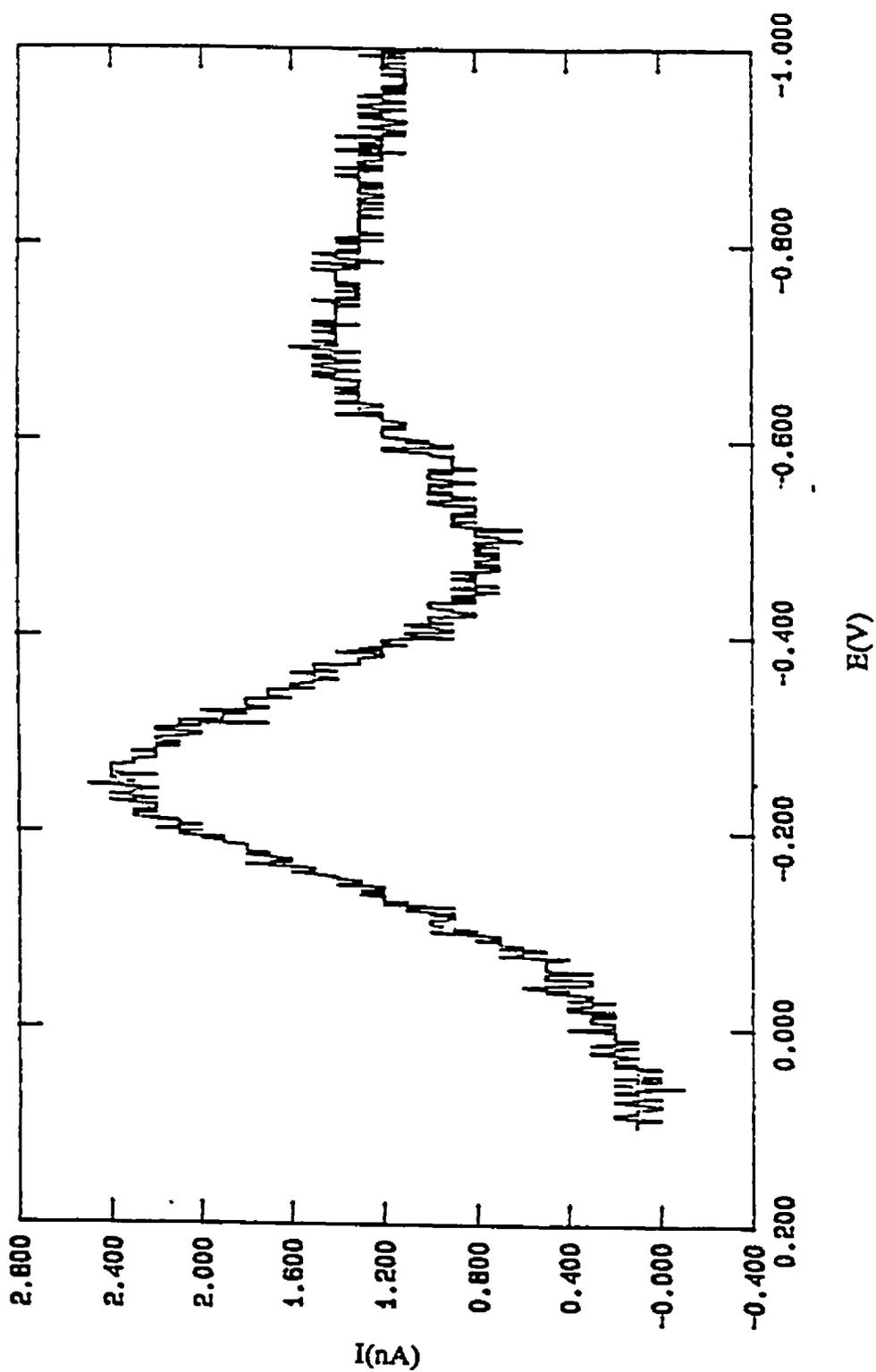
Figure 12 Diagram of CV of $\text{Cu}_3(\text{bdmap})_2\text{Cl}$



also was studied by the technique of differential pulse voltammetry (DPV). The DPV diagram of **2**, which is shown in Figure 13, indicated the $E_{1/2}$ value of -0.25V.

II.4. Conclusion

The bdmaph ligand can react with CuCl_2 in a 1:1 ratio to produce a dimeric Cu(II) compound, $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ **1**. The molecule of **1** is a dizwitterion. The additional N atom coordination centre in bdmaph ligand probably leads to the formation of the dizwitterion. The dimeric Cu(II) compound is a very good starting material in the synthesis of the trimer $[\text{Cu}_3(\text{bdmap})_2\text{Cl}_4]$ **2**. The bdmaph ligand can link more than two metal centres. Both dimer and trimer display antiferromagnetic exchange behaviour and irreversible electrochemical behaviour.

Figure 13 Diagram of DPV of $\text{Cu}_3(\text{bdmap})_2\text{Cl}$ 

Chapter III

Homonuclear Copper Complexes with a Cyclic Cu^{II}₄ Unit

III.1. Introduction

The discovery of high-temperature cuprate-based superconductors^{1,2} and of superconducting metal oxides with T_c values in excess of 77K has stimulated intense scientific and technological interest in the preparation of high quality, superconducting, high T_c thin films by MOCVD and sol-gel processes.¹⁰⁶⁻¹⁰⁷ Studies have suggested that hetero-metallic complex might be important intermediates in the MOCVD technique and chemical sol-gel processes. Several heteronuclear metal complexes related to the precursors of high T_c superconductors have been reported recently. They are $\text{Ba}\{\text{Cu}[\text{OCMe}(\text{CF}_3)_2]_3\}_2$ ¹²⁵; the most volatile Ba-Cu complex, $(\text{CuO})_3\text{Ba}_2\text{Y}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_7$ ¹²⁶; used in the synthesis of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor, and $\text{Ba}_2\text{Cu}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4(\text{acac})_4(\text{HOCH}_2\text{CH}_2\text{OCH}_3)_2$ ⁴³; isolated from the precursor solution to $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin films. The structure of a heteronuclear Y_2Cu_8 complex has been reported by our group.⁴⁴ The central core structure of this compound remarkably resembles that of the 1-2-3 superconductor. A Ba-Cu complex has been synthesized¹⁰⁸ in our lab, and a very soluble precursor, $\text{Y}_2\text{Cu}_6(\text{CF}_3\text{COO})_8(\text{bdmap})_{10}$ ¹⁰⁹ has also been prepared in our group. However, the application of the processes mentioned above suffers from the limited availability of precursor compounds and a lack of understanding of the solution chemistry involved in the processes. Our group has been particularly interested in the syntheses of heteronuclear metal complexes with metal composition and structures resembling those of 1-2-3 superconductors. Such complexes can not only be used as precursors for superconductors but also can be used as molecular models for the study of the chemical and physical properties of superconductors. The problem associated with the synthesis of these hetero-nuclear metal complexes is that there is not much control in the structures of the products due to the electrostatic nature of barium-ligand and yttrium-ligand

bonds. The precursors obtained by these methods are often discrete molecular species and their structures may have very little resemblance to those of 1-2-3 superconductors. For this reason, it is believed that an alternative approach is necessary for the preparation of oriented high-temperature cuprate superconductors in which the crystallographic orientation of the superconducting phase may be at least partially controlled by the structure of the precursors.

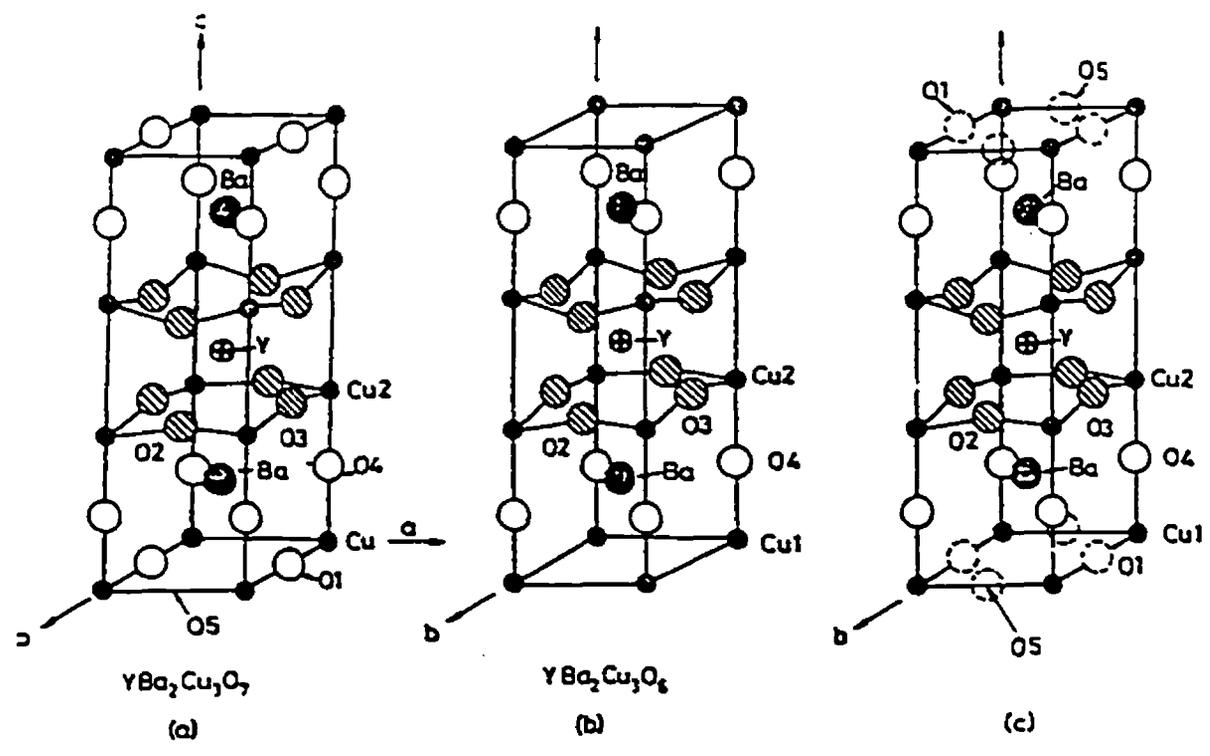
It is well known that the 1-2-3 superconductor has a layered structure¹¹³ shown in Figure 14. In the unit cell these layers are Cu_4O_2 - BaO_4 - Cu_4O_4 -Y- Cu_4O_4 - BaO_4 - Cu_4O_2 , that is, it consists of Cu_4O_2 units inter-layered by BaO_4 and Y units. It is of interest to examine whether a molecular complex could be used as a building block for the construction of molecular complexes with structures resembling that of the 1-2-3 superconductors in one dimension. Such building blocks should also make it possible to control the addition of different metal atoms to the complex as shown in scheme 3. In this chapter of the thesis, a new class of planar cyclic Cu_4 complexes are presented. The structure of the cyclic Cu_4 unit is similar to the structure of the Cu_4O_4 unit of layers in 1-2-3 superconductors. The details of the syntheses and crystal structures are discussed. These compounds indeed display the potential to form one-dimensional arrays.

III.2. Experimental Section

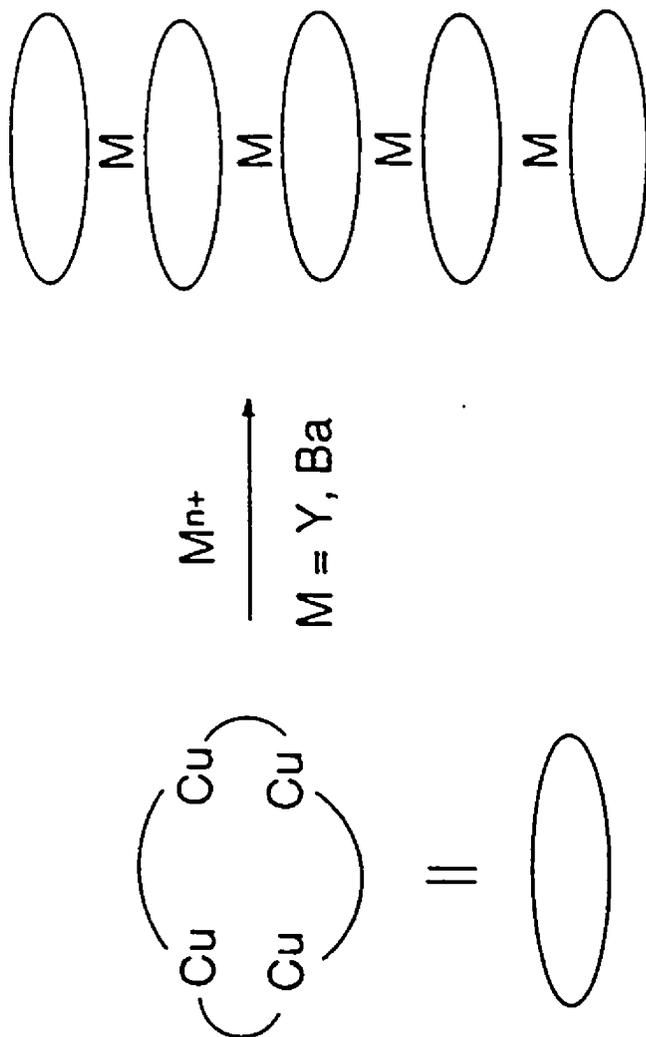
III.2.1. Chemicals and Solvents

All manipulations were carried out using standard Schlenk lines or a nitrogen-filled drybox. All solvents were dried in an appropriate manner under nitrogen prior to use. Cupric

Figure 14. 1-2-3 Superconductor Structure



(a) $\text{YBa}_2\text{Cu}_3\text{O}_7$, orthorhombic (b) $\text{YBa}_2\text{Cu}_3\text{O}_6$ (c) $\text{YBa}_2\text{Cu}_3\text{O}_7$, tetragonal



Scheme 3

acetate was purchased from Fisher Scientific. Silver acetate, 2-hydroxypridine, tetrabutylammonium hexafluorophosphate and the yttrium ethoxide ethanol complex were purchased from Aldrich Chemicals Co.. Thallium(I) hexafluorophosphate was purchased from Strem Chemicals Inc. and it was stored in a desiccator.

III.2.2. Synthesis of $[\text{Cu}^{\text{II}}_4(\text{bdmap})_3(\text{OH})(\text{OAc})_2(\text{HOAc})(\text{H}_2\text{O})][\text{PF}_6]_2$ 3

$\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ 1 (168mg, 0.30mmol) was added to CH_2Cl_2 (30ml). The solution was stirred for about 10 minutes. The light green compound 1 was completely dissolved to give a clear light green solution. Then $\text{Ag}(\text{OAc})$ (150mg, 1.20mmol) was added to this solution. After being stirred for 2 h at 23°C, the colour of the solution changed from light green to blue and a white powder of AgCl formed on the bottom of the flask. TlPF_6 (99mg, 0.28mmol) was added to the filtered solution. The mixture was stirred for an additional 5 h and yielded a grey white powder (TlCl). The solution was then filtered and concentrated to approximately 10ml by pumping the solvent under vacuum. Diethyl ether and toluene were added to the solution. After a few days at 23°C, dark blue crystals of 3 (45mg, yield 12%, m.p. 235°C dec.) were obtained. Elemental analysis: calcd. for $\text{C}_{27}\text{H}_{64}\text{Cu}_4\text{P}_2\text{F}_{12}\text{O}_{11}\text{N}_6$: C%, 26.31; H%, 5.21; N%, 6.58. Found: C%, 26.36; H%, 5.34; N%, 6.42. IR (KBr, cm^{-1}): 3619(m, OH), 3549 (m, OH), 3300 (w, br, OH), 1575 (s, C=O), 1469 (s, C=O), 1439 (s, C=O), 1098 (m, C-O), 850 (vs, P-F).

III.2.3. Synthesis of $[\text{Cu}^{\text{II}}_4(\text{bdmap})_2(\text{OAc})_3(\text{OH})_2(\text{H}_2\text{O})][\text{PF}_6]_4$ 4

$\text{Cu}_2(\text{bdampH})_2\text{Cl}_4$ 1 (140mg, 0.25mmol) was completely dissolved in CH_2Cl_2 (100ml); a clear light green solution was obtained after stirring for ten minutes. Then $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$

(196mg, 0.49mmol) was added to this solution. After being stirred for 1 h, the blue crystals of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ disappeared completely, and the light green colour of the solution turned to dark blue green. Then $\text{Ag}(\text{OAc})$ (327mg, 1.90mmol) was added to this blue green solution. After being stirred for an additional 1 h, the AgCl precipitation was removed by filtration. A dark blue solution was obtained. $\text{Y}(\text{OEt})_3$ -ethanol (132mg, 0.49mmol) was added to the blue solution. After stirring for 0.5 h, TIPF_6 (162mg, 0.49mmol) was added to the solution which was then filtered again and concentrated. A small amount of the solvents diethyl ether and toluene were added to the solution. After standing at room temperature for about two weeks, small dark blue crystals of **4** (10mg, m.p. 145°C dec.) had crystallized for the solution mixture. Elemental analysis: calcd. for $\text{Cu}_4\text{C}_{20}\text{H}_7\text{O}_{11}\text{N}_2\text{PF}_6$; C%, 26.09; H%, 5.11; N%, 6.09. Found: C% 25.70; H%, 4.77; N%, 5.82. IR (KBr, cm^{-1}): 3270 (m, OH), 1559 (m, C=O), 1471 (m, C=O), 1442 (m, C=O), 840 (vs, P-F).

III.2.4. Synthesis of $[\text{Cu}^{\text{II}}_4(\text{bdmap})_2(\text{OAc})_4][\text{PF}_6]_2$ **5**

Method A: $\text{Cu}(\text{OMe})_2$ (70mg, 0.56mmol) and bdmapH (164mg, 1.12mmol) were dissolved in CH_2Cl_2 (100ml) solvent as stirred for about 2 h. Then CuCl_2 (76mg, 0.56mmol) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (224mg, 1.12mmol) were added to the solution. After being stirred for 1 h, a dark blue solution was obtained. TIPF_6 (176mg, 0.53mmol) was added to the blue solution and a white powder (TlCl) was removed by filtration. Then diethyl ether and toluene were added to the filtered solution. The solution was allowed to stand at 23°C for a few weeks. Dark blue crystals of compound **5** were obtained (yield < 5%, m.p. 265°C dec.). Elemental Analysis: Calcd for $\text{Cu}_4\text{C}_{22}\text{H}_{46}\text{O}_{10}\text{N}_4\text{P}_2\text{F}_{12}$, C%, 24.63%; H%, 4.29; N%, 5.22. Found: C%, 25.11; H%,

4.12; N%, 5.38. IR (KBr, cm^{-1}): 1567 (s, C=O), 1433 (s, C=O), 836 (vs, P-F). ^1H NMR (acetone- d_6 solvent, ppm): 2.70 (single, broad), 2.04 (quintet).

Method B: $\text{Cu}(\text{OMe})_2$ (200mg, 1.60mmol), CuCl_2 (72mg, 0.53mmol), bdmaph (156mg, 1.07mmol) and HOAc (128mg, 2.13mmol) were dissolved in CH_2Cl_2 (100ml), and stirred for 2 h. A dark blue solution was obtained. Then TlPF_6 (325mg, 1.07mmol) was added to this blue solution. The solution was stirred continuously for 0.5 h. The white powder of TlCl was removed by filtration. The solution was concentrated and after the addition of diethyl ether and toluene, the solution was allowed to stand at room temperature for a few weeks. Dark blue crystals of compound 5 (40mg, 7% yield) were obtained.

Method C: $\text{Cu}(\text{OMe})_2$ (100mg, 0.80mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (213mg, 1.07mmol), bdmaph (156mg, 1.07mmol) and CuCl_2 (36mg, 0.27mmol) were dissolved in MeOH (100ml) as solvent by stirring for 2 h. A dark blue solution was obtained. Then TlPF_6 (167mg, 0.50mmol) and NR_4PF_6 (207mg, 0.54mmol) were added to the blue solution. The filtered solution was concentrated. Diethylether was added to it and after standing for 2-3 days at 23°C , crystals of 5 (46mg, 8% yield) were collected.

III.2.5. Synthesis of $[\text{Cu}_6(\text{bdmap})_3(\text{OAc})_5(\text{PyOH})(\text{PyO})_2][\text{PF}_6]_2$ 6

A sample of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ 1 (150mg, 0.27mmol) was dissolved in CH_2Cl_2 (150ml) by stirring. Then $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (107mg, 0.54mmol) was added to this solution. After being stirred for 1 h at room temperature, the blue solid of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ completely dissolved to

give a dark blue solution. $\text{Bi}(\text{C}_6\text{H}_5)_3$ (117mg, 0.27mmol) and PyOH (101mg, 1.06mmol) were added to the solution and stirred for 0.5 h. AgOAc (134mg, 0.80mmol) and TIPF_6 (88mg, 0.27mmol) were added to the solution above. A white solid formed immediately and precipitated from the solution which was then filtered and concentrated. Diethyl ether and toluene were added and subsequently blue green crystals of **6** (17% yield, m.p. 243°C dec.) were collected from the mixture. Elemental analysis: Calcd. C%, 33.50. H%, 4.79. N%, 7.65. Found: C%, 34.71. H%, 4.99. N%, 7.01. IR (KBr, cm^{-1}): 3380 (m, OH), 1656 (s, C=O), 1475 (s, C=O), 1435, 1570 (vs, C=C and C=N), 838 (vs, P-F).

III.2.6. Instruments

Elemental analyses were carried out at the Guelph Chemical Laboratories Ltd.. Infrared spectra were recorded as KBr pellets using a Nicolet 5DX FT-IR spectrometer in the range of wave number from 400cm^{-1} and 4000cm^{-1} . Melting points were determined on a Fisher-John melting point apparatus. The ^1H NMR spectrum of compound **5** was recorded on a Bruker AC-300 spectrometer.

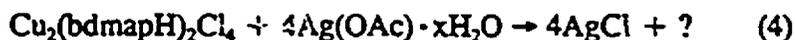
X-ray Diffraction Analysis: Single crystals of **3** with rectangular shapes were grown by slow diffusion of diethyl ether into the CH_2Cl_2 /toluene solution of **3** at room temperature. Dark blue crystals of **4** with a thin plate shape were obtained from the solution of CH_2Cl_2 /diethyl ether/toluene at room temperature. Dark blue single crystals of **5** were obtained from the solution of CH_2Cl_2 , diethyl ether and toluene at room temperature. Blue green crystals of **6** with rectangular shapes were obtained from the solution of CH_2Cl_2 /diethyl ether/toluene at room

temperature. The crystals of 3-6 were mounted on glass fibres and sealed with epoxy. Data were collected on a Rigaku AFC6-S diffractometer with graphite-monochromatized Mo K α radiation and processed on a VAX workstation 3520 using the TEXAN crystallographic package (version 5.0). Data were corrected for Lorentz-polarization effects. The X-ray diffraction analyses were performed by Dr. Wang.

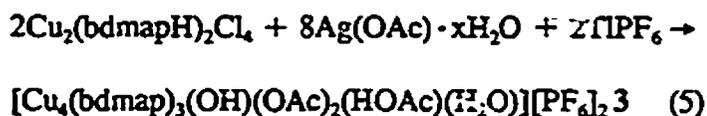
III.3. Results and Discussion



Synthesis: The dicopper complex $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ has been used to synthesize the trinuclear Cu(II) compound 2, by remove the proton of the ammonium group. If the chlorine ligands in the dimeric compound 1 can be removed, more coordination sites would be created so that more metal centres could be put in. The first reaction designed is shown in equation (4).



Here Ag^+ ions would be expected to precipitate out as AgCl while the OAc^- anions might provide another kind of coordination ligand. No crystals were obtained from reaction (4). The second reaction designed is shown in equation (5). It was hoped that the PF_6^- anion would help the product to crystallize. The tetranuclear copper compound 3 was synthesized by the reaction (5) of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ with AgOAc and TlPF_6 in a 1:4:1 ratio.



The formation of the hydroxy ligand in this complex may arise from trace amounts of water in the solvent or in $\text{Ag}(\text{OAc}) \cdot x\text{H}_2\text{O}$ providing the source of the OH^- ligand. The presence of excess of AgOAc appeared necessary for the formation of the hydroxy ligand.

X-ray Crystal Structure: The structures of copper(II) compounds have been studied extensively. Several hundred have been determined by single-crystal X-ray analyses. For tetranuclear $\text{Cu}(\text{II})$ complexes only four types have been structurally identified. The four structural types are (i) linear, (ii) zigzag or stepped, (iii) planar and (iv) tetrahedral.

Compound 3 has been characterized by single-crystal X-ray diffraction analysis. The diagram for the Cu_4 cation of 3 is given in Figure 15. Selected bond distances and angles are given in Table 6 and Table 7. The cation of 3 consists of four Cu^{II} ions bridged by two acetate ligands and two *bdmap* ligands in a cyclic fashion. The *bdmap* ligand functions as a tridentate ligand and bridges two copper atoms through oxygen and two nitrogen atoms. A similar bonding situation has been observed in the trinuclear compound¹²⁴ $\text{Cu}_3(\text{bdmap})_2\text{Cl}_4$. The twelve-membered ring formed by the four copper atoms, two CO_2 groups, and two oxygen atoms from the *bdmap* ligands is essentially planar with the maximum deviation ($\pm 0.37\text{\AA}$) of O(3) from the plane. Cu(2) and Cu(3) are further bridged by an oxygen atom from the additional *bdmap* ligand, while Cu(1) and Cu(4) are further bridged by a hydroxy ligand. The four copper atoms have an approximate rectangular arrangement, $\text{Cu}(1)\text{-Cu}(2) = 3.695(3)\text{\AA}$, $\text{Cu}(2)\text{-Cu}(3) = 3.307(3)\text{\AA}$, $\text{Cu}(3)\text{-Cu}(4) = 3.694(3)\text{\AA}$, $\text{Cu}(1)\text{-Cu}(4) = 3.149(3)\text{\AA}$. In comparison with the $\text{Cu}(1)\text{-Cu}(2)$ and $\text{Cu}(3)\text{-Cu}(4)$ distances, the shorter Cu-Cu separations between $\text{Cu}(2)\text{-Cu}(3)$ and $\text{Cu}(1)\text{-Cu}(4)$ can be

Figure 15. Structure of Compound 3

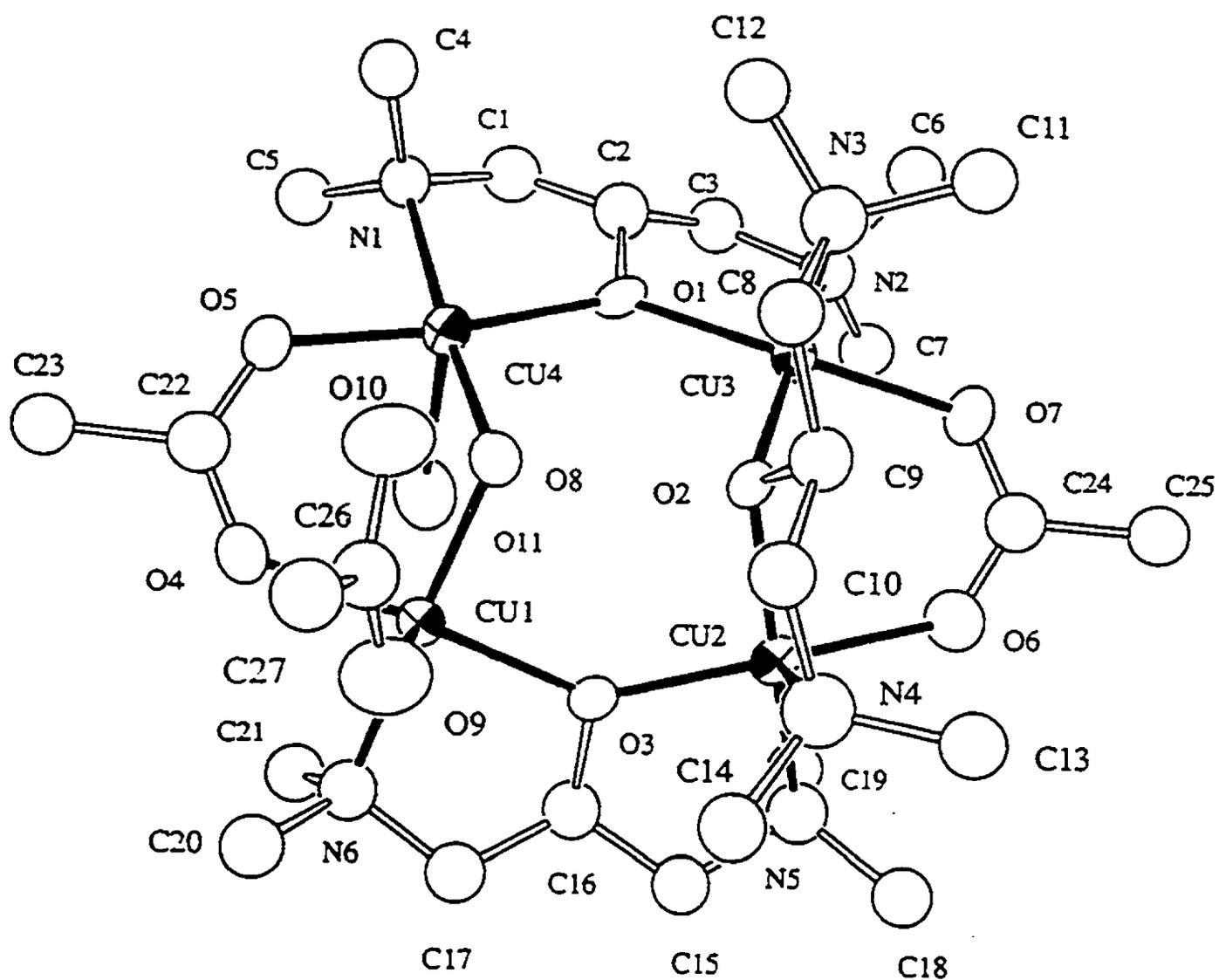


Table 6 Selected Bond distances of Compound 3

atom	atom	distance	atom	atom	distance
CU1	O3	1.970(9)	CU2	N4	2.41(1)
CU1	O4	1.97(1)	CU4	O11	2.47(1)
CU1	O8	1.92(1)	CU1	CU2	3.695(3)
CU1	N6	2.02(1)	CU3	CU4	3.694(3)
CU2	O2	1.954(9)	O1	C2	1.40(2)
CU2	O3	1.96(1)	O2	C9	1.43(2)
CU2	O6	1.98(1)	O3	C16	1.43(2)
CU2	N5	2.00(1)	O4	C22	1.23(2)
CU3	O1	1.988(9)	O5	C22	1.25(2)
CU3	O2	1.96(1)	O6	C24	1.24(2)
CU3	O7	1.96(1)	O7	C24	1.25(2)
CU3	N2	1.99(1)	O9	C26	1.20(3)
CU4	O1	1.95(1)	O10	C26	1.30(3)
CU4	O5	1.94(1)	N1	C1	1.48(3)
CU4	O8	1.92(1)	N5	C15	1.48(3)
CU4	N1	2.01(1)	N5	C19	1.42(3)
CU3	N3	2.42(1)	N6	C20	1.40(3)
CU1	O9	2.68(2)	C1	C2	1.38(3)
CU1	CU4	3.149(3)	C8	C9	1.50(2)
CU2	CU3	3.307(3)	C15	C16	1.43(3)
C2	C3	1.46(3)	C22	C23	1.53(2)
C9	C10	1.50(3)	C26	C27	1.45(4)
C16	C17	1.42(3)			
C24	C25	1.50(2)			

atom	atom	distance	atom	atom	distance
N1	C4	1.44 (3)	N1	C5	1.44 (3)
N2	C3	1.49 (3)	N2	C6	1.46 (3)
N2	C7	1.46 (3)	N3	C8	1.43 (2)
N3	C11	1.48 (2)	N3	C12	1.48 (2)
N4	C10	1.43 (2)	N4	C13	1.48 (2)
N4	C14	1.46 (3)			
N5	C18	1.45 (3)			
N6	C17	1.45 (2)			
N6	C21	1.41 (3)			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 7 Bond Angles of Compound 3

atom	atom	atom	angle	atom	atom	atom	angle
O3	CU1	O4	173.8 (5)	CU3	O1	CU4	139.3 (5)
O3	CU1	O8	93.1 (4)	CU3	O1	C2	109.3 (8)
O3	CU1	N6	87.1 (5)	CU4	O1	C2	111.3 (8)
O4	CU1	O8	91.9 (4)	CU2	O2	CU3	115.4 (5)
O4	CU1	N6	88.1 (5)	CU2	O2	C9	111.3 (8)
O8	CU1	N6	176.4 (5)	CU3	O2	C9	110.6 (9)
O2	CU2	O3	94.4 (4)	CU1	O3	CU2	140.0 (5)
O2	CU2	O6	90.6 (4)	CU1	O3	C16	107.7 (9)
O2	CU2	N5	168.9 (5)	CU2	O3	C16	112.1 (8)
O3	CU2	O6	166.1 (5)	CU1	O4	C22	132 (1)
O3	CU2	N5	86.3 (5)	CU4	O5	C22	128.9 (9)
O6	CU2	N5	86.3 (5)	CU2	O6	C24	134 (1)
O1	CU3	O2	94.5 (4)	CU3	O7	C24	131 (1)
O1	CU3	O7	172.1 (5)	CU1	O8	CU4	110.3 (5)
O1	CU3	N2	86.6 (5)	CU4	N1	C1	103 (1)
O2	CU3	O7	90.5 (5)	CU4	N1	C4	110 (1)
O2	CU3	N2	165.4 (5)	CU4	N1	C5	115 (1)
O7	CU3	N2	87.0 (5)	CU3	N2	C3	109 (1)
O1	CU4	O5	173.0 (4)	CU3	N2	C6	113 (1)
O1	CU4	O8	93.8 (4)	CU3	N2	C7	114 (1)
O1	CU4	N1	85.7 (5)	N5	CU2	N4	109.8 (6)
O5	CU4	O8	91.2 (4)	O2	CU3	N3	80.0 (5)
O5	CU4	N1	88.4 (5)	N2	CU3	N3	114.4 (5)
O8	CU4	N1	168.9 (5)				

atom	atom	atom	angle	atom	atom	atom	angle
CU2	N5	C15	104(1)	CU1	N6	C17	104(1)
CU2	N5	C18	117(1)	CU1	N6	C20	113(1)
CU2	N5	C19	106(1)	CU1	N6	C21	111(1)
O6	CU2	N4	96.1(5)				
O7	CU3	N3	93.1(5)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

attributed to the double bridges over these two pairs of Cu atoms. Such bridging effects on Cu-Cu distances have been frequently observed^{69,114,123}. The most common arrangement of tetranuclear copper (II) compounds is tetrahedral.⁸¹ For example, the class of $[\text{CuX}(\text{OCH}_2\text{CH}_2\text{NR}_2)_n]$ compounds ($X=\text{Cl, Br, NCS and NCO}$; $R=\text{Me, Et, Pr}^n$, or Bu^n . $n=2, 4$ or ∞) except for the dimer and polymer, are tetrameric cuban-type molecules (Table 1). The rectangular planar arrangement of tetranuclear Cu(II) compounds with Cu(II) atoms in close proximity is rare. Among the few known examples are¹¹² $[\text{Cu}_4(\text{mpz})_4(\text{acmpz})_2(\text{NO}_3)_2]$, $\text{mpzH}=3(5)$ -methylpyrazole and $\text{acmpzH}=1$ -(1-ethanoyl)-5-methylpyrazole, and¹¹³ $\text{Cu}_4\text{Zr}_4\text{O}_3(\text{O}^i\text{Pr})_{18}$, in which the arrangement of the four Cu(II) atoms resembles that found in 3.

By comparing the Cu-Cu distances of double bridges in dimer 1, trimer 2 and tetramer 3, it is found that the Cu-Cu distances in double bridges follow a order of dimer < trimer < tetramer. In the dimer $[\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4]$ 1, two Cu atoms are bridged by two bdmapH ligands which are almost parallel and have a cis configuration in respect to the Cu-Cu' vector. There is no crowdedness effect between ligand and ligand or ligand and copper atoms. In trimer $[\text{Cu}_3(\text{bdmap})_2\text{Cl}_4]$ 2, although two Cu atoms [Cu(1) and Cu(3)] are also bridged by two oxygen atoms from two bdmap ligands, Cl(2) atom is very closed to the plane of Cu(3)O(1)Cl(4)N(3)O(2), and the dihedral angle between the plane of O(1)Cl(2)Cl(3)N(2) and the plane of O(1)O(2)N(3)Cl(4) is nearly 80°, which results in steric effect. On the other hand, both N(1) and N(4) atoms from the two bdmapH ligands in 2 coordinate to Cu(1) atom at the same time. These two $-\text{N}(\text{CH}_3)_2$ groups increase steric effect. These make the bdmap ligand distorted and weaken the bridging ability of this bdmap ligand. Therefore, the Cu-Cu distance

in double bridges of dimer 1 is much shorter than that in trimer 2. In the tetramer 3, one of the double bridge ligands is an acetate ligand which bridges each pair of Cu atoms through two oxygen atoms. The Cu-Cu distance with double bridges in 3 is longer than those of 1 and 2.

Each copper atom in 3 is five-coordinate with a square-pyramidal geometry. The four copper-ligand bonds in the plane have normal bond distances, while the fifth ligand coordinates to the Cu centre with a long copper-ligand bond length. Cu(2) and Cu(3) are both weakly coordinate by a nitrogen atom from the bdmmap ligand. Cu(2)-N(4)=2.41(1)Å, Cu(3)-N(3)=2.42(1)Å. Cu(1) is coordinated weakly by an oxygen atom from an acetic acid ligand, Cu(1)-O(9)=2.68(2)Å. Cu(4) is coordinated by an H₂O ligand. Cu(4)-O(11)=2.47(1)Å. Five-coordinate copper(II) complexes often display trigonal-bipyramidal structures. Square-pyramidal structures are relatively less common. The assignments of the acetic acid and water ligands are based on the charge of the cation and long Cu-O distances. It has been well established that a neutral ligand tends to occupy the fifth position in square-pyramidal Cu(II) complex.^{81,114} A hydrogen bond⁷⁷⁻⁷⁹ is present between the hydroxy ligand and the acetic acid ligand, as evidence by the C(26)-O(10)-O(8) angle of 106(1)° and O(8)-O(10) distance of 2.61(2)Å, much shorter than the sum of the van der Waals radii⁷⁶ of oxygen atoms (2.80Å). Such an unusual hydrogen bond between an acid and a strong base is apparently stabilized by the coordination of hydroxy group to the Cu atoms. The hydroxy ligand and the bdmmap ligand on the ring are cis to each other. Hence, the other two bdmmap ligands are cis to each other as well. The bdmmap ligand bonded to the Cu₄ ring may be used to incorporate other metal centres through the two nitrogen atoms that are weakly bonded to the copper centres.

IR Spectrum Analysis: The IR spectrum of compound 3 is shown in Figure 16. There are three medium-intensity bands at 3619cm^{-1} (sharp), 3549cm^{-1} (sharp) and 3300cm^{-1} (broad), which could be caused by three different frequencies arising from the OH stretching vibrations of the three different hydroxy groups in 3. These three types of hydroxy groups arise from the hydroxy, water and acetic acid ligands in 3. In the molecular structure of compound 3 the oxygen atom of the hydroxy ligand is bonded to Cu(1) and Cu(4) atoms. The hydroxy ligand also forms an intramolecular hydrogen bond with the carbonyl group of the acetic acid. Its vibrational frequency should be relatively lower than those of hydroxy group in the water and acetic acid ligands. The absorption band of this group should also be broader than other OH groups. Therefore, the broad peak at 3390cm^{-1} was assigned to the hydroxy ligand stretching frequency. The sharp bands at 3549cm^{-1} and 3619cm^{-1} were assigned to the OH stretch in the water and acetic acid ligands.

The infrared spectra of complexes of carboxylic acids have been studied extensively.⁹³ In examining the effect of coordination on C-O stretching frequency of the carboxylic group, it is important to interpret the results on the basis of the structure of compounds as determined by X-ray analysis. The acetate anion coordinates with a metal ion usually in one of following manners:

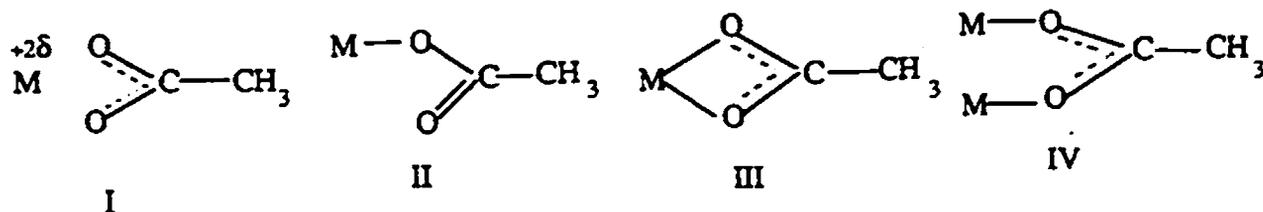
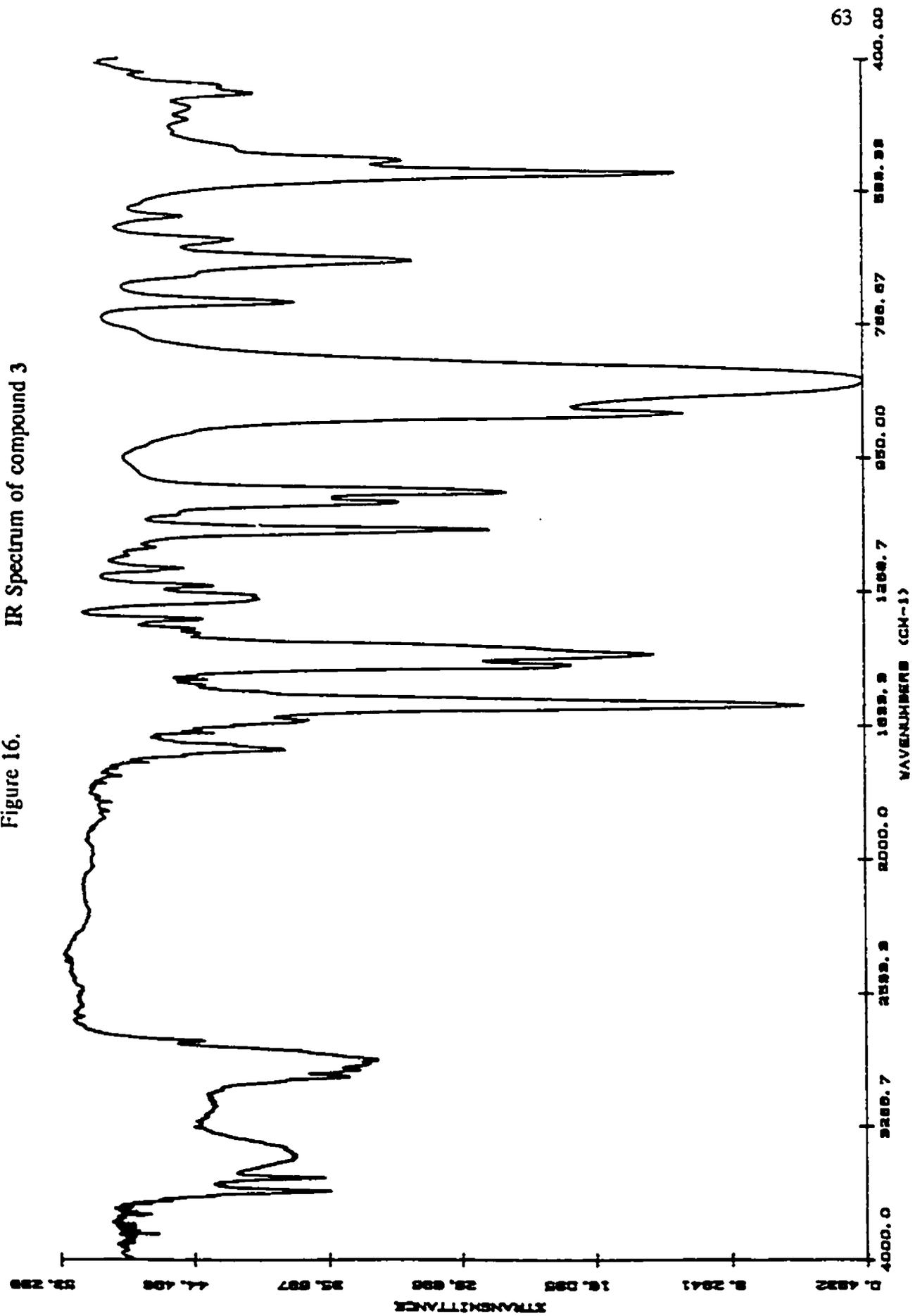


Figure 16. IR Spectrum of compound 3



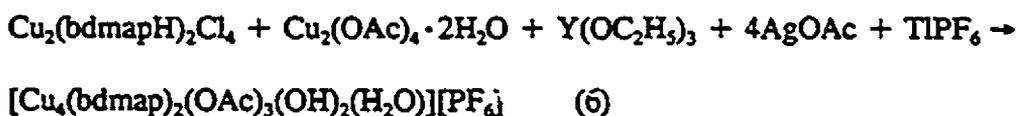
According to the crystal structure of compound 3, the bonding of RCOO^- and Cu(II) atoms belongs to the type IV. A series of compounds having type IV structures have been studied extensively by Nakamoto and co-workers.⁹³ For example, the antisymmetric and symmetric COO stretching frequencies in $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$ were assigned to 1590cm^{-1} and 1440cm^{-1} respectively. In the IR spectrum of compound 3, the absorption bands at 1575cm^{-1} and 1439cm^{-1} could be caused by antisymmetric and symmetric COO stretching frequencies. A absorption band at 1469cm^{-1} was assigned to the $\text{C}=\text{O}$ stretching frequency in HOAc and the absorption band at 1098cm^{-1} to the C-O stretching vibration⁹¹.

Compounds containing the P-F bond have been studied by a number of researchers.⁹² As is expected the range is a wide one, which Thomas puts at $940\text{-}740\text{cm}^{-1}$. This can be subdivided into pentavalent phosphorus and trivalent phosphorus compounds. The former absorb between $940\text{-}794\text{cm}^{-1}$ and the latter between $800\text{-}740\text{cm}^{-1}$. In the spectrum of compound 3, a very intensive absorption band at 850cm^{-1} is assigned to the P-F vibration in PF_6^- .⁹²

$[\text{Cu}^{\text{II}}_4(\text{bdmap})_2(\text{OAc})_3(\text{OH})_2(\text{H}_2\text{O})][\text{PF}_6]_4$

Synthesis: The tetrameric copper compound 3 was synthesized by the reaction of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ 1 with AgOAc and TlPF_6 in a 1:4:1 ratio. $\text{Ag}(\text{OAc})$ was used to precipitate the Cl^- anion in the dimer 1. The acetate anions OAc^- provided an additional coordinating ligand and also reacted with the protons in bdmapH . The anion, PF_6^- , was used for the crystallization of 3.

It was hoped that the reaction of $\text{Cu}_2(\text{bdmapH})_2\text{Cl}_4$ **1** with $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$, $\text{Y}(\text{OC}_2\text{H}_5)_3$, AgOAc and TIPF_6 in a 1:1:1:4:1 would result in the synthesis of a Y-Cu complex. However, the homonuclear compound **4** was actually obtained from this reaction as is shown in equation (6). The functions of AgOAc and TIPF_6 are the same as those in the synthesis of **3**. The compound $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$ could provide additional Cu metal centres and OAc^- ligands. $\text{Y}(\text{OC}_2\text{H}_5)_3$ might have caused the formation of hydroxy ligands in the product **4** by reacting with the trace amount of water in the solution. The yield of the product varied with the reaction conditions. Independent synthesis was unsuccessful. However, in the presence of $\text{Y}(\text{OC}_2\text{H}_5)_3$ the synthesis was reproducible.



X-ray Crystal Structure: The compound **4** was fully characterized by single-crystal X-ray analysis. The structure of the cation is shown in Figure 17. Selected bond lengths and angles are given in Table 8 and Table 9.

The features of the twelve-membered ring in the cation are similar to that of **3**. There are two hydroxy ligands bridging two pairs of Cu atoms. The two hydroxy groups have a cis configuration with respect to the twelve-membered ring. An H_2O ligand and an acetate ligand bridge Cu(2)/Cu(3) and Cu(1)/Cu(4), respectively through the formation of two long Cu-O bonds, $\text{Cu}(2)\text{-O}(11)=2.37(1)\text{\AA}$, $\text{Cu}(3)\text{-Cu}(11)=2.50(1)\text{\AA}$, $\text{Cu}(1)\text{-O}(9)=2.45(2)\text{\AA}$, $\text{Cu}(4)\text{-O}(9)=2.44(2)\text{\AA}$. The distances of $\text{Cu}(2)\text{-Cu}(3)=3.109(5)\text{\AA}$, $\text{Cu}(1)\text{-Cu}(4)=2.998(5)\text{\AA}$ are much

Figure 17. Structure of compound 4

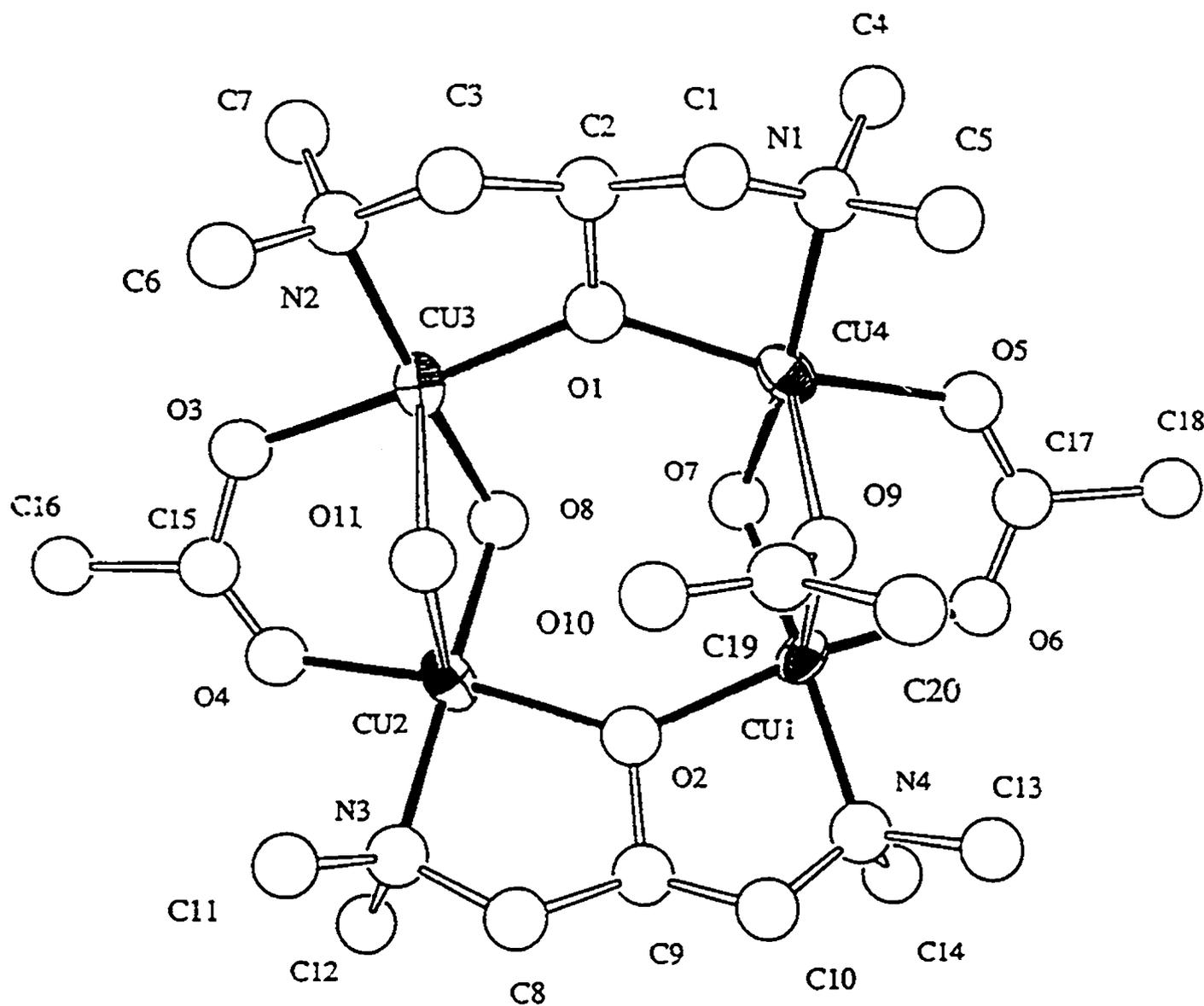


Table 8 Bond Distances of Compound 4

atom	atom	distance	atom	atom	distance
CU1	CU4	2.998 (5)	C8	C9	1.50 (3)
CU1	O2	1.98 (1)	C9	C10	1.52 (3)
CU1	O6	1.98 (1)	C15	C16	1.54 (3)
CU1	O7	1.92 (1)	C17	C18	1.54 (3)
CU1	O9	2.45 (2)	O1	C2	1.36 (2)
CU1	N4	2.03 (2)	O2	C9	1.41 (2)
CU2	CU3	3.109 (5)	O3	C15	1.25 (2)
CU2	O2	1.99 (1)	O4	C15	1.19 (2)
CU2	O4	1.97 (1)	O5	C17	1.20 (2)
CU2	O8	1.94 (1)	O6	C17	1.22 (2)
CU2	O11	2.37 (1)	O9	C19	1.23 (2)
CU2	N3	2.00 (2)	O10	C19	1.22 (2)
CU3	O1	2.02 (1)	N1	C1	1.44 (3)
CU3	O3	2.00 (1)	N1	C4	1.50 (3)
CU3	O8	1.92 (1)	N1	C5	1.49 (3)
CU3	O11	2.50 (1)	N2	C3	1.44 (3)
CU3	N2	1.99 (2)	N2	C6	1.46 (3)
CU4	O1	2.01 (1)	N2	C7	1.47 (3)
CU4	O5	1.99 (1)	N3	C8	1.46 (3)
CU4	O7	1.90 (1)	N3	C11	1.49 (3)
CU4	O9	2.44 (2)	N3	C12	1.44 (3)
CU4	N1	1.98 (2)	N4	C10	1.41 (2)
C1	C2	1.49 (3)	N4	C13	1.47 (3)
C2	C3	1.50 (3)	N4	C14	1.43 (3)
C19	C20	1.52 (3)			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 9 Bond Angles of Compound 4

atom	atom	atom	angle	atom	atom	atom	angle
CU4	CU1	O2	110.9 (4)	O4	CU2	N3	88.6 (7)
CU4	CU1	O6	79.2 (5)	O8	CU2	O11	83.9 (5)
CU4	CU1	O7	37.9 (4)	O8	CU2	N3	175.7 (7)
CU4	CU1	O9	52.1 (4)	O11	CU2	N3	100.3 (6)
CU4	CU1	N4	151.8 (5)	CU2	CU3	O1	107.7 (4)
O2	CU1	O6	169.4 (6)	CU2	CU3	O3	75.8 (4)
O2	CU1	O7	94.5 (5)	CU2	CU3	O8	36.7 (3)
O2	CU1	O9	99.2 (5)	CU2	CU3	O11	48.5 (3)
O2	CU1	N4	83.7 (6)	CU2	CU3	N2	145.1 (5)
O6	CU1	O7	91.7 (6)	O1	CU3	O3	175.1 (6)
O6	CU1	O9	89.7 (6)	O1	CU3	O8	92.2 (5)
O6	CU1	N4	88.7 (7)	O1	CU3	O11	92.8 (5)
O7	CU1	O9	87.4 (5)	O1	CU3	N2	85.5 (6)
O7	CU1	N4	169.6 (7)	O3	CU3	O8	92.6 (5)
O9	CU1	N4	103.0 (7)	O3	CU3	O11	87.0 (5)
CU3	CU2	O2	112.7 (4)	O3	CU3	N2	89.7 (6)
CU3	CU2	O4	78.3 (4)	O8	CU3	O11	80.9 (5)
CU3	CU2	O8	36.2 (3)	O8	CU3	N2	177.6 (6)
CU3	CU2	O11	52.1 (3)	O11	CU3	N2	100.1 (6)
CU3	CU2	N3	147.8 (5)	CU1	CU4	O1	112.9 (4)
O2	CU2	O4	167.2 (6)	CU1	CU4	O5	77.5 (4)
O2	CU2	O8	94.0 (5)	CU1	CU4	O7	38.6 (4)
O2	CU2	O11	98.3 (5)	CU1	CU4	O9	52.4 (4)
O2	CU2	N3	84.9 (6)	CU1	CU4	N1	150.7 (5)
O4	CU2	O8	91.7 (6)	O1	CU4	O5	167.1 (5)
O4	CU2	O11	93.6 (5)	O1	CU4	O7	91.9 (5)

(cont)

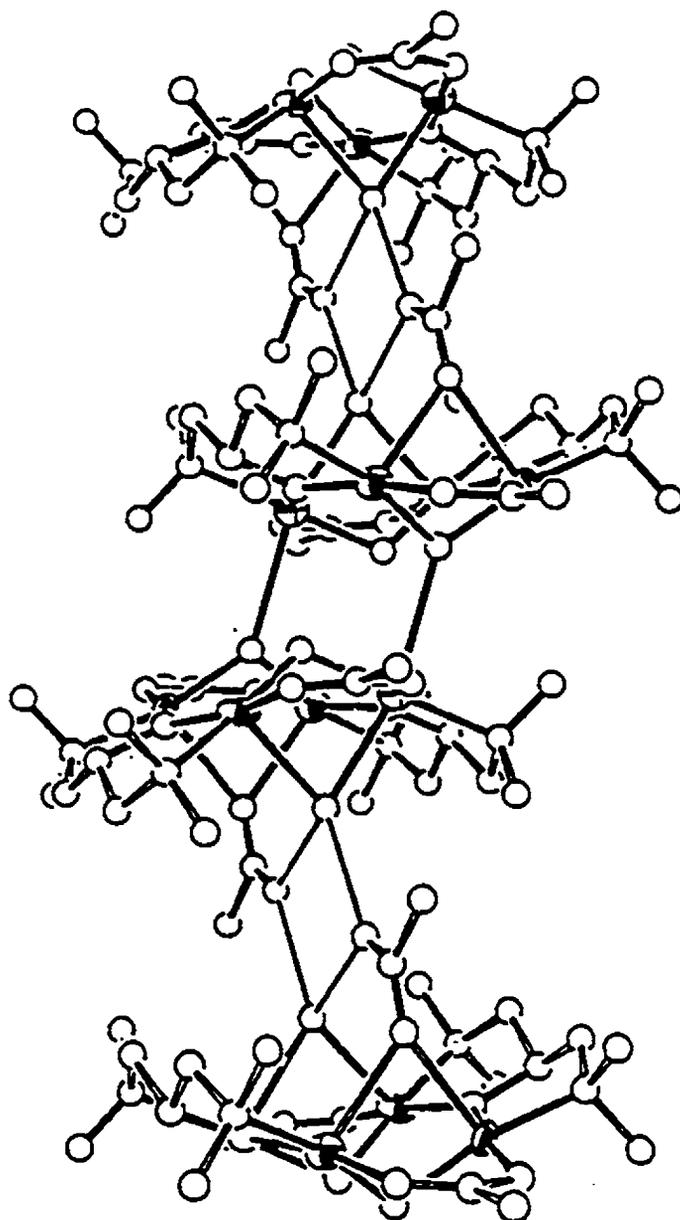
atom	atom	atom	angle	atom	atom	atom	angle
O1	CU4	O9	105.9(5)	CU1	O2	CU2	135.6(7)
O1	CU4	N1	83.6(6)	CU1	O2	C9	112(1)
O5	CU4	O7	92.4(6)	CU2	O2	C9	112(1)
O5	CU4	O9	86.3(5)	CU3	O3	C15	127(1)
O5	CU4	N1	90.3(6)	CU2	O4	C15	127(2)
O7	CU4	O9	88.2(5)	CU4	O5	C17	127(1)
O7	CU4	N1	170.7(6)	CU1	O6	C17	125(1)
O9	CU4	N1	100.8(6)	CU1	O7	CU4	103.5(6)
CU3	N2	C3	105(1)	CU2	O8	CU3	107.1(5)
CU3	N2	C6	117(1)	CU1	O9	CU4	75.5(5)
CU3	N2	C7	110(1)	CU1	O9	C19	135(2)
CU2	N3	C8	105(1)	CU4	O9	C19	137(2)
CU2	N3	C11	112(1)	CU2	O11	CU3	79.3(4)
CU2	N3	C12	108(1)	CU4	N1	C1	108(1)
CU1	N4	C10	106(1)	CU4	N1	C4	113(2)
CU1	N4	C13	115(2)	CU4	N1	C5	115(2)
CU1	N4	C14	107(2)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

shorter than the distances of $\text{Cu}(1)\text{-Cu}(2)=3.676(6)\text{\AA}$, $\text{Cu}(3)\text{-Cu}(4)=3.746(5)\text{\AA}$. This is mainly caused by triple bridges. However, the distance of $\text{Cu}(1)\text{-Cu}(4)=2.998(5)\text{\AA}$ is slightly shorter than the distance of $\text{Cu}(2)\text{-Cu}(3)=3.109(5)\text{\AA}$. Since H_2O is a neutral ligand, acetate is a ligand with one negative charge, the acetate ligand as an anion has a much stronger affinity to $\text{Cu}(\text{II})$ cation than H_2O ligand does, and the bridging ability of acetate ligand is also stronger than that of H_2O . Although a water molecule as a bridging ligand is rare in transition-metal complexes, several examples are known in alkali- and alkaline-earth-metal complexes.^{77,105} In comparison with the Cu-Cu distances in 3, the distances of $\text{Cu}(2)\text{-Cu}(3)=3.109(5)\text{\AA}$, $\text{Cu}(1)\text{-Cu}(4)=2.998(5)\text{\AA}$ in 4 are much shorter than the distances of $\text{Cu}(2)\text{-Cu}(3)=3.307(3)\text{\AA}$, $\text{Cu}(1)\text{-Cu}(4)=3.149(3)\text{\AA}$ in 3, this is caused by triple bridges. The geometry of each copper atom is approximately square-pyramidal. The plane $\text{Cu}(1)\text{O}(2)\text{O}(7)\text{O}(6)\text{N}(4)$ and the plane $\text{Cu}(2)\text{O}(2)\text{O}(8)\text{O}(4)\text{N}(3)$ are nearly coplanar with a dihedral angle of 4.5° . The plane $\text{Cu}(3)\text{O}(1)\text{O}(3)\text{O}(8)\text{N}(2)$ has a dihedral angle of 7.5° with the plane $\text{Cu}(4)\text{O}(1)\text{O}(5)\text{O}(7)\text{N}(1)$. The dihedral angles between the $\text{Cu}(1)$ plane and the $\text{Cu}(4)$ plane, and the $\text{Cu}(2)$ plane and $\text{Cu}(3)$ plane are 60.1° and 58.0° , respectively.

The most important feature of the molecule 4 is that the Cu cations form a one-dimensional structure in the solid state, as shown in Figure 18. This one-dimensional structure is achieved through the face to face and back to back dimerization by two sets of intermolecular bonds. One set are intermolecular hydrogen bonds between the H_2O and acetate ligands. $\text{O}(10)\cdots\text{O}(11')=2.72(2)\text{\AA}$, $\text{C}(19)\text{-O}(10)\cdots\text{O}(11')=142(2)^\circ$, and perhaps two weak intermolecular hydrogen bonds between the hydroxy ligand $\text{O}(8')$ and the $\text{O}(1)$ atom of the

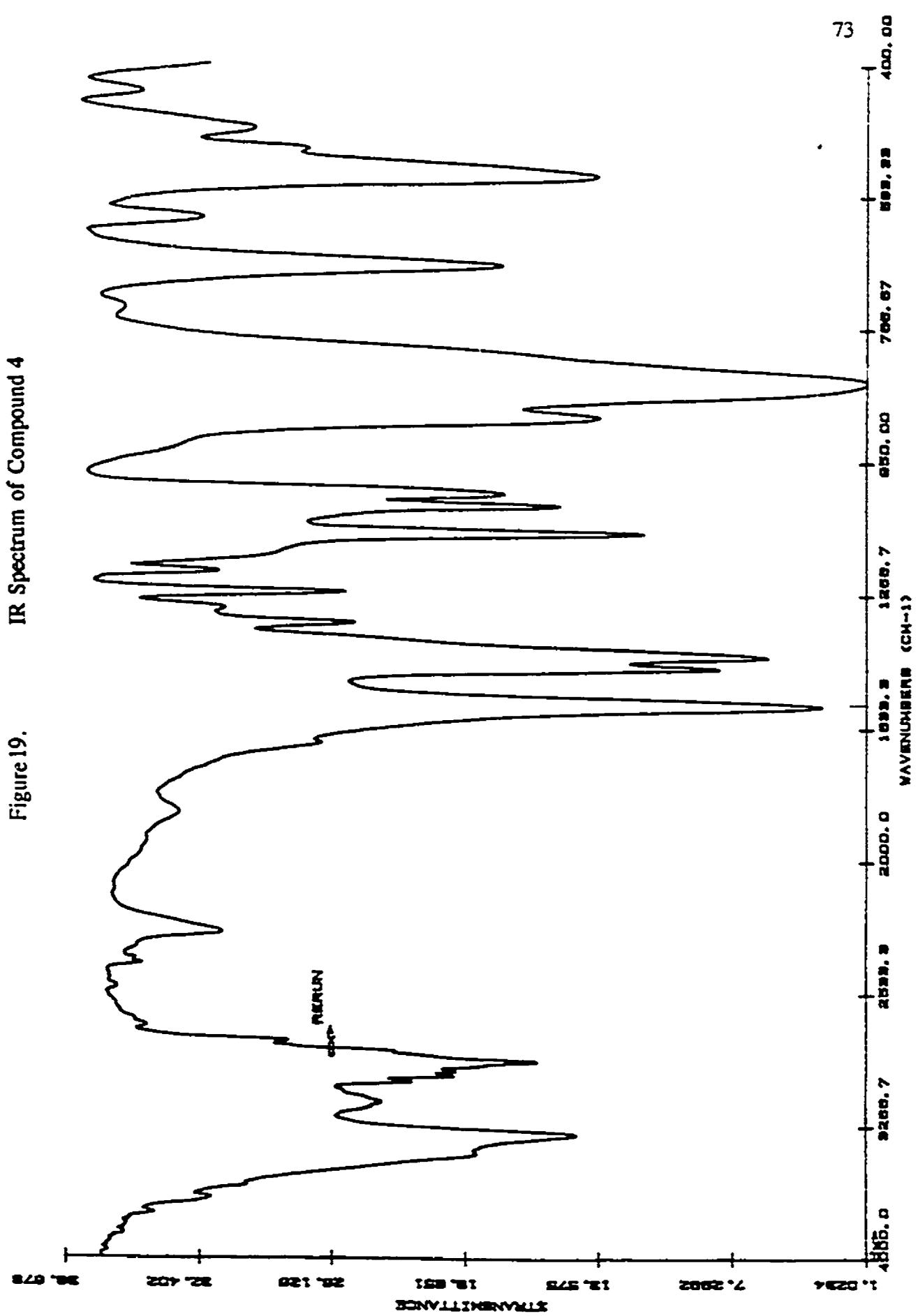
Figure 18. One Dimensional Structure of Compound 4



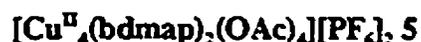
bdmap ligand, $O(1) \cdots O(8) = 2.92(2) \text{ \AA}$, $C(2)-O(1) \cdots O(8') = 113(1)^\circ$. $O(10)$ also forms an intramolecular hydrogen bond with the H_2O ligand, as evidenced by the $O(10) \cdots O(11)$ distance of $2.71(2) \text{ \AA}$ and the $C(19)-O(10) \cdots O(11)$ angle of $127(2)^\circ$. The other set of bonds are two long intermolecular Cu-O bonds, $Cu(3)-O(7') = 2.81(1) \text{ \AA}$. The shortest intermolecular Cu-Cu distance is $3.910(5) \text{ \AA}$ for $Cu(3)-Cu(4')$, comparable to the intramolecular Cu-Cu distances of $Cu(3)-Cu(4)$, $3.746(6) \text{ \AA}$, and $Cu(1)-Cu(2)$, $3.676(6) \text{ \AA}$. Hydrogen bonds between a water molecule and an acetate have been observed previously in inorganic and organic hydrates such as oxalic acid dihydrate where the water molecule is the donor of two protons.⁷⁹ The use of hydrogen bonds to control the assembly of molecules has been one of the widely-used strategies in the synthesis of supramolecules.¹¹⁶⁻¹¹⁷ The synthesis of low-dimensional polymeric compounds, especially those containing metal atoms in one-dimensional arrays, has also been a very active research area.¹¹⁸⁻¹¹⁹ Low-dimensional materials are very attractive to chemists not only because they display interesting anisotropic properties but also because they may have important applications as new materials. Most of the known one-dimensional inorganic compounds have a staggered, one-metal-centred chain structure in the solid state.¹¹⁸⁻¹²⁰ One-dimensional inorganic compounds which contain multiple-metal-centre units arranged along one dimension are rare. The compound **4** represents a new polymeric inorganic material.

IR Spectra Analysis: Compound **4** has been characterized by IR as shown in Figure 19. The OH frequencies of the two hydroxy ligands and a water molecule in **4** were overlapped at between 3300 cm^{-1} and 3200 cm^{-1} . By comparison with the OH frequencies in **3**, the absorption frequencies in **4** were lower than those of **3**. This could be caused by the presence of intra- and

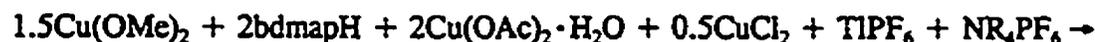
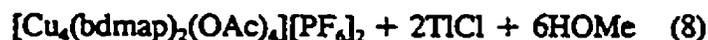
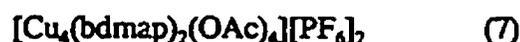
Figure 19. IR Spectrum of Compound 4



inter- hydrogen bonds among hydroxy ligands, the water molecule and the acetate ligand in 4. The absorption bands at 1559cm^{-1} and 1442cm^{-1} were assigned to the antisymmetric and symmetric COO stretching frequencies. The absorption band at 1471cm^{-1} was assigned to the stretching frequency of C=O in the COO⁻¹ bridging ligand containing O(9) in 4. The very intensive band at 840cm^{-1} was assigned to the P-F stretching frequency in PF₆⁻¹ anion.



Synthesis: The tetrameric copper(II) compound 5 has been synthesized by the methods of A, B and C. The appropriate equations are shown in (7), (8) and (9).



In reaction (7), the two equivalents of OMe⁻ only neutralized the two equivalents of H⁺ from the bdmapH ligand. Two equivalents of Tl⁺ were required for the precipitation of the two equivalents of Cl⁻ in CuCl₂. In reaction (8), six equivalents of OMe⁻ not only neutralized the two equivalents of H⁺ from the bdmapH ligand, but also removed the four equivalents of H⁺ from acetic acid. Two equivalents of Tl⁺ precipitated the two equivalents of Cl⁻ in CuCl₂. The yields by methods A and B were quite low. In reaction (9), only three equivalents of OMe⁻ were required for the removal of two equivalents of H⁺ from the bdmapH ligand, leaving an excess

of one equivalent of OMe^- in the reaction. One equivalent of Tl^+ precipitated one equivalent of Cl^- in CuCl_2 . The two equivalents of PF_6^- anion came from TlPF_6 and NR_4PF_6 . Although the yields of the copper(II) compound **5** by methods A, B and C were less than 10%, the yield by method C was a little better than the yields by methods B and C. The reaction mechanisms are not understood, but the low yield might be caused by the poor solubility of the product **5**. Most of product **5** was lost due to the coprecipitation with TlCl .

X-ray Crystal Structure: The compound **5** was fully characterized by X-ray analyses. The molecular structure is shown in Figure 20. Bond lengths and angles are listed in Table 10 and Table 11, respectively. The molecule of **5** has an inversion centre. Two acetate ligands and two *bdmap* ligands bridge the four copper atoms in a square-planar arrangement, $\text{Cu}(1)\text{-Cu}(2)=3.435(3)\text{\AA}$, $\text{Cu}(1)\text{-Cu}(2')=3.305(2)\text{\AA}$. Interestingly, the double-bridged $\text{Cu}(1)\text{-Cu}(2)$ distance is slightly longer than the single-bridged $\text{Cu}(1)\text{-Cu}(2')$ distance. The twelve-membered ring composed of the four copper atoms, two CO_2 units, and two oxygen atoms is similar to those of compound **3** and **4**. This ring unit is essentially planar with the maximum deviation ($\pm 0.44\text{\AA}$) of $\text{O}(1)$ from the plane. In **3** and **4**, the additional ligands bridge the two pairs of Cu atoms bridged by the acetate ligands. In contrast, the two additional acetate ligands in **5** bridge $\text{Cu}(1)$ and $\text{Cu}(2)$ or $\text{Cu}(1')$ and $\text{Cu}(2')$ that are bridged by the *bdmap* ligands. Several factors might contribute to the preference of bridging $\text{Cu}(1)$ and $\text{Cu}(2)$ instead of $\text{Cu}(1)$ and $\text{Cu}(2')$. First of all, each $\text{Cu}(\text{II})$ centre requires a square-planar geometry. Secondly, the geometry of the *bdmap* ligand requires that the oxygen and nitrogen atoms coordinate to the $\text{Cu}(\text{II})$ centre in a *cis* fashion. As a result, the oxygen atoms from the acetate ligands have to coordinate to the

Figure 20 Cation Structure of Compound 5

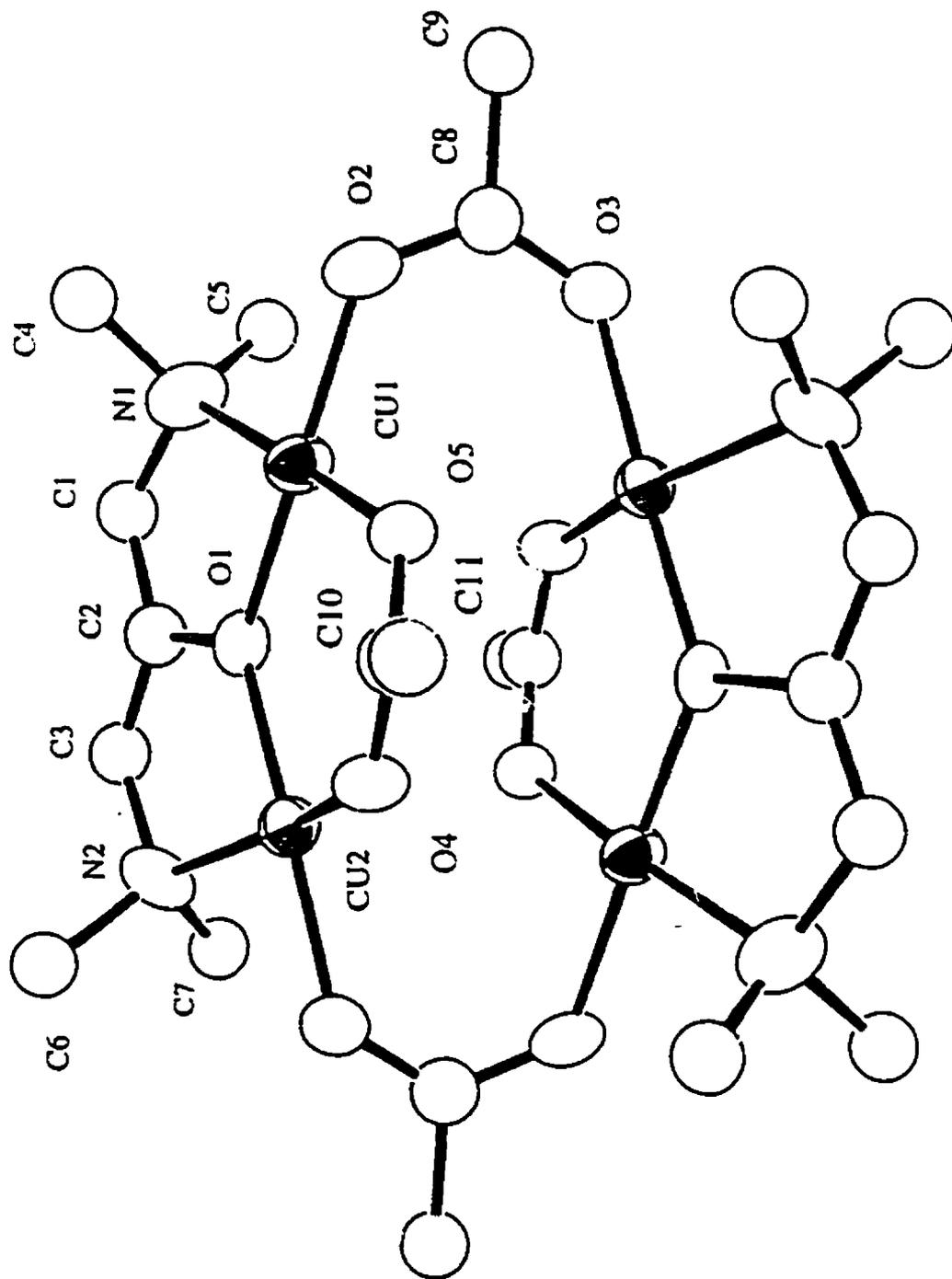


Table 10 Bond Distances of compound 5

atom	atom	distance	atom	atom	distance
CU2	O1	1.874 (8)	O2	C8	1.26 (1)
CU2	O3'	1.919 (8)	O3	C8	1.23 (1)
CU2	O5	1.961 (8)	O4	C10	1.27 (1)
CU2	N2	2.02 (1)	O5	C10	1.24 (1)
CU1	O1	1.884 (8)	N1	C1	1.45 (3)
CU1	O2	1.938 (9)	N1	C4	1.41 (2)
CU1	O4	1.949 (8)	N1	C5	1.46 (2)
CU1	N1	2.01 (1)	N2	C3	1.44 (2)
P1	F1	1.53 (1)	N2	C6	1.46 (3)
P1	F2	1.46 (1)	N2	C7	1.46 (2)
P1	F3	1.55 (1)	C1	C2	1.36 (2)
P1	F4	1.51 (1)	C2	C3	1.35 (2)
P1	F5	1.45 (1)	C8	C9	1.48 (2)
P1	F6	1.53 (2)	C10	C11	1.49 (2)
O1	C2	1.40 (2)			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 11 Bond Angles of Compound 5

atom	atom	atom	angle	atom	atom	atom	angle
O1	CU2	O3	174.9(4)	F5	P1	F6	173(1)
O1	CU2	O5	95.1(3)	CU2	O1	CU1	132.1(4)
O1	CU2	N2	85.7(4)	CU2	O1	C2	114.7(8)
O3	CU2	O5	89.9(3)	CU1	O1	C2	113.1(8)
O5	CU2	N2	89.7(4)	CU1	O2	C8	128.7(9)
O5	CU2	N2	159.8(4)	CU2	O3	C8	132.4(9)
O1	CU1	C2	174.5(4)	CU1	O4	C10	131.2(8)
O1	CU1	O4	94.8(3)	CU2	O5	C10	132.2(8)
O1	CU1	N1	85.9(4)	CU1	N1	C1	107(1)
O2	CU1	O4	89.9(4)	CU1	N1	C4	114(1)
O2	CU1	N1	89.9(4)	CU1	N1	C5	112(1)
O4	CU1	N1	173.4(4)	C1	N1	C4	109(2)
F1	P1	F2	177(1)	C1	N1	C5	110(2)
F1	P1	F3	90.2(6)	C4	N1	C5	105(1)
F1	P1	F4	90.2(7)	CU2	N2	C3	105(1)
F1	P1	F5	89(1)	CU2	N2	C6	111(1)
F1	P1	F6	84(1)	CU2	N2	C7	113(1)
F2	P1	F3	89.9(7)	C3	N2	C6	115(2)
F2	P1	F4	89.8(7)	C3	N2	C7	106(1)
F2	P1	F5	94(1)	C6	N2	C7	107(1)
F2	P1	F6	93(1)	N1	C1	C2	117(2)
F3	P1	F4	177.7(9)	O1	C2	C1	117(2)
F3	P1	F5	91.3(8)	O1	C2	C3	114(2)
F3	P1	F6	86.7(8)	C1	C2	C3	129(2)
F4	P1	F5	86.4(9)	N2	C3	C2	121(2)
F4	P1	F6	96(1)	O2	C8	O3	126(1)

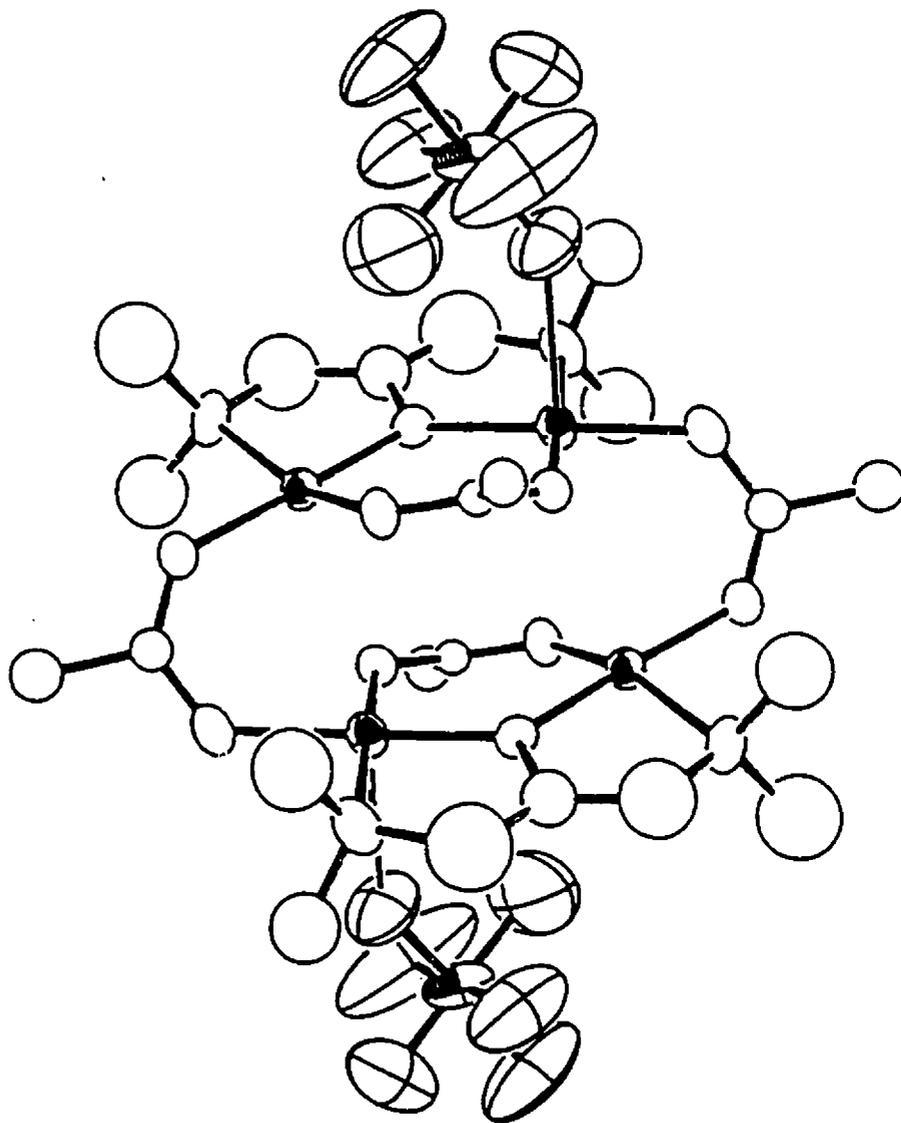
Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Cu(II) centre in a cis fashion as well. It can be demonstrated easily by simple molecular models that in order to minimize the steric interactions of ligand atoms, the acetate bridging of Cu(1) and Cu(2) is the preferred geometry. The two dimeric units of $\text{Cu}_2(\text{bdmap})(\text{OAc})$ are parallel to each other. The dihedral angle between the twelve-membered ring and the plane defined by Cu(1) and Cu(2) and atoms coordinated to these two copper atoms is about 45° . The two acetate ligands coordinate to the ring in a trans configuration. As a consequence, the two bdmap ligands are trans to each other. The O(4') atom is weakly bonded to Cu(2), $\text{Cu(2)-O(4')} = 2.549(8)\text{\AA}$. The geometry of Cu(2) is square-pyramided. The shortest contact between the ligand atoms and the Cu(1) atom are between Cu(1) and O(5') [$2.830(8)\text{\AA}$], and Cu(1) and F(3) of the PF_6^{-1} anion [$2.771(1)\text{\AA}$]. These O(5') and F(3) atoms occupy the fifth and sixth positions of the Cu(1) atom, as shown in Figure 21. As a result the geometry of Cu(1) is an elongated octahedrons. All other contact distances between the Cu atoms and the PF_6^{-1} anion are larger than 3.60\AA and therefore can be ignored. A similar PF_6^{-1} anion interaction with a Cu(II) centre has been reported recently.¹²¹

The common feature of the structures 3-5 is the presence of the cyclic unit composed of four copper(II) ions, two acetate ligands, and two bdmap ligands. The structures of 3-5 illustrate that the cyclic Cu_4 unit is capable of accommodating a variety of ligands. It is believed that the ligand environments on the ring can be modified such that heterometal ions such as Y^{3+} or Ba^{2+} can be readily incorporated into the Cu_4 complexes.

¹H NMR Spectrum: The ¹H NMR spectra of the compound 5 is shown in Figure 22.

Figure 21. Interaction of the PF_6^- Anions with Cation of Compound 5



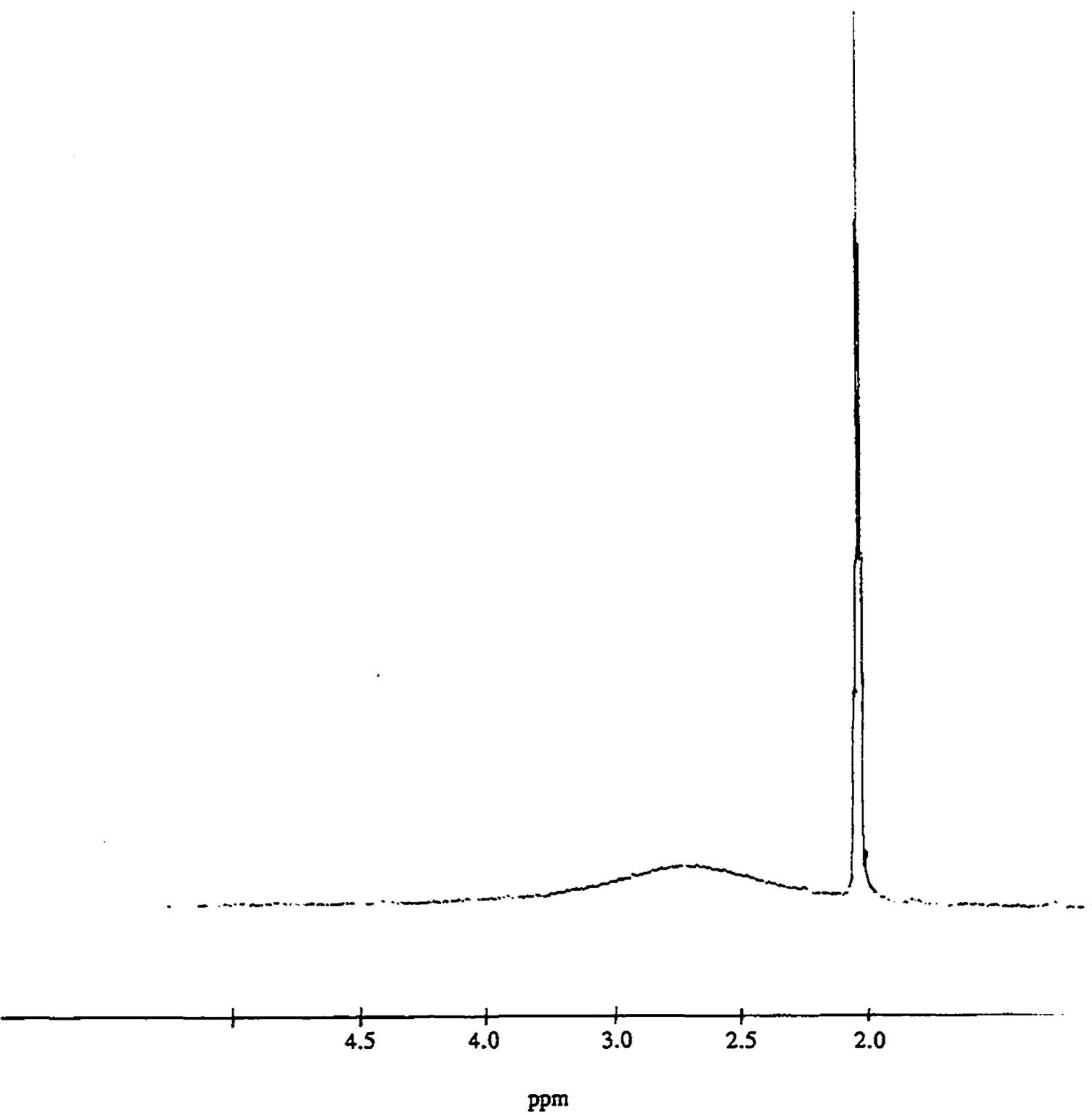


Figure 22. ^1H NMR Spectrum of Compound 5

Only two regions of signals were observed in acetone- d_6 for the compound **5**. A quintet at 2.04 ppm is the typical peak of the acetone- d_6 solvent. The other region is a very broad peak around 2.7 ppm, which is due to the proton chemical shifts of the bdmap and acetate ligands. The broadness of these chemical shifts was apparently caused by the paramagnetic behaviour of the tetramer in solution at room temperature.

This phenomenon has also been observed in the ^1H NMR spectrum of the tetranuclear Cu(II) compound, $[\text{Cu}^{\text{II}}_4(\text{bdmap})_2(\text{OAc})_2(\text{OH})_2][\text{Hg}(\text{OAc})\text{Cl}_2]_2[\text{HgCl}_2]$. The structure of the Cu_4Hg_3 tetramer is shown in Figure 23. This structure is similar to the structure of **5**. The two bdmap, two OAc^- and four Cu(II) atoms formed a twelve-membered ring, which is the same as the twelve-membered ring in **5**. The two pairs of Cu(II) atoms in this compound are bridged by two hydroxy ligands instead of two acetate ligands in **5**. The ^1H chemical shifts from the ligands are very broad in ^1H NMR spectrum apparently due to the similar paramagnetic shift.

IR Spectrum Analysis: The IR spectrum of compound **5** is shown in Figure 24. It was established from the X-ray crystal structure of compound **5** that the bonding of OAc^- ligands and Cu(II) atoms belongs to the type IV (page62). The antisymmetric and symmetric OAc^- stretching frequencies in **5** might be assigned at 1567cm^{-1} and 1433cm^{-1} . The very intensive absorption band at 836cm^{-1} was assigned to the P-F vibration in PF_6^- . The broad band at 3430cm^{-1} might be caused by the small amount of water in KBr.



Figure 23. Cu_4 Structure of $[\text{Cu}_4(\text{bdmap})_2(\text{OAc})_2(\text{OH})_2][\text{Hg}(\text{OAc})\text{Cl}]_2[\text{HgCl}_2]$

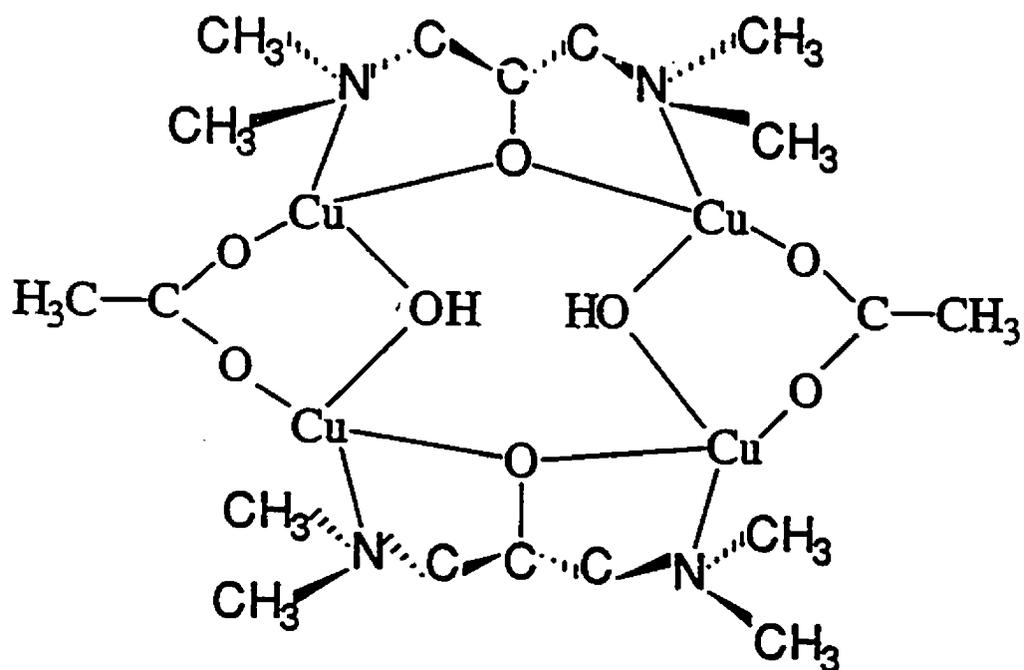
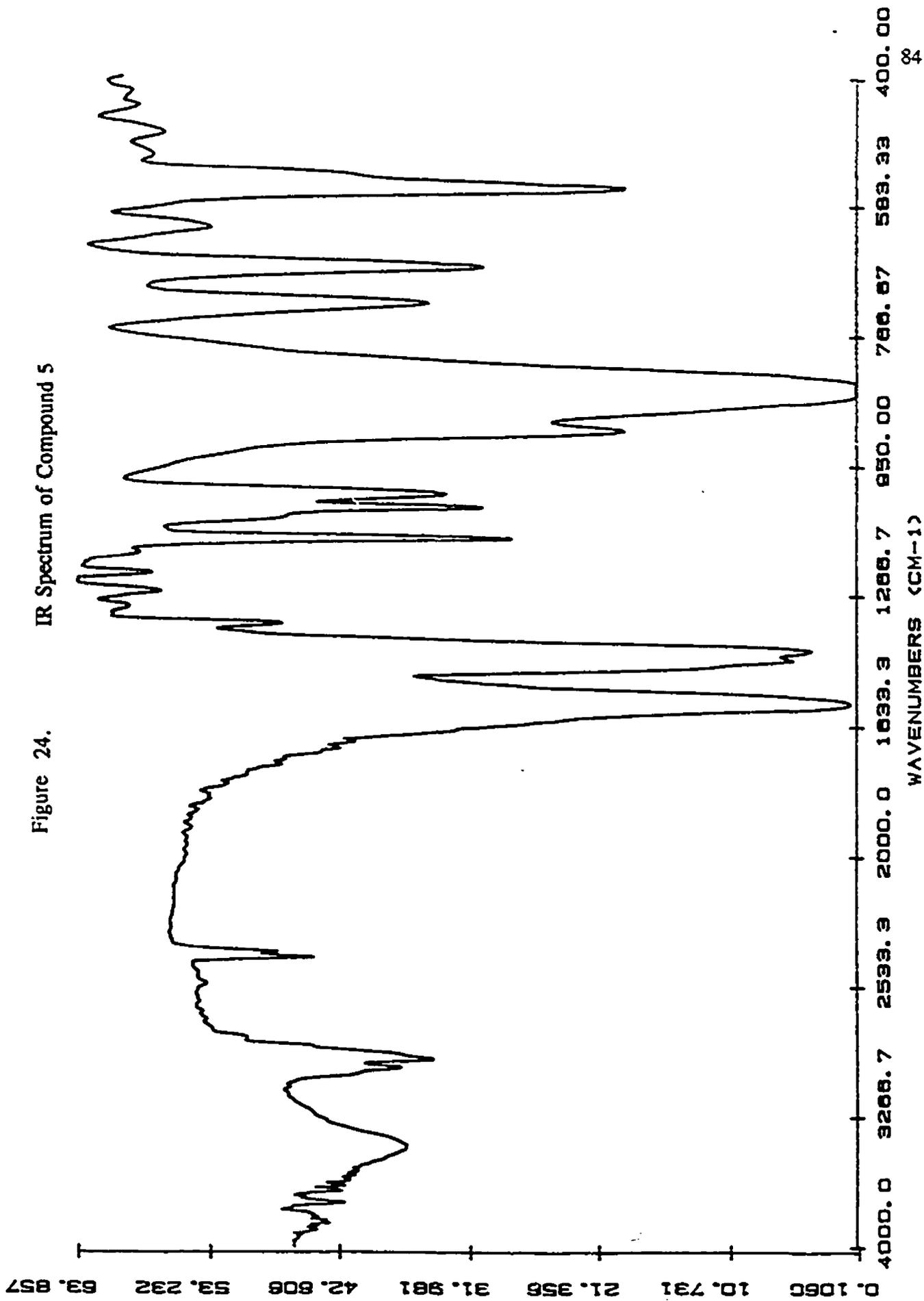
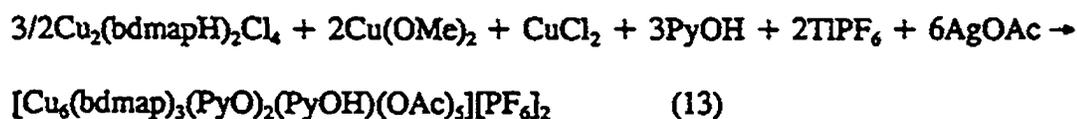
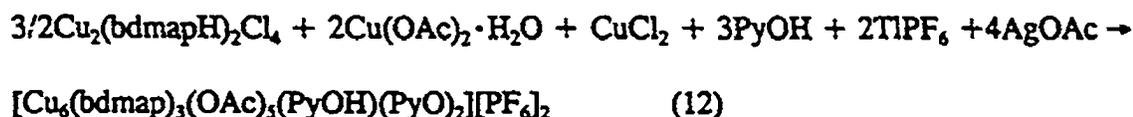
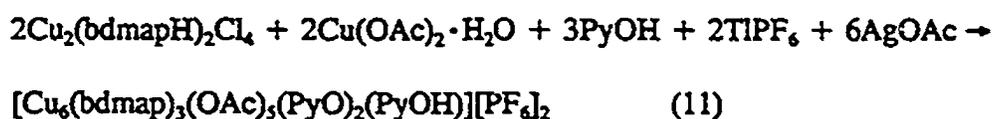
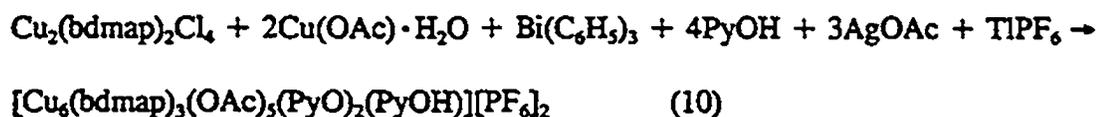


Figure 24. IR Spectrum of Compound 5



WAVENUMBERS (CM-1)

Synthesis: It has been shown that the Cu(II) atoms in the planar tetrameric compounds of 3-5 were linked by the mixed ligands of acetate and bdmmap ligands. If one more ligand is introduced, and the soluble source of Bi(C₆H₅)₃ is added, Bi-Cu complex should be synthesized. This is the synthetic strategy involved in the design of reaction (10). However, a hexanuclear Cu^{II} compound 6 was obtained from the reaction (10) instead of the proposed Bi-Cu complex. The crystals of 6 were not very good. Due to contamination by impurities we were unable to obtain reliable magnetic susceptibility data. With the hope to synthesize the compound 6 in a pure form, the reactions (11), (12) and (13) were designed. However, green blue powders were obtained from these reactions, and in neither case a single product was isolated.



It has been determined by single-crystal X-ray crystal analysis that the hexanuclear Cu(II) compound 6 contains a tetramer $[\text{Cu}_4(\text{OAc})_2(\text{bdmap})_2(\text{PyO})_2]$ unit and a dimer unit $[\text{Cu}_2(\text{OAc})_3(\text{bdmap})]$. The dimer unit is similar to that of $[\text{Cu}_2(\text{OAc})_3(\text{bdmap})]$ synthesized by our group¹²⁷. If the tetramer can be synthesized independently, the hexamer might be obtained by

mixing the tetramer unit with the dimer unit in organic solvent. The reactions of (14) and (15) were designed for the synthesis of the tetramer, $[\text{Cu}_4(\text{bdmap})_2(\text{OAc})_2(\text{PyO})_2][\text{PF}_6]_2$.



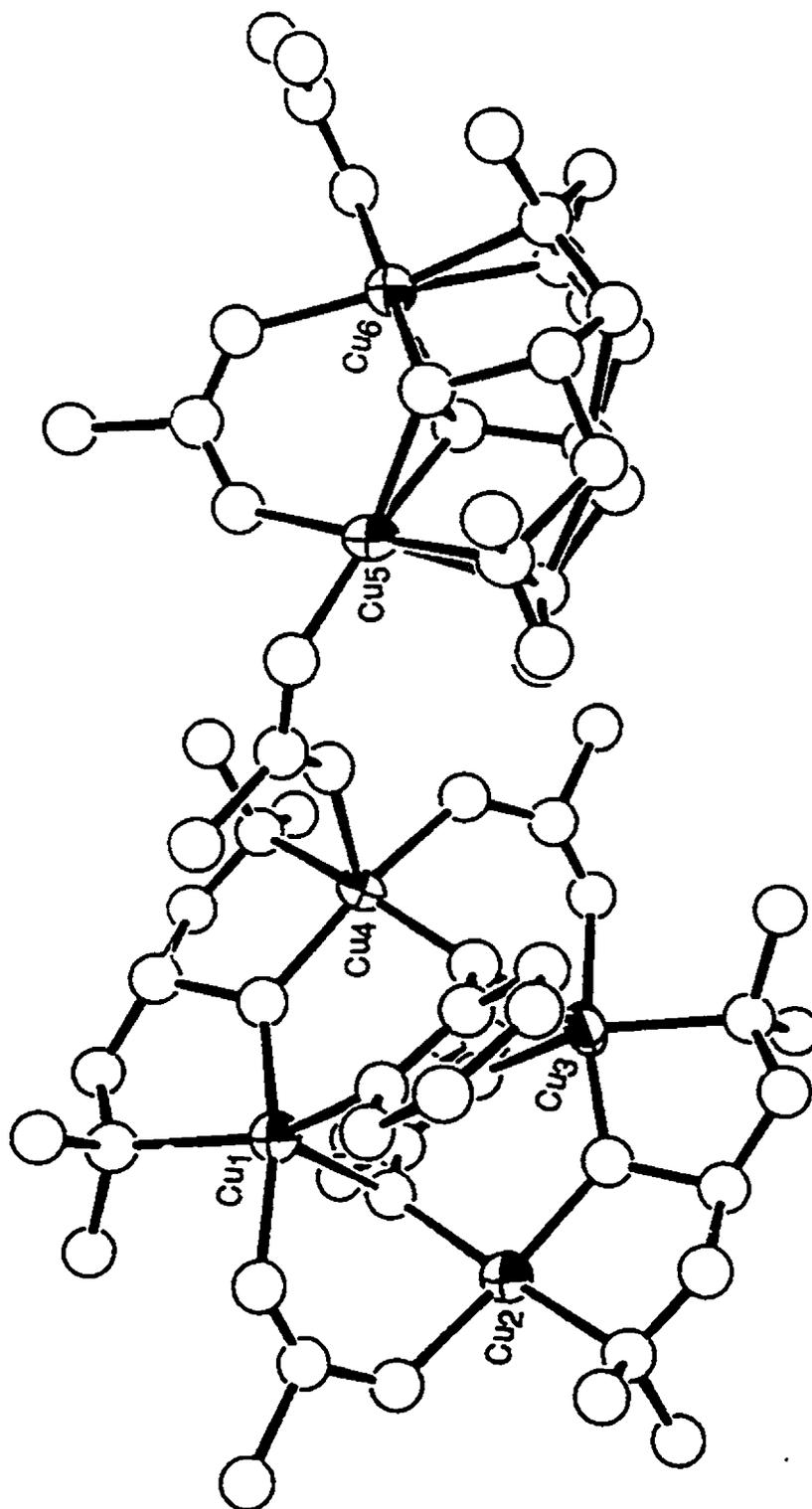
Unfortunately, it was very difficult to obtain crystals from (14) and (15). The reaction (14) produced a blue green powder. The reaction (15) produced a green blue solution. However, in neither case could a single product be isolated.

The dimer, $\text{Cu}_2(\text{bdmap})(\text{OAc})_3$, can be synthesized by reaction (16). A very soluble blue solution was obtained. However, when the solutions from (15) and (16) were mixed together, no crystals of compound 6 were obtained.



X-ray Crystal Structure: The compound 6 has been characterized by single-crystal X-ray analyses. The partially finished structure of the cation of 6 is shown in Figure 25. The most interesting feature of this compound is that the structure contains a Cu^{II}_4 unit and a Cu^{II}_2 unit. The Cu^{II}_4 unit is very similar to the structure of 1-3. Four Cu(II) ions are coplanar. A twelve-membered ring was formed by the four copper(II) atoms, two CO_2 group from acetate ligands and two oxygen atoms from bdmap ligands. The twelve-membered ring is the same as the rings

Figure 25. Structure of Compound 6

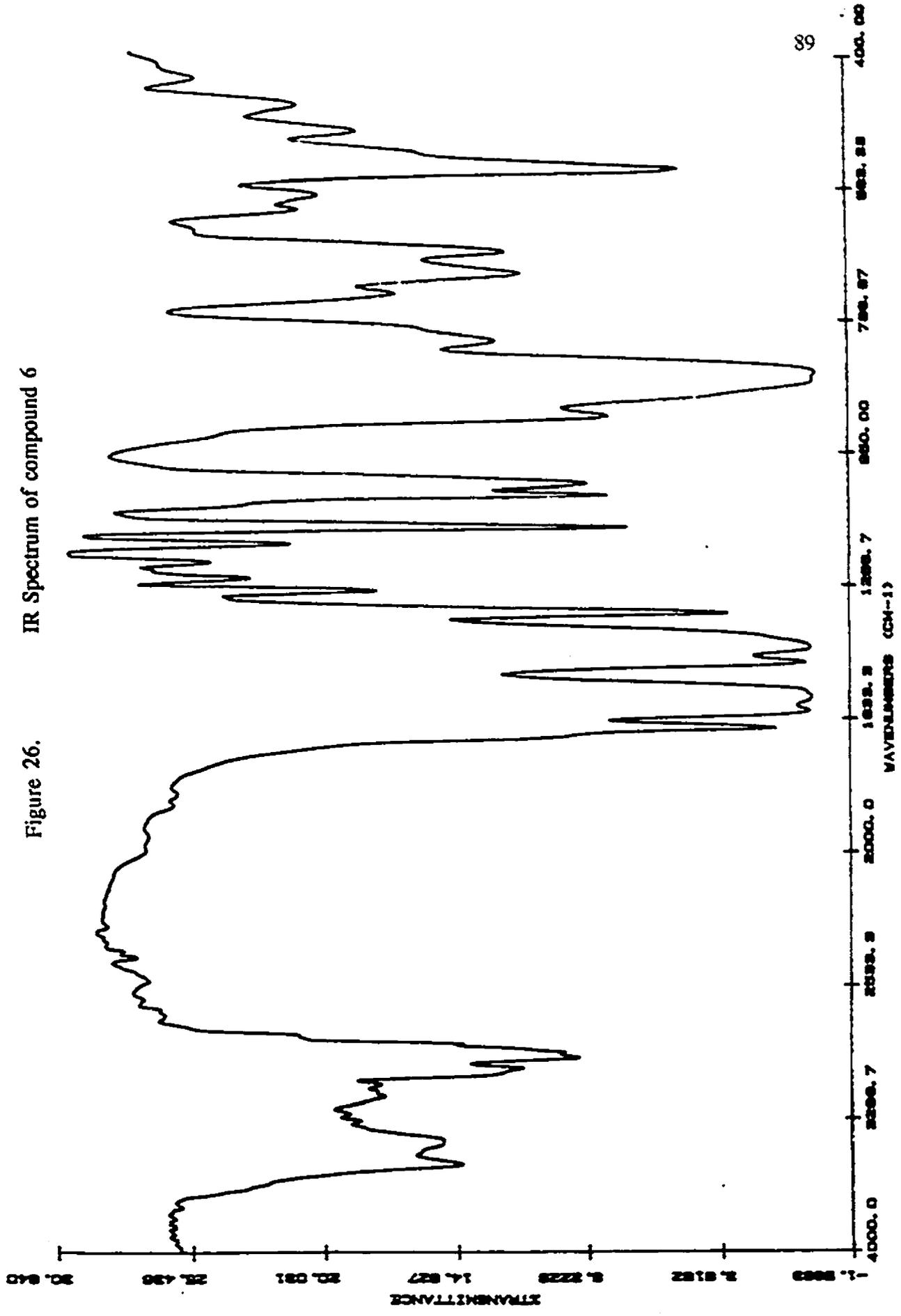


in 3-5. The two oxygen atoms from two PyO⁻ ligands bridge two pairs of copper atoms, Cu(1)/Cu(2) and Cu(3)/Cu(4). The nitrogen atoms of the two PyO⁻ ligands are coordinated to Cu(1) and Cu(3) atoms. In the dimeric unit, the acetate ligand bridges Cu(5) and Cu(6) atoms by two oxygen atoms. The oxygen atom from the bdmaph ligand also bridges the Cu(5) and Cu(6) in the opposite side. The Cu^{II}₄ unit and Cu^{II}₂ unit were linked together by an acetate ligand to form a one dimensional structure in the solid state. Hexanuclear Cu₆ units are very limited in Cu(II) structures.⁶⁹ The one example reported previously is [Cu₃O(dpeo)₃]₂¹³⁹, where dpeo = 1,2-diphenyl-2-(methylamino)ethanone-1-oxime. Two trinuclear [Cu₃O(dpeo)₃] units dimerize to form this compound.

IR Spectrum Analysis: The IR spectrum of 6 is shown in Figure 26. The band at 3380cm⁻¹ was assigned to the OH stretch of PyOH in 6. The antisymmetric and asymmetric OAc⁻ stretching frequencies in 6 were assigned to 1656cm⁻¹ and 1475cm⁻¹ respectively. By comparison with the IR spectrum of a pure sample of PyOH, the bands at 1435cm⁻¹ and 1570⁻¹ were assigned to the aromatic C=C and C=N stretching in PyO⁻ or PyOH. The very intensive absorption band at 838cm⁻¹ was assigned to the P-F vibration in PF₆⁻ anion.

III.4. Conclusion

A new class of cyclic tetranuclear Cu(II) complexes has been synthesized. The dimeric compound, Cu₂(bdmapH)₂Cl₄ 1, is very good starting material for the syntheses of 3 and 4 in the presence of mixed ligands of OAc⁻ and bdmaph. These complexes are capable of forming one-dimensional arrays in the solid state if appropriate ligands and metal ions are present. They are



potential precursors for the synthesis of heteronuclear metal complexes with compositions and structures resembling those of high T_c superconductors.

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